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Mariam TLAISS

Photochemistry of diarylethenes under different environnements
studied by time resolved absorption spectroscopy: from
polyoxometalate molecular cages to electropolymers.

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DR. PASCALE CHANGENET	Polytechnic Institute of Paris	Reviewer
DR. CHANTAL ANDRAUD	ENS of Lyon	Reviewer
Pr. LAURENT RUHLMANN	University of Strasbourg	Examiner
Pr. AURELIE PERRIER	Paris-Cité University	Examiner (President of the Jury)
MCF. STEPHANE ALOISE	University of Lille	PhD Supervisor

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Mariam TLAISS

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étudiée par spectroscopie d'absorption résolue dans le temps: des
cages moléculaires à base de polyoxométallates
aux électropolymères.

Soutenue le **4 Décembre 2025** devant la commission d'examen:

DR. PASCALE CHANGENET	Ecole Polytechnique de Paris	Rapporteur
DR. CHANTAL ANDRAUD	ENS de Lyon	Rapporteur
Pr. LAURENT RUHLMANN	Université de Strasbourg	Examineur
Pr. AURELIE PERRIER	Université Paris-Cité	Examineur (Président de Jury)
MCF. STEPHANE ALOISE	Université de Lille	Directeur de Thèse

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Abstract

This thesis investigates the ultrafast photoinduced dynamics of pyridyl-based diarylethene (DAE) photochromic systems, with particular emphasis on the influence of molecular structure, confinement, and environment. Owing to their bistability and fatigue resistance, DAEs are widely used as molecular switches in photonic and electronic applications. Their reversible photochromic behavior is based on carbon-carbon electrocyclization between an open form (OF) and a closed form (CF). UV light induces photocyclization, while visible light triggers photoreversion to regenerate the OF. Because these transformations occur on the ultrafast timescale, femtosecond transient absorption spectroscopy was therefore employed to resolve (i) the primary photoinduced events initiating the switching reaction and (ii) the role of molecular environment and structural confinement in modulating the excited-state pathways. To address these objectives, three levels of structural complexity were investigated.

At the molecular level, two closely related DAE derivatives were investigated in solution: DAE1 without and DAE2 with an additional phenyl spacer between the pyridyl groups and the photochromic core. For both systems, the reactive antiparallel (AP) conformer is dominant and the contribution of parallel (P) forms is limited. From the Franck-Condon region, and depending on the laser power, DAE1 follows either a direct or sequential photocyclization pathway (~ 0.4 - 0.6 ps), reaching the conical intersection either directly or after relaxation to lower singlet states. In contrast, DAE2 undergoes only a slower sequential mechanism (~ 2 - 10 ps), yet retains a good quantum yield. Photoreversion in both systems is ultrafast and proceeds through the relaxed S_1 state, whose involvement is evidenced by a transient stimulated emission band in the infrared region of the spectrum, consistent with TD-DFT calculations.

Structural confinement was next introduced using polyoxometalate (POM)-based supramolecular capsules (MB, MC1, and MC2), in which DAE1 serves as the switching core in MB and MC1, whereas DAE2 forms the switching core of MC2. These architectures markedly reshape the excited-state landscape. In MB, structural locking in PC suppresses photocyclization entirely, and excitation leads only to an ultrafast charge-transfer (CT) process (~ 0.8 ps) from the DAE unit (donor) to the POM unit (acceptor). In contrast, the other two capsules follow a sequential photocyclization mechanism. In MC1, which adopts predominantly the AP configuration, photocyclization becomes less efficient ($\Phi \approx 0.07$), and a CT process to the POM occurring on the (~ 35 ps) timescale. Conversely, MC2, exhibiting AP and pseudo-P conformations, shows no detectable CT; instead, localized excitation gives rise to emission from the lateral pyridyl-phenyl-thiophene chain with similar photoswitching performance ($\Phi \approx 0.11$). Moreover, photoreversion remains fast in both MC1 and MC2.

Finally, porphyrin-DAE electropolymers (P1 and P2), derived from DAE1 and DAE2 respectively, were examined to probe architectures and medium effects. In the solid state, these polymers are not photochromic but recover photochromism in solution. In thin films, excitation predominantly triggers photoinduced electron transfer (PET) from isoporphyrin radicals to pyridinium cations, followed by internal conversion (IC) and back-electron transfer (BET), suppressing photocyclization. In solution, however, photochromism is restored: alongside ultrafast PET, a direct ring-closure pathway emerges on the (~ 1 - 2 ps) timescale, followed by a slower indirect cyclization process around (~ 15 ps) before BET restores the ground state.

Overall, this work highlights how molecular structure, supramolecular confinement, and environment modulate the competition between photoisomerization and charge-transfer pathways in DAE-based systems.

Résumé

Cette thèse étudie les dynamiques photoinduites ultrarapides de systèmes photochromes de type diaryléthène (DAE) fonctionnalisés par des groupements pyridyles, en mettant l'accent sur l'influence de la structure moléculaire, du confinement et de l'environnement. Grâce à leur bistabilité et à leur résistance à la fatigue, les DAE sont largement utilisés comme interrupteurs moléculaires dans des applications photoniques et électroniques. Leur photochromisme réversible repose sur une électrocyclisation carbone-carbone entre une forme ouverte (OF) et une forme fermée (CF) : l'irradiation UV induit la photocyclisation tandis que la lumière visible déclenche la photoréversion régénérant la forme OF. Ces transformations se produisant à l'échelle ultrarapide, la spectroscopie d'absorption transitoire femtoseconde a été utilisée afin d'identifier (i) les processus photoinduits primaires initiant la commutation et (ii) le rôle de l'environnement moléculaire et du confinement structural dans la modulation des voies de relaxation des états excités. Trois niveaux de complexité structurale ont ainsi été étudiés.

Au niveau moléculaire, deux dérivés de DAE étroitement apparentés ont été étudiés en solution : DAE1 sans, et DAE2 avec, un espaceur phényle supplémentaire entre les groupements pyridyles et le cœur photochromique. Dans les deux systèmes, le conformère antiparallèle réactif (AP) est dominant tandis que la contribution des formes parallèles (P) reste limitée. À partir de la région de Franck-Condon et selon la puissance du laser, DAE1 suit une photocyclisation directe ou séquentielle ($\sim 0,4\text{-}0,6$ ps), atteignant l'intersection conique soit directement, soit après relaxation vers des états singulets plus bas. DAE2 suit uniquement un mécanisme séquentiel plus lent ($\sim 2\text{-}10$ ps) tout en conservant un bon rendement quantique. Dans les deux cas, la photoréversion est ultrarapide et passe par l'état S_1 relaxé, mis en évidence par une émission stimulée transitoire dans l'infrarouge, en accord avec les calculs TD-DFT.

Un confinement structural a ensuite été introduit à l'aide de capsules supramoléculaires à base de polyoxométalates (POM) (MB, MC1 et MC2), dans lesquelles DAE1 constitue le cœur photochromique de MB et MC1, tandis que DAE2 constitue celui de MC2. Dans MB, le verrouillage structural supprime la photocyclisation et l'excitation conduit uniquement à un transfert de charge ultrarapide ($\sim 0,8$ ps) du DAE (donneur) vers le POM (accepteur). Les capsules MC1 et MC2 suivent en revanche un mécanisme de photocyclisation séquentiel. Dans MC1, majoritairement en configuration AP, la photocyclisation devient moins efficace ($\Phi \approx 0,07$) et un transfert de charge vers le POM apparaît sur ~ 35 ps. MC2, présentant des conformations AP et pseudo-P, ne montre aucun transfert de charge détectable ; l'excitation localisée conduit à une émission de la chaîne latérale pyridyle-phényle-thiophène avec une efficacité de commutation comparable ($\Phi \approx 0,11$). La photoréversion reste rapide dans MC1 et MC2.

Enfin, des électropolymères porphyrine-DAE (P1 et P2), dérivés respectivement de DAE1 et DAE2, ont été étudiés afin d'évaluer l'effet de l'architecture polymérique et du milieu. À l'état solide, ces polymères ne sont pas photochromes mais retrouvent cette propriété en solution. Dans les films minces, l'excitation déclenche principalement un transfert d'électron photoinduit des radicaux isoporphyrine vers les cations pyridinium, suivi d'une conversion interne et d'un transfert d'électron inverse, supprimant la photocyclisation. En solution, le photochromisme est rétabli : parallèlement au transfert d'électron ultrarapide, une fermeture directe du cycle apparaît ($\sim 1\text{-}2$ ps), suivie d'une cyclisation indirecte plus lente (~ 15 ps) avant que le transfert inverse ne restaure l'état fondamental. Ce travail montre comment la structure moléculaire, le confinement supramoléculaire et l'environnement modulent la compétition entre photoisomérisation et transfert de charge dans les systèmes à base de DAE.

LIST OF ABBREVIATIONS

ACN	Acetonitrile
AP	Antiparallel conformer
BET	Back Electron Transfer
CaF₂	Calcium Fluoride
CF	Closed Form
CI	Conical Intersection
CT	Charge Transfer
CV	Cyclic Voltammetry
DAE	Diarylethene
DCE	Dichloroethane
DCM	Dichloromethane
DFT	Density Functional Theory
DMF	Dimethylformamide
DTE	Dithienylethene
EQCM	Electrochemical Quartz Crystal Microbalance
ESA	Excited-State Absorption
ϵ	Molar absorptivity
FC	Franck-Condon
fs-TAS	Femtosecond Transient Absorption Spectroscopy
FWHM	Full Width at Half Maximum
GSB	Ground-State Bleaching
GVD	Group Velocity Dispersion
HOMO	Highest Occupied Molecular Orbital
IC	Internal Conversion
IR	Infrared
IsoP	Isoporphyrin
ISC	Intersystem Crossing

ITO	Indium Tin Oxide
λ_{max}	Maximum absorption wavelength
LUMO	Lowest Unoccupied Molecular Orbital
MB	Molecular Basket
MC	Molecular Cage
μJ	Microjoule
μM	Micromolar
NMR	Nuclear Magnetic Resonance
nm	Nanometer
OF	Open Form
OPA	Optical Parametric Amplifier
P	Parallel Conformer
P1/2	Polymers
PET	Photoinduced Electron Transfer
QY, ϕ	Quantum Yield
POM	Polyoxometalate
PPT	Pyridyl-Phenyl-Thiophene
ppm	Parts per million
ps	Picosecond
PSS	Photostationary State
Py	Pyridinium
SE	Stimulated Emission
SEC	Spectroelectrochemistry
τ	Characteristic Time Constant
TD-DFT	Time-Dependent Density Functional Theory
UV-Vis	Ultraviolet-Visible
WLC	White-Light Continuum

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General Introduction

Photochromism is the reversible transformation of a chemical compound between two forms with distinct absorption spectra upon exposure to light. This phenomenon, typically triggered by ultraviolet or visible radiation, results in a visible color change. Photochromic materials have attracted significant scientific interest because of their dynamic optical properties and their ability to respond rapidly and reversibly to external stimuli. They are widely employed in applications such as smart windows, optical data storage, and UV-sensitive lenses.

The most familiar example is photochromic sunglasses that darken under sunlight and regain transparency indoors. However, photochromic molecules extend far beyond this everyday use. Their reversible structural transformations can induce profound changes in physical and chemical properties, including conductivity, fluorescence, and polarity. These alterations allow precise control of molecular behavior using light, opening new avenues for the design of smart and photoresponsive materials. As a result, photochromic systems now play a central role in emerging fields such as molecular electronics, sensors, and nanodevices.

Since the pioneering work of Professor Masahiro Irie in 1988 on diarylethene (DAEs) derivatives (1), DAEs have emerged as one of the most reliable and extensively studied families of photochromic compounds. Their photochromism arises from a reversible photoinduced carbon-carbon electrocyclization that interconverts two thermally stable isomers: the open form (OF) and the closed form (CF). DAEs are characterized by their exceptional thermal stability, high fatigue resistance, and bistability, as both forms are stable at room temperature. The reversible transformations between OF and CF known as photocyclization and photoreversion, respectively, occur on ultrafast timescales and induce pronounced changes in the absorption, emission, and electronic properties of the molecules. These unique features are the one that makes DAEs exceptionally versatile molecular photoswitches for applications in optical data storage, molecular electronics, and photonic devices.

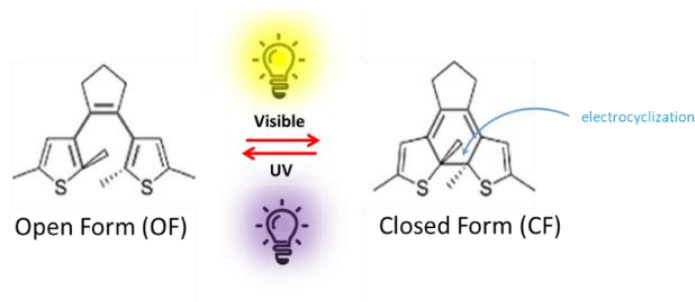


Figure: Light-Controlled Molecular Switching in DAEs.

Mechanistic studies have shown that these photoinduced transformations occur through ultrafast excited-state dynamics governed by the shape of the potential energy surfaces and the presence of conical intersections (CIs) that enable internal conversion between electronic states. During photocyclization, UV excitation promotes the OF to a Franck-Condon (FC) state, which rapidly relaxes on the S_1 surface and crosses a CI to yield the closed form (CF). The process occurs on a femtosecond-picosecond timescale, proceeds without an activation barrier, and exhibits high quantum yields (QY) (0.3-0.9) (12-15). In contrast, photoreversion is slower and less efficient, involving relaxation within S_1 (CF), crossing of an energy barrier, and internal conversion to the OF, consistent with its lower QY (0.01-0.1) and temperature dependence (13,19).

The efficiency of both reactions is strongly influenced by the molecular conformation of the OF. Only the antiparallel (AP) conformer can undergo the conrotatory electrocyclization, while the parallel (P) conformer is photochemically inactive and responsible for fluorescence emission (~ 100 ps) (29). Femtosecond transient absorption spectroscopy (fs-TAS) confirmed the coexistence of a direct photocyclization from the FC region and a sequential pathway via the relaxed S_1 minimum, as shown by Aloïse et al. (28) and Hamdi et al., who also revealed competing ultrafast singlet and triplet channels. Overall, the balance between reactive (AP) and non-reactive (P) conformers, together with their interconversion rate, governs the overall photochromic efficiency. However, despite their well-established photochemical framework, the excited-state dynamics of DAEs are highly sensitive to their local environment, molecular conformation, and electronic coupling to neighboring units. These parameters can significantly modify reaction efficiency, open competing pathways such as charge transfer (CT), or significantly alter the photoactivity. Understanding how such factors reshape DAE photophysics is essential for designing advanced photoresponsive systems that integrate DAE switches within functional molecular or polymeric architectures.

The objective of this thesis is therefore to investigate how molecular environment and structural confinement influence the ultrafast photoinduced processes of DAEs, using a combination of steady-state spectroscopy, fs-TAS, and time-dependent density functional theory (TD-DFT) calculations. The study follows a progressive approach that examines three structural levels of increasing complexity: (i) free DAE molecules, (ii) supramolecular capsules incorporating polyoxometalate (POM) clusters, and (iii) extended electro-polymeric systems coupling free DAEs with porphyrinic moieties.

Chapter 1 provides the fundamental definitions and general principles of photochromism, together with an overview of the main photochromic families. Particular emphasis is then placed on DAEs, describing their structural features, conformational behavior, and photochemical mechanisms in both solution and solid states. The chapter also reviews the contribution of theoretical and ultrafast spectroscopic studies in elucidating photocyclization and photoreversion pathways, highlighting the key topological points such as CIs that govern their excited-state dynamics. Finally, it discusses the influence of the molecular environment on DAE photochromism and summarizes representative examples of supramolecular and hybrid systems based on bis-pyridyl DAE units, including their integration with polyoxometalate (POM) clusters and porphyrinic frameworks systems that form the basis of the present thesis.

Chapter 2 establishes the experimental basis of the thesis, presenting the preparation of molecular and polymeric samples and the spectroscopic and spectro-electrochemical techniques used to characterize them. DFT and TD-DFT calculations are employed to support and interpret the experimental data. Particular emphasis is placed on fs-TAS, which serves as the central technique for resolving ultrafast excited-state dynamics. Together, these methods form a coherent analytical framework that is systematically applied to all studied systems.

Chapter 3 builds upon the methodological foundation of Chapter 2 by investigating the intrinsic photoreactivity of two structurally related bis-pyridyl diarylethenes, DAE1 and DAE2, the pyridyl groups being essential for linking the photochromic molecules with other moieties. Beyond the expected results for such simple DAEs, we will see that DAE1 exhibits an interesting power-dependent effect. The comparison with DAE2 then highlights how the addition of a phenyl

linker modifies the photocyclization and photoreversion mechanisms, notably giving rise to novel transient features. The results obtained by fs-TAS and TD-DFT establish the photophysical reference framework, which will be essential for evaluating the effects of supramolecular caging in the subsequent chapters.

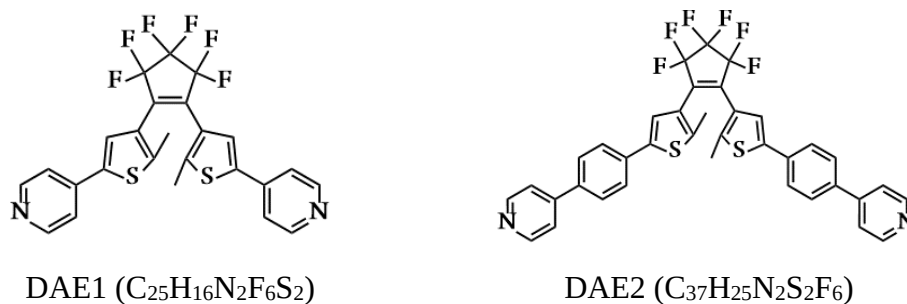


Figure: Diarylethene derivatives, DAE1 and DAE2.

Chapter 4 extends the investigation from free isolated molecules to supramolecular assemblies combining DAEs with inorganics polyoxometalate (POM) clusters. These hybrid capsules serve as model systems to explore how structural confinement and inorganic-organic coupling affect photochromism. fs-TAS measurements reveal that encapsulation stabilizes specific conformers, modifies photocyclization efficiency, and introduces charge-transfer and back-transfer pathways between the DAE and POM units. By direct comparison with Chapter 3, this part demonstrates how confinement can suppress or promote selected excited-state channels depending on the molecular geometry.

Chapter 5 extends the investigation from discrete supramolecular capsules to extended polymeric architectures, where the DAE switches are integrated into porphyrinic backbones through electropolymerization, forming the conjugated systems P1 and P2. fs-TAS, performed in solution and solid state, is employed to examine how the polymer state, excitation wavelength (UV, Soret, or Q bands), and structural rigidity influence the excited-state dynamics and the accessibility of photocyclization toward the CF. Building on the molecular insights from Chapters 3 and 4, this study connects the behavior of free and confined DAEs to their polymeric counterparts, highlighting how the surrounding further modulate the excited-state pathways first identified in the simpler systems.

The results of this work provide an overall understanding of how molecular structure and environment control the ultrafast photoinduced behavior of DAE systems. From individual molecules to supramolecular capsules and polymers, each level introduces its effects that influence photocyclization and relaxation pathways. These findings establish clear structure-dynamics relationships that can guide the development of future photoresponsive materials with adjustable optical and electronic properties.

Chapter 1. State of the Art on Diarylethene

Photochromism

This chapter aims to review the definitions and concepts surrounding photochromism, with a presentation of several families of photochromic compounds, followed by a specific focus on diarylethenes.

Subsequently, the literature related to the fundamental mechanisms of DAEs, namely electrocyclization and cycloreversion will be presented, distinguishing between the contributions of theoretical calculations and transient spectroscopy. Particular attention will be given to the DTE molecule.

We will also examine the influence of the environment (viscous solutions, polymer matrices) on the photoswitching mechanisms, and present examples of supramolecular systems incorporating DAEs.

1.1. General Overview of Photochromism

1.1.1 Definitions

The history of photochromes began in the 19th century, with the first publications describing reversible color changes induced by sunlight (2). However, it was not until 1950 that Hirshberg finally proposed the appropriate term to describe this phenomenon: photochromism (3).

Photochromism. Photochromism of a chemical species is the reversible transformation induced by light between two forms, A and B, each possessing a different absorption spectrum (2). The interconversion between the two states is usually accompanied by changes in the physical properties of the chemical species, such as refractive index, solubility, viscosity, surface wettability, or dielectric constants (2). As shown in **Figure 1.1**, the thermodynamically stable form A is transformed by irradiation into the less stable form B, which has a different absorption spectrum and can be reconverted to form A by thermal and/or photochemical means. More precisely, if both A and B are thermodynamically stable (bistable compounds), the system is referred to as a Type P photochrome, with photoinduced reversion. If B is thermodynamically unstable, the photochrome is of Type T, and reversion occurs thermally. Typically, for most photochromic compounds, the stable form is colorless or pale yellow and becomes colored upon irradiation (positive photochromism). Some photochromic compounds, however, exhibit a colored A form and a colorless B form (negative photochromism), or show a reversible change between different colors.

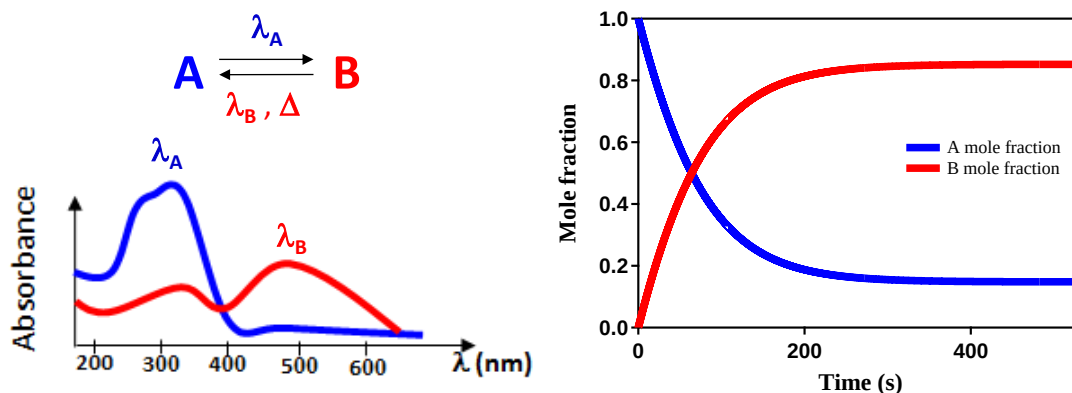


Figure 1.1. (left) Photochromism concept with the two forms A and B displaying different absorption spectra and; (right) the kinetic.

Photochromic parameters. It is important to quantify the efficiency of photochromic molecules, and naturally, in addition to the classical photochemical parameters (λ_A , λ_B) and extinction coefficients (ϵ_A , ϵ_B), it is essential to refer to the QY of the formation of B (or A) after excitation of A (or B), as follows:

$$\phi_{A \rightarrow B} = \frac{\# \text{ B molecules photoinduced}}{\# \text{ photons absorbed by A}} \quad \phi_{B \rightarrow A} = \frac{\# \text{ A molecules photoinduced}}{\# \text{ photons absorbed by B}}$$

By anticipation, in the case of photoinduced electrocyclization photochromism, $\phi_{A \rightarrow B}$ refers to photocyclization QY while $\phi_{B \rightarrow A}$ refers to photoreversion QY.

Photosationary state (Pss). Corresponds to the thermodynamic equilibrium state of the photochromic reaction, obtained after light irradiation for a sufficiently long period of time as illustrated to the **Figure 1.1**, right.

Fatigue of Photochromes. Although photochromism is a fully reversible process, secondary reactions may occur. This photodegradation, even if minor, that develops over time or under prolonged irradiation, is responsible for the gradual loss of photochromic properties. This loss of performance, often caused by oxidation of the compound, is referred to as photochrome fatigue. One way to quantify this fatigue is to determine the number of photo-reaction/photo-reversion cycles, $A \leftrightarrow B$, that the system can undergo without significant photodegradation of A.

1.1.2 Different Photochromic Families

It is not the intention here to provide an exhaustive list of the different families of photochromes. The reader is referred to specialized books (2,4) and comprehensive reviews (2). However, it seems appropriate to present a few examples of photochromes that will also help illustrate certain points discussed later in this manuscript. The various families of photochromes can be classified according to the type of chemical reaction responsible for the structural and therefore spectral modification.

Photochromism by cis-trans Isomerization. An important family of photochromes is based on the photoinduced cis-trans isomerization of double bonds: C=C in stilbenes or N=N in azobenzenes, the latter being by far the most widely studied in the literature. The spectral change between the trans and cis forms of azobenzenes, induced by UV radiation, is generally moderate due to the similar π -electron delocalization in both isomers. However, the large geometric difference between the trans and cis forms makes these molecules particularly useful for applications requiring material displacement (actuators, surface relief gratings, etc.).

Photochromism by Particle or Molecular Group Transfer. For these families of photochromes, generally of Type T, the photoreaction is based on the transfer of an electron, a proton (as in anils), a hydrogen atom (as in quinolone-ketone systems), or a chemical group (as in quinones), among others. Naturally, this type of photochromism is highly sensitive to the surrounding environment.

Photochromism Based on a Pericyclic Reaction. Several important families of photochromes are based on electrocyclic reactions, which are electronic rearrangements involving the conversion of a π bond into a σ bond or vice versa. Whether concerted or not, photoelectrocyclic reactions typically involve six π -electrons and six atoms. Spiropyrans and spirooxazines (see **Figure 1.2**) are Type T photochromes, while fulgides, fulgimides, and diarylethenes are generally Type P photochromes. Naturally, the principles of this family will be discussed in more detail later in this work.

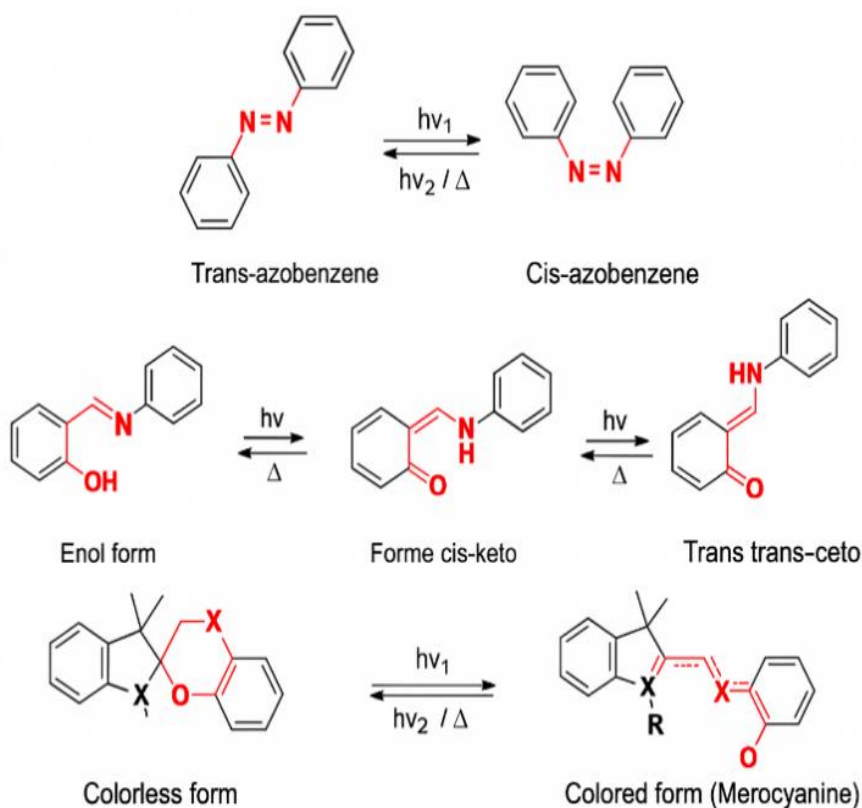


Figure 1.2. Different photochromic families.

1.2. Photochromism of Diarylethenes

Definitions. Diarylethene are cis-stilbene derivatives featuring a central C=C double bond substituted with two aryl groups. The photochromic behavior of DAEs originates from an electrocyclic reaction of the 1,3,5-hexatriene system, which is formed by the aryl-ethylene-aryl framework, as illustrated in **Figure 1.3**. A particularly well studied class of diarylethenes in the literature is the family of dithienylethenes (DTE), which incorporate thiophene rings ($Y=C$; $X=S$) and a perfluorocyclopentane bridge. These compounds are renowned for their excellent thermal stability and reversible photochromic properties.

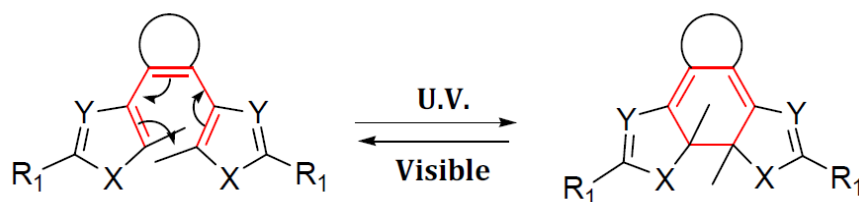


Figure 1.3. DAE photocyclization/photoreversion. When $X=S$, we refer as DTE molecules.

This reaction follows the Woodward–Hoffmann selection rules (5), as summarized in **Table 1.1**. Accordingly, in the case of diarylethenes, since the electrocyclic reaction involves six π -electrons, it would be theoretically allowed through a thermal disrotatory mechanism, and through a photochemical process, known as photocyclization, via a conrotatory mechanism. However, computational studies reveal that the high energy barrier between the reactant and the product prevents the thermal cyclization from occurring, and therefore, only the photochemical pathway efficiently leads to the cyclized product.

Table 1.1. Woodward-Hoffmann Selection Rules.

π -Electron System	Thermal Process	Photochemical Process
$4n$	Conrotatory	Disrotatory
$4n + 2$	Disrotatory	Conrotatory

1.2.1 Different Types of Conformers

Due to the intrinsic structural nature of DAEs and the carbon-carbon electrocyclization reaction, a specific terminology is employed. In general, the thermodynamically most stable form is the OF, which is typically colorless and exhibits a dominant absorption band in the UV region. Upon excitation of this UV absorption band, photocyclization is induced, leading to the formation of the CF, which is colored and displays a new absorption band in the visible region. While the Closed Form generally exists as a single conformation, the OF can adopt two conformations, depending on the relative orientation of the aryl groups: a parallel conformer, denoted P (or cis), and an antiparallel conformer, denoted AP (or trans), as illustrated in **Figure 1.4**.

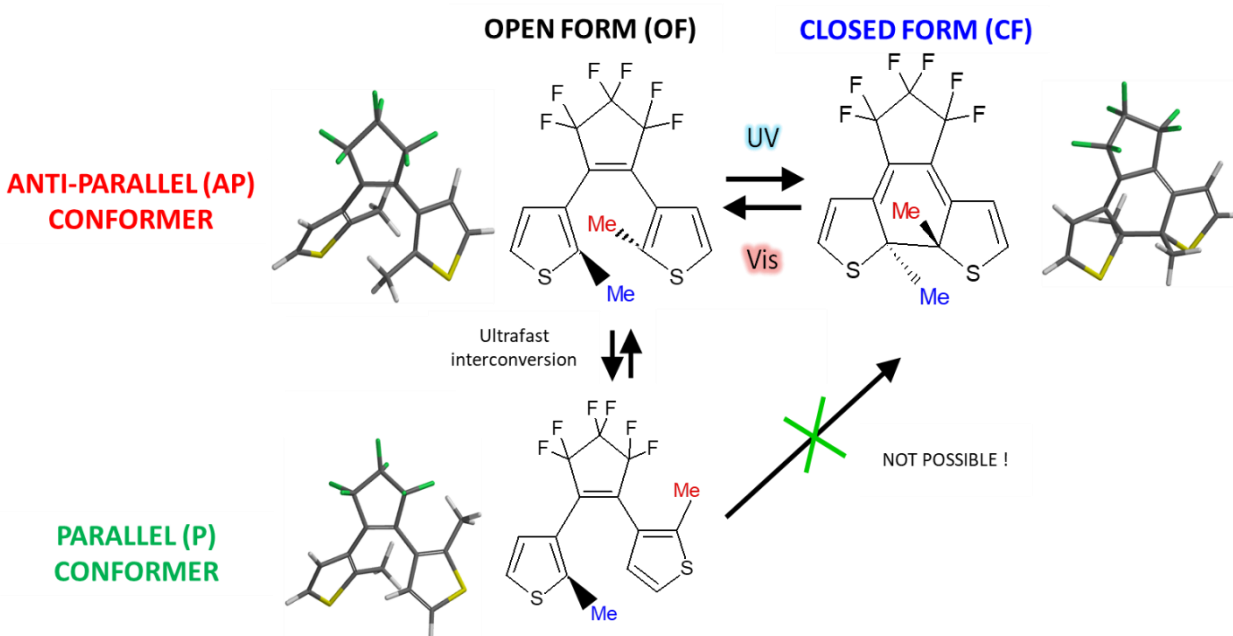


Figure 1.4. Different conformers for DAE.

According to the Woodward-Hoffmann rules described above, the photocyclization reaction can occur only from the AP conformation. In general, the proportion of each conformer in solution is approximately 50%, particularly for DAEs with minimal steric hindrance around the photoactive carbons. Consequently, the QY of cyclization cannot theoretically exceed 0.5. A major challenge for many researchers is to overcome this conformational limitation in order to achieve QYs approaching unity. Improvements in quantum efficiency have been extensively discussed in the book by Professor Irie, the inventor of these photochromic molecules.

1.3. Spectrokinetic Characterization of DAE

The characterization of the photochromism of a DAE first requires the photochemical characterization of the ground-state species, OF and CF species. This involves determining the fundamental photochromic parameters: molar extinction coefficients, wavelengths of maximum absorption for both species, QYs of photoconversion, and thermal back-reaction rate constants (together with their activation energies). Since the OF $\rightarrow$ CF conversion occurs in the excited state (according to the Woodward-Hoffmann rules), it is necessary to employ transient spectroscopy techniques to identify the various intermediate states and to study their dynamics. In recent years, excited-state calculations (CASSCF, TDDFT) have become indispensable tools for achieving a deeper understanding of the photo-opening and photo-closing mechanisms of the central ring.

In the following section, we present several spectrokinetic data for representative DAE and then discuss the photocyclization and photoreversion mechanisms previously reported in the literature.

1.3.1 OF and CF Characterizations

Conformer P vs AP. The relative proportion of the P and AP conformers is always a crucial parameter to determine before beginning the study of a DAE. Since the P conformer is photochemically inactive, its fraction in solution directly influences the observed photochemical parameters. The preferred technique for evaluating the percentage of P and AP conformers is proton NMR spectroscopy (^1H NMR), provided that the interconversion between AP and P is slower than the NMR timescale. For instance, in the case of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (DTE), Irie et al. determined that the P and AP populations are 52% and 48%, respectively, in chloroform solution (6) (see **Figure 1.5**).

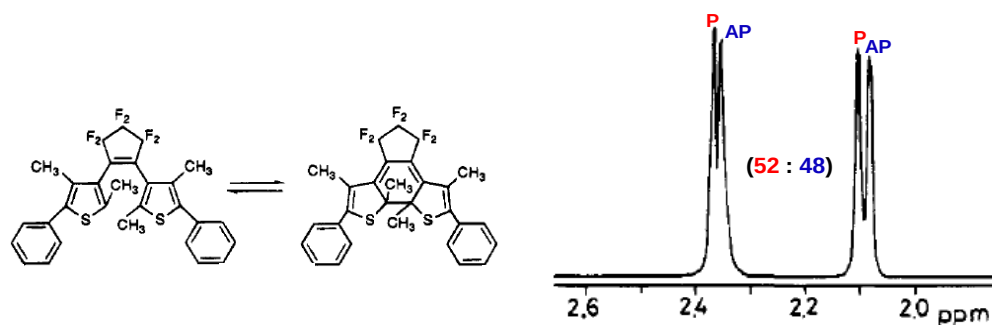


Figure 1.5. (Left) Molecular structure of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene.

Electronic and structural features. A typical example of the electronic and geometric structural changes occurring in a diarylethene is shown in **Figure 1.6**. The chemical structures of the OF and CF isomers, along with their absorption spectra, are presented in **Figure 1.6, a**. Upon irradiation, the compound changes from a colorless solution in the open form ($\lambda_{\text{max}} \approx 300$ nm) to a red solution in the closed form ($\lambda_{\text{max}} \approx 500$ nm).

In OF, the π orbitals are localized over each thiophene ring, and the absorption spectrum resembles that of a substituted thiophene. In contrast, in the closed form, the π orbitals are delocalized across the entire molecule, reducing the HOMO-LUMO energy gap and thus shifting the absorption to longer wavelengths. The red color of the CF is therefore attributed to the extended π -conjugation throughout the molecule. Simultaneously, the geometric structure of the molecule changes significantly. As illustrated in **Figure 1.6,c**, the height of the triangular framework (blue dashed line) increases from 0.49 to 0.56 nm, while the base width decreases from 1.01 to 0.90 nm. The side view further indicates that the molecular thickness decreases upon conversion from the OF to the CF.

The relevant parameters for several typical normal DTEs summarized in **Table 1.2**, all containing the Perfluorocyclopentene Bridge. For inverse DTEs, the reader is referred to previously published studies. This table includes the photochromic cores of A1 and A2, i.e., the DTE molecule, as well as its analogue lacking phenyl substituents (DTE- β) and its positional isomer (DTE- α). Finally, the commercially available compound 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BT) is also listed.

Within this series, the λ_{max} of the OF varies by more than 70 nm, whereas that of the closed form changes by only about 30 nm, reflecting the greater flexibility of the former. Regarding QYs, the photocyclization values are consistently higher than those of photoreversion, with the notable exception of BT. In the case of DTE, the very low photoreversion QY (0.018) compared to that of photocyclization (0.45) warranted a more detailed mechanistic investigation.

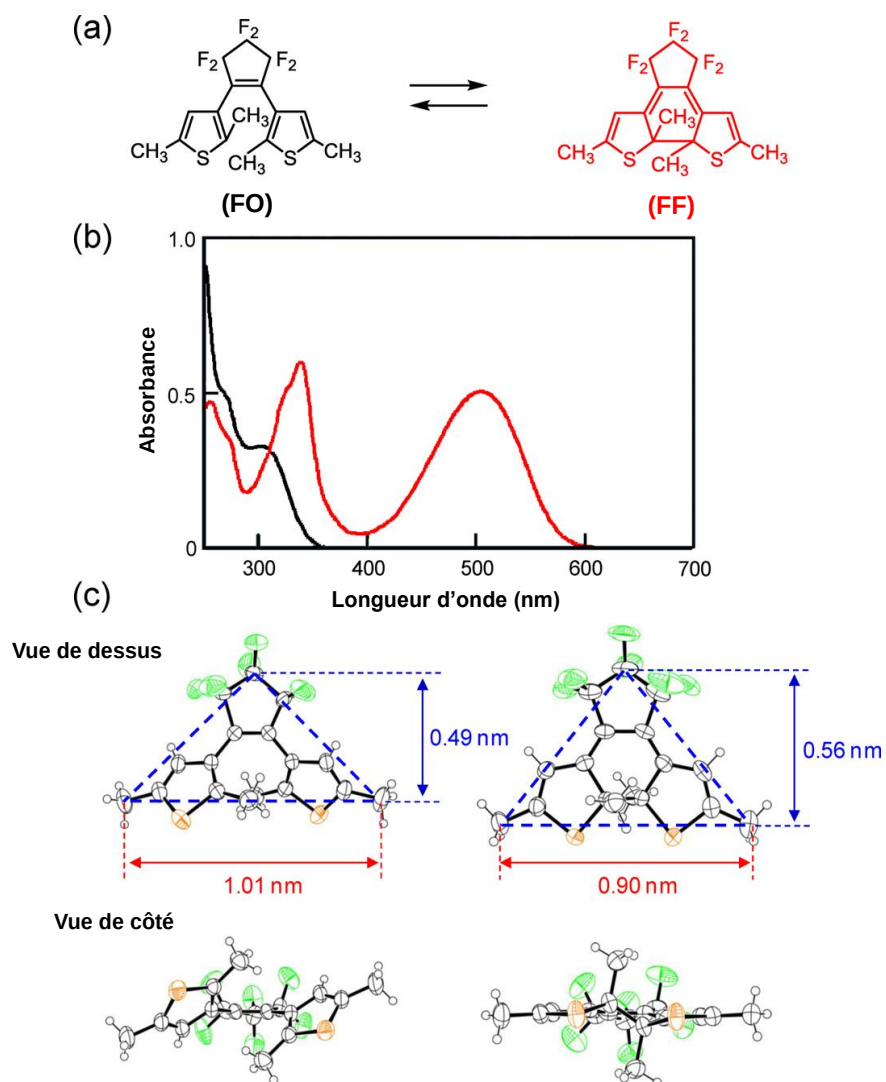
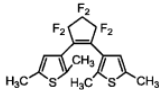
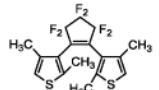
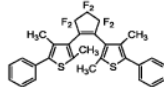
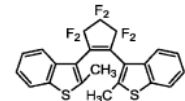


Figure 1.6. (a) Chemical structure of the open- and closed-ring isomers of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene. (b) Steady-state absorption spectra of the OF (black line) and CF (red line). (c) Top and side views of the geometric structures of the open and closed isomers in the crystalline form.

Table 1.2. Photochemical parameters of selected DAE.

		OF		CF		In solution		Crystal		Ref
		$\lambda_{\max}$ (nm)	ϵ (M ⁻¹ cm ⁻¹)	$\lambda_{\max}$ (nm)	ϵ (M ⁻¹ cm ⁻¹) ¹⁾	ϕ_{cycl}	ϕ_{rev}	ϕ_{cycl}	ϕ_{rev}	
DAEa		303	5300	505	8000	0.40	0.12	0.80	0.10	(7,8)
DAEb		234	13000	534	5000	0.21	0.13	0.51	0.12	(9)
DAEc		268	28400	562	10900	0.45	0.018	0.96	0.027	(8,10)
BT		258	15200	516	10000	0.31	0.29	0	--	(10)
DAE1	?	?	?	?	?	?	?			

1.3.2 Solid State Photochromism

A photochromic molecule in solution is not necessarily photochromic in the crystalline state. The crystal lattice, along with steric and conformational constraints, can modify the photochromic parameters, either enhancing or reducing them, or even suppressing the photochromism entirely. **Table 1.2** compares the photochromic behavior of several compounds in n-hexane and in the crystalline state. When photochromism is retained in the solid state, the cyclization QY (ϕ -cycl) is significantly improved, while the reversion QY (ϕ -rev) remains essentially unchanged, as observed for DTE- α and DTE- β .

For DTE, the photocyclization QY approaches the theoretical limit of unity, whereas the reversion yield remains modest. In contrast, for BT, the photochromism disappears completely in the crystalline phase. Given the complexity of solid-state effects, the reader is referred to specialized reviews for a more detailed discussion (11). Nevertheless, it can be concluded that the crystal lattice imposes a structural constraint that significantly affects the photocyclization process, while the photoreversion process is only slightly influenced.

1.4. Ultrafast Photoswitching Mechanism

To begin with, it should be recalled that the photoswitching behavior of DAEs in general and of DTEs in particular is based on a photoinduced carbon-carbon electrocyclization reaction, occurring either in the ring-closing direction (photocyclization) or in the ring-opening direction (photoreversion) (see **Figure 1.7**). To achieve a comprehensive understanding of the mechanistic pathways and possible competing processes, a combined approach involving time-resolved spectroscopy and theoretical calculations is required. Indeed, theoretical studies have played a crucial role in elucidating the electronic structure of diarylethenes, including the topology of the ground and excited states and the presence of CIs (as discussed later). Although the excited-state dynamics have been investigated using both classical and quantum molecular dynamics simulations, it is undoubtedly time-resolved absorption spectroscopy that has most significantly advanced our understanding of the photochromic switching mechanisms.

1.4.1 Theoretical Calculations: Important Topological Points

Semi-empirical calculations. Among the earliest semi-empirical excited-state calculations on DAEs (12), the work of Ern et al., using a Collective Electronic Oscillator-Austin Model 1 (CEO-AM1) approach, provided the foundational insights for understanding the photoswitching mechanisms. Their objective was to interpret transient absorption results for both cyclization (13) and cycloreversion (14). By performing calculations of the ground state (S_0) and the two lowest excited states (S_1 and S_2) as functions of the carbon-carbon distance (reaction coordinate q), the authors obtained the results shown in **Figure 1.7**.

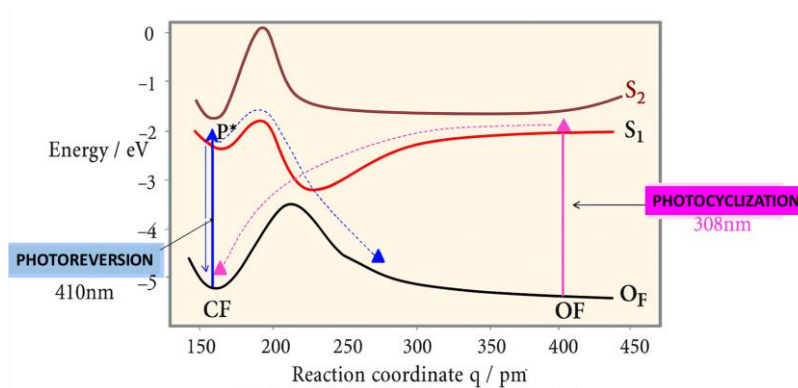


Figure 1.7. Potential energy surfaces of the S_0 , S_1 , and S_2 states as a function of the reaction coordinate (q).

Photocyclization: the UV excitation produces a FC state on the S_1 surface, $S_1^{FC}(OF)$ which relaxes to a potential minimum, $S_1^{min}(OF)$ before yielding the closed form (FF) within 2.3 ps. The absence of an activation barrier was therefore used to explain the rapidity of the process and its high QY (0.86).

Photoreversion: Irradiation of the closed form (CF) in the visible region produces the FC state, $S_1^{FC}(CF)$, which relaxes within 1 ps to the potential minimum $S_1^{min}(OF)$. At this stage, the lifetime of this state (13 ps) is governed by two parallel processes: (i) internal conversion (IC) to S_0 , and (ii) an activation barrier crossing toward the topological point leading to ring opening, occurring within 325 ps. The presence of this activation barrier could explain the low QY (0.04) and the slower rate constant compared to the cyclization process.

Although these excited-state calculations were performed under strong approximations, they had the merit of providing a first qualitative picture of the reaction pathways.

Post-Hartree-Fock Methods: toward Conical Intersections. The simplest ab initio method is the Hartree-Fock approach, in which the electron-electron Coulomb repulsion is not explicitly taken into account; only its average effect is included in the calculation. For excited-state computations, it is essential to include electron correlation through so-called post-Hartree-Fock methods. Unlike the ground state, the description of excited states requires the treatment of open electronic configurations, which may demand multiconfigurational calculations. Considering that the computational cost, depending on the level of theory, can scale as N^4 to N^7 (where N is the number of basic functions), it is easy to understand why such calculations have long represented a significant challenge.

A particularly important study was that of Boggio-Pasqua et al. (2003), who investigated DAEs at the CASSCF (Complete Active Space Self-Consistent Field) level of theory, complemented by Molecular Mechanics Valence Bond (MMVB) calculations (15). This study clearly highlighted the crucial role of **CI**s, which can be viewed as “funnels” between two different potential energy surfaces (an avoided crossing), enabling an ultrafast transfer of the wave packet from one surface to the other (typically S_1 to S_0). These particular topological points, characterized by complex geometries, have been reported for various dienes (16–18).

In the study by Boggio-Pasqua et al., five CIs were identified, and the molecular geometries associated with these states were explicitly described. One CI appears particularly interesting because of its position along the reaction pathway and its similarity to that found in the case of the cycloreversion of cyclohexa-1,3-diene (16,19): CI_3 . The shape of the potential energy surfaces shown in **Figure 1.8** is also recovered, notably with the presence of an activation barrier (2ATS) that must be overcome during the cycloreversion reaction. In contrast, no barrier is observed for the cyclization reaction. The MMVB studies starting from the $2A_0$ and 2ATS states therefore make it possible to investigate the dynamics of the cyclization and cycloreversion reactions, respectively.

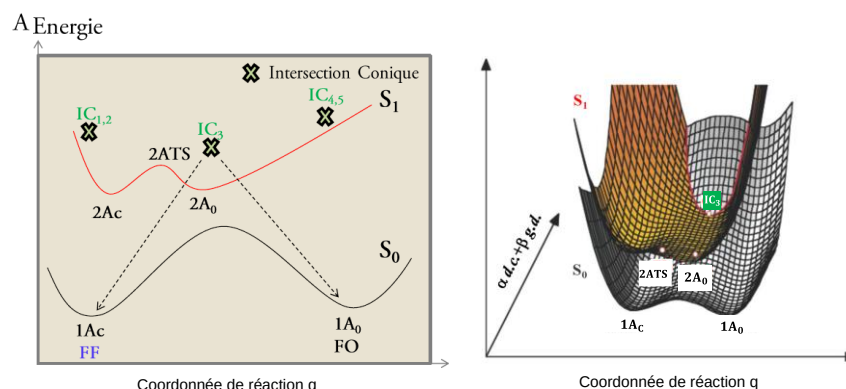


Figure 1.8. Potential energy diagram of the S_0 and S_1 states of diarylethenes along a reaction coordinate q , shown in two dimensions (left) and three dimensions (right).

For the cyclization reaction, excitation to the S_1 state by UV irradiation is followed by relaxation to the local minimum $2A_0$, then passage through CI_3 to reach the $1AC$ state (S_0 of the closed form, CF). Excitation may also lead to transitions through CI_4 or CI_5 before the relaxation of $2A_0$. In this case, the system returns to the ground state $1A_0$. This mechanism accounts for the rapidity of the cyclization process (a few picoseconds), the high QY, and the absence of temperature dependence of the latter. Moreover, some molecules remain in the S_1 state for several tens of picoseconds, making fluorescence properties conceivable.

For the cycloreversion reaction, excitation may either lead to relaxation toward CI_1 and CI_2 , or to relaxation toward $2AC$ (the local minimum of S_1 corresponding to the closed form, CF). In the first case, the system returns to the ground state (S_0 of the CF), whereas in the second case, it may overcome the activation barrier to reach CI_3 and then $1A_0$. The other de-excitation pathways, however, do not lead to CI_3 . This explains the lower QY compared to cyclization, as well as its

temperature dependence. Furthermore, the absence of fluorescence in the CF is explained by the efficient relaxation through CI₁ or CI₂, which prevents the system from remaining long enough in the S₁ state.

However, this major study suffered from a limitation related to the use of the CASSCF level of theory alone, without correction for the loss of electron correlation resulting from the truncation of the active space.

Electronic Correlation taken into account. With this objective, Perrier et al. (2013) carried out high-level calculations at the CASSCF/6-31G(d) level, complemented by corrective CASPT2 (Complete Active Space Second-Order Perturbation Theory) computations, focusing on the photocyclization process (see **Figure 1.9**) for model DTEs (without fluorine substituents), both in the normal and inverse forms.

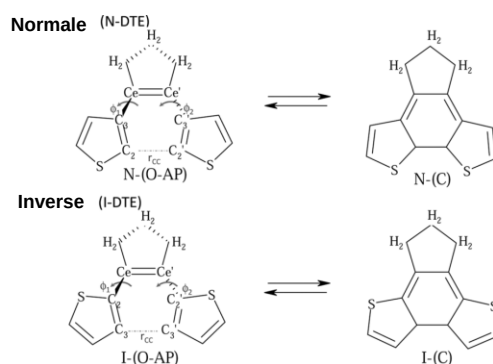


Figure 1.9. Representation of the two DTEs: normal (top) and inverse (bottom).

The authors were able to optimize both the excited states (S₂ and S₁) and the ground state (S₀), as well as the transition states (TS) and the CIs. Both P and AP conformers were considered. Moreover, they identified two conical intersections, CI(S₂/S₁) and CI(S₁/S₀), corresponding to the molecular geometries shown in **Figure 1.10**. Several important conclusions arise from this study. Starting from the OF, regardless of the electronic excitation (S₁ or S₂), there exists a reaction pathway leading to the CF. It is not necessary to pass through S₁^{rel}, N-S₁(O-AP) to reach the reactive CI (see **Figure 1.10**). The equilibrium geometries of the electronic states for the P conformer vary only slightly. The transition state between the OF and CF on the S₁ surface, N-S₁(O-AP) in **Figure 1.10**, is significantly lowered compared to the previous study. That said, the

authors suggest that this topological point should ideally be re-optimized at the CASPT2 level (a calculation that is currently almost unfeasible).

It will therefore be important to take these results into account in the following chapters.

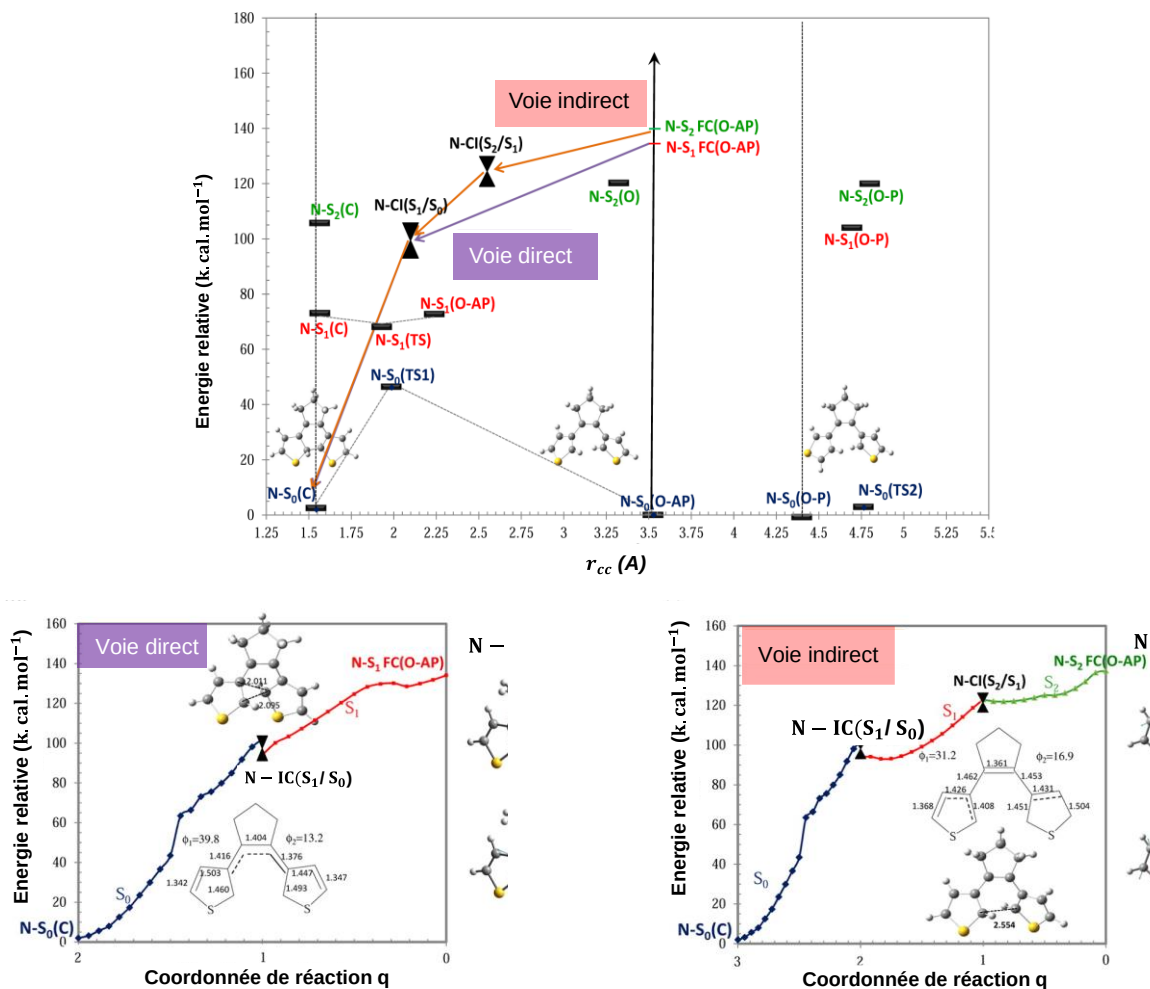


Figure 1.10. (Top) Potential energy surfaces of the S_0 , S_1 , and S_2 states of normal diarylethenes as a function of the reactive carbon distance. (Bottom) Illustration of the two pathways: direct and indirect, via CIs.

1.4.2 Ultrafast Spectroscopies to Study Photocyclization

Once the key topological features have been established computationally, it becomes essential to probe the population dynamics underlying photocyclization and photoreversion processes. Time-resolved spectroscopic techniques enable the investigation of these processes across timescales ranging from femtoseconds to seconds. In the following, we briefly summarize the main findings reported in the literature for both processes and highlight the existence of alternative pathways in addition to the commonly accepted mechanisms. In recent years, the photocyclization mechanism, both in solution (20–23) and in the crystalline phase (24,25), has been extensively explored using a combination of complementary spectroscopic approaches.

Photocyclization via Franck-Condon State. In the late 1990s, transient absorption spectroscopy studies of various DAEs in solution reported photocyclization times, following excitation to the S_1 (OF) state, on the order of 1-10 ps (20,26,27). However, in more recent years, several groups have reported significantly shorter timescales. Aloïse et al. observed photocyclization times ranging from 90 to 150 fs for a series of inverse DTEs (28). Contrary to the mechanism proposed by Boggio-Pasqua, they suggested that cyclization may occur directly from the FC region via a CIs. Similarly, Miyasaka et al. reported a time constant of 450 fs for the BT molecule (29). Similarly,

Parallel Conformer. Irie and Miyasaka demonstrated that the P conformation is responsible for the photochromic fluorescence. Upon UV excitation, the S_1 P excited state is populated and relaxes with a time constant of approximately 150 ps, either to the ground state or via intersystem crossing to a triplet state with a lifetime of about 1 μ s (**Figure 1.11**). Since both the fluorescence lifetime and the cyclization QY are independent of the solvent viscosity, it can be concluded that the P conformation does not participate in the cyclization process. Furthermore, experiments conducted under inert atmosphere conditions show no variation in the cyclization QY, indicating that the triplet state does not play a significant role in the cyclization mechanism. In contrast, Aloïse et al. investigated an inverse DTE system constrained by polyester bridges, where the AP:P conformational ratio was modulated. In this study, fluorescence was still observed even in the absence of the P conformer, suggesting that fluorescence emission may originate from other conformational states or involve alternative relaxation pathways.

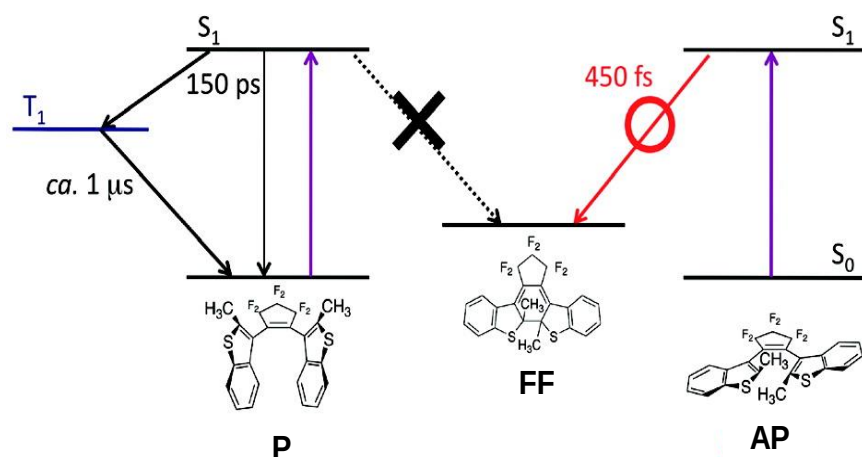


Figure 1.11. Photophysics of *P* vs Photochemistry of *AP* conformers for *BT* molecule (29).

Photocyclization of molecule *DAEc* in solution (29) was further reinvestigated by Hamdi et al. (30) using both fs-TA and chemometric data analysis to elucidate the photochemical behavior of the *P* and *AP* conformers. It has been shown that photocyclization the overall deactivation pathway of both *AP* and *P* conformers of the *OF* (1:1 in solution) has been resolved and rationalized starting from the *FC* region to the ground state recovery. For the photo-excited *P* conformer, after ultrafast relaxation (B200 fs) towards the *S*₁ relaxed state, an expected ISC occurred (55 ps) to produce a triplet state, 3*P*, the latter relaxing within 2.5 ms. Concerning the *AP* conformer, the photocyclization reaction is reported to proceed immediately (100 fs) starting from the *FC* region while the relaxed singlet state is populated in parallel. For the first time, we discovered that the latter state evolves through an unexpected ISC process (1 ps) giving rise to a second triplet state, 3*AP* (**Figure 1.12**)

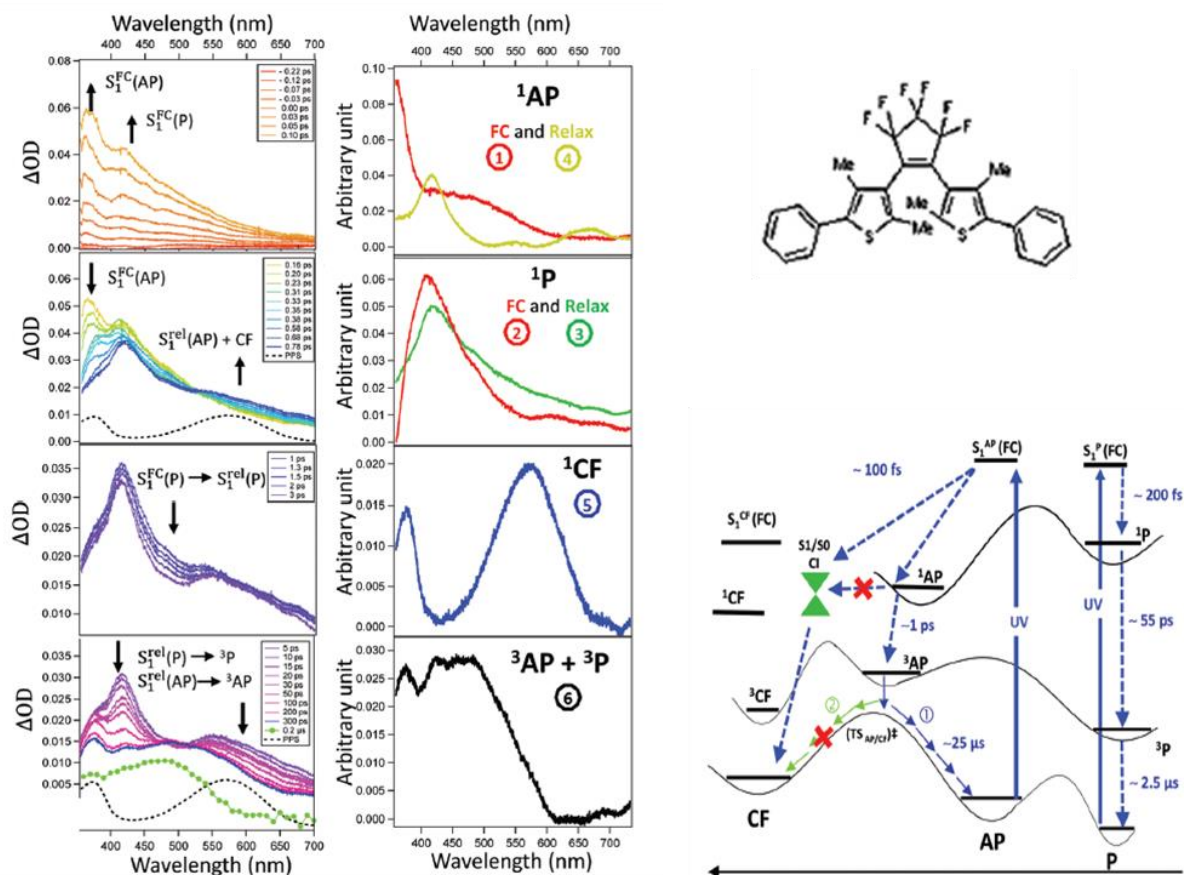


Figure 1.12. (left) Subpicosecond time-resolved absorption spectra of DTE (left) in chloroform using 320 nm excitation wavelength (all spectra are corrected from the GVD), and spectra (right) of the 6 excited state species of DTE identified by MCR-ALS analysis. (left) Schematic representation of photochemical pathways for AP and P conformers after UV excitation.

1.4.3 Ultrafast Spectroscopies to Study Photoreversion

Transient spectroscopy applied to the FF with visible laser excitation makes it possible to study the photoinduced ring-opening mechanism (which requires breaking the C-C bond). As we have seen, theoretical calculations predict an activation barrier between the FC region and the CI leading to the OF. In general, publications investigating the photoreversion process by ultrafast spectroscopy report bi-exponential decays of 4 ps and 22 ps, as observed for the BT molecule (in hexane) studied by transient absorption and fluorescence. Indeed, the temperature dependence (or not) of the cyclization and ring-opening reactions of BT was indicative. The ring-opening reaction varies significantly with temperature over the range 253-343 K, whereas this parameter has no effect on the cyclization process. This indicates that the ring-opening reaction encounters an energy barrier in the excited state and proceeds via the same CI as the cyclization reaction (see **Figure 1.13, left**). In the same vain, the cycloreversion dynamics of the DAEC molecule were

studied by Ward et al. (31) using ultrafast absorption spectroscopy with a two-photon pump (pump-repump-probe) setup. The transient data were interpreted in terms of ultrafast relaxation from the FC region (~ 100 fs), relaxation of the excited S_1 state, crossing of an energy barrier (~ 3 ps), final internal conversion (IC), and return to the ground state (~ 9 ps). At this stage, no spectral signature distinguishing the FC region from a relaxed state has been proposed (see **Figure 1.13, right**). This point will be important for the next chapters.

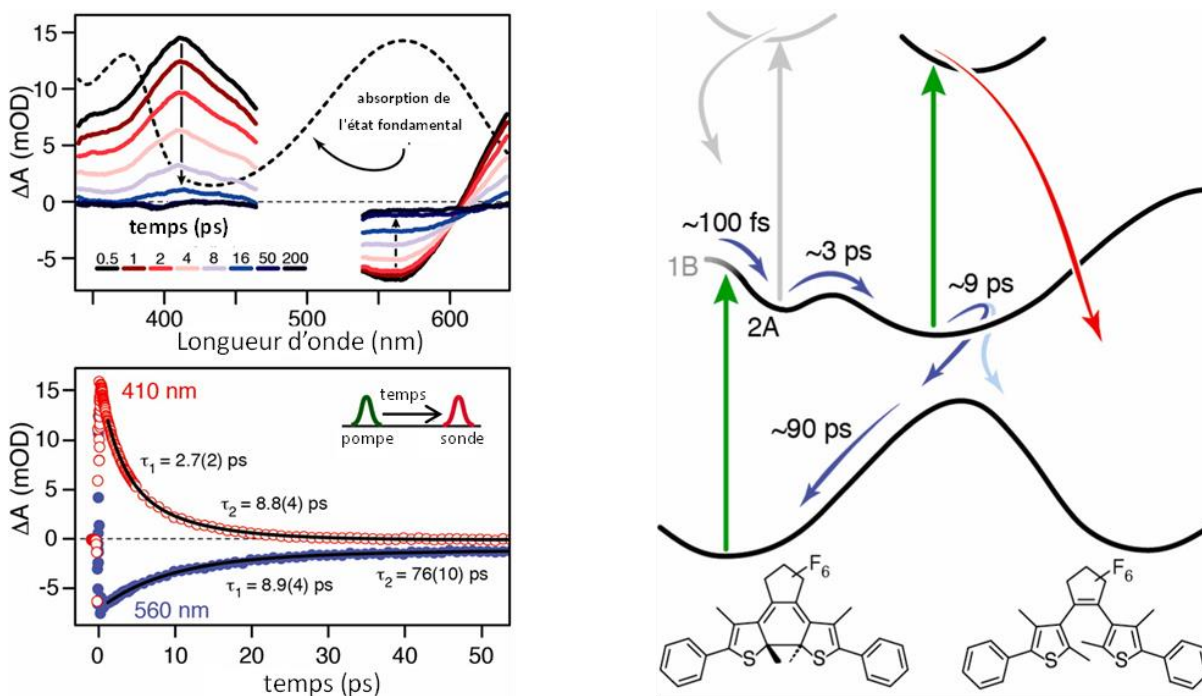


Figure 1.13. (left) Transient absorption signal of the closed form after laser excitation at 500 nm. The upper panel shows the transient spectra together with the ground-state absorption spectrum of the closed form. The lower panel shows the temporal evolution at 410 nm (red $\circ$) and 560 nm (blue $\bullet$). (right) Schematic representation of the reaction dynamics for one-photon and two-photon excitation of the closed form. Straight arrows represent optical excitation and re-excitation at 500 nm; blue arrows indicate reaction pathways, with time scales determined experimentally.

1.5. Focusing on Bis-Pyridyl DAE Supramolecular System

About DAE1 molecule. This thesis is dedicated to different molecular system that originate from DAE1 and DAE2 starting building blocks. During the last 25 years, several groups have used DAE1 and DAE2 to build photoresponsive supramolecular diad or more sophisticated assemblies. In 2001, as a pioneering work, Branda et al. reported a supramolecular dyad combining DAE1 with a ruthenium porphyrin (**Figure 1.14, a**). This group demonstrated that: (i) despite the strong Soret and Q bands of the porphyrin moieties, the spectral signatures of the CF of the photochromic units were distinguishable (**Figure 1.14, b**); and (ii) the emission properties of the porphyrin moieties were switchable according to the state of the photochromic units (**Figure 1.14, c**). This latter result indicated that the emission behavior of the porphyrin is clearly sensitive to the linearly π -conjugated chromophore created upon ring-closing of DAE1.

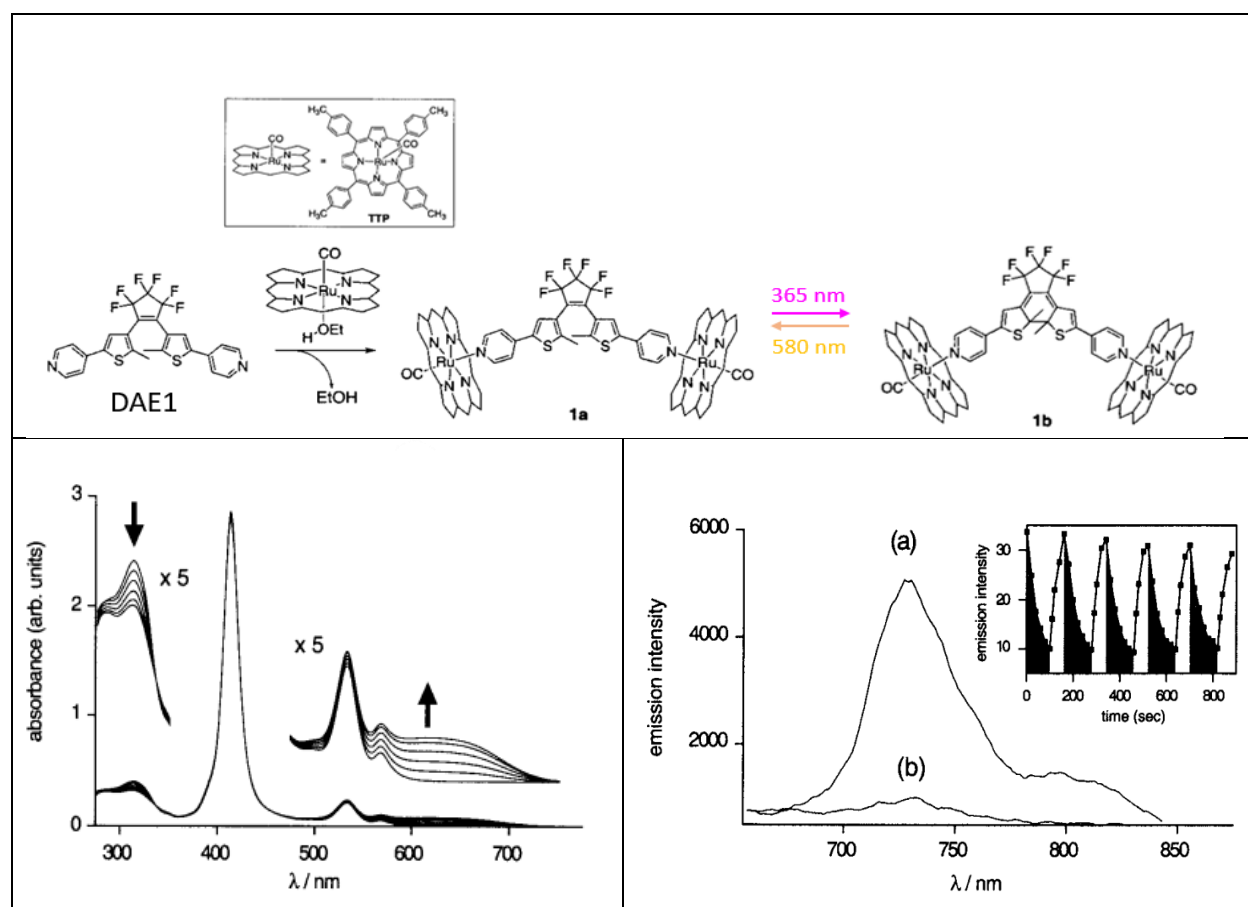


Figure 1.14. (a) Chemical structures of the OF (1a) and CF (1b) isomers of DAE1, along with reversible photoisomerization triggered by 365 nm and 580 nm irradiation; (b) Changes in the UV-vis absorption spectra of a benzene solution of 1a (6×10^{-6} M) upon irradiation at 365 nm for various durations (0, 210 s); (c) Emission spectra of 1a and 1b (1×10^{-6} M) in benzene, showing modulated fluorescence upon alternate irradiation at 365 nm and >580 nm. Inset: Emission intensity oscillation over time indicating reversible switching.

Similar supramolecular complexes using Pt(II) atoms have been used to modulate the DNA interacting properties and cytotoxic behaviors (32). In 2016, DAE1 molecules have been used to generate Rhombicuboctahedral Sphere by combining photochromic molecules in CF with 24 Pd(II) cations (see **Figure 1.15**). Interestingly, this complex's supramolecular architecture was still photochromic with some unexpected properties. Unlike the kinetic of photoreversion (closed to open), the kinetic of photocyclization (open to closed) was strongly slow down (see **Figure 1.15**) with an additional induction period. This effect was rationalized by the presence of quasi P conformer (twisted conformation) that required long and gradual shifting of the dynamic equilibrium between P and AP conformers (33).

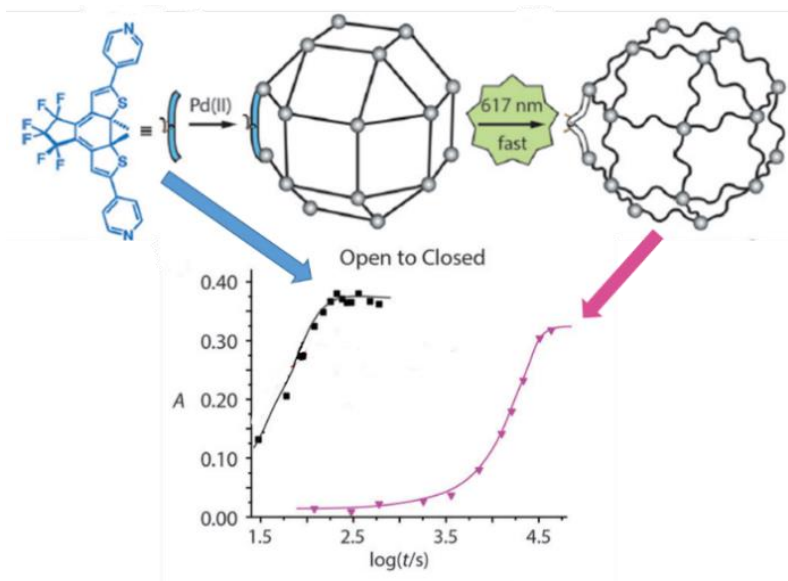


Figure 1.15. Photochromic Behavior of a DAE1-Based Rhombicuboctahedral Supramolecular Cage.

About DAE2 molecule. In the literature, the DAE2 molecule has been less studied. Fu et al. reported a light- and acid-responsive luminescent system combining DAE2 with a sulfonate-merocyanine photoacid (**Figure 1.16**). When the photoacid generates protons under light irradiation, the protonated OF of DAE2 (OF-DAE2·H⁺) shows visible fluorescence, while all other forms (OF-DAE2, CF-DAE2, and CF-DAE2·H⁺) remain non-emissive. This system was used to create logic gates and fluorescent inks, showing promise for information encryption.

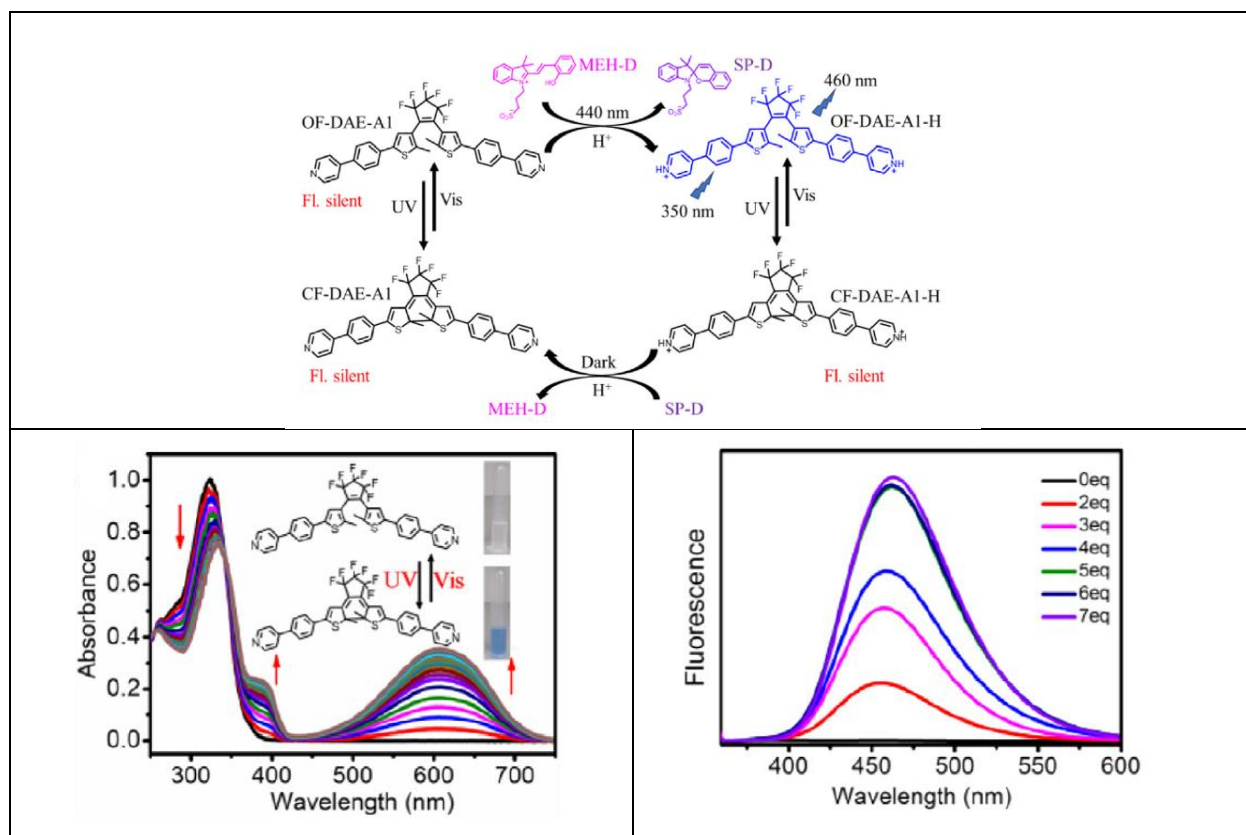


Figure 1.16. a) illustration of multi-stimuli-responsive luminescent system. b) UV-Vis spectra of DAE-2 ($10\mu\text{M}$) in DCM upon 254 nm light excitation. c) Fluorescence spectra ($\lambda_{\text{ex}} = 350\text{ nm}$) of DAE2 with different equivalents of MEH-D (photoacid) after 10 s of 440 nm light irradiation (trigger of H^+ release).

DAE1-POM Systems. In 2018, Chris Ritchie Group in Australia, has combined one DAE1 molecule with two Co(II) borotungstates polyoxometalate anions. The new supramolecular assembly was thoughtfully characterized by a battery of analytical techniques (NMR, electrospray ionization quadrupolar TOF-MS, SAXS...etc). The supramolecular assembly was thermodynamical stable and clearly photochromic with however very low QYs. Indeed, the QY for photocyclization and photoreversion were 0.097 and 0.00022 far from the typical values of classical DAE (see **Figure 1.17**). These poor performances were attributed to the significant electron-withdrawing capacity of the coordinated polyanion.

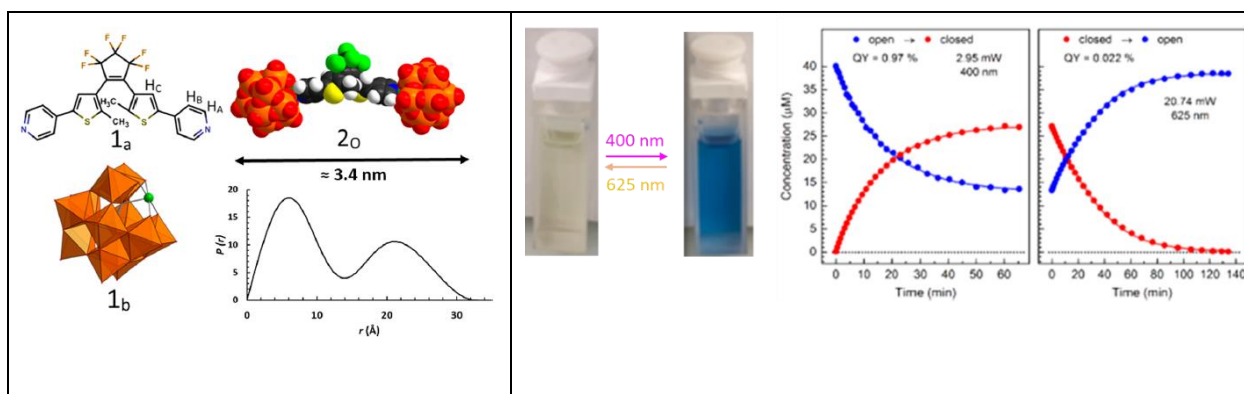


Figure 1.17. (Left) ChemDraw and polyhedral representations of the pyridylcontaining diarylethene ligand ($C_{25}H_{16}N_2F_6S_2$) (1a) and the polyanion $[B_{III}W_{VI}IO_{39}Co_{III}]^{6-}$ (1b) that constitute the photochromic coordination complex $[(C_{25}H_{16}N_2F_6S_2)(BW_{11}O_{39}Co_{III})_2]^{12-}$ (2o), shown in a space-filling diagram. The coordinatively unsaturated Co(III) ion of 1b is shown as a green sphere. Pair-distance distribution function analysis of experimental SAXS data (bottomright of 2o) indicates that the dominant structure of 2o in solution is that of monodispersed molecular dumbbells in the photoactive conformation. Color code: carbon, black; hydrogen, white; nitrogen, blue; boron, pink; cobalt, dark green; fluorine, lime green; sulfur, yellow; oxygen, red; tungsten, orange. (Right) Change of color due to photochromic equilibrium together with UV-Vis photokinetic curves.

More recently, Chris Ritchie Group in collaboration with the LASIRE laboratory have investigated a more sophisticated DAE1-POM system that consists on three DAE1 molecules combined with the trilacunary heteropolyoxomolybdate $[PMo_9O_{31}(pyridine)_3]^{3-}$ to yield a molecular capsule/cage $[(PMo_9O_{31})_2(DAE)_3]^{6-}$. X-ray structure have been obtained showing that the three DAE1 in AP conformation are c linked in the both sides via covalent Nitrogen-Molybdenum bonds (**Figure 1.18**).

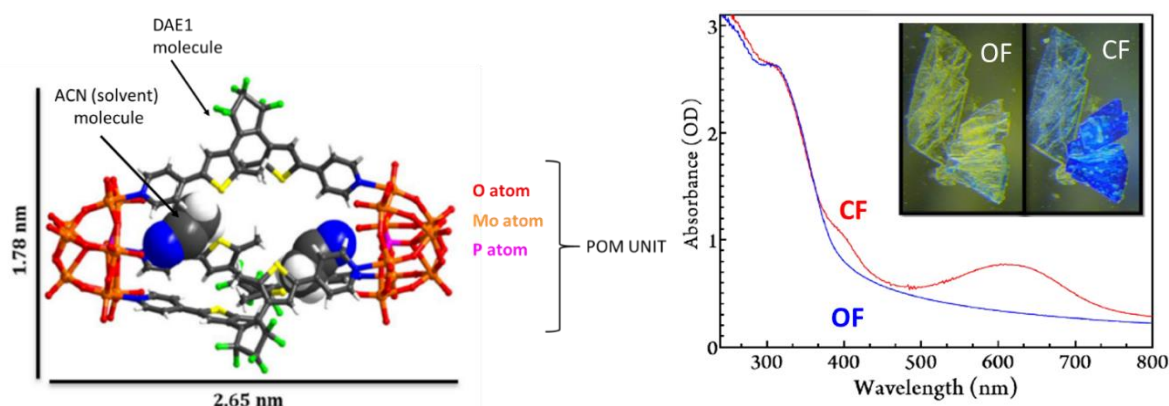


Figure 1.18. Graphical representation of the molecular capsule $(DAE1)_3-(POM)_2$ with dimensions obtained from single crystal X-ray diffraction structure determination. Solid-state transmittance Spectroscopy of and optical photographs of $(DAE1)_3-(POM)_2$ in OF and CF in crystalline forms.

Apart, classical analytical techniques, the system $(\text{DAE1})_3\text{-(POM)}_2$ has been analyzed with spectroelectrochemistry, fs-TAS and state-of-the-art DFT calculations. In **Figure 1.19**, the spectroelectrochemical results are displayed. Cyclic voltammetry conducted on $(\text{OF})_3\text{-(POM)}_2$ when cycling toward positive potentials reveals an irreversible two-electron oxidation at ca. 1.26 V vs. SCE (**Figure 1.19**), while a quasireversible reduction peak is noted at 0.77 V and a peak with low intensity is evident at ca. -0.50 V. The wave at 1.26 V is attributed to the oxidation of the OF of the DAE subunits to yield the radical cation $(\text{OF})_2(\text{CF})^+$ form of the ligand within the complex. The radical cation can be reduced at 0.77 V, returning the species to the starting state $((\text{OF})_3\text{-(POM)}_2)$ or can be converted via radical coupling to $(\text{OF})_1(\text{CF})_2^{2+}$. The reduction of this oxidized species is achieved at ca. -0.50 V. Thus, for potential well below 1.26 V and under UV-visible illumination, the solution is in the steady-state composed of a mixture of $((1(\text{OA})_x(\text{C})_z); x+z=3)$ driven by the equilibrium between the open and the closed form of the DAE subunits (blue-curve, **Figure 1.19**). In fact, the spectroelectrochemical results have been decisive to understand the ultrafast spectroscopic results.

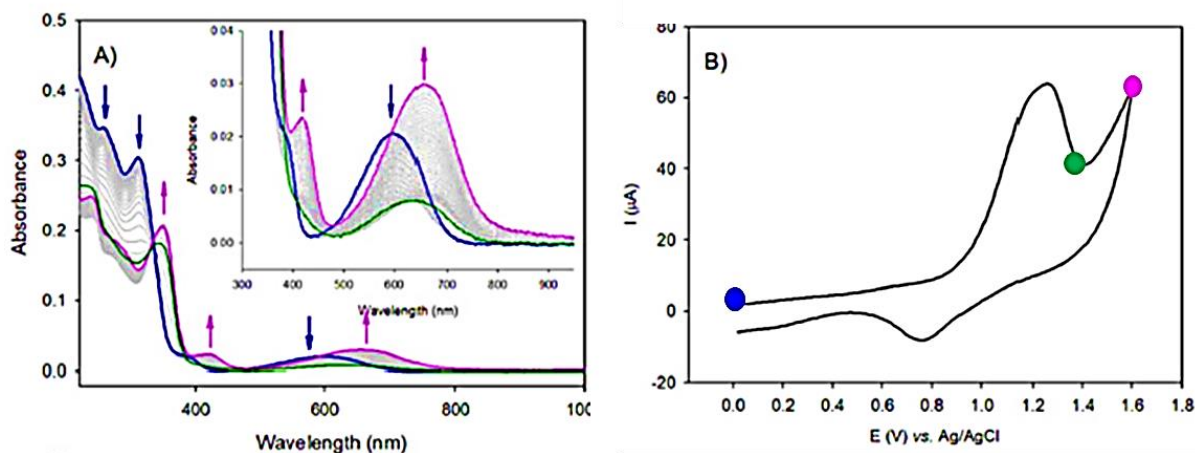


Figure 1.19. Spectroelectrochemical Characterization of the $(\text{DAE1})_3\text{-(POM)}_2$ System.

The fs-TAS of $(\text{DAE1})_3\text{-(POM)}_2$ in acetonitrile (ACN) is displayed on **Figure 1.20**. The data are displayed according to three distinct temporal windows. After the expected ultrafast photocyclization (first temporal window) and expected vibrational relaxation (second temporal window), it has been found that a successive process occurred with the rise of the new feature peaking near 560 nm. Such process has been recognized as a CT from the DTE to the POM units. Indeed, Interpretation of spectral features observed in the transient data in conjunction with spectroelectrochemical analysis indicates that the 560 nm band along with the lateral shoulder at

520 nm is related to the triplet spectra obtained for thiophene fragment indicated. Furthermore, we can assign the second broad band at 640 nm as the DAE radical cation (DAE1)^{•+}, which we suggest coincides with the absorption band of the reduced POM identified during the spectroelectrochemical analysis. Using a linear combination of normalised (DAE(C)), (L1) normalised triplet, (DAE1)^{•+}, and reduced (POM)⁻ spectra, a qualitative reconstruction of the normalised transient trace at 1000 ps was proposed, see **Figure 1.20** right. In summary, when the molecular capsule (1) is excited with UV light within 60 ps the photochromic process is completed for one DAE unit, followed by charge separation and electronic decoupling of the thiophene moieties. We propose that this first electrocyclisation and the resulting asymmetrisation of the assembly induces stretching of the remaining two DAE ligands and electronic decoupling of the DAE, resulting in the characteristic thiophene fragment photophysics described for (L1) and charge separation yielding (DAE⁺ and POM⁻). In this paper, under continuous illumination, it has been postulated that (CF)₃-(POM)₂ is obtained due to the sequential ring-closure of each DAE rather than via simultaneous ring-closure.

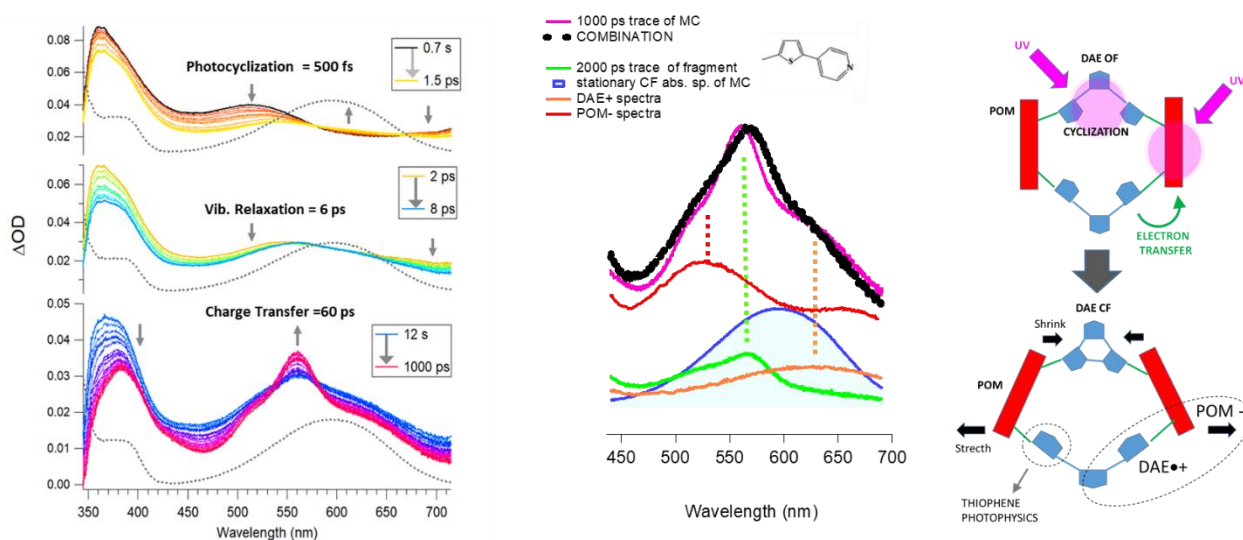


Figure 1.20. (Left) fs absorption data for (OF)₃-POM₂ in dry ACN for a laser excitation of 330 nm displayed as three separated temporal windows [0.7–1.5 ps] (top) [2–8 ps] (middle) and [12–1000 ps] (bottom). The absorption spectra for the PPS solution is appended (gray dashed line) for comparison. (Right) Qualitative Reconstruction of the transient trace of at 1000 ps (Figure 5) making a linear combination with a CF spectrum, the transient trace of L1 (2000 ps-Figure S18); the spectroelectrochemical traces for POM⁻ and POM^{•+} spectra.

In this thesis, we will reinvestigate this molecular capsule but with several challenges: i) one need to identify the Back Charge transfer (BCT) process by probing the system beyond the 1 ns delay time ii) during fs-TAS experiments, one need to explore a broader region in order to gain more insights about the overall process. iii) The photoreversion must be investigated.

Chapter 2. Experimental Methods and Characterization.

This chapter introduces the molecular systems investigated in our study, all of which are based on diarylethene photochromic cores. These systems are categorized into two main groups: (i) Simple DAE derivatives, which serve as fundamental photoresponsive units; and (ii) Complex hybrid assemblies, in which the DAE units are integrated with either polyoxometalate clusters or polymeric porphyrins, thereby enhancing their electronic and photophysical properties.

Experimental studies were conducted on samples prepared either in solution, based on solubility considerations determined by the synthetic groups, or as thin films for solid-state investigations. Steady-state spectroscopic characterizations, including UV-Vis absorption and emission studies, were performed to probe the ground-state properties. In a complementary way, the excited-state dynamics were subsequently investigated through femtosecond transient absorption spectroscopy, supported by complementary Density Functional Theory and Time-Dependent Density Functional Theory calculations to provide theoretical insights into the experimental results.

2.1. Materials and Studied Systems

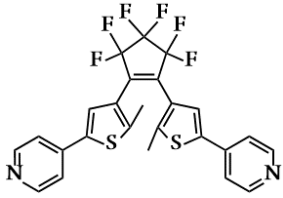
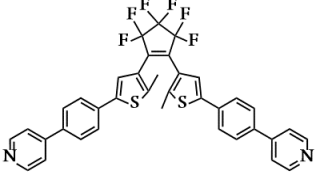
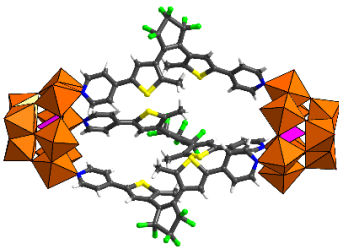
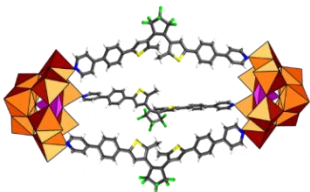
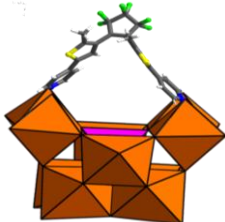
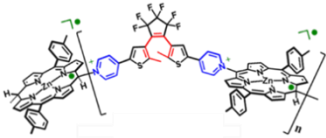
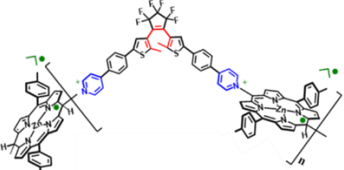
This study examines seven photochromic molecules and macromolecular systems synthesized by two distinguished research groups. The complete list of these photochromic systems is presented in **Table 2.1**.

The first group, led by Professor Chris Ritchie at the School of Chemistry, Monash University (Australia), developed the two parent diarylethene molecules, DAE1 and DAE2. These compounds contain terminal pyridyl nitrogen atoms that act as anchoring sites, making them fundamental precursors for the more elaborate architectures discussed later. In other words, DAE1 and DAE2 represent the photochromic cores from which the subsequent systems were derived.

Based on their earlier studies, Ritchie's group extended this work by combining the DAE molecules with polyoxometalate (POM) units to form larger assemblies. By bridging two POM fragments in a face-to-face arrangement with three DAE linkers in between, they obtained molecular cages, designated MC1 (from DAE1) and MC2 (from DAE2). In these cages, all DAE units are expected to adopt the AP conformation, which is the photoactive geometry. In parallel, a 1:1 complex between a POM and a single DAE1 molecule was prepared, forming a basket-like structure named MB, where DAE1 adopts a P conformation. Among these assemblies, DAE1 and MC1 had already been reported in the literature, while DAE2, MC2, and MB1 were newly developed as part of this work.

Within the same collaborative framework, Ritchie's group provided DAE1 and DAE2 samples to Professor Laurent Ruhlmann's team at the LECPCS, University of Strasbourg (France), to initiate the synthesis of new photochromic electropolymers, P1 and P2, respectively. These polymers incorporate the DAE cores into extended conjugated frameworks, and their synthesis and characterization are detailed in the following sections.

Table 2.1. List of the DAE-based molecules and polymers studied in this work.

Molecule abbreviation	Structural Code	Structural formula	Molecular Weight (g/mol)
DAE 1	$C_{25}H_{16}N_2F_6S_2$		522.53
DAE 2	$C_{37}H_{25}N_2S_2F_6$		674.72
MC1	$TBA_6[(PMO_9O_{31})_2(C_{25}H_{16}F_6N_2S_2)_3]$		5803.42
MC2	$TBA_6 (PMO_9O_{31})_2(C_{37}H_{25}F_6N_2S_2)_3]$		6259.72
MB	$TPP_3[(PMO_{10}O_{34})(C_{25}H_{16}N_2S_2F_6)]$		3075.06
P1	Poly-DAE(Py ⁺) ₂ ZnT2IsoP [•]		-
P2	Poly-DAE(ph-Py ⁺) ₂ ZnT2IsoP [•]		-

2.2. Molecules Synthesis and Sample Preparation

2.2.1 Synthesis of all DAE derivatives

DAE1 and DAE2. The diarylethene derivatives DAE1 and DAE2 were synthesized following established procedures. The synthesis of DAE1 was carried out by Ritchie et al. group according to a previously published method, the reaction pathway is shown in **Figure 2.1** (33). A complete description of the experimental conditions and purification steps undergo on this molecule can be found in the supplementary section of this article (34).

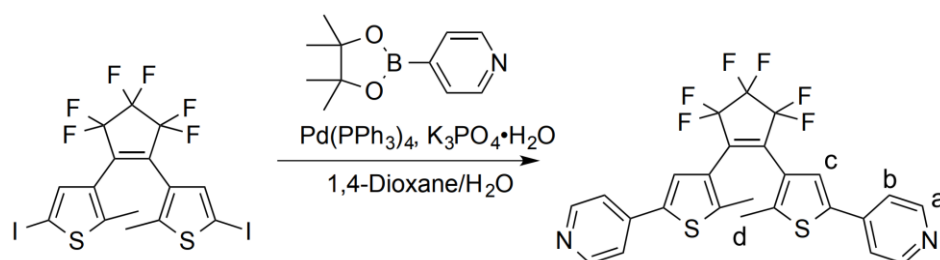


Figure 2.1. Synthetic route for the preparation of DAE1.

In contrast, the synthesis of DAE2 followed a modified methodology developed by the same research group. The corresponding reaction pathway is illustrated in **Figure 2.2**, with further experimental details provided in this thesis (35).

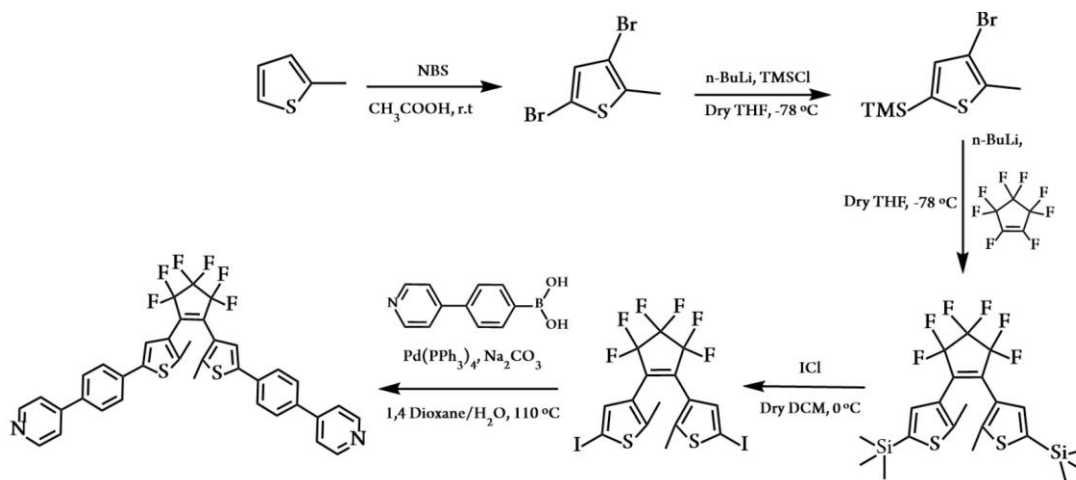


Figure 2.2. Synthetic pathway for the preparation of DAE2.

Molecular Cages, MC1 and MC2. The synthesis of MC1 and MC2 was carried out using a refined strategy inspired by the work of Ritchie et al. (35). This method is based on a ligand-exchange approach in which the polyoxometalate (POM) component, specifically the heteropolyoxomolybdate unit $[\text{PMo}_9\text{O}_{31}(\text{py})_3]^{3-}$ (abbreviated as $\{\text{PMo}_9\}$), selectively coordinates with pyridyl-functionalized DAE ligands. Through a self-assembly process, this coordination leads to the formation of a stable, cage-like architecture, ensuring the exclusive binding of the photoactive antiparallel DAE rotamer to the POM framework.

The resulting supramolecular assembly consists of two $\{\text{PMo}_9\}$ units located at opposite ends, connected by three DAE ligands, thereby forming a POM-(DAE)₃-POM capsule. Depending on the specific DAE ligand used, two structurally distinct systems were obtained: MC1, incorporating DAE1; MC2, incorporating DAE2. This configuration not only stabilizes the desired photoactive geometry but also promotes enhanced electronic communication between the photochromic ligands and the POM framework.

MB. The synthesis of $[(\text{PMo}_{10}\text{O}_{34})_2(\text{C}_{25}\text{H}_{16}\text{N}_2\text{S}_2\text{F}_6)_2]^{6-}$ involves the stepwise assembly of one DAE1 ($\text{C}_{25}\text{H}_{16}\text{N}_2\text{S}_2\text{F}_6$) unit with one polyoxometalate clusters $[\text{TPP}_6(\text{PMo}_{10}\text{O}_{34})]$, arranged in a P configuration. Initially, DAE1 is functionalized at its reactive sites to enable selective attachment to the POMs. The reaction is carried out under controlled conditions, typically employing anhydrous solvents and an inert atmosphere to prevent unwanted side reactions. The coupling between DAE1 and the POM units is facilitated through coordination chemistry or covalent bonding strategies, resulting in a stable molecular structure. Following synthesis, the product is purified by chromatography and recrystallization. Comprehensive characterization is performed using UV-Vis spectroscopy, FTIR, NMR, and mass spectrometry, confirming the successful formation of MC-P with its parallel POM attachment (36).

ElectroPolymers P1 and P2. The synthesis of diarylethene-isoporphyrin copolymers, poly-DAE(Py)₂-ZnT₂isoP and poly-DAE(Ph-Py)₂-ZnT₂isoP, was achieved by Prof. Laurent Rhulmann group through the electropolymerization of zinc tetratolylporphyrin (ZnT₂P) in the presence of pyridine-substituted diarylethenes DAE(Py)₂ or DAE(Ph-Py)₂. These DAE units (DAE1/DAE2), previously described, are the same ones incorporated during the polymerization process. The electropolymerization was carried out within an optimized cyclic voltammetry

potential window ranging from -1.1 V to +1.0 V vs. the Saturated Calomel Electrode (SCE), allowing for the oxidation of ZnT₂P and the generation of radical cations that selectively couple with pyridine-functionalized DAE units. This process facilitated the formation of conjugated pyridinium-bridged architectures, while effectively preventing over-oxidation.

Polymer growth was systematically monitored using Electrochemical Quartz Crystal Microbalance (EQCM), confirming controlled film deposition in the range of 17-22 $\mu\text{g}/\text{cm}^2$. Further spectroscopic analyses confirmed the successful incorporation of both isoporphyrin and diarylethene units into the copolymeric framework, offering insights into their structural integration and photoresponsive behaviour in solution (36). The resulting filmed materials is presented below in **Figure 2.3**.

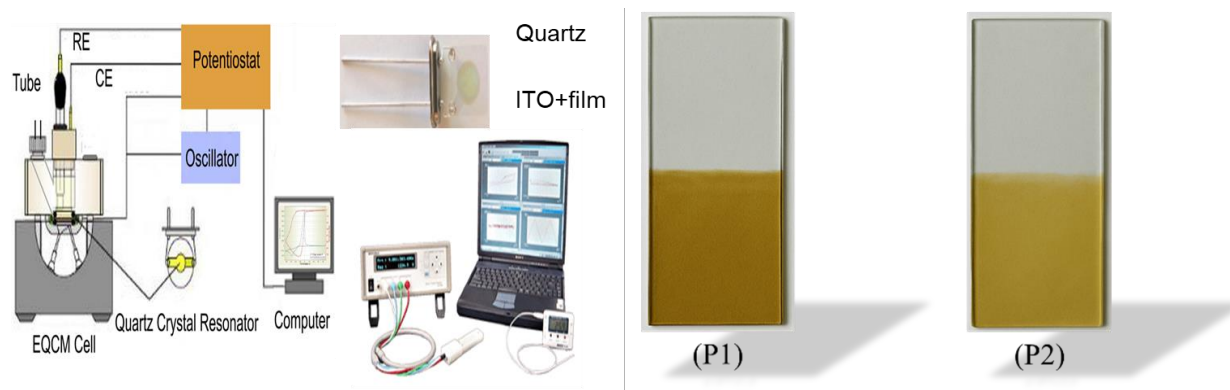


Figure 2.3. EQCM-monitored electropolymerization of P1 and P2 thin films on ITO glass.

2.2.2 Solvent Selection

The choice of solvent plays a crucial role in ensuring both the solubility and structural stability of the studied photochromic systems. Since the molecules investigated in this work include both discrete DAE-based assemblies and polymeric architectures incorporating POM and porphyrin components, a systematic solubility evaluation was performed prior to spectroscopic characterization. It is important to note that these solubility assessments were established in the doctoral studies of Dr. Manjiri Choudhari (35) and Dr. Ning Jiang thesis (36), whose results served as the reference for selecting the appropriate solvents.

DAE and MC Systems. The selection of an appropriate solvent was critical to ensuring both the stability of the POM capsules and the solubility of the DAE ligands in the simple and complex systems. Among the solvents evaluated, anhydrous ACN, dichloromethane (DCM), and dichloroethane (DCE) were identified as suitable options, offering good solubility and maintaining structural stability across all studied compounds (DAE1, DAE2, MC1, MC2, and MC-P). Ultimately, ACN was chosen as the universal solvent throughout this work due to its accessibility, practicality, and comparable performance to DCM and DCE.

P1 and P2 Systems. The selection of an appropriate solvent was essential for preparing stable solutions of the photoswitchable porphyrin/isoporphyrin copolymers, poly-DAE1-ZnT₂isoP[•] and poly-DAE2-ZnT₂isoP[•], particularly to preserve their structural integrity, radical stability, and photoresponsive properties. Dimethylformamide (DMF) was identified as the most suitable solvent, as it allowed complete dissolution of both copolymers.

2.2.3 Sample preparation for Spectroscopic measurements

DAE-based systems. Based on the solubility evaluation described above, anhydrous ACN was selected as the main solvent for all DAE-based molecular systems, including DAE1, DAE2, MC1, MC2, and MB1. In some experiments, anhydrous DCE was also used to compare the behavior of certain molecules in different solvent environments. Both ACN and DCE provided complete dissolution of the samples while preserving the integrity of the polyoxometalate frameworks. For all spectroscopic measurements, the powdered compounds were accurately weighed and dissolved in the appropriate solvent.

Polymer solid. The polymer films deposited on indium-tin-oxide (ITO) substrates were directly mounted in the optical path for solid-state measurements.

Polymer solutions. The polymer films electropolymerized on ITO slides were dissolved in DMF to obtain clear molecular solutions. Each coated ITO slide was immersed in DMF and gently handed until complete dissolution of the deposited polymer film was achieved. The resulting solutions were degassed with nitrogen for 30 minutes to remove dissolved oxygen prior to spectroscopic analysis. When oxygen-free conditions had to be maintained during measurements, a nitrogen-filled balloon was connected to the sample, ensuring oxygen-free conditions and preserving the stability of the radical isoporphyrin units.

2.3. Stationary Spectroscopic Techniques

2.3.1 UV-Vis absorption spectroscopy

UV-Vis absorption spectroscopy serves as a fundamental tool to investigate the optical properties and photochromic response of the studied photochromic systems (37). In this study, all UV-Vis spectra were recorded using an Agilent Cary 100Bio spectrophotometer in the 190-900 nm range, using 1 mm quartz cuvettes at room temperature (38). The lower detection limit of 190 nm reflects instrumental constraints, as light sources and detectors become inefficient in the deep UV region. The instrument was controlled using Cary WinUV software, known for its speed, flexibility, and reliability. The spectrophotometer is equipped with a deuterium lamp for UV wavelengths and a tungsten lamp for the visible region. A monochromator that isolates specific wavelengths to ensure accurate spectral resolution, and a photomultiplier tube (PMT) detector is used for its high sensitivity and fast response time (39). To ensure accurate baseline correction, a reference cuvette containing the same solvent as the sample was used.

2.3.2 Emission spectroscopy

In this study, emission measurements were performed using an Agilent Cary Eclipse fluorescence spectrophotometer, operating over a 200-1100 nm spectral range. The instrument is equipped with a pulsed xenon flash lamp, providing high-intensity excitation (40). The excitation wavelength was chosen based on the compound's absorption spectrum, typically at a strong absorption maximum to ensure efficient excitation. The choice of excitation wavelength also influences emission intensity and spectral characteristics, depending on whether higher or lower excited states are accessed. The spectrometer features a double monochromator system: one selects the excitation wavelength, and the other isolates the emitted light to improve spectral resolution. Emission is detected using a PMT, known for its high sensitivity and ability to amplify weak emission signals. To prevent interference from scattered excitation light, the detector is positioned at a 90° angle relative to the excitation beam. All measurements were conducted at ambient temperature using 1 cm quartz cuvettes, which ensure excellent optical transparency throughout the measured spectral region.

2.3.3 Quantum Yield Measurements

The kinetic measurements to deduce quantum yield were performed using an Agilent Cary 100 UV-Vis spectrophotometer. The reaction progress was monitored by recording time-dependent changes in absorbance at a typical wavelength of the CF (590 nm). To ensure homogeneous irradiation, the cuvette was placed on a magnetic stirrer equipped with a small stir bar, maintaining uniform mixing throughout the experiment (**Figure 2.4**). A 565 nm low pass optical filter was mounted at the entrance of the photodetector to restrict noise from the irradiated light during the measurement. The irradiation wavelengths were selected according to the absorption characteristics of the analyte, 310 nm for the OF and 550 nm for the CF.

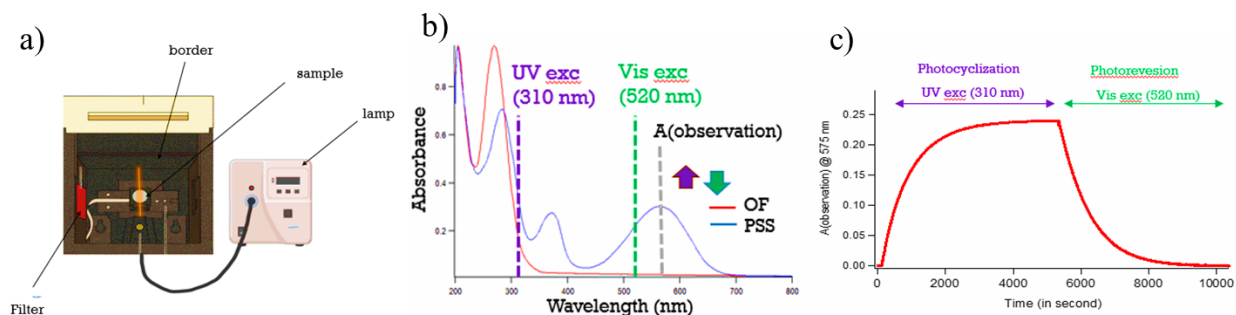


Figure 2.4. a) Schematic representation of the experimental setup used for spectro-kinetic measurements; b) Typical spectra of OF and CF; c) Spectrokinetic curves that will be fitted to deduce QY.

Absolute kinetic analysis (fitting procedure). Quantitative analysis of the kinetic data was performed using a fitting program implemented in IGOR Pro, developed by Métivier et al. (41). The model requires input parameters including the sample concentration and volume, excitation and observation wavelengths, mole fraction of the reactant (set to 1.0 for photocyclization), the power of the UV and visible lamps used for the ring-closure and ring-opening reactions, respectively, as well as the experimental time frame and the optical path length of the cuvette. The molar extinction coefficients of both isomers at the excitation and observation wavelengths were obtained from their steady-state absorption spectra. Thermal rate constants were assumed to be negligible.

The software numerically solves the coupled differential equations describing the time evolution of the OF (Concentration C_A) and CF (Concentration C_B) forms:

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = -\Phi_{B \rightarrow A} I_B^{\text{abs}} + \Phi_{A \rightarrow B} I_A^{\text{abs}} \quad (1)$$

where Φ_{A-B} / Φ_{B-A} refer to photocyclization/photoreversion yield four UV excitation or the reverse order for the visible excitation.

From this fitting, the photocyclization and photoreversion QYs are obtained along with the simulated temporal evolution of both isomer concentrations. Each reaction was analyzed separately: since the mole fraction of the OF is known at the onset of photocyclization, this reaction was fitted first, followed by the photoreversion process.

2.4. Spectroelectrochemistry (SEC)

SEC is a powerful technique that combines electrochemical control with spectroscopic monitoring, enabling real-time investigation of electronic and structural changes during redox reactions. In this study, in situ UV-Vis-NIR spectroscopy was employed to probe the redox behaviour of the studied copolymers by capturing their absorption spectra during controlled oxidation and reduction. This approach provided direct insight into their electronic transitions and associated structural modifications (36).

The experiments were conducted by Strasbourg University using an optically transparent thin-layer electrochemical cell, specifically designed to allow simultaneous electrochemical and spectroscopic measurements. The setup consisted of a gold (Au) mini-grid working electrode, a platinum (Pt) mini-grid counter electrode, and an Ag/AgCl reference electrode, with CaF₂ optical windows enabling efficient light transmission for spectroscopic analysis.

To investigate electrochemical properties, cyclic voltammetry (CV) was used to apply controlled potentials to the cell, initiating redox events (oxidation and reduction) in the copolymer films. These redox processes induced changes in the materials' electronic structures, which can be detected as shifts in the UV-Vis-NIR absorption spectra. The SEC system continuously monitored these spectral variations, establishing a direct correlation between the applied potential and the corresponding optical transitions.

By integrating CV and SEC, a comprehensive evaluation of the copolymers' redox behaviour was achieved. CV identified key redox potentials associated with electron transfer, while SEC spectroscopic data confirmed the related electronic transitions and structural transformations. This combined approach provided valuable insights into the electronic structure of the copolymers and highlighted their potential for applications in electrochemical and optoelectronic systems.

2.5. Femtosecond Transient Absorption Spectroscopy (fs-TAS)

While steady-state UV-vis spectroscopy provides valuable information about the final electronic states of photochromic systems, it lacks the temporal resolution required to capture ultrafast dynamics and transient intermediates (42). Many photophysical and photochemical processes occur on the femtosecond to picosecond timescale, far outside the capabilities of conventional spectroscopic techniques. To overcome this limitation, ultrafast spectroscopic techniques most notably fs-TAS are employed. This technique enables real-time monitoring of excited-state dynamics by recording time-resolved changes in a molecule's absorption spectrum following photoexcitation with sub-picoseconde resolution.

At the LASIRE laboratory (University of Lille), fs-TAS has been a central research tool for more than two decades. The group was among the first in France to implement fs-TAS using a home-built Ti:sapphire regenerative amplifier system, which enabled pioneering studies on photoinduced molecular dynamics (22,23,28,34,43–46) . Since 2022, a new commercial fs-TAS setup has been installed at LASIRE, providing an extended temporal window and enhanced spectral detection capabilities. The following section presents the operating principle of the femtosecond pump-probe technique used throughout this work.

2.5.1 General Introduction: pump probe configuration

fs-TAS operates on the pump-probe principle, allowing real-time investigation of ultrafast photoinduced processes. In general, a femtosecond pump pulse first excites the sample, promoting molecules from the ground state to an electronically excited state ($A + \text{pump} \rightarrow A^*$). After a controlled delay, a probe pulse passes through the sample, detecting the absorption of the excited state ($A^* + \text{probe} \rightarrow A^{**}$) (47). Note that the probe can also induce stimulated emission. By systematically varying the delay time between the pump and probe pulses, a time-resolved map of the molecular dynamics is constructed. This provides detailed insights into the formation, transformation, and decay of excited states and short-lived intermediates with femtosecond temporal resolution.

Modern fs-TAS systems typically use Ti:sapphire or Yb-doped femtosecond lasers as the primary source. Their output pulses are spectrally tuned via nonlinear optical processes such as

optical parametric amplification (OPA), enabling broadband excitation and probing across the UV-Vis-NIR spectral range.

To generate pulses with durations on the order of tens of femtoseconds, mode-locked oscillators are used to synchronize multiple laser modes in phase. The pulses are then amplified using chirped pulse amplification, a technique that increases pulse energy while preventing optical damage to system components. This configuration allows fs-TAS to achieve both high temporal and spectral resolution, making it a powerful method for tracking excited-state dynamics in real time (48).

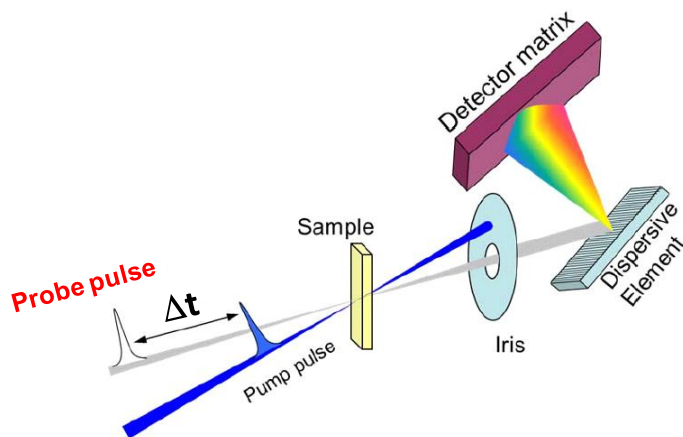


Figure 2.5. Pump-probe configuration for fs-TAS technique.

2.5.2 Experimental fs-TAS set-up used in this study

fs-TAS measurements were performed using a HELIOS pump-probe spectrometer (Ultrafast Systems), a modular setup optimized for ultrafast kinetic studies and broadband spectral detection. This system is fully compatible with amplified femtosecond laser sources that offers high temporal precision alongside with excellent spectral resolution. One of its major advantages is its fully automated optical alignment and spectral calibration, which improves measurement reproducibility and significantly reduces setup time. A schematic representation of the fs-TAS experimental setup is shown in **Figure 2.6**.

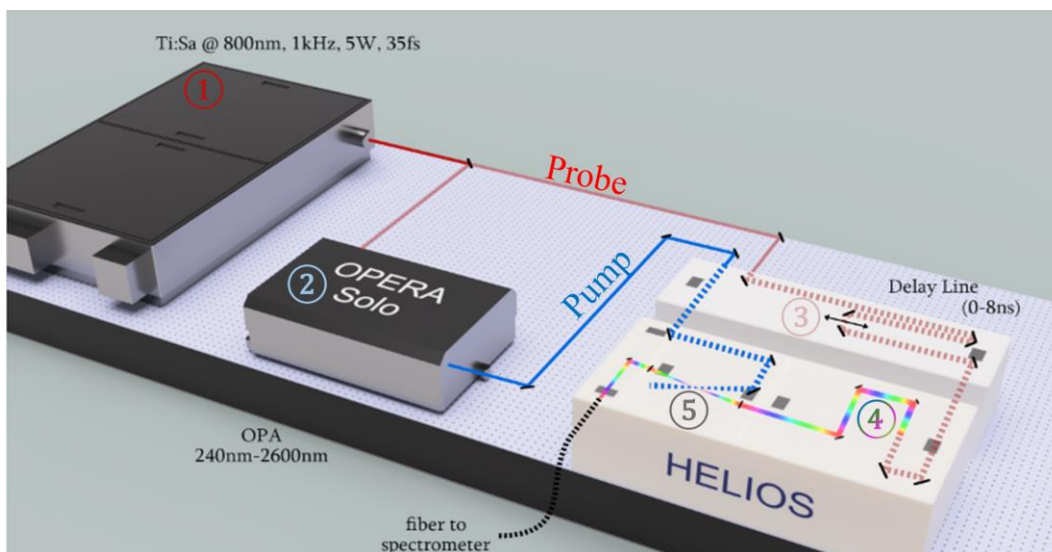


Figure 2.6. 3D schematic representation of the experimental fs-TAS setup used in this study.

Pump Beam. The laser source equipped in the system was a Ti:sapphire regenerative amplifier, ①, delivering femtosecond pulses at a 1 kHz repetition rate, with a pulse duration of 35 fs, average power of 5 W, and a central wavelength of 800 nm. The output beam was split into two paths: One part was directed into an optical parametric amplifier (OPA, ②) to generate tunable pump pulses across a wide spectral range (240-2600 nm), enabling excitation in the UV, visible, and near-infrared regions. In this study, two excitation wavelengths, in the UV (between 310-330 nm) or in the visible (between 570-660 nm) were selected based on the steady-state absorption profiles of the investigated compounds. An example of the pump pulse spectrum obtained after the OPA setup is shown in **Figure 2.7** for a target wavelength of 425 nm. A Gaussian fit yields a central wavelength of 425.4 ± 0.1 nm with a spectral width of approximately 6 nm.

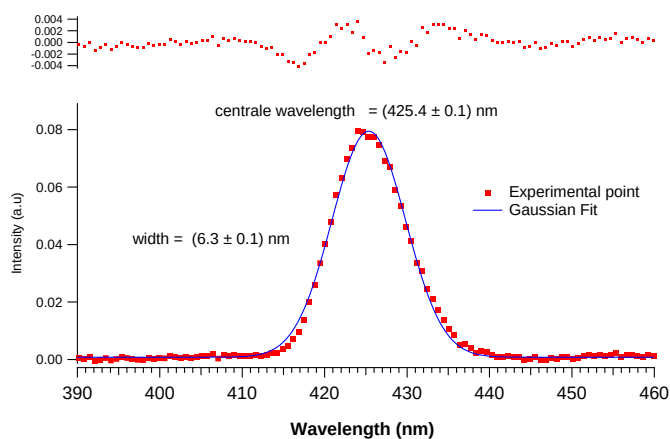


Figure 2.7. Pump spectral distribution for a target wavelength of 425 nm. The signal is fitted with a Gaussian function.

Probe beam. The second part of the 800 nm beam was used to generate the probe pulse. After passing through a motorized optical delay line (comprising a fixed and a moving mirror, ③), it was focused into a CaF₂ crystal to produce a stable white-light continuum (WLC, ④), was used to record the absorption spectra of the excited-state species. Two key features of the setup are noteworthy: (i) the WLC technology of our system enables broadband spectral acquisition over 320-1600 nm. (ii) the long optical delay line provides a temporal window ranging from 0 to 8 ns. It should be noted that such a wide spectral range cannot be detected using a single detector.

Pump-probe overlap. Before crossing with the pump, the probe beam was then split in two using a periscope: one part is the measurement beam for probing the excited sample (with pump), while the other is the reference beam (without pump) to enable differential absorbance (ΔA) measurements. The pump and measurement beams were carefully overlapped in the sample to detect and maximize the transient signal. Both pump and probe beams were aligned at the magic angle (54.7°) to eliminate polarization-related artifacts due to molecular reorientation. Optical filters were introduced in the detection path to attenuate scattered pump light and suppress second-order contributions, ensuring artifact-free spectral acquisition.

Sample stage ⑤. Two experimental configurations were employed depending on our objective, whether measurements were performed in solution or in the solid state.

In the **liquid-phase setup**, a 0.5 mm pathlength flow cuvette was connected to a peristaltic pump via C-Flex, Viton, or PTFE tubing materials selected according to solvent compatibility, to ensure continuous sample circulation (**Figure 2.8**). This setup effectively prevented local heating, photoproduct accumulation, and degradation. Notably, the cuvette featured a 100 μm optical face to minimize group velocity dispersion (GVD) distortion.

In the **solid-state configuration**, thin films were directly mounted in the beam path for fs-TAS measurements of film samples.

A secondary light source of Asahi xenon lamp was positioned along the sample path to control the photochromic state of the diarylethene units. When the pump laser operated in the UV region, the lamp was filtered to provide visible light, whereas under visible excitation, a UV filter was applied. This configuration maintained the DAE moieties in their desired isomeric (open or closed) form during data acquisition and prevented unwanted photoisomerization that could interfere with the transient signals.

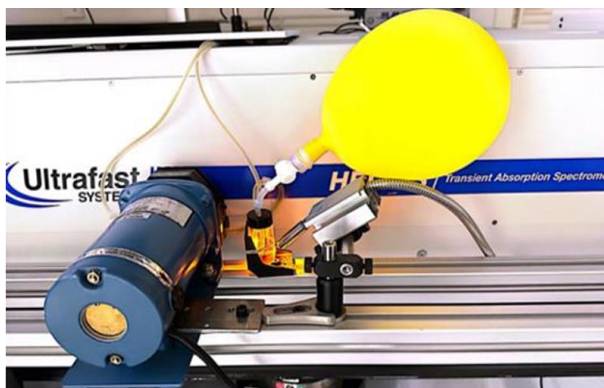


Figure 2.8. Liquid-phase fs-TAS configuration.

Detectors and Data Processing. Detection was performed using CCD or CMOS detectors for the UV or Vis range, and a separate SWIR detector for the near-infrared region. The output data consisted of a two-dimensional matrix of differential absorbance (ΔA) values, plotted as a function of probe wavelength and pump-probe delay time.

ΔA spectra were calculated using the following equation:

$$\Delta A(\lambda, t) = A_{pump+probe}(\lambda, t) - A_{probe}(\lambda, t) \quad (2)$$

where $A_{pump+probe}(\lambda, t)$ is the absorbance after excitation at delay time t , and $A_{probe}(\lambda, t)$ is the probe-only ground-state spectrum.

Data processing and analysis were conducted using Surface Xplorer (Ultrafast Systems) software, which provides modules for chirp correction, target analysis and kinetic modeling from the ΔA matrix, kinetic traces at specific wavelengths and transient absorption spectra at selected delay times, allowing detailed characterization of excited-state lifetimes and ultrafast dynamic processes.

2.5.3 Temporal resolution determination using Raman signal

The temporal resolution of a fs-TAS setup refers to the shortest time delay between the pump and probe pulses that can be experimentally resolved. It is a key factor for accurately capturing ultrafast processes and is typically defined by the Full Width at Half Maximum (FWHM) of the instrument response function (IRF). This IRF is derived from the pump-probe cross-correlation curve, which represents the temporal overlap of the two pulses and is commonly modeled by a Gaussian function $G(t)$:

$$G(t) = G_0 \exp\left(\frac{-t^2}{\tau^2}\right) \quad (3.1)$$

with the Gaussian width Γ , related to the full width at half maximum, FWHM, according to:

$$\Gamma = \frac{\tau_{FWHM}}{2\sqrt{\ln 2}} \quad (3.2)$$

In pump-probe spectroscopy, certain signals such as stimulated Raman scattering (SRS), two-photon absorption (TPA), and cross-phase modulation (XPM) appear only when the pump and probe pulses are temporally coincident. Because these are instantaneous nonlinear processes, their temporal profiles directly reflect the cross-correlation function (49).

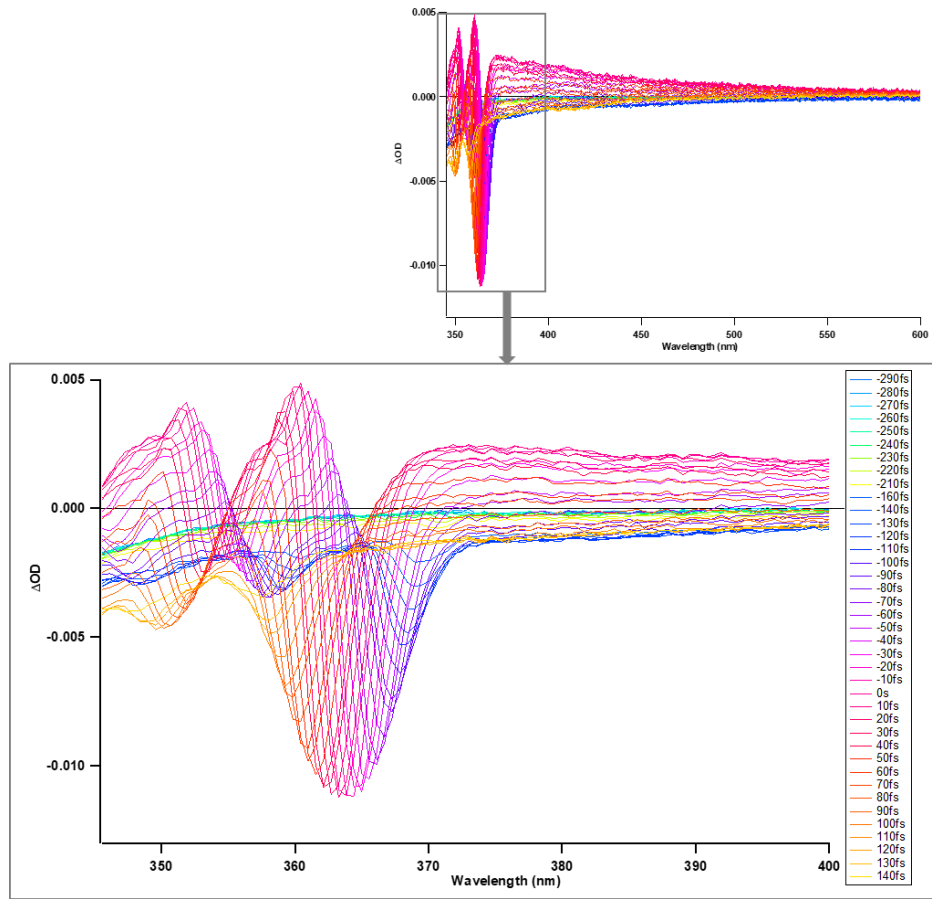


Figure 2.9. Transient SRS of pure ACN excited at 330 nm (0.4 μ J) for delays between -290 fs and +140 fs.

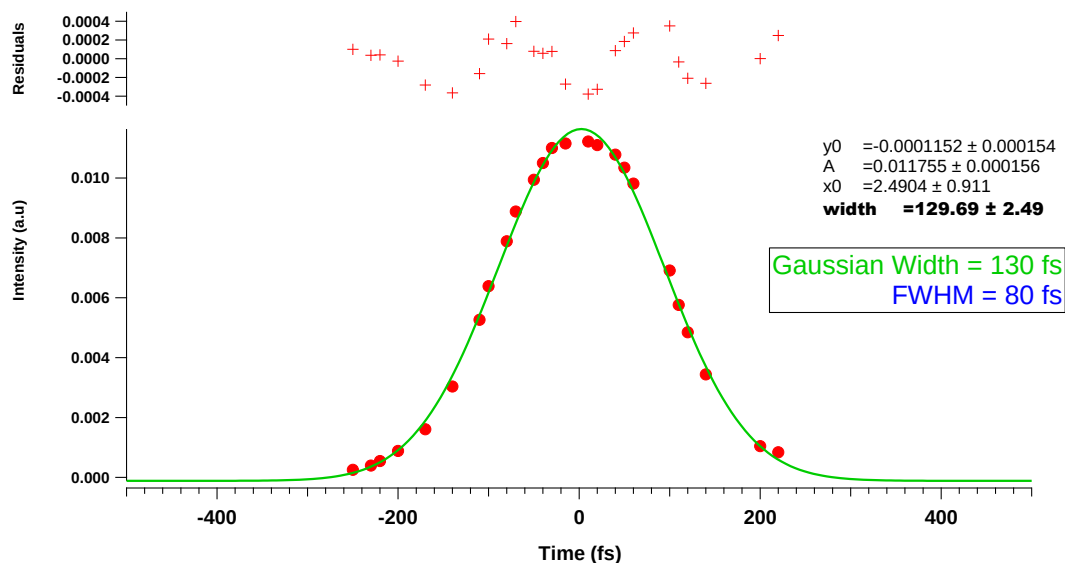


Figure 2.10. Gaussian fit of the SRS signal (maximum of the peak intensity versus delay time), used to determine the pump-probe correlation function.

In this work, the pump-probe correlation function was determined using the SRS signal of pure ACN. This Raman feature is an instantaneous virtual process appears as a sharp negative peak in the transient absorption spectrum and is independent of excited-state population, making it a precise marker for time-zero. By tracking the maximum intensity of the peak as a function of time, the signal was fitted with a Gaussian function, yielding a Gaussian width (Γ) of 130 fs, corresponding to a temporal resolution of 80 fs (FWHM) for our fs-TAS setup (**Figure 2.9, Figure 2.10**).

2.5.4 Spectral Signatures and Data Interpretation in fs-TAS

fs-TAS probes the ultrafast evolution of photoexcited species by measuring differential absorbance (ΔA) as a function of the time delay between pump and probe pulses as mentioned in the section before. Because ΔA is calculated as the difference in absorbance before and after excitation, both positive and negative features can appear in the resulting spectra. Upon excitation, the system undergoes rapid changes in electronic structure, which manifest as distinct spectral signatures that reflect photophysical and photochemical processes evolving on femtosecond to nanosecond timescales.

The principal spectroscopic features characteristic of fs-TAS are illustrated in **Figure 2.11** and summarized below:

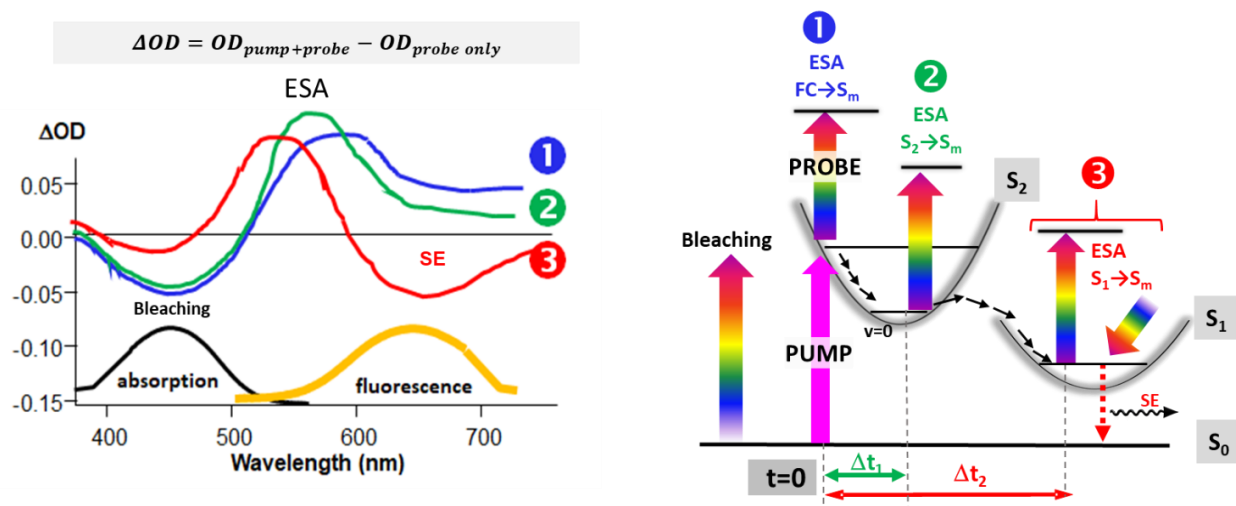


Figure 2.11. Typical Transient data explain with an energy diagram.

Ground-State Bleaching (GSB) appears as a negative signal at wavelengths corresponding to the molecule's steady-state absorption. It results from the depletion of ground-state population: once molecules are promoted to excited states by the pump pulse, fewer remain in the ground state to absorb the probe light. This reduction in absorbance leads to a negative ΔA signal. The GSB feature typically mirrors the steady-state absorption spectrum, but with inverted sign.

Excited-State Absorption (ESA) appears as a positive signal when excited molecules absorb additional photons from the probe to reach higher-lying excited states. These transitions reflect the formation and evolution of excited-state species and are often broad and dynamic. ESA features may shift over time due to processes such as internal conversion, intersystem crossing, or chemical transformations. It appears as a positive signal when excited molecules absorb the WLC (probe) to reach higher-lying excited states. The main objective is to record the excited-state absorption spectra at various pump-probe delay times (e.g., FC State $\rightarrow S_m$, $S_2 \rightarrow S_m$, $S_1 \rightarrow S_m$, as illustrated in **Figure 2.11**). These transitions reflect the formation and temporal evolution of excited-state species and are often broad and dynamic. ESA features may shift over time due to processes such as internal conversion, intersystem crossing, or photoinduced chemical transformations.

Stimulated Emission (SE) contributes as a negative signal in spectral regions corresponding to the molecule's fluorescence emission. It occurs when the probe pulse induces emission from the excited state back to the ground state, increasing the transmitted probe intensity. Like GSB, the SE signature often resembles the steady-state emission spectrum, but with reversed sign.

In practice, these spectral features frequently overlap in both time and wavelength domains, which can complicate direct assignments (50). For instance, ESA may obscure GSB, and SE can overlap with ESA, making it difficult to isolate individual processes. Therefore, careful experimental design including optimization of excitation wavelengths, pulse energy, and fluence is essential to minimize spectral congestion and avoid misinterpretation.

To extract meaningful kinetic and spectral information from overlapping features, advanced data analysis techniques such as global fitting and target modeling are often required. Moreover, several instrumental artifacts including white-light chirp, scattering, and coherent artifacts can distort the transient response if not properly corrected during data processing. Thus, the reliability of fs-TAS analysis depends critically on proper baseline correction, artifact suppression, and fitting models that accurately reflect the real excited-state dynamics of the system. To support this process, commercial software platforms such as Surface Xplorer software as previously introduced provide user-friendly and powerful interfaces for chirp correction, data visualization, enabling accurate extraction of transient spectra and kinetic traces with precision and reduced uncertainty (47).

2.5.5 Transient Data Processing

fs-TAS data were processed using Surface Xplorer software of Ultrafast Systems, which interfaces directly with the HELIOS spectrometer. Final global fitting and kinetic analysis were conducted in IGOR Pro. Prior to modelling, the raw datasets underwent critical pre-processing to remove experimental artifacts and define the appropriate spectral and temporal ranges for accurate analysis.

Basic Correction. A common artifact observed was a non-zero spectral baseline that persisted across delay times. This background signal may result from long-lived excited states, thermal lensing due to the excitation beam, or drift and noise in the detection system. To isolate the true transient absorption signals, a background correction was performed by averaging spectra

from a delay region where no significant kinetic response was expected and subtracting this average from the entire dataset. This step ensured that only the photoinduced dynamics were retained. In addition, the WLC probe pulse exhibited a Gaussian intensity profile, with reduced spectral power and higher noise at the edges. In some regions, strong sample absorption also diminished the probe transmission, further degrading the signal-to-noise ratio. To improve spectral clarity, poorly transmitting and noisy regions typically at the spectral boundaries were excluded through spectral cropping. This also extended to removing temporal segments that were signal-free or dominated by noise (47).

GVD Correction. A further particularly important artifact that required correction was group velocity dispersion, which arises due to wavelength-dependent propagation delays in the WLC probe as it passes through the CaF₂ crystal and other dispersive optics, resulting different wavelength components travel at different group velocities. Because longer wavelengths (redder light) travel faster than shorter wavelengths (bluer light), resulting a tilted data, a phenomenon known as chirp. This fundamental concept has been described during early developments of fs-pump-probe techniques by Nakayama and Hamanoue (51). This principle is illustrated in **Figure 2.12**, where red, green, and blue components of the probe arrive at different times after passing through a dispersive medium.

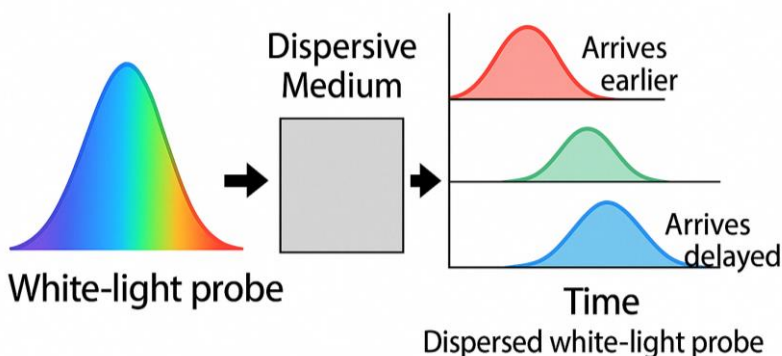


Figure 2.12. Schematic representation of GVD in a white-light continuum probe.

In the 3D surface plots generated by Surface Xplorer, this chirp manifests as a tilted angle in the transient absorption signal across wavelengths (**Figure 2.13, panel A**). If left uncorrected, this spectral misalignment leads to inconsistent time-zero points across the dataset and distorts kinetic analysis. To address this, GVD correction was applied using the built-in algorithms in Surface Xplorer, realigning the spectral components such that all wavelengths were mapped to a

consistent pump–probe delay (**Figure 2.13, panel B**). This correction was critical for enabling synchronized kinetic traces and accurate spectral assignments during global analysis.

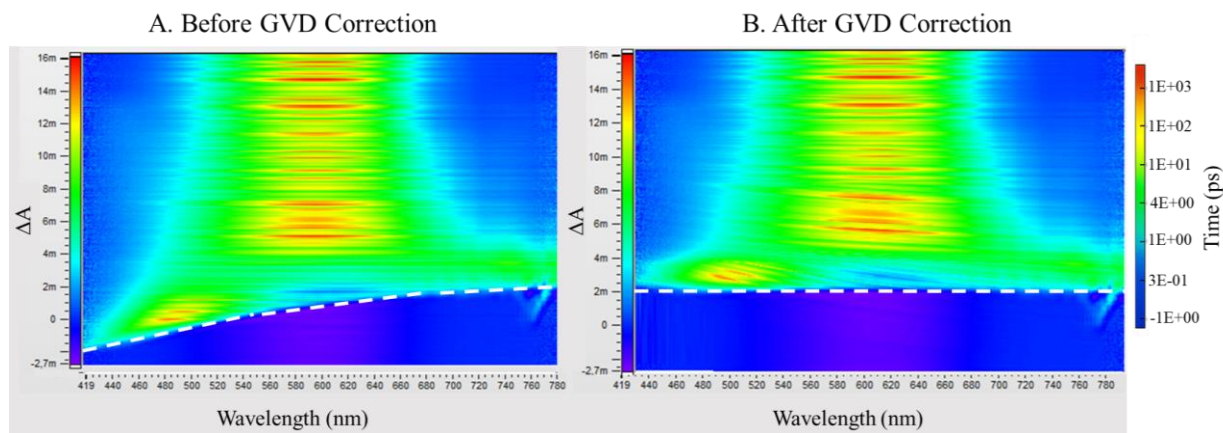


Figure 2.13. 3D Representation of Transient Absorption Data (Panel A, left) Before GVD correction, (Panel B, right) After GVD Correction.

2.5.6 Combining Spectral Window

To obtain a complete transient absorption spectrum covering the full UV-Vis-NIR range, the datasets recorded in different detection windows were combined using Surface Xplorer (Ultrafast Systems). Since each detection range (UV, Vis, and NIR) is registered as an independent measurement file in the HELIOS system, careful data alignment and correction were required prior to merging.

Each dataset was first pre-processed individually following identical steps, including background subtraction, chirp correction, and time-zero alignment, to ensure consistent baseline, temporal calibration, and synchronization across all spectral regions. The crucial step for accurate merging consisted of identifying a common reference point, typically corresponding to a region near time zero or exhibiting similar ΔA amplitude in the overlapping spectral zones. This ensured that the datasets were aligned at equivalent temporal and spectral positions, avoiding discontinuities or artificial intensity jumps at the junctions between spectral windows.

Once the reference points were established, the individual UV-Vis-NIR files were combined using the Combine Windows function in Surface Xplorer. This operation produced a single, continuous transient absorption map with smooth transitions across the full detection range, providing a global view of the excited-state dynamics with minimal or no spectral artifacts (**Figure Figure 2.14**).

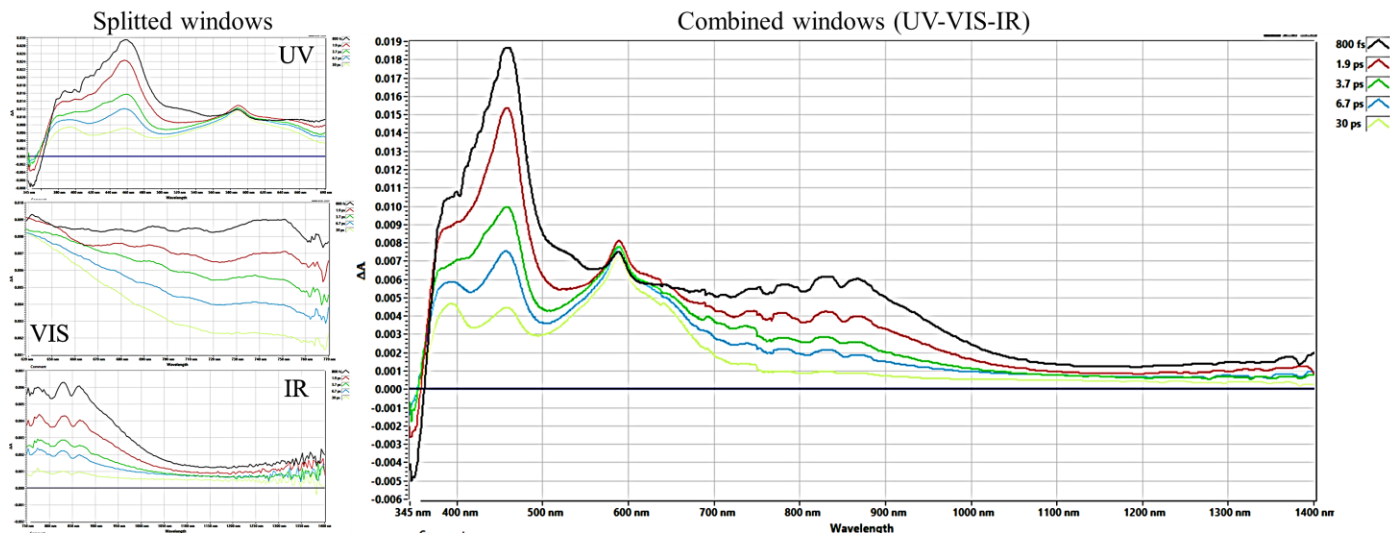


Figure 2.14. Combination of UV, Vis, and IR detection ranges using Surface Xplorer to obtain a continuous TA spectrum across the full UV-Vis-IR region.

2.5.7 Data analysis: Fitting Method

Basic fitting. The transient absorption dataset consists of a spectro-kinetic matrix $\Delta A_{(ij)} = f(\lambda_i, t_j)$, which can be initially analysed in a “spectral” mode at given times:

$$\Delta A(t_j) = f(\lambda) \quad (4.1)$$

Or in a “kinetic” mode at specific wavelengths:

$$\Delta A(\lambda_i) = f(t) \quad (4.2)$$

This second case is the most straightforward to handle. In practice, the basic fitting is the simplest approach consists of fitting each kinetic trace, $\Delta A(\lambda_i) = f(t)$, individually with a sum of simple exponential functions, possibly including a signal offset (S_0) and a time offset (t_0).

$$\begin{cases} S^\lambda(t) = S_0^\lambda + \sum_i a_i^\lambda e^{-k_i^\lambda(t-t_0)} \\ k_i^\lambda = \frac{1}{\tau_i^\lambda} \end{cases} \quad (5)$$

where k_i^λ (τ_i^λ) are rate constants (characteristic times) for a given kinetic at a specific wavelength than can be related to the photophysical or photochemical processes of the chemical system. Note that the number of exponential components must be sufficient to account for all the distinct temporal events identified in the spectral domain.

Global fitting. To ensure the reliability and consistency of the extracted kinetic parameters, global fitting was subsequently employed. In this approach, multiple kinetic traces were simultaneously analyzed using a unified kinetic model for each wavelength. In this case, unlike pre-exponential factors, the kinetic constant does not depend on the detection wavelength anymore which allow to modify the previous equation as:

$$S^\lambda(t) = S_0^\lambda + \sum_i a_i^\lambda e^{-\frac{(t-t_0)}{\tau_i}} \quad (6)$$

An important aspect of global fitting concerns the careful selection of probe wavelengths, both in number and position. The chosen kinetics should be representative enough to capture all relevant transient features associated with the chemical intermediates (OF*, CF*, triplet, etc.) that appear and decay throughout the temporal window.

Deconvolution. As previously described, the pump-probe convoluted function can be represented by a Gaussian function $G(t)$ (Equation 3.1). During the global fitting process, in order to accurately reproduce the entire temporal range, including the negative delay region, the kinetic model $S^\lambda(t)$ must be convolved with this Gaussian function to yield the overall response function $F(t)$.

$$F(t) = S^\lambda(t) \otimes G(t) = \int_0^\infty S^\lambda(t') G(t - t') dt' \quad (7.1)$$

The resulting equation is given as follow:

$$F_\lambda(t) = G_0 \sum_i \left[F_0^\lambda + a_i^\lambda \exp\left(\frac{\Gamma^2}{4\tau_i^2} - \frac{t-t_0}{\tau_i}\right) \times \left\{ 1 - \operatorname{erf}\left(\frac{\Gamma}{2\tau_i} - \frac{t-t_0}{\tau_i}\right) \right\} \right] \quad (7.2)$$

Where in this expression, the global parameters are the time constants (τ_i), the time origin (t_0), and the pump-probe cross-correlation width (Γ), which was fixed at 130 fs. The wavelength-dependent parameters, referred to as local parameters, are the pre-exponential factors (a_i) and the baseline offsets or plateaus represented by the term F_{0i} .

A comparative example is shown in (**Figure 2.15**), illustrating three fitting approaches: a basic bi-exponential fit, a global tri-exponential fit, and a global tri-exponential fit convolved with a Gaussian function. In the latter case, the full temporal window including negative delay times is accurately reproduced, enabling the extraction of ultrafast time constants.

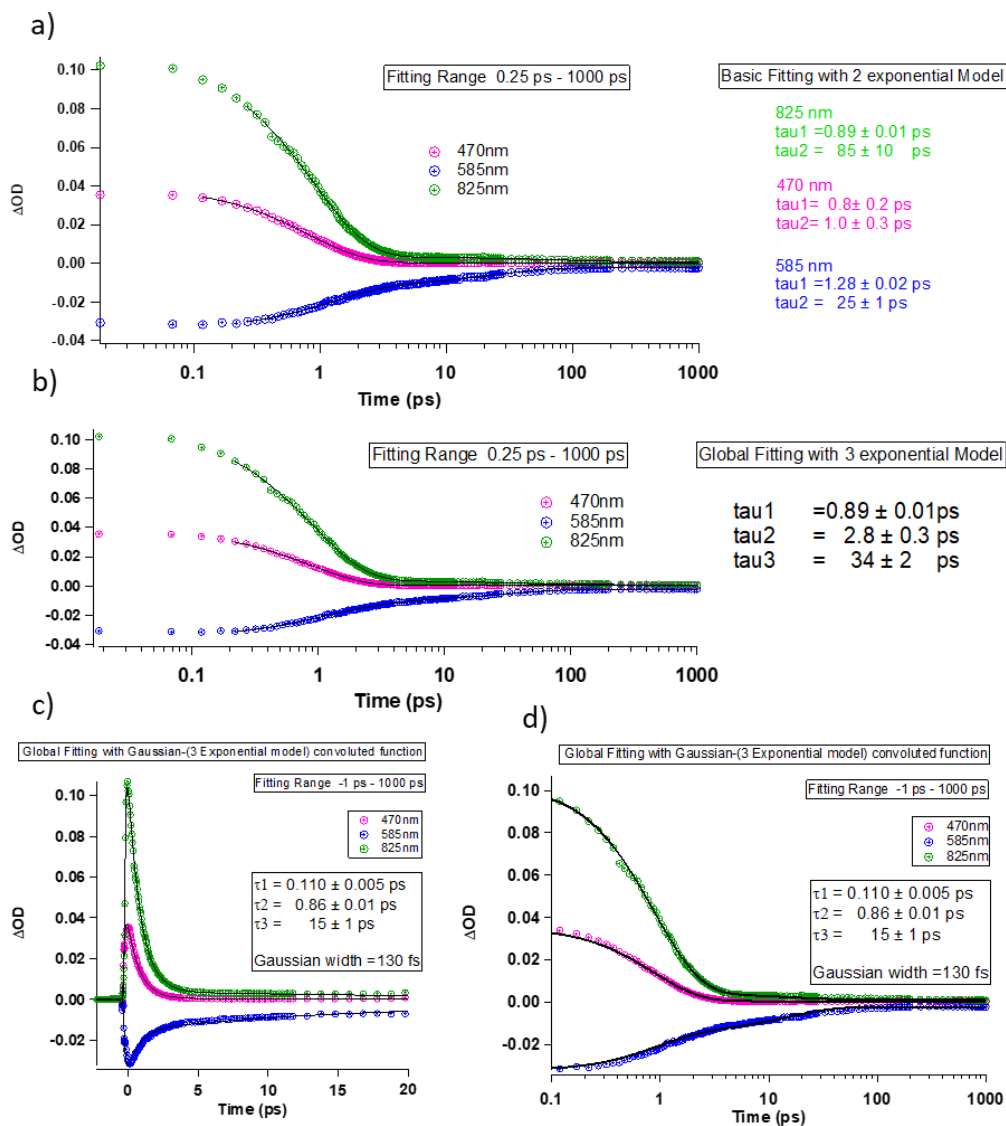


Figure 2.15. Fitting of three representative kinetics: (a) basic fitting using a bi-exponential model within the [0.25 to 1000 ps] range; (b) corresponding global fitting using a tri-exponential model; and (c-d) global fitting with a three-exponential Gaussian-convoluted model over the [-1 to 1000 ps] window, shown in linear (c) and logarithmic scales (d). Gaussian width=130 fs.

2.6. Computational Methods: Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) for Electronic Analysis

Computational chemistry is a subfield of theoretical chemistry that focuses on solving chemical problems using computer-based calculations. It involves building molecular models and applying quantum mechanical methods to study properties and reactivity. Rather than developing new theories, it uses established methods to interpret and predict experimental results.

One of the most widely used methods in computational chemistry is DFT. DFT simplifies the complex many electrons problem by focusing on electron density instead of wavefunctions, making it less computationally demanding than traditional methods like Hartree-Fock (HF). This efficiency has made DFT a popular tool for studying molecular geometries, energies, reaction mechanisms, and spectroscopic properties. DFT is especially valuable when used alongside experimental work. It can confirm interpretations, distinguish between possible mechanisms, and even predict properties that have not yet been experimentally measured. While standard DFT is primarily applied to ground-state properties, TD-DFT extends its utility to excited-state phenomena, such as absorption spectra and electronic transition energies (52).

To complement our experimental investigations on DAE molecules, computational calculations were carried out by our collaborator, Prof. Aurélie Perrier, from the Laboratoire Interdisciplinaire des Énergies de Demain (LIED) at Université Paris Cité. These simulations provided valuable insights into the electronic structure and photoresponsive behavior of the systems under study (DAE1/2, MC1/2, MCP), supporting and enriching our interpretation of the spectroscopic data.

Chapter 3. Ultrafast Photoswitching Mechanisms of Bis-Pyridyl Diarylethenes

This chapter focuses on the ultrafast photodynamics and electronic structure of two simple Bis-Pyridyl diarylethene derivatives, DAE1 and DAE2. Using femtosecond transient absorption spectroscopy, we investigate their photocyclization and photoreversion processes under varying excitation conditions, with particular attention to excitation power effects on relaxation pathways.

The organization of this chapter follows a conventional yet systematic approach. First, steady-state spectroscopic measurements and quantum yield determinations are presented to establish the photochemical efficiencies of both molecules. In parallel, DFT calculations are used to evaluate their conformational distributions (AP vs. P), while TD-DFT calculations provide the assignment of vertical transitions for the open and closed forms. Subsequently, the fs-TAS results are discussed for each compound, beginning with the photocyclization process and followed by photoreversion. Together, these complementary approaches enable a direct comparison between DAE1 and DAE2, emphasizing how structural extension modulates their photoswitching mechanisms and relaxation pathways. Particular attention is given to comparing these findings with the preliminary results previously reported in Chemical Science (34) and summarized in the following page.

3.1. Introduction

In Chapter II, we introduced the various DAE based photochromic systems examined throughout this thesis. DAEs are among the most extensively studied photochromic dyes and have been widely reported in the literature for their reversible light-induced switching capabilities. Recently, our team investigated the ultrafast dynamics of a simple photoswitchable DAE derivative, DAE1, using fs-TAS, focusing specifically on the photocyclization process in the UV-visible region (34). The aim of that study was to understand the intrinsic photochemistry of DAE1 and compare its dynamics with those of a molecular cage system, in which three DAE1 units are confined between two POM clusters. Notably, only the forward (photocyclization) process was explored, without addressing photoreversion. The key findings revealed a cyclization event occurring within 0.5 ps, followed by vibrational relaxation on a 40 ps timescale, and a slower internal conversion attributed to the P conformer.

In this chapter, we extend our investigation to explore the full photochemical and photophysical behavior of DAE1, encompassing both photocyclization and photoreversion, across an extended spectral range that includes the near-infrared (NIR) region. In addition, we introduce and examine a second photoswitchable system, DAE2, which differs structurally from DAE1 by the insertion of a phenyl spacer between the thiophene and pyridyl rings. As illustrated in **Figure 3.1**, both DAE1 and DAE2 share a common hexafluorocyclopentene photochromic core, with thiophene units on either side. In DAE1, the thiophenes are directly bonded to pyridyl groups, while in DAE2, a phenyl linker is introduced between the thiophene and pyridyl units. This structural variation raises several central questions: How do the excited-state photoswitching dynamics and competitive pathways differ between DAE1 and DAE2, and what role does the phenyl spacer play in modulating these dynamics?

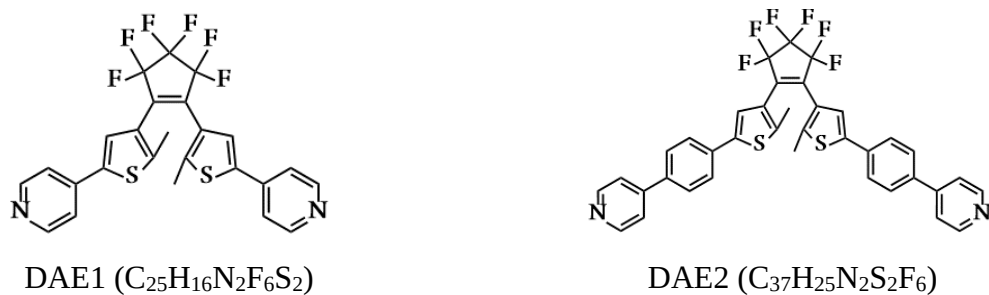


Figure 3.1. Chemical structures of the diarylethene derivatives, DAE1 and DAE2.

To address these questions, we evaluated the photochemical and photophysical properties of both compounds. Photocyclization QYs were determined to assess switching efficiency, while molar absorptivity, steady-state absorption and emission spectra, and time-resolved spectroscopic data were used to investigate their electronic behavior. These experimental insights were further complemented by NMR spectroscopy and supported by theoretical calculations to gain a deeper understanding of the electronic structure and dynamics.

In the following sections, we present and analyze the spectral evolution associated with the photoinduced conversion and reversion of DAE1 and DAE2, aiming to clarify how structural modifications affect the overall photoswitching performance.

3.2. General Photochromic Properties of DAE1 and DAE2

To access the photochromic parameters of DAE1 and DAE2, steady-state UV-Vis absorption was performed to characterize the optical spectra of the OF and CF species during xenon lamp irradiation. In parallel, QYs were determined from photo-kinetic measurements. These experiments also guided the selection of appropriate excitation wavelengths for the fs-TAS studies discussed in subsequent sections.

The temporal evolution of the absorption spectra (**Figure 3.2**) for both DAE1 and DAE2, highlights the spectral changes associated with the photoinduced ring-closure (photocyclization, top panels) and ring-opening (photoreversion, bottom panels) processes. It is also worth noting that no experimental emission was observed for DAE1, whereas DAE2 exhibited a measurable emission signal, which will be discussed in more detail later in this chapter.

For DAE1. The steady-state UV-Vis absorption spectra of DAE1 (400 μM in dry ACN), shown in **Figure 3.2** (left, top), illustrate a clear photochromic transformation upon continuous irradiation at 330 nm UV wavelength.

Before irradiation, DAE1 exists predominantly in its OF as a colorless solution which is characterized by a strong absorption band ($\epsilon = 3.47 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) centered around 301 nm in the UV region. As continuous irradiation proceeds, this band progressively decreases, while a new broad absorption band appears and intensifies in the visible region around 592 nm, red shifted relative to the initial band, giving the solution a blue color associated with the CF ($\epsilon = 1.47 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). An isosbestic point observed at 325 nm throughout the irradiation

confirms a clean conversion from the OF to the CF, without the accumulation of detectable intermediates.

After 185 seconds of continuous UV irradiation, the absorbance of the CF red band no longer increases, indicating that the system has reached the photostationary state (PSS), where both OF and CF coexist.

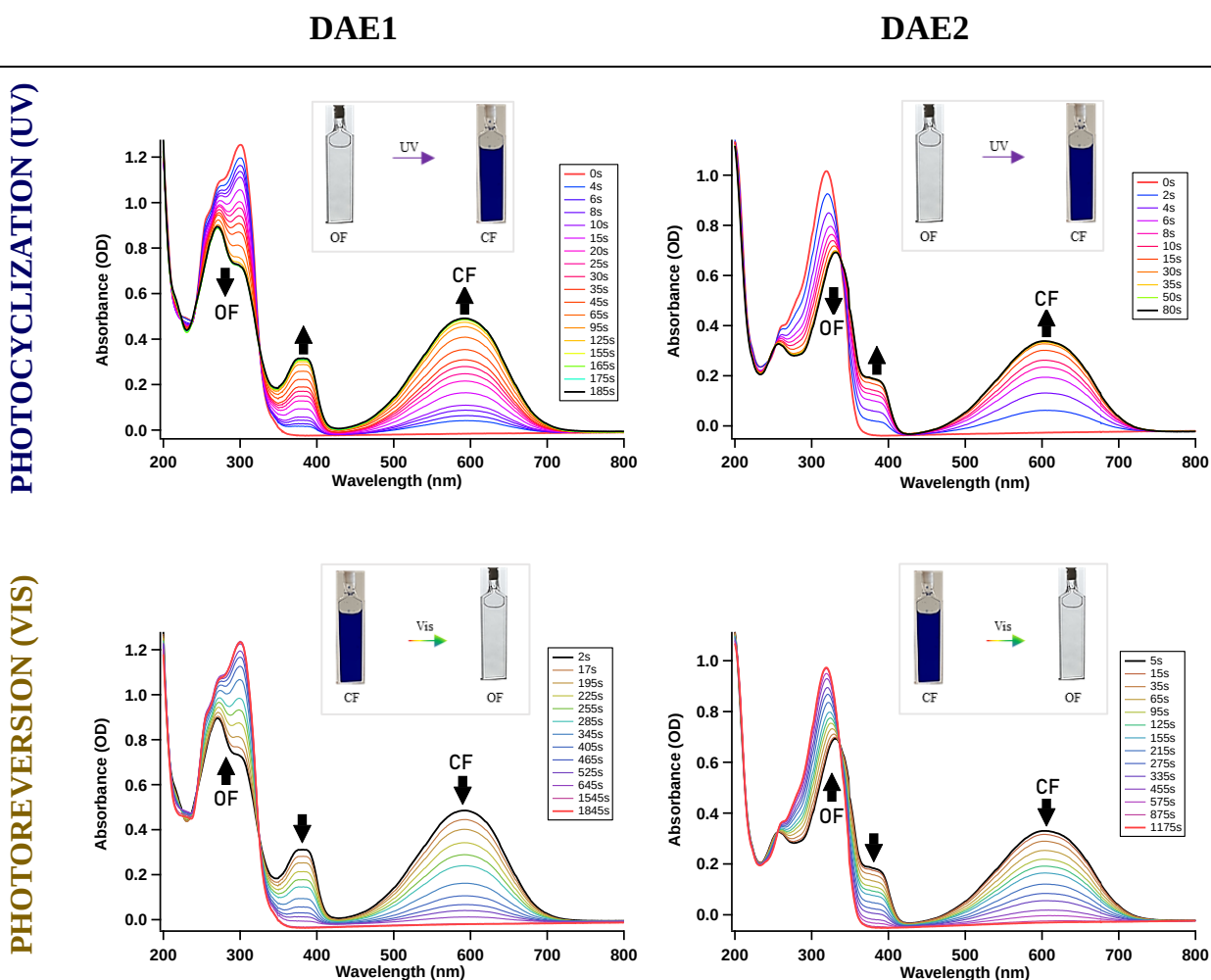


Figure 3.2. Temporal evolution of the steady-state UV-Vis absorption spectra in dry ACN for DAE1 [400 μ M] (left) and DAE2 [264 μ M] (right) under 330 nm UV irradiation (top) and 590 nm visible irradiation (bottom), corresponding to the photoinduced ring closure (OF $\rightarrow$ CF) and ring opening (CF $\rightarrow$ OF) reactions, respectively. Arrows indicate the spectral changes over time.

To demonstrate the reversibility of this process after reaching the PSS, the spectral response of DAE1 were subsequently monitored under continuous visible-light irradiation at 590 nm to induce the ring opening reaction (CF $\rightarrow$ OF), as shown in **Figure 3.2** (left, bottom). Initially, the spectrum is dominated by a broad CF absorption band. Upon visible irradiation, this band gradually decreases in intensity, while a sharp absorption band re-emerges in the UV region around 301 nm, indicating the regeneration of the OF and the recovery of the colorless state. The same 325 nm isosbestic point as in the photocyclization stage is observed.

After 1845 seconds of continuous visible light exposure, the spectral changes stabilize, indicating full ring opening and restoration of the OF dominated state, thereby completing the reversible photochromic cycle.

For DAE2. Under identical conditions, DAE2 (264 μ M in dry ACN) exhibits the same qualitative photochromic response as DAE1 during both cyclization at 330 nm UV (right, top) and reversion at 590 nm visible light (right, bottom). The OF absorption maximum appears at 319 nm, shifting to a CF band at 602 nm upon UV irradiation, with a well defined isosbestic point at 338 nm indicating a clean two state interconversion. The PSS state is reached within $\sim$ 80 s for the forward reaction and $\sim$ 1175 s for the reverse.

The main photochemical parameter, namely the photocyclization QY, together with the photophysical parameters derived from steady-state absorption (λ_{max} and molar absorptivity), are summarized in **Table 3.1** for DAE1 and DAE2. The photocyclization QY of DAE2 is found to be (0.66), slightly higher than for DAE1 (0.5), whereas the photoreversion shows the opposite (0.007 vs 0.011). These results, confirm that both molecules share the same reversible photoswitching mechanism, with minor spectral differences.

Table 3.1. List of the optical parameters determined for the simple diarylethene derivatives DAE1 and DAE2 in different solvents, absorption maxima, QYs, and molar absorptivities.

Molecules	Solvents	λ_{max}, OF	λ_{max}, CF	$\Phi_{cycl.}(UV)$	$\Phi_{rev.}(Vis)$	$\epsilon_{OF} \text{ at } \lambda_{max}$	$\epsilon_{CF} \text{ at } \lambda_{max}$
		nm				$(\times 10^4) \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	
DAE 1	ACN	301	592	0.50	0.011	3.32	1.59
DAE 2	ACN	319	602	0.66	0.007	3.96	2.29
	DCE ^a	322	607	0.67	-	7.74	2.63

a: Data taken from the doctoral thesis of Manjiri (35).

3.3. Distribution of AP/P Conformers for DAE1 and DAE2

The photoswitching behavior of DAE1 and DAE2 is influenced not only by their chemical structures, but also by the conformational distribution present in the OF. As established in the literature, simple diarylethenes in the OF exist in a dynamic equilibrium between two geometries: AP and P conformers (53). However, only the AP conformer adopts a reactive geometry that allows efficient photocyclization upon irradiation, while the P conformer remains photoinactive. Since conformational distribution directly impacts the overall photoswitching efficiency and consequently the QY, it is essential to evaluate the presences of each isomer. To this end, ^1H NMR measurements were performed for both DAE1 and DAE2 in CDCl_3 at room temperature, and the experimental spectra are shown in **Figure 3.3**. These results are complemented by DFT-calculated chemical shifts.

The analysis focused on two key regions: the central methyl protons (Hd^*) and the aromatic protons (Hc^*/He^*) of the thiophene ring, which are known diagnostic markers for conformational assignment. In the AP geometry, the two methyl groups expected to be chemically equivalent due to molecular symmetry, resulting in a single NMR signal. In contrast, the P conformation would place the methyl groups in non-equivalent environments, leading to two distinct singlets.

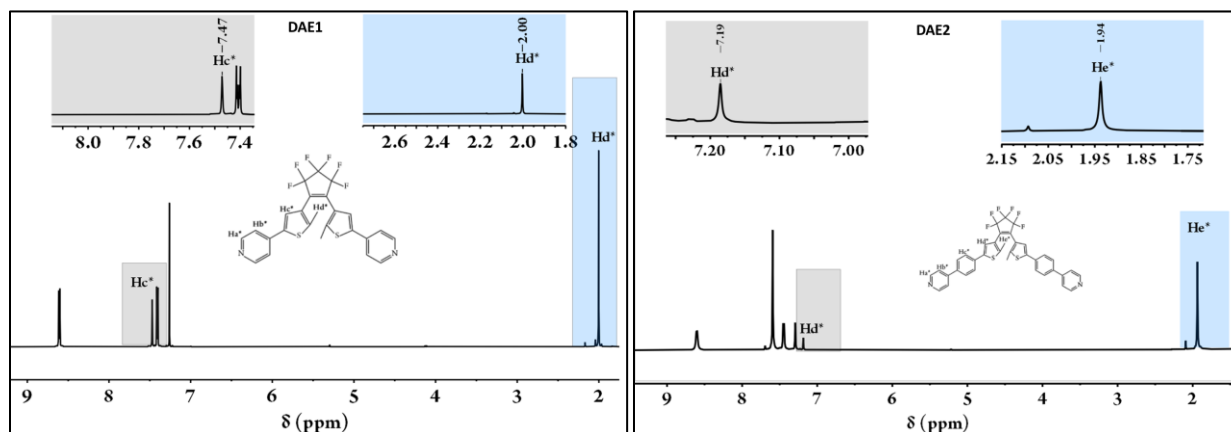


Figure 3.3. ^1H NMR spectrum of DAE1 (left) and DAE2 (right) in CDCl_3 at room temperature, highlighting the diagnostic methyl and aromatic protons signals.

For DAE1, the experimental spectrum (left) displays sharp singlets at $\delta \approx 2.00$ ppm (Hd*, highlighted in blue) and $\delta \approx 7.47$ ppm (Hc*, highlighted in grey). Likewise, DAE2 (right) exhibits signals at $\delta \approx 1.94$ ppm (Hd*) and $\delta \approx 7.37$ ppm (He*). In both cases, no additional peaks as doublet presence or splitting patterns indicative of the P conformer were detected. This observation raises several possibilities: (i) Only the AP conformer is present in solution (AP = 100%); (ii) both AP and P conformers exist, but the P conformer could be undetectable due to rapid interconversion with the AP form, occurring on a timescale faster than what NMR resolution. As a result, the observed spectrum reflects only the AP geometry (43); (iii) P conformer is present at a concentration below the detection limit of ^1H NMR (NMR sensitivity typically $< 100 \mu\text{M}$).

To try to distinguish between these hypotheses, theoretical DFT calculations of ^1H NMR spectra were computed for both AP and P geometries. The chemical shifts results were gathered along with the experimental data found in **Table 3.2** below for comparison.

Table 3.2. Comparison of experimental and DFT-calculated ^1H NMR chemical shifts (δ , ppm) for Me–Hd* and Hc*/He* protons of DAE1 and DAE2.

	DAE1		DAE2	
Protons	Me Hd*	Proton Hc*	Me Hd*	Proton He*
Experimental	2.00	7.47	1.94	7.37
DFT- AP	1.89	8.15	1.87	7.93
DFT- P	2.81	7.19	2.81	8.00

For DAE1, the calculated shift for the AP methyl proton (Hd*) ($\delta\text{-calc} \approx 1.89$ ppm) closely aligns with the experimental value ($\delta\text{-exp} \approx 2.00$ ppm) attributed to the AP conformer, while deviating significantly from the P prediction ($\delta\text{-calc} \approx 2.81$ ppm), strongly supporting the predominance of the AP geometry. In contrast, the aromatic proton (Hc*) appears experimentally at 7.47 ppm, which lies between the calculated shifts for AP ($\delta\text{-calc} \approx 8.15$ ppm) and P ($\delta\text{-calc} \approx 7.19$ ppm), making its assignment less definitive. For DAE2, both calculated methyl (Hd*) and aromatic (He*) proton signals from the AP geometry match well with the experimental values, clearly indicating that the AP conformer is the dominant species in solution.

These combined experimental and theoretical results strongly support that DAE1 and DAE2 predominantly adopt the AP conformation, with no experimental evidence for the presence of the P form under the studied conditions, or at most a population below 10%.

3.4. Photocyclization dynamics of DAE1

Building upon the preliminary insights discussed in our previous work (34), we now re-examine the photocyclization dynamics of DAE1 using a newly implemented fs-TAS setup at the LASIRE laboratory. In addition to the UV-Visible range, this upgraded system extends into the near-infrared (NIR), enabling the tracking of transient species that were previously inaccessible. The effect of excitation power was also systematically investigated to assess any multiphoton effects.

This section begins with TD-DFT calculations that help clarify the nature of the electronic transitions targeted in our experiments, followed by a detailed analysis of the fs-TAS results.

3.4.1 Electronic Excited State Involved (TDDFT)

Theoretical results were analyzed based on oscillator strengths and orbital contributions, with particular focus on the key orbitals participating in the electronic transitions. This analysis provides a detailed description of the absorption and emission features. To optimize the geometries and visualize the frontier orbitals for both absorption and emission processes, TD-DFT calculations were performed using a polarizable continuum model to account for solvent effects.

Absorption: The calculated absorption spectra for the AP conformer of DAE1 reveal distinct electronic transitions, each occurring at characteristic wavelengths with varying oscillator strengths (f), as summarized in **Figure 3.4** (left).

Among these transitions, the most intense band appears at 282 nm ($f = 1.311$), corresponding to an $S_0 \rightarrow S_2$ excitation involving a combination of $H \rightarrow L+2$ and $H-1 \rightarrow L+1$ contributions. A moderately intense transition at 281.31 nm ($f = 0.1257$) is assigned to an $S_0 \rightarrow S_3$ excitation involving $H-1 \rightarrow L$ and $H \rightarrow L+1$. And a last weaker absorption band is found at 292.39 nm ($f = 0.0801$), corresponding to the $S_0 \rightarrow S_1$ transition, dominated by a $H \rightarrow L$ configuration.

The spatial distribution of the involved molecular orbitals are illustrated in **Figure 3.4** (right). The S_1 state is found to be predominantly localized on the central photochromic core, while the S_2 and S_3 states show more delocalized character involving the lateral pyridyl groups.

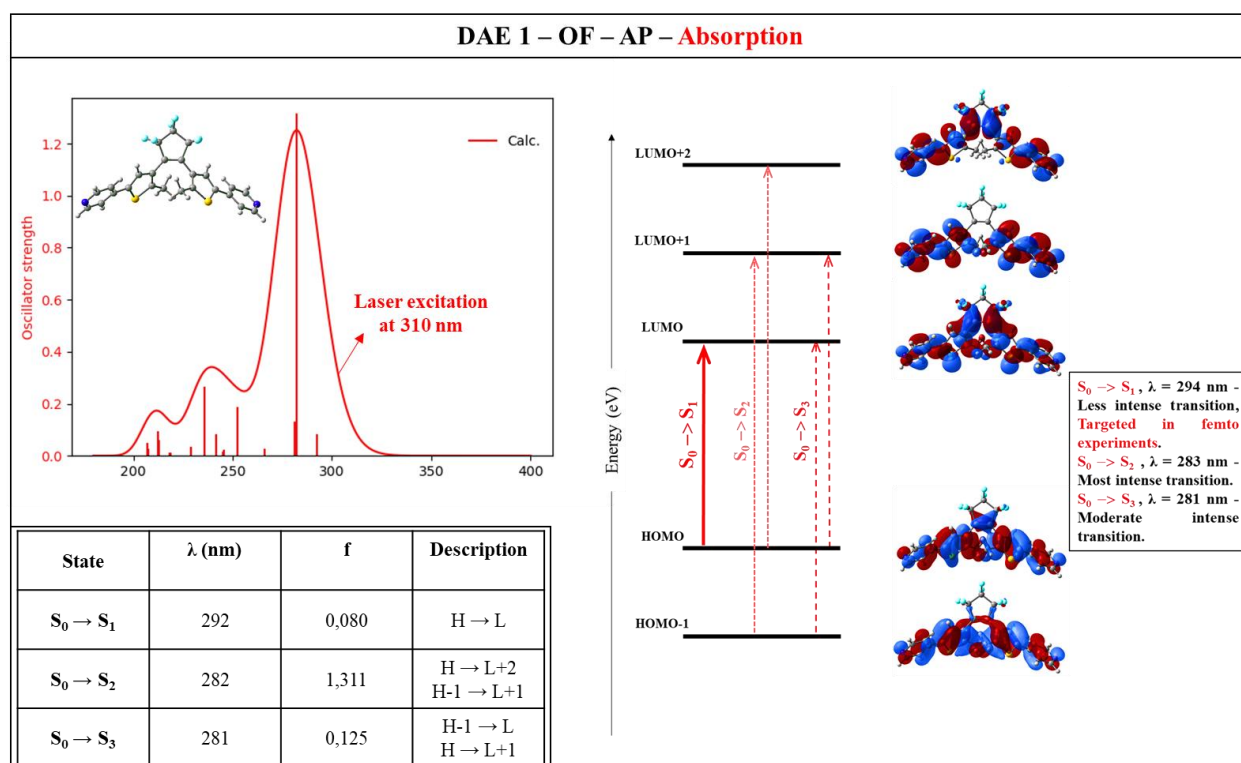


Figure 3.4. Theoretical Absorption Transitions with Orbital Contributions for DAE2.

Given that the excitation wavelength used in our fs-TAS experiments was 310 nm, the most relevant calculated transition is the $S_0 \rightarrow S_1$ band at 292.4 nm ($f = 0.0801$), suggesting that the excitation likely populates the first singlet excited state under our conditions. However, the proximity of S_2 and S_3 transitions implies that some contribution from higher-lying states may also occur, particularly under high power excitation.

This distinction in the orbital localization may have implications on the excited state behavior discussed in the next sections, where we compare the dynamics under different excitation conditions and assess potential deviations from the standard photocyclization mechanism.

3.4.2 Transient absorption data at low excitation power

To better understand the photochromic properties of DAE1, time-resolved experiments were performed to identify the exact mechanisms of the photochromic and competing reactions, and to characterize the intermediates along with their associated timescales. Based on the steady-state absorption spectrum of DAE1 discussed above in section 3.2, excitation pulses at 310 nm near the absorbance band of the OF species with an energy of 0.1 μ J were used. The resulting transient absorption spectra of DAE1 in dry ACN are shown in **Figure 3.5.A**. For comparison, the corresponding steady-state spectra OF and CF are shown in **Figure 3.5.B**, providing a basis for assigning the observed dynamical events. For clarity, the main relaxation pathways and characteristic times extracted from these measurements are summarized in the energy diagram shown in **Figure 3.10**.

fs-TAS measurements were conducted over a spectral range of 320-1600 nm and a temporal window from [-1 ps to 3000 ps], using a DAE1 solution at a concentration of 600 μ M. For clarity, the data are divided into three temporal windows, with color coded traces ranging from red to black. Each trace represents the delay time between the pump and probe pulses, capturing the evolution of the excited state dynamics from early events through intermediate stages to long lived processes: [-1 to 0.2 ps] (top panel), [0.2 to 3.3 ps] (middle panel), [3.3 to 3000 ps] (bottom panel).

Characteristic time constants were extracted by global fitting of the transient signals at five representative wavelengths (376-437-588-894-1190nm) using a five-exponential model convoluted with a Gaussian instrument response function as shown in **Figure 3.6** above, yielding five time components: $\tau_1 = 0.250 \pm 0.030$ ps, $\tau_2 = 0.40 \pm 0.04$ ps, $\tau_3 = 4.5 \pm 0.4$ ps, $\tau_4 = 80 \pm 10$ ps and $\tau_5 = 880 \pm 70$ ps. For clarity, all extracted lifetimes associated with the photocyclization process are summarized in **Table 3.3** below.

In the top panel [-1 to 0.2 ps], immediately after pump excitation of the OF colorless solution, broad ESA features appear across the spectrum. Three distinct peaks are observed at 415 nm (band A), 885 nm (band B), and 1135 nm (band C). Given that both AP and P conformers exist in DAE1, these ESA bands are expected to contain contributions from both conformers. Based on the analysis presented in the following temporal windows, band A and band B are

assigned to the rise of the FC state of the AP conformer, $S_1^{AP}(FC)$, while band C is attributed to the P conformer, $S_1^P(FC)$, probably belonging to the S_1 manifold according to TD-DFT results.

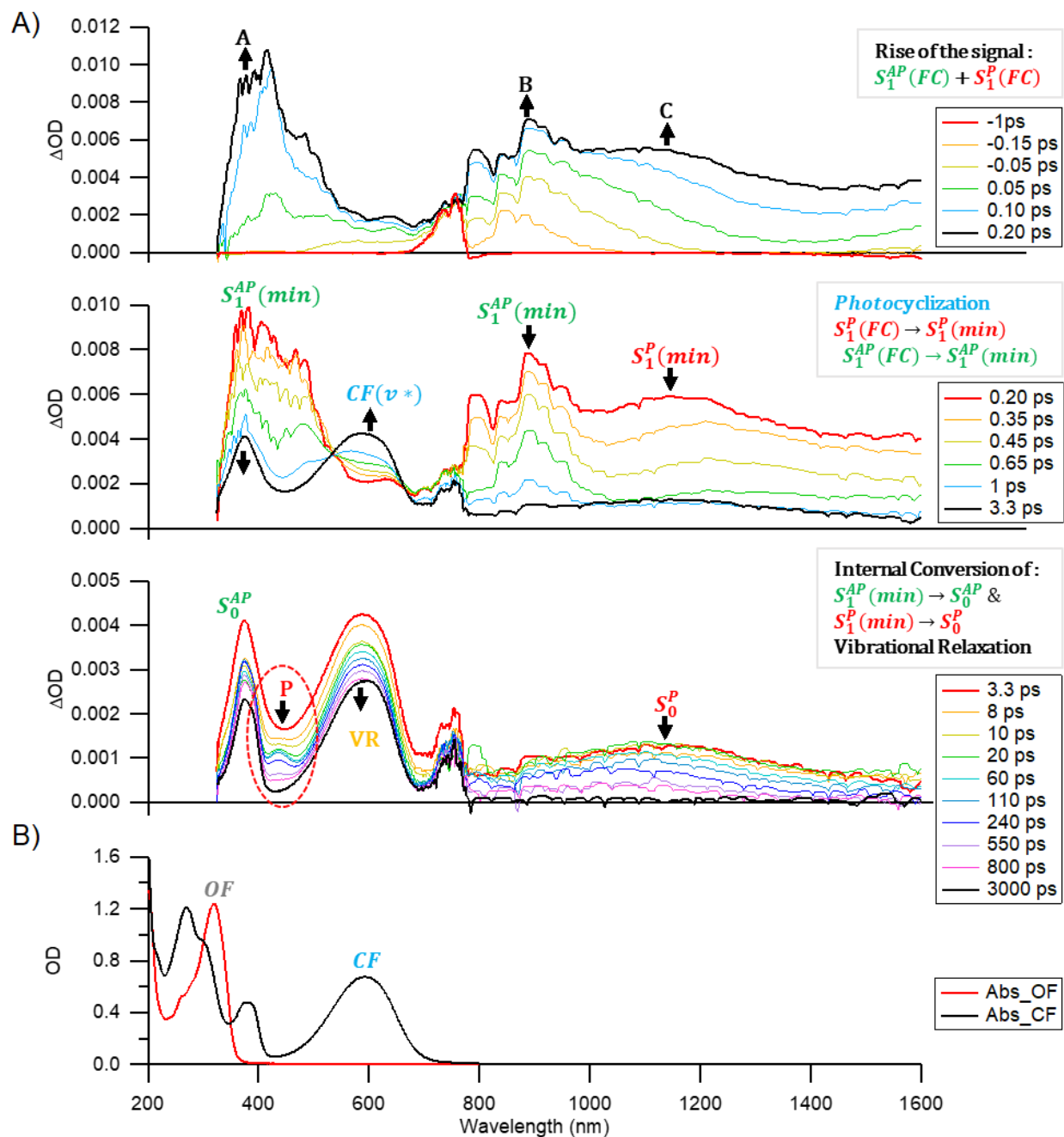


Figure 3.5. (A) fs-TA spectra of DAE1 in dry ACN (600 μ M), recorded upon 310 nm laser excitation with a power of 0.1 μ J. The color gradient from red to black represents the spectral evolution over time, grouped into three distinct temporal windows: top panel [-1 ps to 0.2 ps], middle panel [0.2 ps to 3.3 ps], and bottom panel [3.3 ps to 3000 ps]; (B) Steady-state UV-Vis absorption spectra of DTE1 in its open (red) and closed (black) forms, included for reference.

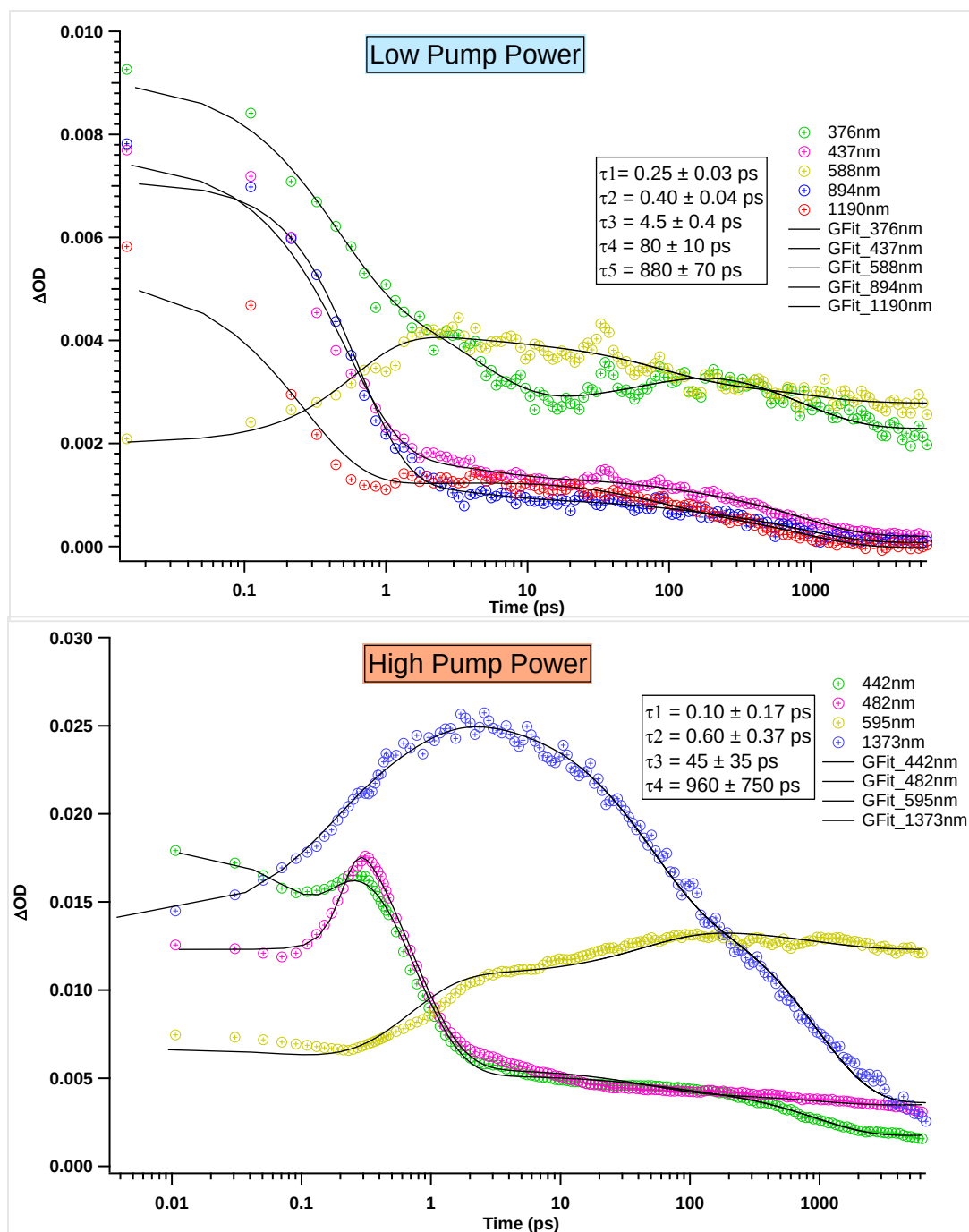


Figure 3.6. Global fitting of transient absorption kinetics of DAE1 at five selected wavelengths (low power) and at four selected wavelengths (high power).

Table 3.3. Global fit lifetimes (τ_1 to τ_5 , in ps) obtained from multi-exponential analysis of fs-TA data for DAE1 and DAE2, measured at different excitation powers and in various solvent environments (ACN, DCE). Error bars are given in parentheses.

Molecules	Solvents	Power (μJ)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	τ_5 (ps)
DAE 1	ACN	0.10	0.25(3)	0.40(4)	4.5(4)	80(10)	880(70)
DAE 1	ACN	1.20	0.1(2)	0.6(4)	-	45(30)	960(800)
DAE 2	ACN	0.10	0.2(1)	1.00(5)	10(3)	70(20)	3100(1000)
DAE 2	ACN	1.20	0.180(5)	1.00(1)	2.30(2)	20(1)	1640(100)
DAE 2	DCE	0.02	0.66(2)	5.5(4)	-	100(100)	1330(100)

The middle panel [0.2 to 3.3 ps], captures the intermediate relaxation dynamics after the initial excitation, showing the three ESA bands (A, B, and C) progressively decreasing in intensity over time. The decay of band C is attributed to the relaxation of the $S_1^P(FC)$ state toward the $S_1^P(min)$ state, with a characteristic time constant $\tau_1 = 0.25$ ps. At the same time, the decay of bands A and B, associated with the photoactive AP conformer, gives rise to a new band centered at 592 nm, accompanied by two isosbestic points at 534 nm and 660 nm, indicating a clean spectral conversion between two forms. This new spectral feature matches the CF absorption position in the stationary spectra, allowing a straightforward identification of the photocyclization process. The characteristic time for this process is $\tau_2 = 0.4$ ps, providing clear evidence that the transformation proceeds from the $S_1^{AP}(FC)$ state via a CI giving CF(v*), without involvement of the relaxed $S_1^{AP}(min)$. This finding is consistent with previously reported dynamics for DAEc (29). Such a well-resolved ultrafast rise of the CF signal is rarely observed in the literature ((22), Figure 2, page 2226), owing to strong spectral overlap from AP* or P* species. In parallel to the photocyclization event, part of the AP population is expected to relax from the $S_1^{AP}(FC)$ region to the $S_1^{AP}(min)$ state, from which internal conversion to the ground electronic state can occur later.

In the bottom panel [3.3 to 3000 ps], further relaxation processes are observed. After an expected relaxation from the $S_1^{AP}(FC)$ region to the $S_1^{AP}(min)$ state, a further decaying of bands A and B suggesting an internal conversion from $S_1^{AP}(min)$ to S_0^{AP} with $\tau_3 = 4.5$ ps. After around 20 ps trace, the spectrum from this time window is dominated by contributions from the P conformer. Furthermore, the ESA band of the CF species centered at 592 nm undergoes vibrational

relaxation, as indicated by the narrowing of the band edges while the central maximum shows as relatively stable, forming vibrationally relaxed CF, **Figure 3.7**. This behaviour reflects a redistribution of the excited-state population from higher to lower vibrational levels, with a characteristic time of $\tau_4 = 80$ ps.

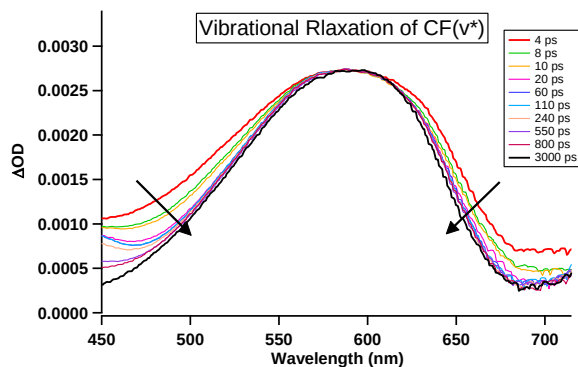


Figure 3.7. Normalized ESA band traces at the maximum 592 nm, showing a decrease at the band edges with a concurrent rise toward a stable central maximum, characteristic of vibrational relaxation of CF band.

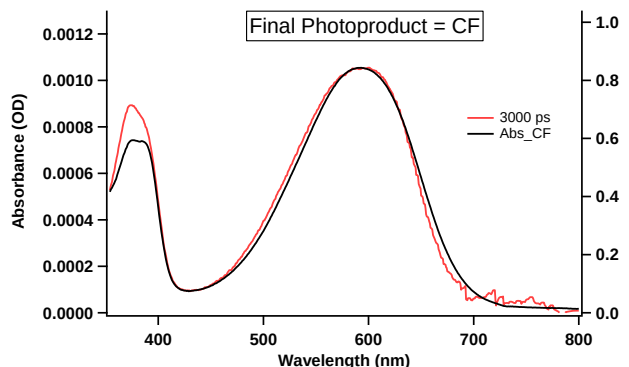


Figure 3.8. Spectral overlap between the transient absorption spectrum at 3000 ps (red) and the steady-state CF absorption spectrum (black) for DAE1 under low power laser excitation, confirming complete formation of the closed form photoproduct.

In the same temporal window, once the vibrational relaxation of the CF is underway, a weak transient band emerges around 435 nm (highlighted by a dashed red circle) from approximately 20 ps onward. This feature is attributed to the P conformer and gradually decays within the 20-240 ps range, disappearing in parallel with the other ESA bands assigned to the P state. The final time constant, attributed to internal conversion from $S_1^P(min) \rightarrow S_0^P$, is $\tau_5 = 880$ ps. It is worth noting that, unlike in DAEc where the P conformer transient band appears intense and broad, here its markedly weaker intensity aligns with NMR results, which indicate that the P conformer represents only a minor population (below 10%).

All these relaxation processes reach a stationary profile around approximately 3000 ps, confirming the complete formation and full recovery of the CF photoproduct, with no evidence of competing processes, in agreement with the steady-state spectrum, **Figure 3.10**.

3.4.3 fs-TAS of DAE1: high excitation power case

Fs-TAS measurements of DAE1 in dry ACN were repeated under higher pump power (1.2 μ J) to assess the impact of excitation energy on the observed dynamics (**Figure 3.9**).

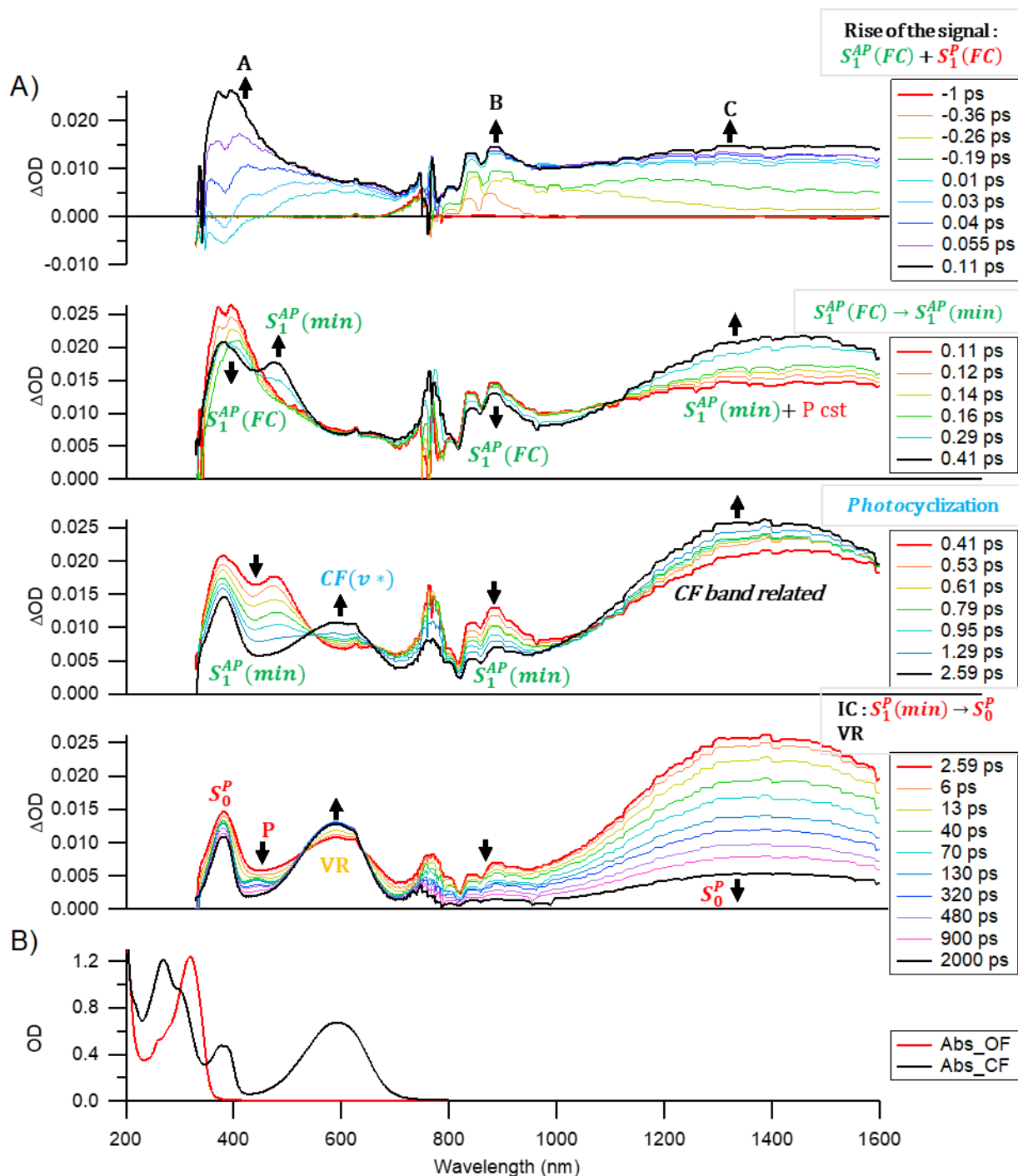


Figure 3.9. (A) Fs-TAS of DAE1 in dry ACN (220 μ M), recorded upon 310 nm laser excitation with a power of 1.2 μ J. The color gradient from red to black represents the spectral evolution across four segmented temporal window s: top panel [-1 ps to 0.11 ps], second [0.11 ps to 0.41 ps], third [0.41 ps to 2.59 ps], and bottom panel [2.59 ps to 2000 ps]; (B) Steady-state UV-Vis absorption spectra of DAE1 in its OF (red) and CF (black) forms, included for reference.

Although the underlying excited-state processes remained consistent with those observed at lower power, the increased excitation energy introduced additional complexity. Under high-power conditions, multiphoton absorption is likely occurring, which may lead to population of higher excited states beyond S_1 . As a result, subtle changes in certain relaxation pathways were revealed, and the clarity of spectral features, as well as the temporal resolution of key intermediates, was significantly enhanced. This improvement enabled the resolution of an additional temporal window for the same molecule. The spectral evolution is separated into four temporal windows: [-1 to 0.11 ps] (top panel), [0.11 to 0.41 ps] (second panel), [0.41 to 2.59 ps] (third panel), and [2.59 to 2000 ps] (bottom panel). Global fitting of the transient signals at 424, 482, 595, and 1373 nm yielded four characteristic time constants: $\tau_1 = 0.100 \pm 0.170$ ps, $\tau_2 = 0.600 \pm 0.370$ ps, $\tau_3 = 45 \pm 35$ ps and $\tau_4 = 960 \pm 750$ ps, **Figure 3.6**.

The first Temporal Window [-1 to 0.11 ps]: The spectra reveal the same three ESA bands observed under low power excitation, band A (~390 nm), band B (~885 nm), and band C (~1380 nm), originating from the FC states of both AP and P conformers in the open form [$S_1^{AP}(FC)$ and $S_1^P(FC)$].

The second TW [0.11 to 0.41 ps]: This newly resolved time window was absent in the low power experiment. The spectrum exhibits two successive isosbestic points at 442 nm and 555 nm, framing the rapid decay of bands A (~390 nm) and B (~885 nm), both attributed to the $S_1^{AP}(FC)$ state. This concerted decay feeds the rise of a new feature at 480 nm, assigned to the relaxed minimum of the AP conformer in the excited state $S_1^{AP}(min)$. A newly third isobestic point at 1120 nm accompanies the spectral changes, preceding the emergence of a strong band in IR region that was not present in low power probably related to the same $S_1^{AP}(min)$ rise with P being constant. The rise of the $S_1^{AP}(min)$ feature occurs within 0.1 ps.

The third TW [0.41 to 2.59 ps]: This time window captures the photocyclization process with the rise of the CF(v*) band at 592 nm, perfectly matching its position in the steady-state spectrum and consistent with the low power measurements. However, unlike the low power case where CF(v*) formation proceeds directly from the $S_1^{AP}(FC)$ state probably via a CI, here the CF(v*) originates from the decay of the $S_1^{AP}(min)$ state, passing through a new CI (54), which effectively suppresses the internal conversion pathway of the AP conformer. This decay is

evidenced by the loss of two prominent ESA, A and B bands at ~460 nm and ~880 nm. The spectral transformation is sharply defined by two isosbestic points at 545 nm and 658 nm. In parallel, an additional band grows in the IR at ~1380 nm. To determine whether this IR growth (that was not pronounced for low power) is part of the same process, a kinetic analysis restricted to this time window was carried out at four representative wavelengths, each corresponding to one of the ESA bands observed. The results show that all features evolve with similar kinetics, suggesting that the IR growth is indeed linked to CF formation. The only exception is the 592 nm CF band, which exhibits a slightly longer lifetime, likely due to contributions from vibrational relaxation that shows to be more pronounced under high excitation power and beginning to influence the kinetics at this stage as well. The CF rise time is measured at ~0.6 ps.

The final time window [2.59 to 2000 ps] exhibits dynamics closely matching those in the low power experiment's bottom panel, beginning with the vibrational relaxation of the CF band. This effect is more pronounced under high power excitation, showing a clear decrease at the band edges accompanied by a rise toward a stable central maximum, with a characteristic time of 45 ps. In parallel, the ESA features at ~378 nm, ~444 nm, and ~1380 nm, associated with the P conformer, undergo a pronounced decay, attributed to internal conversion to the ground state with a time constant of 960 ps. Notably, the IR band around 1380 nm becomes significantly more intense under high excitation power, indicating that the contribution of the P conformer to the photocyclization pathway increases with excitation power. The spectral changes are further defined by two sharp isosbestic points at 527 nm and 635 nm.

3.4.4 DAE1 photocyclization: from direct to sequential pathways

At higher excitation power, the dynamics of DAE1 reveal an additional relaxation channel not observed at low power: the rise of the $S_1^{AP}(min)$ state within ~0.1 ps, **Figure 3.10**. This state becomes the precursor to CF formation, giving rise to a new photocyclization pathway that differs from the low power case. Under low excitation, CF originates directly from the $S_1^{AP}(FC)$ state in ~0.40 ps, with AP internal conversion ($\tau \approx 4.5$ ps) occurring happening after. By contrast, at high power, CF emerges from $S_1^{AP}(min)$ with a characteristic time of ~0.60 ps, while AP internal conversion is essentially negligible. Thus, although the photocyclization itself remains ultrafast

under both conditions, its mechanistic route shifts from a direct FC process at low power to a sequential $S_1^{AP}(FC) \rightarrow S_1^{AP}(min) \rightarrow CF$ pathway at high power.

In addition, the vibrational relaxation of the CF band accelerates significantly ($\tau \approx 80$ ps $\rightarrow$ 45 ps), reflecting more efficient redistribution of excess energy under stronger excitation. The P conformer internal conversion dynamics at high power was more pronounced but the times remains largely unchanged within error (≈ 880 ps vs. 960 ps). Altogether, these results highlight that high excitation power reshapes the photocyclization mechanism of DAE1 by stabilizing $S_1^{AP}(min)$ as a reactive intermediate, while also accelerating CF vibrational relaxation without strongly affecting the long live P decaying.

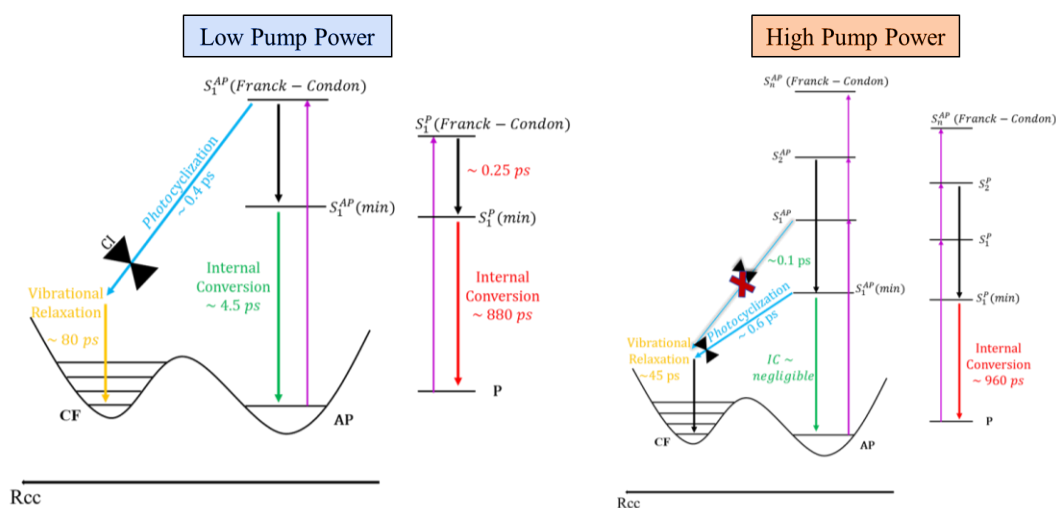


Figure 3.10. Comparative energy diagrams of DAE1 under low and high excitation power, illustrating the main relaxation pathways and characteristic times for the AP/P conformers and CF species as a function of the reactive coordinate (R-cc).

Relying on all the observations discussed above, DAE1 emerges as a textbook example of DAE photochemistry, offering remarkably clean and well-resolved transient absorption features across a broad spectral window from the UV to the IR. Notably, the photocyclization process is clearly resolved and temporally isolated, followed by a well-defined vibrational relaxation phase of the CF band compare to recent literature results (54). As in many previously studied DAEs, including commercial derivatives and the work by Aloïse et al. (22,28,44), or Miyasaka group (42), the transient spectral signature of photocyclization is overlap by the ESA signals from AP* and P* species.

In contrast, the transient signals of DAE1 clearly enables us to monitor the full progression of the photocyclization, from the initial rise of the CF band to its vibrational relaxation, with exceptional clarity. Such a clean and interpretable photochemical response across multiple timescales and spectral regions makes DAE1 an ideal model system for studying ultrafast photoinduced processes in DAEs.

3.5. Photocyclization Dynamics of DAE2

Having established a detailed understanding of the excited-state dynamics and photocyclization pathways of DAE1, we now turn to DAE2, a structurally modified analogue featuring an additional phenyl spacer. This added aromatic unit is expected to influence or introduce new transient features in the excited-state. In the following sections, we investigate how these structural differences impact the overall photochemical response of DAE2 using steady-state and femtosecond time-resolved spectroscopy, supported by theoretical modeling.

3.5.1 Electronic State Involved (TD-DFT) and Emission in DAE2

Absorption : For the OF of DAE2, the calculated absorption spectrum for the AP conformer (**Figure 3.11**, on the left panel) displays its most intense transition for the AP conformer appears at 302.15 nm, with a high oscillator strength ($f = 0.7943$), mainly attributed to a $H \rightarrow L$ configuration. Given that our experimental excitation wavelength is 325 nm, it likely excites the S_1 state. However, nearby higher-energy transitions (S_2 , S_3) remain accessible due to their close proximity in energy and may also be weakly populated.

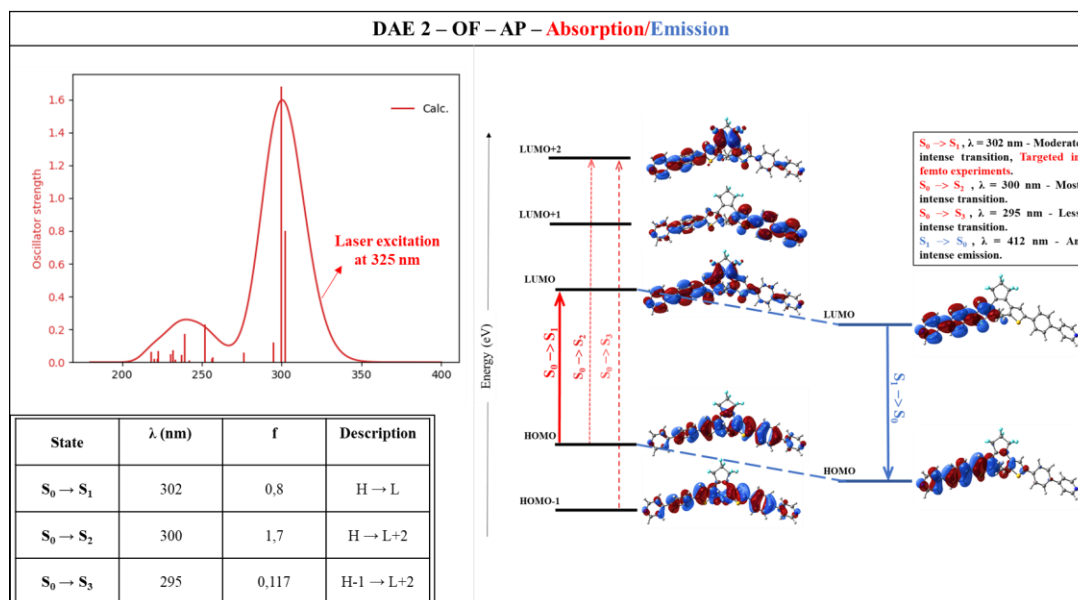


Figure 3.11. Theoretical Absorption and Emission Transitions with Orbital Contributions for DAE2.

Emission. Surprisingly, the OF of DAE2 exhibits a measurable and unexpected fluorescence band in the 410 nm range, an emission entirely absent in DAE1 under identical conditions. As shown in **Figure 3.12**, this emission becomes clearly observable when exciting at 400 nm. However, the corresponding excitation spectrum recorded for this emission (blue trace) does not match the full shape of the OF absorption spectrum (red trace). This spectral mismatch suggests that the emission originates from a specific chromophoric region within the molecule, supporting the presence of two distinct chromophoric units in DAE2: the central photochromic core, analogous to DAE1 (which does not show emission), and a lateral unit based on the pyridyl-phenyl-thiophene (PTT) moiety. The absence of this lateral group in DAE1 likely explains the lack of detectable emission in that system.

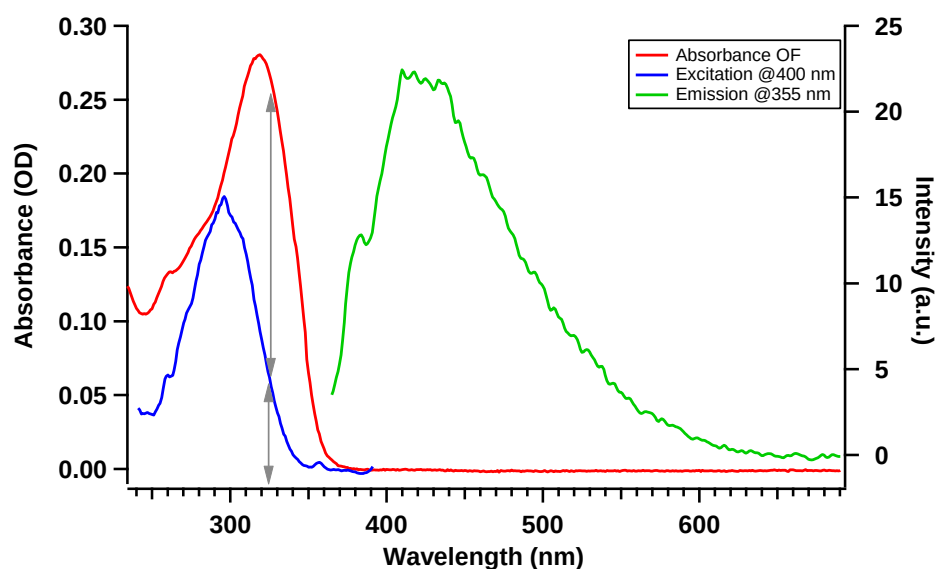


Figure 3.12. Steady-state emission spectra of the OF of DAE2 in ACN.

To confirm the chromophoric origin of this emission, TD-DFT calculations were performed. The vertical emission of the AP conformer was predicted at 412 nm, in excellent agreement with the experimental band. Analysis of the excited-state geometry and associated molecular orbitals (**Figure 3.11**, right panel side) reveals that this emission arises from a transition localized on a single molecular arm, specifically the PPT moiety, rather than the central switching core.

This confirms that the experimentally observed fluorescence originates primarily from the lateral PPT chromophore in DAE2, validating the conclusion that emission in this system is structurally driven and fundamentally distinct from that of DAE1.

3.5.2 At low excitation power

The measurements performed in dry ACN (207 μM) upon 325 nm excitation at 1.2 μJ are presented in four temporal windows: [-1 to 0.20 ps], [0.20 to 1 ps], [1 to 45 ps], and [45 to 6000 ps] (**Figure 3.13,A**). The corresponding stationary spectra of the OF (red) and CF (black) are shown in **Figure 3.13,B** for reference. Global fitting at selected probe wavelengths (360-387-451-520-590-895 nm) yielded the characteristic time constants $\tau_1 = 0.180 \pm 0.005 \text{ ps}$, $\tau_2 = 1.00 \pm 0.01 \text{ ps}$, $\tau_3 = 2.30 \pm 0.02 \text{ ps}$, $\tau_4 = 20 \pm 0.02 \text{ ps}$ and $\tau_5 = 1640 \pm 0.02 \text{ ps}$.

For clarity, the main relaxation pathways and characteristic times extracted from these measurements are summarized in the energy diagram shown in Scheme 3.21. Complementary measurements performed at higher excitation power in dry ACN are discussed in Appendix chapter 3, Section S.3.1. Complementary measurements in DCE are also presented there in section S.3.2.

In the earliest time window [-1 to 0.20 ps], immediately after the excitation the spectra show the prompt rise of the AP and P Franck-Condon S_1 state, $S_1^{AP}(FC)$ and $S_1^P(FC)$, accompanied by the appearance of an additional feature (X) in the visible region at 590 nm. Its rise time is determined to be $\sim 0.18 \text{ ps}$. The X feature is likely connected to the new emission reported above, but its exact origin will be further examined in the next chapter 4.

In the following time window [0.20 to 1 ps], the ESA band associated with the $S_1^{AP}(FC)$ state decays rapidly, corresponding to relaxation toward $S_1^{AP}(min)$ with a time constant of 1 ps. During this interval, the X feature remains consistently unchanged in intensity.

The [1 to 45 ps] time window shows the onset of $S_1^{AP}(min)$ ESA band decay, accompanied by the rise of the CF absorption band, which displays a hump maintenance attributed to the X feature. The isobestic points found are: 557nm-664nm. The characteristic photoclosure lifetime is found to be 2.3 ps, approximately one order of magnitude longer than in DAE1, suggesting that CF formation mainly proceeds from the relaxed $S_1^{AP}(min)$ state, as similarly observed under high-power excitation of DAE1.

In the final stage [45 to 6000 ps], Two main relaxation events dominate this time window. First, the CF band undergoes vibrational relaxation, with a characteristic time of $\sim 20 \text{ ps}$. By the end of this time window, the spectrum reaches a stationary profile consistent with complete CF formation. In parallel, as already commented above, the P conformer undergoes internal conversion from $S_1^P(min)$ to $S_0^P(IC)$. This process results in the disappearance of the strong P

related signatures, accompanied by the simultaneous loss of the X feature hump, with a characteristic time of ~ 1640 ps.

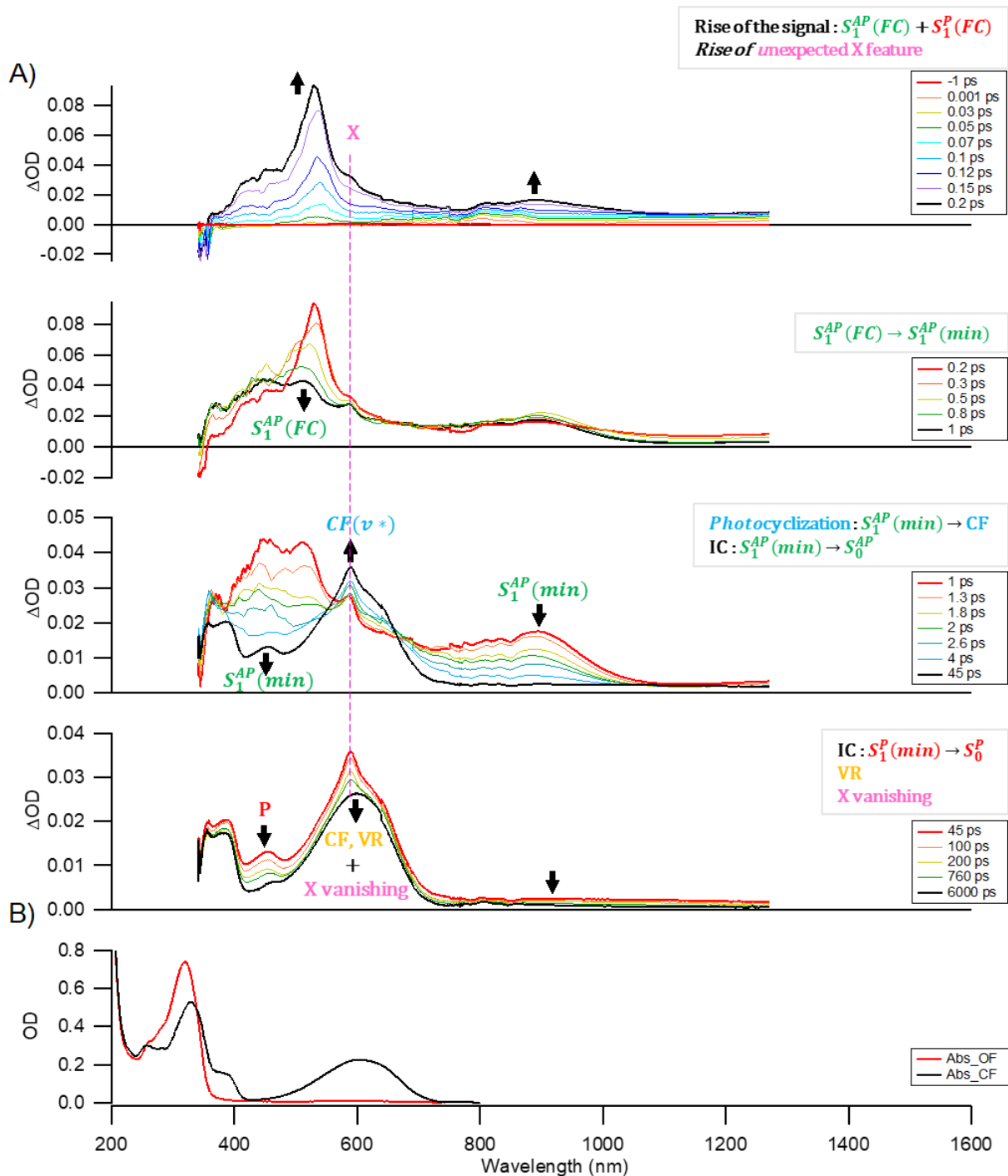


Figure 3.13. (A) fs-TA spectra of DAE2 in dry ACN (100 μM), recorded upon 325 nm laser excitation with a power of 0.1 μJ . The color gradient from red to black represents the spectral evolution over time, grouped into five distinct temporal windows: top panel [–1 ps to 0.14 ps], second panel [0.14 ps to 0.38 ps], third panel [0.38 ps to 1.13 ps], fourth panel [1.13 ps to 45 ps], and bottom panel [45 ps to 6000 ps]; (B) Steady-state UV-Vis absorption spectra of DTE2 in its open (red) and closed (black) forms, included for reference.

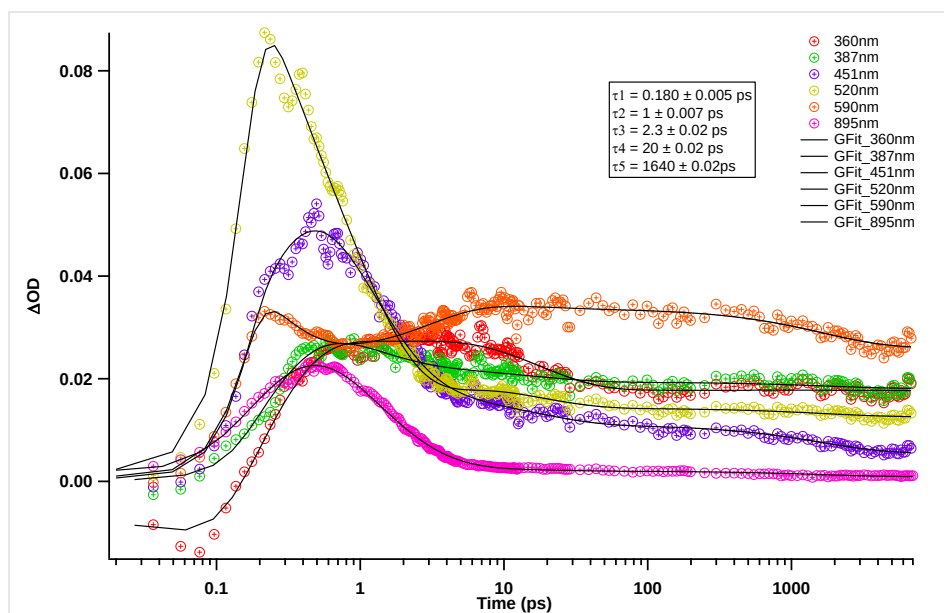


Figure 3.14. Global fitting of transient absorption kinetics of DAE2 (low power) at five selected wavelengths.

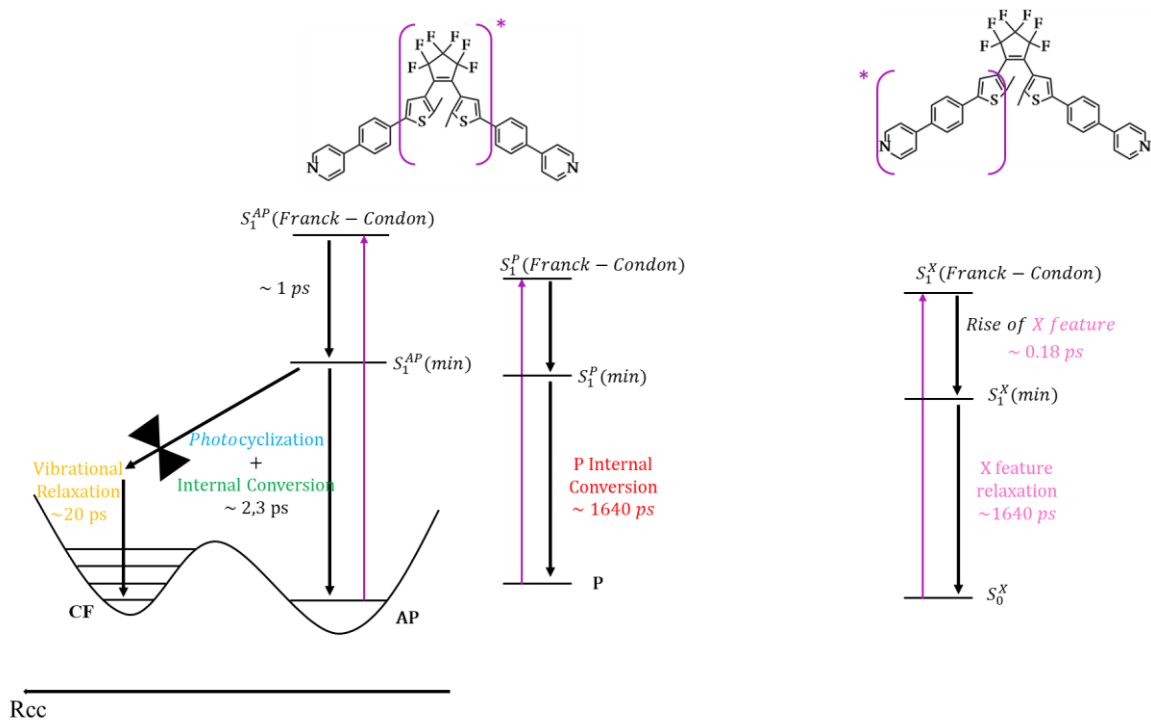


Figure 3.15. Energy diagram for the AP/P conformers, X feature and CF species as a function of the reactive coordinate (Rcc) of DAE2 at low power, highlighting the main relaxation pathways and characteristic times.

3.6. Comparative Ultrafast Dynamics: DAE1 vs DAE2

The overall relaxation dynamics of DAE1 and DAE2, obtained from global fitting of the fs-TAS data, are summarized in **Table 3.3** above, while a direct comparison between the two systems is presented in **Table 3.4**. This comparison aims to elucidate how the additional phenyl spacer in DAE2 reshapes the excited-states and photocyclization mechanism relative to DAE1.

At low power, DAE1 cyclizes almost rapidly, $\tau \approx 0.40$ ps, directly from $S_1^{AP}(FC)$, producing CF, whereas DAE2 requires prior relaxation $S_1^{AP}(FC) \rightarrow S_1^{AP}(min)$ before closing. In the following, we will refer to:

-Direct photocyclization mechanism as the pathway $S_1^{AP}(FC) \rightarrow CF$,

-Sequential photocyclization mechanism as the pathway $S_1^{AP}(FC) \rightarrow S_1^{AP}(min) \rightarrow CF$.

This extra step clearly slows down the CF formation by one order of magnitude $\tau \approx 2.3$ ps.

At high power, both molecules proceed via the sequential mechanism but with distinct kinetics. In DAE1, $S_1^{AP}(min)$ forms almost instantaneously (~ 0.1 ps) and drives CF formation in 0.6 ps. In contrast, DAE2 display ultrafast relaxation more slowly (~ 1 ps), and CF forms in ~ 2.3 ps along directly with AP internal conversion, reflecting a less efficient pathway.

Vibrational relaxation of the CF band is essentially comparable at low power (DAE1: 80 ps; DAE2: 70 ps), but both molecules relax faster under high power, with DAE1 reaching 45 ps and DAE2 an even shorter 20 ps.

Overall, DAE1 is faster and cleaner ultrafast CF formation, while DAE2 is slower and more complex, shaped by the extra phenyl spacer.

Do the mechanistic differences able to rationalize the higher photocyclization QY of DAE2 (0.66) compared to DAE1 (0.5)? This question remains open; however, the additional phenyl group in DAE2, which favors a sequential pathway, likely introduces extra stabilization factors by modulating the relative energetic positions of the CI and the $S_1^{AP}(min)$ state. To clarify this point, advanced calculations beyond the TD-DFT level would be required. Finally, it is worth noting that the X feature appears exclusively in DAE2, and its precise assignment remains to be established later.

Table 3.4. Side-by-side comparison of ultrafast photocyclization dynamics in DAE1 and DAE2 (ACN- low and high power).

Dynamics	Low Power (0.1 μ J)		High Power (1.2 μ J)	
	DAE1	DAE2	DAE1	DAE2
Photocyclization mechanism	Direct	Sequential	Sequential	Sequential
CF formation time(s)	0.40 ps	<0.13 ps	0.1 ps	1 ps
		10.0 ps	0.60 ps	2.3 ps
AP IC	4.5 ps	10 ps	negligible	2.3 ps
CF VR	80 ps	70 ps	45 ps	20 ps
P IC	880 ps	3090 ps	960 ps	1640 ps
X Feature?	Absent	Present	Absent	Present

3.7. Photoreversion dynamics of DAE1 and DAE2

3.7.1 Electronic States Involved (TD-DFT) and Emission Properties

Absorption DAE1 and DAE2. TD-DFT calculations performed on the CF of DAE1 and DAE2 reveal that both molecules exhibit a dominant $S_0 \rightarrow S_1$ transition in the red region, centered at ~615 nm with high oscillator strengths ($f \approx 0.4$ for DAE1 and 0.7 for DAE2). This transition corresponds to a HOMO $\rightarrow$ LUMO excitation delocalized across the diarylethene backbone and is directly addressed by our experimental pump at 660 nm. The photoreversion of both systems is therefore initiated from the S_1 state, as illustrated in **Figure 3.16** (top for DAE1 and bottom for DAE2).

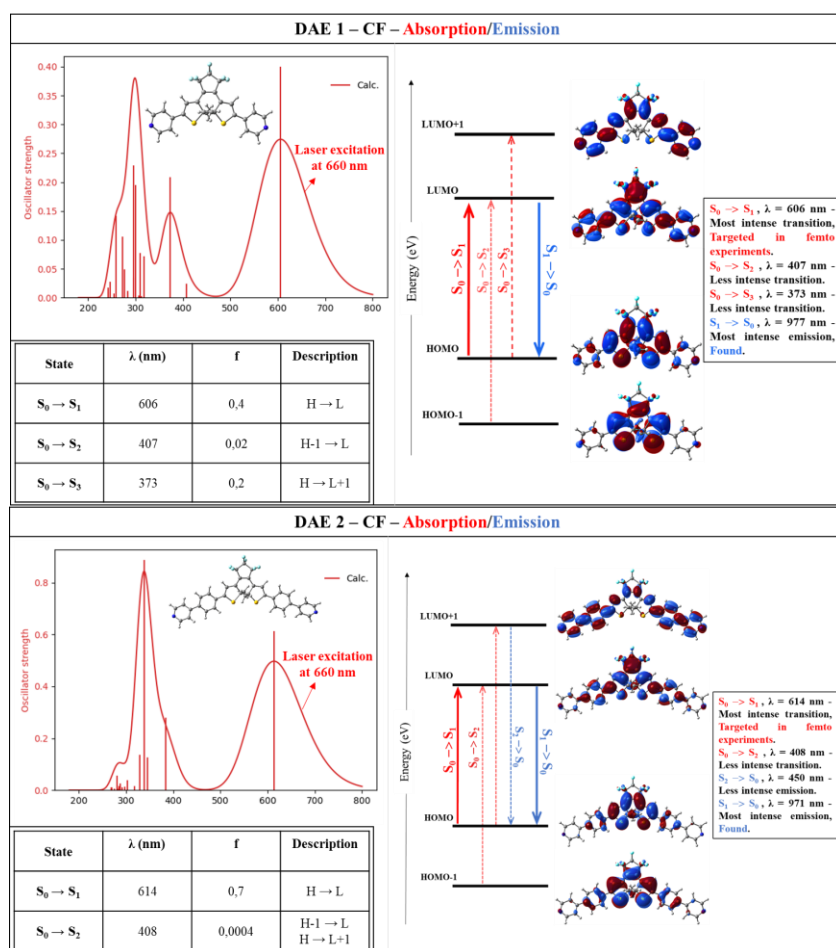


Figure 3.16. Theoretical Absorption/Emission Transitions with Orbital Contributions for DAE1-CF (upper) and DAE2-CF (bottom).

Emission of DAE1 and DAE2. On the emission side, TD-DFT predicts a $S_1 \rightarrow S_0$ transition near 977 nm for DAE1, corresponding to a low-energy radiative decay channel. However, no fluorescence was observed experimentally in the spectral range up to 1000 nm (with excitation tuned at CF band positions), confirming that the CF of DAE1 behaves as a non-emissive species. In contrast, DAE2 displays clear fluorescence experimentally. Selective 540 nm excitation of the CF (red trace in **Figure 3.17**) produces a distinct emission band at 520 nm (green trace). This feature is absent for DAE1, underscoring the unique emissive character introduced by DAE2. From a theoretical perspective, TD-DFT predicts two radiative channels for the CF of DAE2. The first emission, a $S_2 \rightarrow S_0$ transition near 450 nm, aligns closely with the experimentally observed fluorescence at ~ 500 nm, confirming its assignment. It is important to note the violation of the well-known Kasha's rule, representing the first observable effect introduced by the additional phenyl group compared to DAE1. The second emission, $S_1 \rightarrow S_0$ transition predicted around 971 nm, corresponds to the same radiative channel calculated for DAE1. As in the case of DAE1, this emission could not be detected experimentally using steady-state fluorescence measurements. However, as will be shown later, this transition interferes in the fs-TAS experiment through stimulated emission contributions.

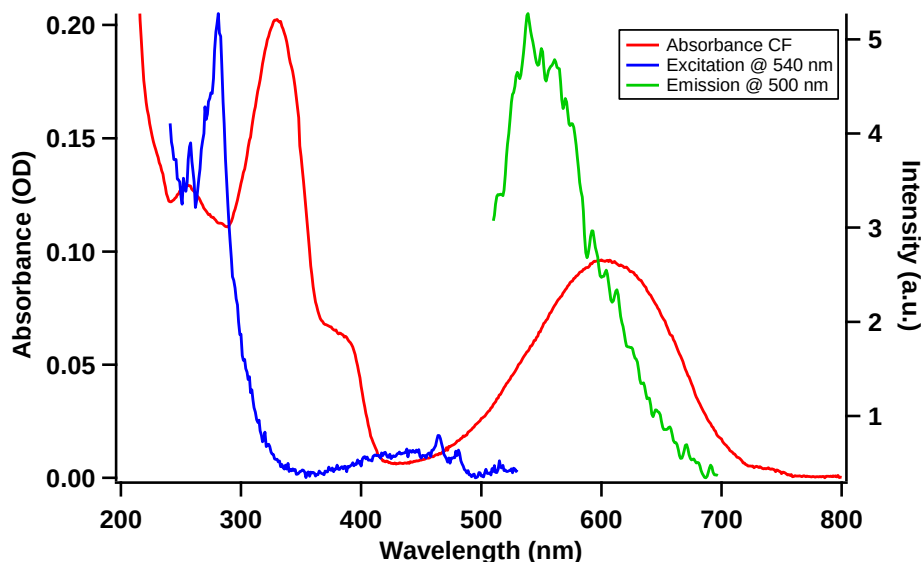


Figure 3.17. Steady-state emission spectra of the closed form DAE2 in ACN.

3.7.2 fs-TAS of DAE1 and DAE2

The photoreversion process (ring opening) of both diarylethenes was investigated by fs-TAS after excitation of their CF at 660 nm (**Figure 3.18**). Both DAE1 and DAE2 display closely similar spectral and kinetic behavior, indicating that their intrinsic excited-state relaxation sequence is preserved across both molecules. Global analysis of the transient data was fitted using a three-exponential model, and the resulting time constants are summarized in

Table 3.5. Global fit lifetimes (τ_1 to τ_3 , in ps) obtained from multi-exponential analysis of fs-TAS for DAE 1 and DAE 2, measured at different excitation powers. Error bars are given in parentheses.

Molecules	Solvents	Power (μ J)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
DAE 1	ACN	5	0.100(3)	0.900(3)	15(1)
DAE 2	ACN	2.5	0.3(1)	1.00(5)	10 (3)

Although the earliest part of the signal is not presented as a temporal window, a fast rise of the transient features is expected immediately after excitation. This initial process corresponds to the relaxation of the $S_1^{CF}(FC)$ toward its local minimum $S_1^{CF}(min)$, and is captured by the first exponential component of the global fit ($\tau_1 \approx 0.1$ ps and ≈ 0.3 ps for DAE1 and DAE2 respectively; see **Figure 3.19**).

During the TW1 [-1 to 30 ps], two broad positive ESA bands dominate the spectra, one centered at ~ 420 nm in the visible and another in the NIR around ~ 820 - 880 nm. In addition, two broad negative bands can be distinguished: (i) a first band at ~ 590 - 600 nm, immediately assigned to the CF ground-state bleaching (negative image of the CF spectrum); (ii) a second feature in the far-red region, between ~ 1030 and 1110 nm. By comparison with the emission spectra discussed above supported by TDDFT calculations, this band can be confidently attributed to stimulated emission (SE) associated with the $S_1 \rightarrow S_0$ transition reported for DAE1 (~ 977 nm) and DAE2 (~ 971 nm). Although this emission is not detected under steady-state conditions, it clearly appears in the femtosecond transient data, indicating that it is too short-lived to be observed in conventional fluorescence measurements. Over this TW, both ESA signals gradually decay, while the two negative SE band rises back toward zero, evidencing a redistribution of the excited-state population. These spectral changes correspond to a geometric reorganization on the S_1 surface,

where the minimum of the CF excited state overcomes the barrier and evolves toward the OF excited states S_1^{OF} . Global fits indicate lifetimes of ~ 0.9 ps (DAE1) and ~ 1.5 ps (DAE2) for this process. Consequently, the SE feature originating from the same S_1 (CF) state decays with identical kinetics. Notably, such a direct involvement of the $S_1^{CF}(min)$ state, supported by a clear spectroscopic signature, has not been previously reported in the literature.

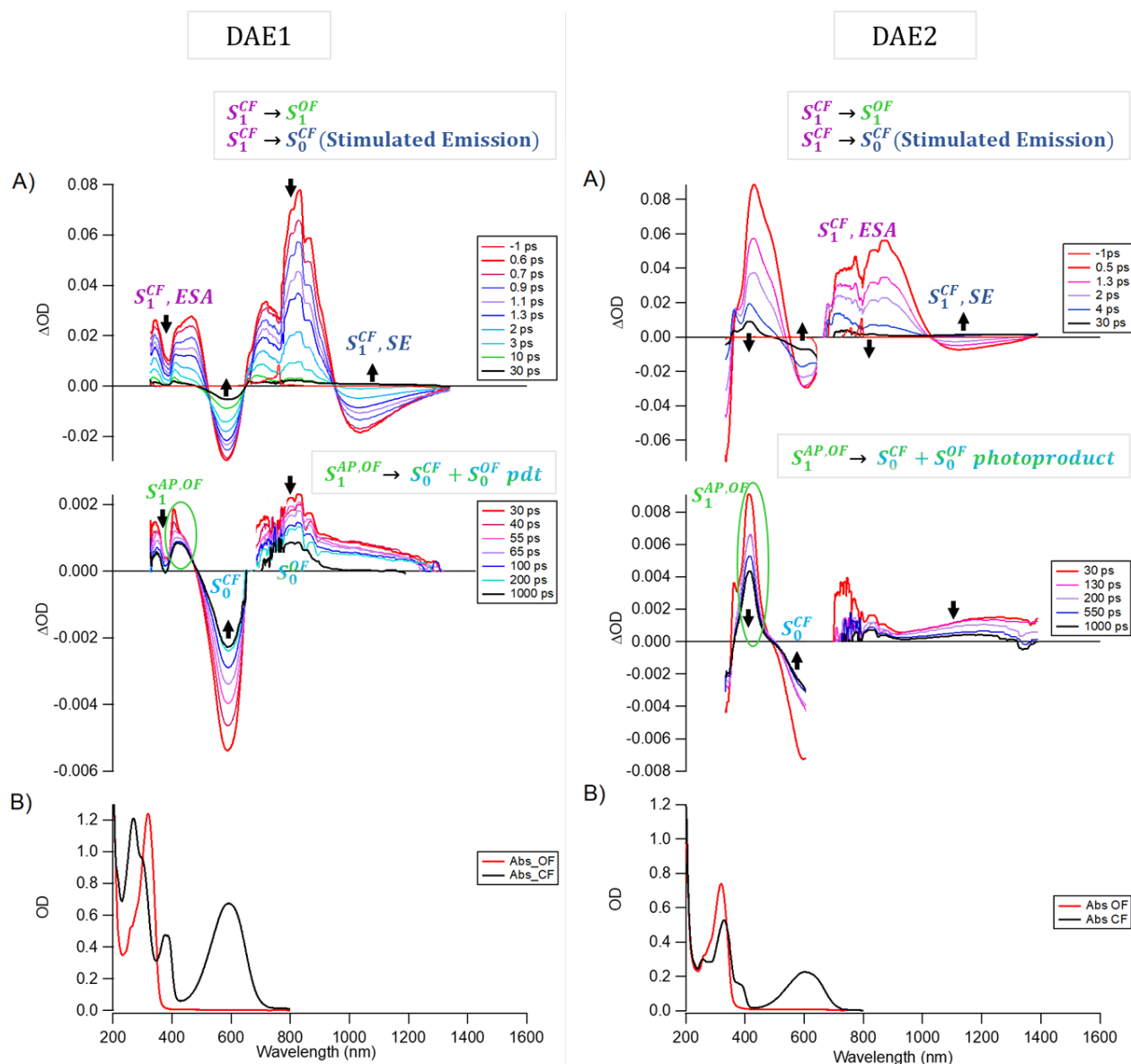


Figure 3.18. (A) fs-TA spectra of DAE1 (left, 5 μ J) and DAE2 (right, 2.5 μ J) in dry ACN, recorded upon 660 nm excitation. The color gradient from red to black represents the spectral evolution over time, segmented into multiple temporal windows. (B) Corresponding steady-state UV-Vis absorption spectra of the open (red) and closed (black) forms are shown for reference.

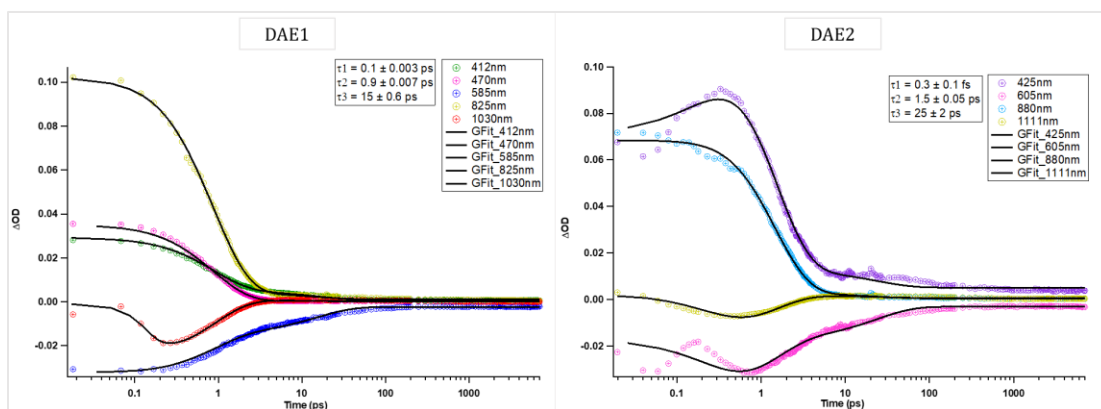


Figure 3.19. Global kinetic fitting of photoreversion dynamics for DAE1 (left) and DAE2 (right).

The TW2 [30 to 1000 ps] is characterized by a continued decay of both ESA bands and a partial recovery of the CF bleach within 15-25 ps. Upon closer inspection, a weak ESA feature peaking at ~ 405 nm can be distinguished. This band may correspond to the residual OF* signal previously observed for DAE1 under high excitation power; namely, the ESA band originating from $S_1^{AP}(min)$ and centered around 480 nm. However, a direct comparison is complicated by the overlap with the bleaching contribution. To further assess this feature, we performed a qualitative reconstruction by subtracting the normalized $S_1^{AP}(min)$ ESA spectrum (320 fs trace from the dataset shown in **Figure 3.20**) from the ground-state absorption of the CF form. The resulting spectrum exhibits a shoulder near 405 nm. While a chemometric analysis will be required in the future, these preliminary observations suggest that after the initial ultrafast process occurring in the first temporal window, the system proceeds within the excited state of the OF species involved in photocyclization. This provides strong evidence that both photoswitching mechanisms proceed through the same reactive geometry.

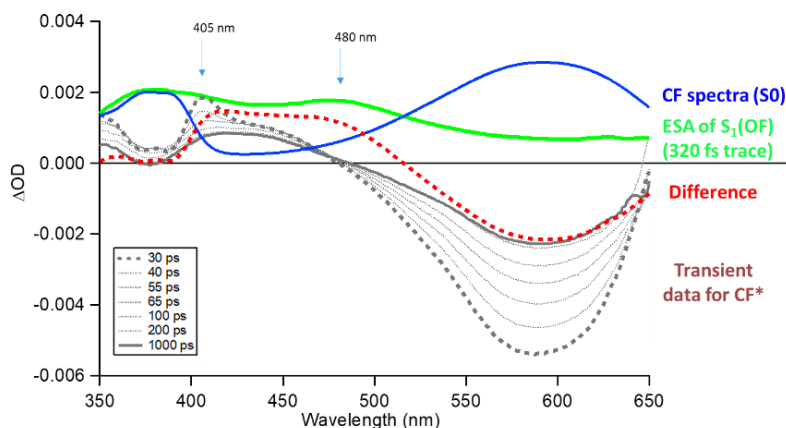
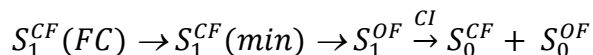


Figure 3.20. Qualitative reconstruction of CF transient data (gray traces) obtained by subtracting the ESA of the OF species detected during the photocyclization experiment from the ground-state absorption spectrum of the CF form.

By analogy with other DAE systems exhibiting similar characteristic times, it is assumed that the final relaxation from $S_1^{AP}(min)$ proceeds through the well-known S_1/S_0 CI, leading to population of either the OF or CF ground states. Altogether, the results summarized in the global fitting (**Figure 3.19**) and the schematic energy-level diagram (**Figure 3.21**) show that both DAE1 and DAE2 follow an analogous photoreversion cascade:



with DAE2 exhibiting slightly slower dynamics owing to its more extended conjugation and higher structural rigidity.

Finally, it is worth recalling the discussion at the beginning of this chapter concerning the QY. The photoreversion QY of DAE2 (0.007) was found to be smaller than that of DAE1 (0.011), even though both molecules appear to follow the same underlying mechanism. The key distinction lies in DAE2, which exhibits a violation of Kasha's rule, suggesting that part of its excited-state population decays through an extra nonradiative pathway from the S_2 electronic state. Future work should focus on measuring the photoreversion QY of DAE2 under different excitation wavelengths, as previously explored for related systems (23).

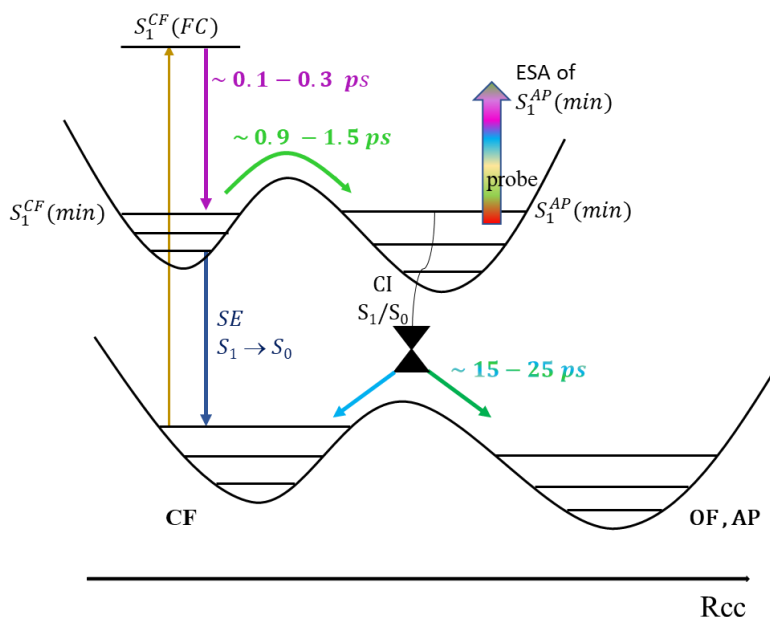


Figure 3.21. Schematic energy level diagram illustrating the ultrafast excited-state dynamics during the photoreversion of DAE1 and DAE2.

3.8. Conclusion

In this chapter, we combined steady-state absorption and emission spectroscopy, NMR spectroscopy, fs-TAS, and quantum chemical calculations to unravel the photoswitching mechanisms of two structurally related diarylethenes: the simple derivative DAE1 and its extended phenyl-pyridyl lateral analogue DAE2.

Conformational analysis via TD-DFT and ^1H NMR spectroscopy demonstrated that both systems adopt the AP and P geometry in solution. However, the presence of non-reactive P conformers, undetected in NMR due to rapid $\text{AP} \leftrightarrow \text{P}$ interconversion on a timescale faster than what NMR can resolve, was confirmed in the transient absorption data through clear P associated signatures.

At the steady-state absorption level, both molecules exhibited clean and fully reversible interconversion between the OF and CF, with no signs of photofatigue. Despite their shared hexafluorocyclopentene core, the insertion of a phenyl spacer in DAE2 significantly accelerated both photocyclization and photoreversion and increased the photocyclization QY (0.66 for DAE2 vs. 0.5 for DAE1). Emission studies further distinguished the two systems: while DAE1 remained non-emissive in its OF, DAE2 exhibited S_2 -state fluorescence localized on its lateral arm, reflecting a violation of Kasha's rule. For the closed form, although TD-DFT calculations predict an $S_1 \rightarrow S_0$ emission channel, no corresponding signal has been detected experimentally using steady-state emission spectroscopy.

fs-TAS measurements revealed pronounced differences in the excited-state dynamics of DAE1 and DAE2, with additional sensitivity to the excitation power.

For DAE1, two distinct photocyclization pathways were identified. At low excitation power, the molecule undergoes an ultrafast direct photocyclization from the FC region, $S_1^{AP}(\text{FC}) \rightarrow \text{CF}$, whereas at higher power, the process follows a sequential pathway, $S_1^{AP}(\text{FC}) \rightarrow S_1^{AP}(\text{min}) \rightarrow \text{CF}$, involving relaxation to the bottom of the S_1 potential well. Such dual photocyclization behavior was first proposed by our group for other DAE derivatives (23).

In contrast, DAE2 exhibits only the sequential photocyclization mechanism, a feature that poses an interesting challenge for computational modeling. The corresponding lifetimes reported for DAE1 and DAE2, ranging from ~ 0.4 ps to 2.3 ps, are consistent with values reported in the literature. Moreover, DAE2 displays a striking additional feature: a transient sharp X feature band centered at ≈ 588 nm, characterized by an ultrafast rise and a decay below 2000 ps. **The nature of this X feature will be discussed in detail in the following chapter.**

Concerning photoreversion, both diarylethenes follow analogous photoreversion dynamics initiated from the S_1 state of the closed form. Excitation of this state leads to a sequential photoconversion process: from the FC region, the system relaxes to the S_1 state within less than 0.3 ps, as evidenced by the stimulated emission band observed at the position of the $S_1 \rightarrow S_0$ transition predicted by TD-DFT in the near-infrared region. Remarkably, such a feature has, to the best of our knowledge, never been reported before. The system then overpasses a potential barrier to reach the $S_1^{AP}(min)$ state, identified through its distinct ESA signature, likely corresponding to the same transient species observed during photocyclization.

Altogether, these results demonstrate how a subtle molecular modification (the insertion of a phenyl spacer) can profoundly alter the efficiency, speed, and complexity of photochromic reactivity. While DAE1 offers faster and simpler dynamics, DAE2 achieves higher yield through slower and more complicate pathways involving additional relaxation channels.

In the next chapter, the influence of confinement is explored as DAE1 and DAE2 are incorporated within inorganic cages, to determine how their photochemical behavior responds to structural and electronic restrictions.

Mechanisms of Diarylethenes Combined with Polyoxometalate Clusters

This chapter investigates the ultrafast photodynamics and electronic behavior of three diarylethene-based supramolecular assemblies; MB, MC1, and MC2; each incorporating DAE1 or DAE2 units within polyoxometalate capsules. Using femtosecond transient absorption spectroscopy, we explore how conformational restriction and molecular encapsulation influence the photocyclization and photoreversion pathways. These systems provide a platform to assess how geometric constraints (enforced P or AP configurations) reshape the excited-state pathways and give rise to new photophysical features such as charge transfer states and long-lived excited species. Complementary steady-state absorption and emission measurements, quantum yield determinations, and TD-DFT calculations are employed to clarify the spectral signatures, assign vertical transitions, and map the excited-state dynamics. Together, these tools provide a comparative picture of the photoreactivity of caged diarylethenes, shedding light on how molecular design and supramolecular architecture govern structural changes.

4.1. Introduction

In Chapter 3, we investigated the fundamental photocyclization and photoreversion dynamics of the simple diarylethene derivatives DAE1 and DAE2. These systems provided a basis for understanding how subtle structural modifications, such as the addition of a phenyl spacer in DAE2, influence the efficiency and mechanistic complexity of photoswitching.

Building on these insights, this chapter turns to more complex architectures where DAE units are integrated into supramolecular capsules constructed from polyoxometalates clusters either $[(\gamma\text{-PMo}_{10}\text{O}_{34})(\text{pyridine})_2]^{3-}$ or $[(\text{A-}\alpha\text{-PMo}_9\text{O}_{31})(\text{pyridine})_3]^{3-}$. Three assemblies are presented in **Figure 4.1**, denoted as MB, MC1, and MC2, which refer respectively to the molecular basket and the two molecular capsules. In MB, a single DAE1 unit is fixed in a restricted geometry on $\text{PMo}_{10}\text{O}_{34}$ unit that enforces the non-photoactive P conformer, through the coordination of its two terminal pyridyl groups to molybdenum atoms. In MC1, three DAE1 units are confined between two $\text{PMo}_9\text{O}_{31}$ unit, an arrangement that enforces exclusively the AP geometry (34). This configuration was clearly confirmed by X-ray crystallography, which showed that all three DAE1 units are fixed in the AP form. As with DAE1, MC1 is reinvestigated here over an extended spectral range to obtain a more deep comprehensive picture of its excited-state dynamics. In MC2, the same capsule design is employed as MC1 but incorporates three DAE2 units together with two POM clusters. However, crystals suitable for X-ray diffraction could not be obtained for MC2, and as a result, its crystal structure remains undetermined. This leaves the conformation of the DAE2 units within the capsule unknown. Therefore, we rely on NMR data, along with theoretical calculations discussed later, to gain structural conformation insight.

Concerning the photochemical characterization by fs-TAS, preliminary transient results for MC1 were obtained in 2022 by Chouadhri et al. (34). Three main characteristic lifetimes were identified: ~ 0.5 ps for photocyclization, ~ 6 ps for vibrational relaxation, and an unexpected ~ 60 ps process marked by a sharp transient feature appearing after photocyclization ((34), Figure 5). By comparison with spectroelectrochemistry and TD-DFT calculations, this process was assigned to a CT from the DAE unit to the POM. No preliminary results were reported for MB or MC2.

The central question guiding this chapter is therefore: How does the encapsulation of DAE units within polyoxometalate architectures influence their ultrafast photoswitching molecule compared to the free DAE molecules? Beyond comparing their excited-state dynamics, we aim to

determine whether both photocyclization and photoreversion are affected in the same way by the inorganic cage environment. In particular, the presence of the POM introduces new charge-transfer interactions that were previously reported for MC1 (34), raising the question of whether this process is accompanied by a subsequent BCT.

Moreover, by extending the study to MC2, we assess whether the insertion of an additional phenyl linker enhances or suppresses this charge-transfer activity. By combining steady-state absorption spectroscopy, fs-TAS, and theoretical modeling, we compare the photochemical and photophysical behavior of confined DAEs directly with the free DAE1/DAE2 benchmarks established in Chapter 3. Before discussing the spectroscopic results, the next section briefly describes the structural and electronic characteristics of the POM frameworks used to construct MB, MC1, and MC2, since these inorganic cores are key to understanding the confinement effects observed later.

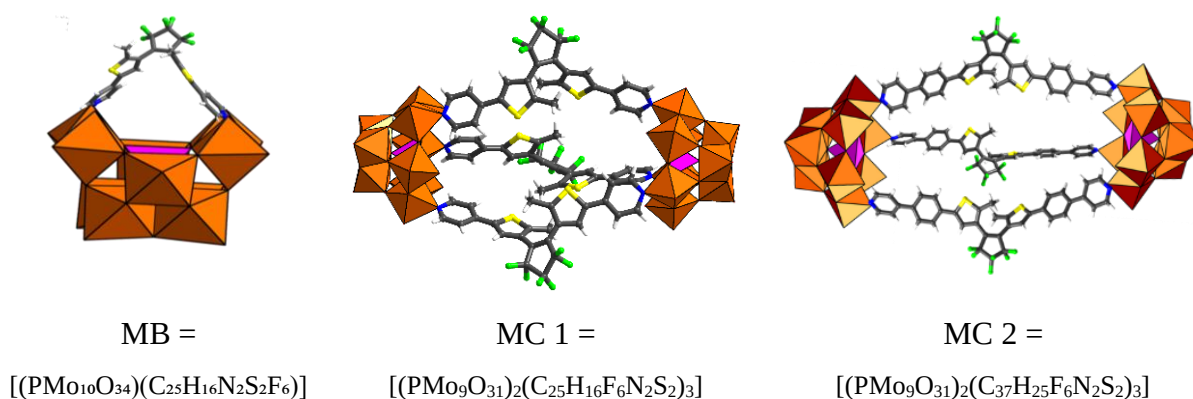


Figure 4.1. Chemical structures of the diarylethene-based capsules MB, MC1, and MC2.

4.1.1 Inorganic Framework: Polyoxometalates

Polyoxometalates are discrete metal-oxygen clusters built from early transition metals such as molybdenum (Mo), tungsten (W), or vanadium (V) in their high oxidation states. These metals form MO_6 octahedra connected through shared oxygen atoms, giving rise to stable and highly tunable polyanionic structures. Among the main structural families: Anderson-Evans, Lindqvist, Wells-Dawson, and Keggin, the Keggin type is the most studied because of its remarkable stability, redox activity, and ability to be functionalized (**Figure 4.2**).

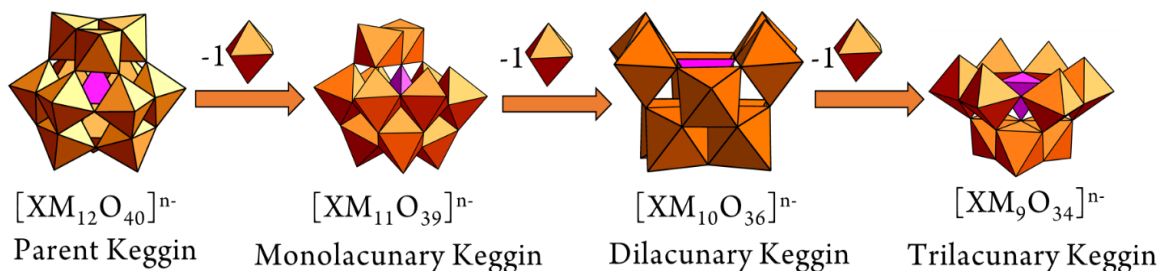


Figure 4.2. Graphical representation of Keggin polyoxometalates and respective lacunary species.

When one or more metal-oxygen units are removed from a POM framework, it results in the generation of lacunary species. Depending on the number of vacant site, the POM can be called as mono-, di-, tri- lacunary (**Figure 4.2**). These vacant sites are often reactive and can coordinate to various metal atoms as well as organic ligands. Therefore, lacunary POMs can be envisioned as a robust platform for the development of inorganic-organic hybrid materials with tunable properties, offering precise control over geometry, charge distribution, and electronic coupling between inorganic and organic components.

In particular, polyoxomolybdate derivatives have long been difficult to functionalize compared to their tungstates analogues due to their hydrolytic stability. However, work by Suzuki et al. introduced a major advance through the preparation of stable pyridine-functionalized molybdate clusters:

$\{PMo_9\} = TBA_3[PMo_9O_{31}(py)_3]$, a tri-lacunary cluster coordinated by three pyridyl ligands.

$\{PMo_{10}\} = TPP_3[PMo_{10}O_{34}(py)_2]$, a di-lacunary species obtained by controlled thermal conversion of $\{PMo_9\}$ in a DMA/pyridine mixture.

These two species serve as the inorganic building blocks for the systems studied in this work: both $\{PMo_9\}$ and $\{PMo_{10}\}$ can act as precursors for the construction of pyridyl-functionalized POM-hybrid architectures (**Figure 4.3**).

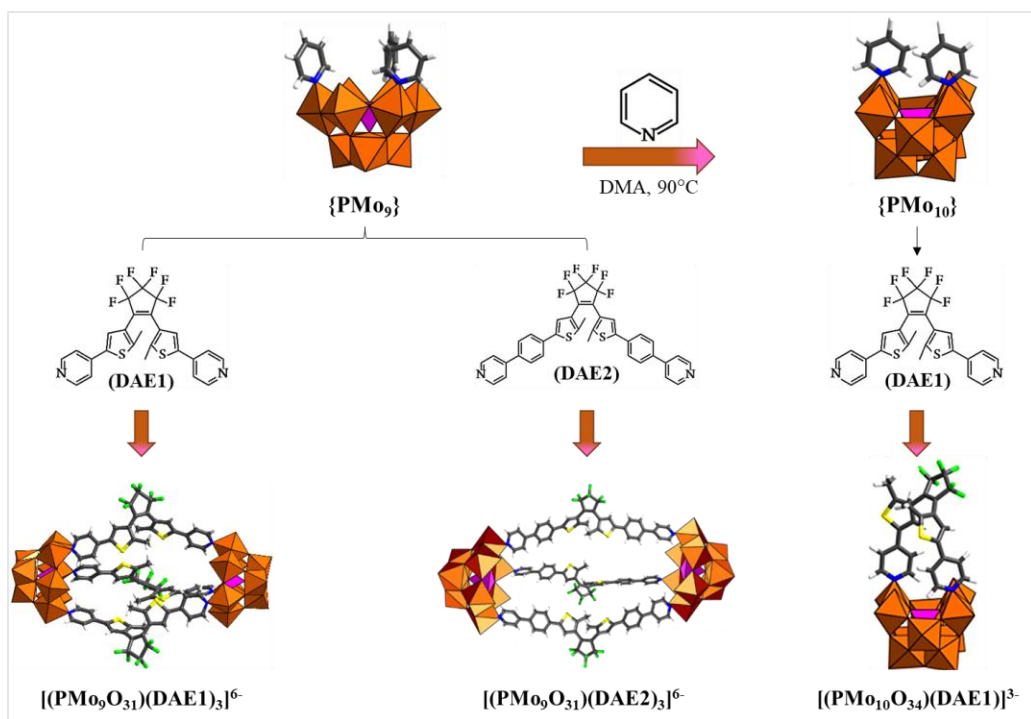


Figure 4.3. Graphical representation of self-assembly of {PMo₉}-based organic architectures.

MC1 and MC2 are based on {PMo₉}, where two POM clusters are bridged by three DAE linkers to form capsule-like architectures that confine the DAE chromophores.

MB is derived from {PMo₁₀}, where a single DAE1 molecule coordinates to PMo₁₀, enforcing the parallel, non-photoactive geometry.

The resulting {PMo₉}- and {PMo₁₀}-based assemblies combine the structural stability of the inorganic POM framework with the reversible photoactivity of the DAE components. This hybrid design enables the study of how confinement and electronic coupling within the POM cage influence the photodynamics of the DAE units.

4.2. General Photochromic Properties of MC1 and MC2

After establishing the photochromic parameters of DAE1 and DAE2 in Chapter 3, we now turn to their encapsulated analogues, MC1 and MC2. The aim is to assess how confinement within POM-based capsules modifies their steady-state absorption profiles, PSS, and QYs, and to compare these directly with the free DAE. While both assemblies preserve the fundamental reversible photochromism of their parent molecules, they also exhibit distinct shifts in spectral position, changes in absorption intensity, and altered switching efficiencies, reflecting the influence of the confined environment. The main photochemical parameter, namely the photocyclization QY,

together with the photophysical parameters derived from steady-state absorption (λ_{max} and molar absorptivity), are summarized in **Table 4.1**.

Figure 4.4 shows the steady-state UV-Vis absorption spectra of MC1 and MC2 during photocyclization (top panels) and photoreversion (bottom panels). As with the free DAE1 and DAE2 systems, clear isosbestic points confirm a clean two-state interconversion between the open and closed forms. However, the confined environment of the MC1 and MC2 capsules leads to notable modifications in the isosbestic points, absorption maxima, spectral intensities, and PSS compositions as shown in **Table 4.1**. It is also worth noting that no experimental emission was observed for MC1, whereas MC2 exhibited a measurable emission signal as found for free DAE2, which will be discussed in more detail later in this chapter.

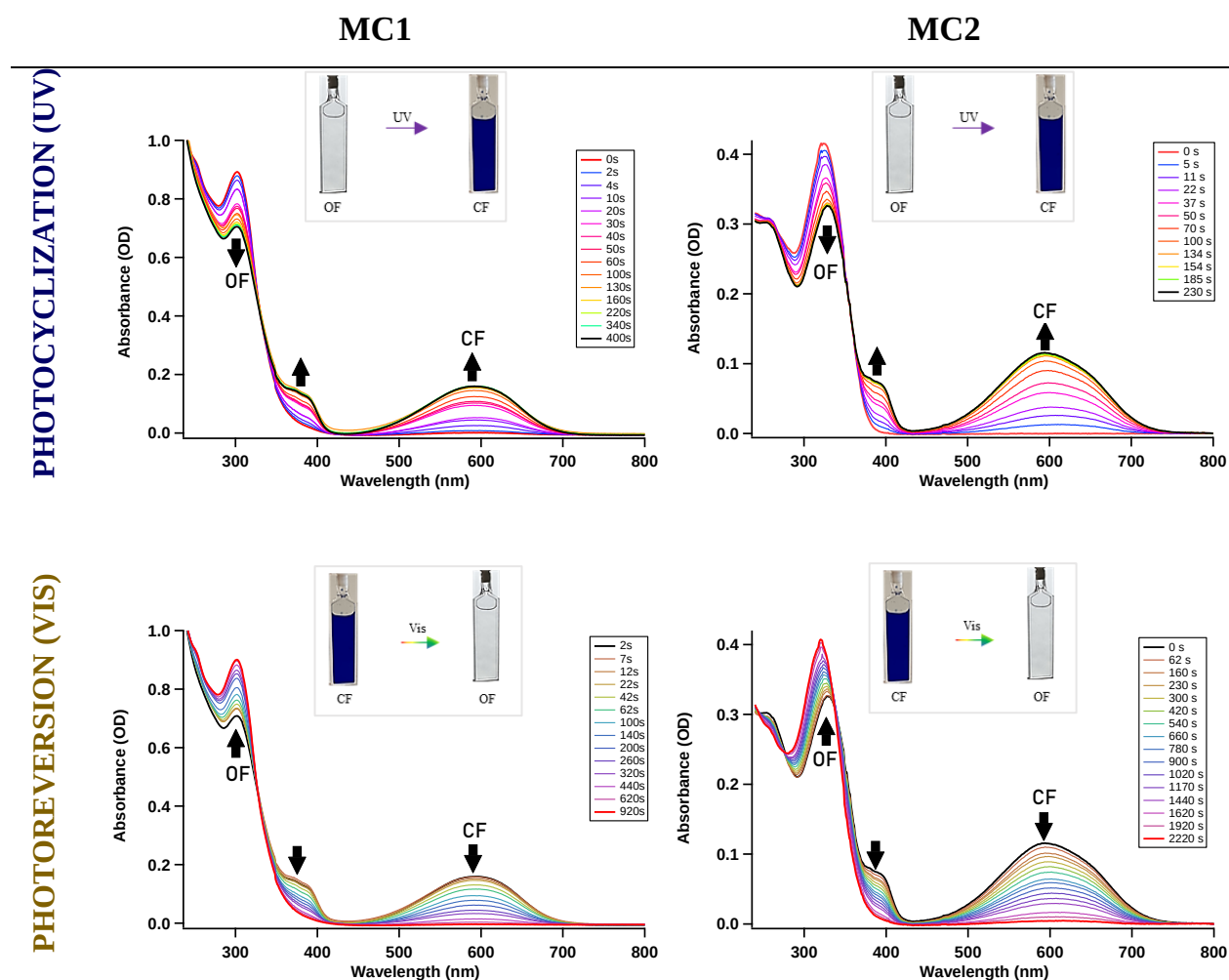


Figure 4.4. Temporal evolution of the steady-state UV-Vis absorption spectra in dry ACN for MC1 [75 μM] (left) and MC2 [20 μM] (right) under 330 nm UV irradiation (top) and 590 nm visible irradiation (bottom), corresponding to the photoinduced ring closure (OF $\rightarrow$ CF) and ring opening (CF $\rightarrow$ OF) reactions, respectively. Arrows indicate the spectral changes over time.

For MC1. The steady-state UV-Vis absorption spectra of MC1 (ACN, 75 μ M), shown in (Figure 4.4, left panel), demonstrate a clear reversible photochromic transformation upon alternating UV (330 nm) and visible (590 nm) irradiation. The OF is characterized by a strong absorption band at 302 nm ($\epsilon = 11.49 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which decreases upon UV irradiation with simultaneous rise of a broad visible band centered at 590 nm ($\epsilon = 3.99 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), corresponding to the CF. An isosbestic point at 330 nm confirms a clean two-state interconversion. The PSS is reached after ~ 400 s (vs ~ 185 s for free DAE1).

Compared to free DAE1 ($\lambda_{\text{max,OF}} = 301 \text{ nm}$, $\lambda_{\text{max,CF}} = 592 \text{ nm}$), MC1 shows essentially the same band positions, indicating that the POM framework does not experimentally significantly alter the HOMO-LUMO energy gap. In contrast, the molar absorptivities are strongly enhanced owing to the cooperative presence of three DAE1 units within the capsule and the contribution of the POM units. Indeed, $\epsilon(\text{OF})$ increases from 3.45×10^4 for DAE1 to $11.49 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for MC1, corresponding to a ratio of ~ 3.3 , slightly above the expected $\times 3$ scaling, suggesting that POM absorption in the UV range is not negligible. In contrast, $\epsilon(\text{CF})$ from 1.65×10^4 to $3.99 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (ratio ≈ 2.4). The latter value is slightly below the expected $\times 3$ scaling, while the OF enhancement remains more pronounced, consistent with modest cooperative effects between the encapsulated DAE1 chromophores.

Despite these higher extinction coefficients and the absence of any P-conformer population, MC1 exhibits a markedly lower photocyclization QY ($\Phi_{\text{cycl}} = 0.07$ vs. ≈ 0.5 for DAE1). This reduced efficiency suggests that: (i) confinement within the POM framework alters the excited-state relaxation pathways, a point examined in detail through ultrafast spectroscopy in the following section; and (ii) part of the incident light is absorbed by the POM units, reducing the effective excitation of the DAE chromophores.

Upon subsequent visible-light irradiation, the CF band at 590 nm diminishes and the sharp OF absorption at 302 nm is restored, with the spectral evolution again passing through an isosbestic point at 330 nm. OF recovery is complete by ~ 920 s, faster than the ~ 1845 s required for free DAE1, indicating that while confinement slows ring-closure, it facilitates the reverse ring-opening process. The QY for photoreversion is 0.003, notably lower than that of DAE1 (0.011), confirming that the POM framework also reduces the efficiency of the visible-induced ring-opening pathway.

For MC2. The observations are exactly the same compare to MC1. Under identical conditions, MC2 (in dry ACN) exhibits the same qualitative photochromic response as its parent

molecule DAE2 during photocyclization at 330 nm UV irradiation (**Figure 4.4**, right panel). The OF absorption maximum appears at 324 nm ($\epsilon_{\text{OF}} = 17.84 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), shifting to a CF band at 594 nm upon irradiation, with a well-defined isosbestic point at 355 nm confirming a clean two-state interconversion. The PSS is reached after ~ 230 s, substantially slower than for free DAE2 (~ 80 s), indicating that confinement in the capsule markedly retards the cyclization process also for MC2. Compared to DAE2 ($\lambda_{\text{max}}(\text{OF}) = 319$ nm, $\lambda_{\text{max}}(\text{CF}) = 602$ nm), MC2 shows similar absorption maxima but a noticeably larger molar absorptivity for the OF band ($\epsilon(\text{OF})$ rises from 3.96×10^4 to $17.84 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; ratio ≈ 4.5), while the CF band rises $\epsilon(\text{CF}) = 2.29 \times 10^4$ to $5.49 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (ratio ≈ 2.4). The latter value is slightly below the ideal $\times 3$ scaling expected for three independent chromophores, whereas the stronger OF enhancement suggests that absorption by the POM units is far from negligible.

Upon subsequent visible-light irradiation at 590 nm, the CF band at 594 nm decreases while the OF absorption at 324 nm recovers, passing through a clear isosbestic point at 340 nm. The overall recovery time for MC2 (~ 2220 s) is slower than that of free DAE2 (~ 1175 s), confirming that confinement within the capsule hinders the ring-opening kinetics. The corresponding photoreversion QY is 0.002, compared to 0.007 for DAE2, further indicating that the encapsulated environment suppresses the efficiency of the visible-triggered re-opening reaction.

In both MC1 and MC2, the photocyclization and photoreversion QYs are markedly reduced compared to their free analogues, confirming that confinement within the POM cage globally dampens both photochemical directions.

Table 4.1. Optical parameters of the free (DAE1, DAE2) and encapsulated (MC1, MC2) diarylethenes in different solvents, including absorption maxima, QYs, and molar absorptivities.

Molecule	Solvents	λ_{max}, OF	λ_{max}, CF	$\Phi_{cycl.}(UV)$	$\Phi_{rev.}(Vis)$	$\epsilon_{OF} \text{ at } \lambda_{max}$	$\epsilon_{CF} \text{ at } \lambda_{max}$
		nm				$(\times 10^4) \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	
DAE 1	ACN	301	592	0.50	0.011	3.45	1.65
DAE 2	ACN	319	602	0.66	0.007	3.96	2.29
	DCE	322	607	0.67	-	7.74	2.63
MC 1	ACN	302	590	0.07	0.003	11.49	3.99
MC 2	ACN	324	594	0.11	0.002	17.84	5.49
	DCE	324	590	-	-	18.11	-

4.3. Distribution of AP/P Conformers for DAE1 and DAE2

The conformational distribution of the diarylethene units in these capsule systems (MB, MC1, MC2) is strongly directed by the confinement imposed by the POM-based architecture. Unlike the free molecules, where both AP and P conformers are in thermodynamic equilibrium, encapsulation restricts conformational freedom and selectively stabilizes one geometry depending on the design of the capsule. To this end, ^1H NMR spectra of MB, MC1, and MC2 were recorded at room temperature in CD_3CN (MB) and CD_2Cl_2 (MC1 and MC2) (**Figure 4.5**), focusing on the diagnostic methyl and aromatic protons that allow assignment of AP versus P conformers. The corresponding experimental chemical shifts are summarized in **Table 4.2**.

Table 4.2. Experimental ^1H NMR chemical shifts (δ , ppm) of MB, MC1 and MC2.

MB		MC1		MC2	
Me Hd*	Proton Hc*	Me Hd*	Proton Hc*	Me He*	Proton Hd*
2.32	7.11	1.94	7.76	1.90	7.52
				1.92	7.54

For MB. The ^1H NMR spectrum of MB displays signals at $\delta \approx 2.32$ ppm (Hd*) and $\delta \approx 7.11$ ppm (Hc*) (**Table 4.2**). Both appear as sharp singlets indicating adoption of one confirmation the PC. This observation matches the expected confined geometry of MB, where the encapsulated single DAE1 is forced into a P arrangement.

For MC1. The ^1H NMR spectrum of MC1, shows a clear singlet for Hd* at $\delta \approx 1.94$ ppm and a sharp signal for Hc* at $\delta \approx 7.76$ ppm. The absence of splitting or additional peaks rules out any detectable population of the P conformer. Thus, all three DAE1 units confined between the POM clusters are locked in the AP geometry, the reactive form. This enforced AP configuration is consistent with the X-ray crystallographic structure, which confirms selective stabilization of the AP form.

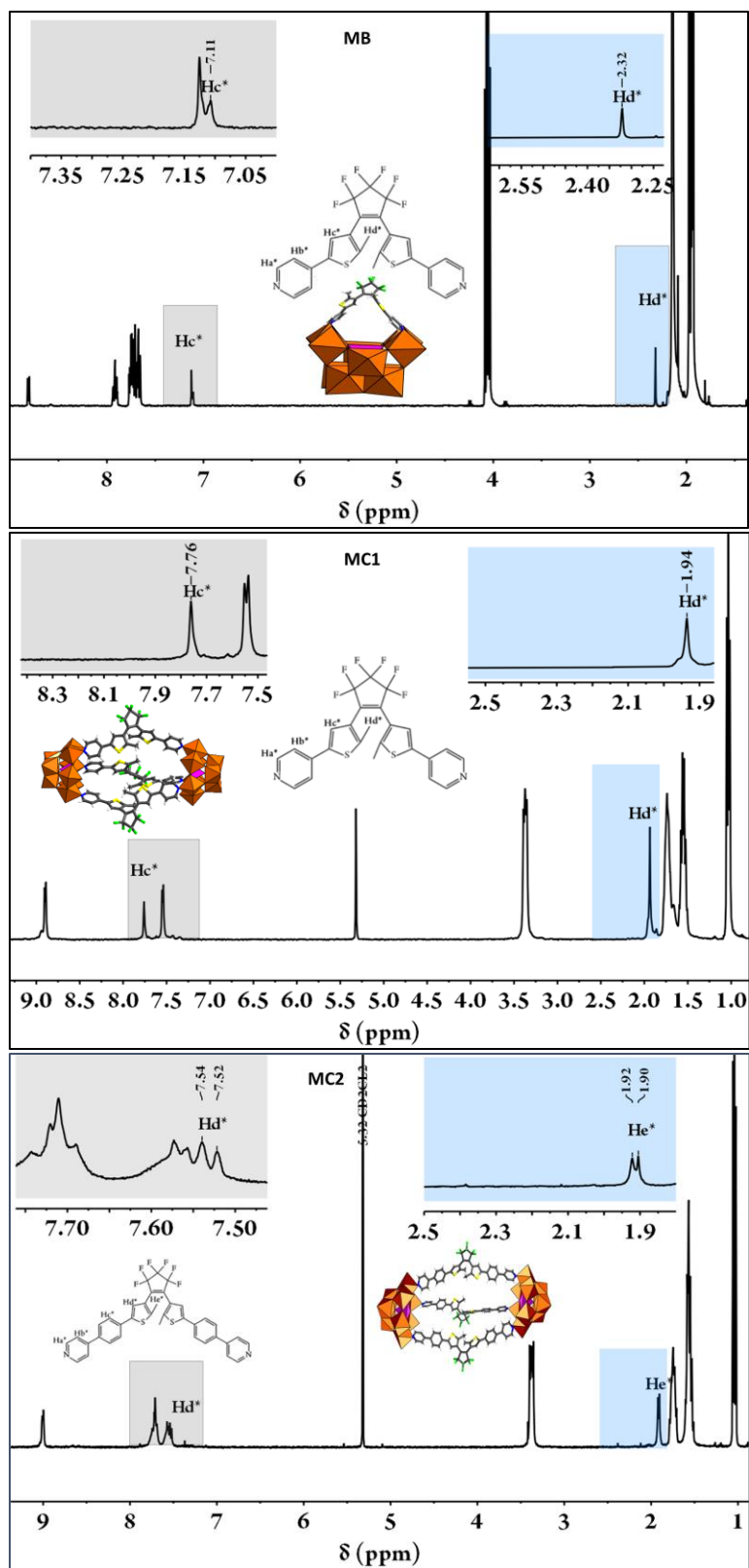


Figure 4.5. ^1H NMR spectra of MB (in CD_3CN) and MC1/MC2 (in CD_2Cl_2) recorded at room temperature highlighting the diagnostic methyl and aromatic protons signals.

For MC2. Unlike DAE2, the diagnostic signals in MC2 appear as doublets at $\delta \approx 1.90/1.92$ ppm (He*) and $\delta \approx 7.52/7.54$ ppm (Hd*). The presence of two distinct peaks for each diagnostic proton indicates the coexistence of both conformers, AP and P, within the capsule, suggesting that a fraction of the encapsulated DAE2 units adopts the P geometry. This stands in contrast to free DAE2, which displayed only single resonances ($\delta \approx 1.94$ and 7.37 ppm) attributed to rapid AP $\leftrightarrow$ P interconversion on the NMR timescale, preventing detection of the P conformer. In MC2, by contrast, the P conformer becomes more pronounced to give distinct resonances, whereas in the other cage MC1 only a single resonance is observed, consistent with an exclusively AP configuration. Following these experimental insights, complementary DFT calculations were relaunched, considering one P conformer and two AP conformers within the capsule.

The optimized geometry (**Figure 4.6**) revealed that this mixed configuration is energetically accessible as the fully AP arrangement, thereby supporting the possibility of coexistence between different conformer distributions. These structural findings are particularly significant and will be considered in the subsequent sections when discussing the excited-state dynamics.

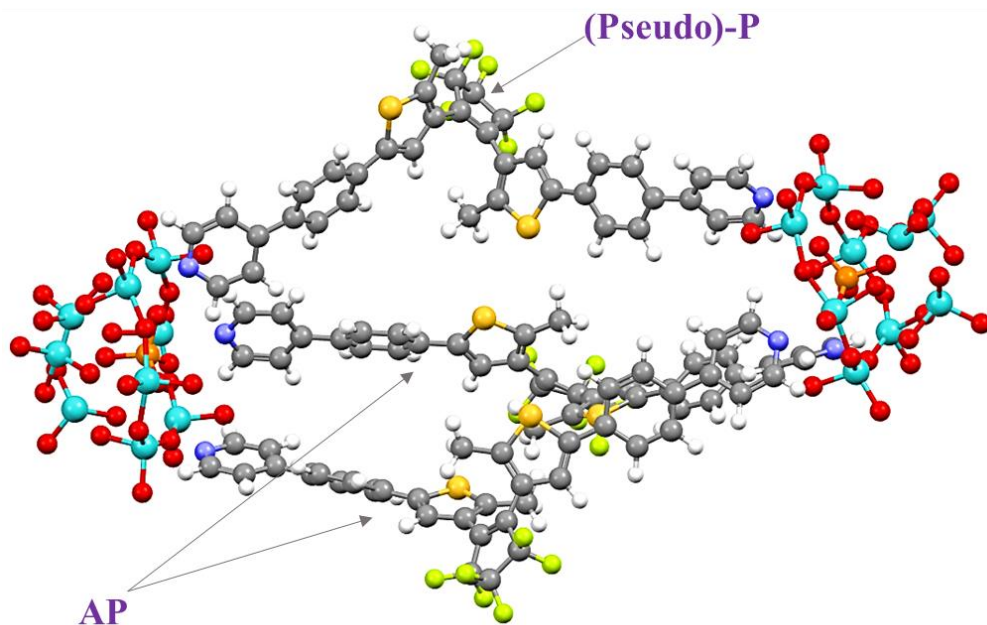


Figure 4.6. DFT-optimized geometry of the MC2 capsule featuring a mixed conformational configuration (2 AP and 1 P DAE2 units).

4.4. Photophysical dynamics of MB

4.4.1 Electronic Excited State of MB (TDDFT)

To rationalize the excited state behaviour of MB, TD-DFT calculations were performed to identify the electronic transitions involved upon laser excitation. The calculated absorption spectrum (**Figure 4.7**, left) reproduces the broad experimental band in the UV region and reveals the contributions of individual electronic transitions.

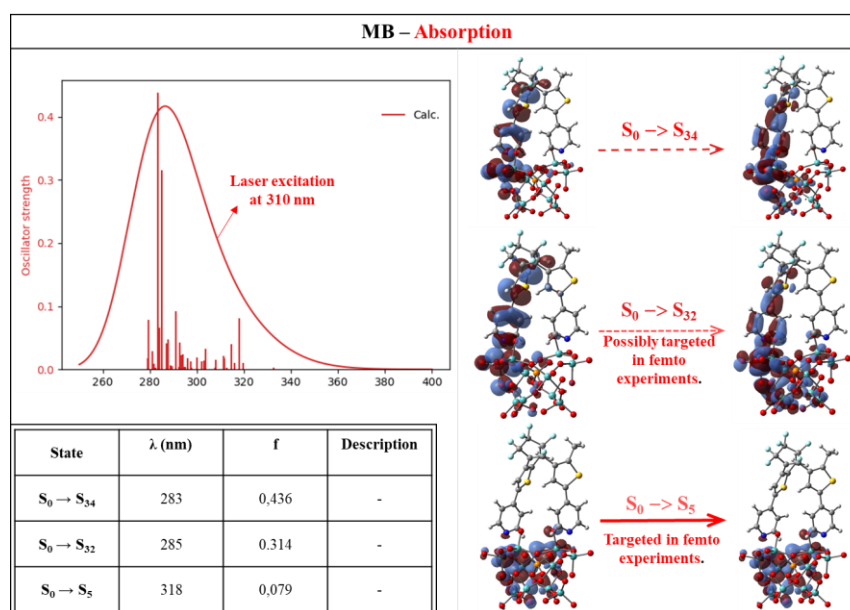


Figure 4.7. Theoretical Absorption Transitions with Orbital Contributions for MB.

The most relevant excitations can be grouped into two main categories. First, $S_3 \rightarrow S_5$ (318 nm, $f = 0.079$): a weak transition predominantly localized on the POM moieties. This transition lies close to the experimental laser excitation wavelength (310 nm) and is therefore the primary channel addressed in our femtosecond experiments. Then, $S_0 \rightarrow S_{32} / S_{34}$ (≈ 283 -285 nm, $f = 0.31$ -0.44): these two close-lying transitions fall within the spectral region of the excitation source. Although less probable than S_5 , their comparable energies and moderate-to-strong oscillator strengths suggest that both states may be partially accessed during the femtosecond experiments, contributing minor excitation channels in addition to the main transition. The diffuse nature of the

accepting orbitals indicates that these high-lying excitations may possess partial Rydberg character, acting as weakly bound doorway states that can interact with nearby valence levels (55).

Molecular orbital analysis (**Figure 4.7**, right) shows that the higher transition S_{32} is delocalized over the lateral chains of DAE1 and **exhibits partial CT character** toward the POM fragment. In contrast, S_5 remains mostly localized on the DAE1 framework with minimal delocalization.

In summary, based on TD-DFT predictions, one can expect that UV excitation will either be localized on the POM or will excite the P conformer, possibly followed by a CT process from the DAE to the POM.

4.4.2 fs-TAS of MB

To directly probe the photophysical dynamics of the parallel conformer, fs-TAS measurements were performed on MB. As evidenced by the NMR results described above, the encapsulated DAE1 is locked in the photoinactive P form. Gaining access to the photophysics of this conformer exclusively through structural constraint is therefore particularly valuable for understanding its intrinsic excited-state behavior. To the best of our knowledge, the photophysics of the parallel conformer alone has never been reported in the literature. Excitation was carried out at 310 nm with a pulse energy of 0.1 μ J in dry ACN at a concentration of 140 μ M. The resulting transient absorption spectra are shown in **Figure 4.8**. To provide a clear overview of the relaxation times extracted from the fs-TAS measurements, the characteristic lifetimes (τ_1 - τ_5) obtained from global multi-exponential fitting are compiled in **Table 3.3**.

The spectra are dominated by broad ESA features extending from the visible into the near-IR region. For clarity, the data are separated into two temporal windows: an initial regime [-1 to 0.2 ps] and a longer relaxation regime [0.2 ps to 6000 ps].

In the early temporal window [TW1: -1 to 0.2 ps], two ESA bands peaking at 385 and 565 nm, together with a broad absorption in the NIR region, rise immediately upon excitation, though with distinct kinetics. In the subsequent windows, a sequence of relaxation processes with different timescales is observed. The overall transient evolution was modeled using global analysis with a four-exponential model, and kinetics were extracted at three strategic wavelengths: 385, 550, and 1000 nm (Appendix 4, Section S.4.1).

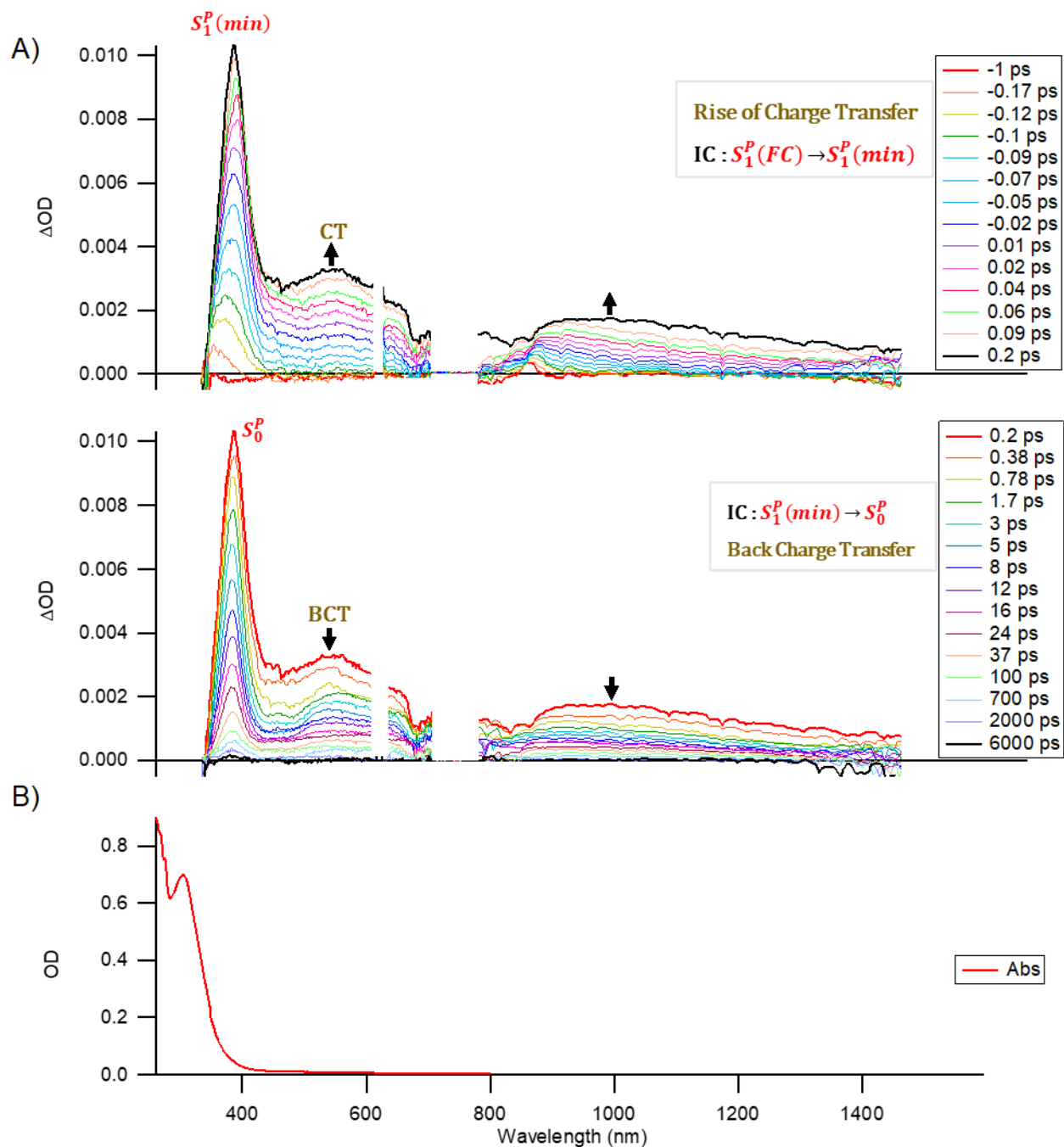


Figure 4.8. (A) Fs-TAS of MB in dry ACN (140 μ M), recorded upon 310 nm laser excitation with a power of 0.1 μ J. The colour gradient from red to black represents the spectral evolution over time, grouped into four temporal windows: top panel [-1 ps to 0.2 ps] and bottom panel [0.2 ps to 6000 ps]. (B) Steady-state UV-Vis absorption spectra of MB shown for reference.

Guided by TD-DFT calculations, the first ultrafast relaxation ($\tau_1 = 0.08$ ps), associated with the rising ESA near 385 nm, is attributed to the relaxation from the FC region of the S_1 state, $S_1^P(FC)$, to its local minimum potential, $S_1^P(min)$. Compared with free DAE1, where the same process occurs in ≈ 0.25 ps, this faster timescale in MB suggests that conformational restriction imposed by the POM modifies the dynamics of the P conformer. It is worth noting that the ESA maximum for the P conformer appears at 385 nm, whereas free DAE1 exhibits its corresponding band near 445 nm. This blue shift reflects the structural constraint exerted by the POM on the encapsulated DAE1 unit, consistent with the TD-DFT predictions discussed above.

As mentioned, the second ESA feature rises gradually from zero and reaches a clear maximum at 565 nm for the 200 fs delay time. The corresponding lifetime associated to this process ($\tau_2 = 0.8$ ps) is tentatively assigned to a CT process. This interpretation is supported by TD-DFT results, which indicate that higher-lying excited states (notably S_{32}) display significant electron delocalization toward the POM fragment. Further support comes from the spectral comparison between MB and MC1 (**Figure 4.9**), which shows that both systems exhibit a largely overlapping CT band centered around ~ 565 nm. This observation is consistent with the DAE $\rightarrow$ POM charge-transfer process previously reported in Chemical Science ((34), Figure 5), where the DAE acts as the donor and the POM as the acceptor. It should be noted that in the case of MC1, this CT feature partially overlaps with additional contributions from the CF species.

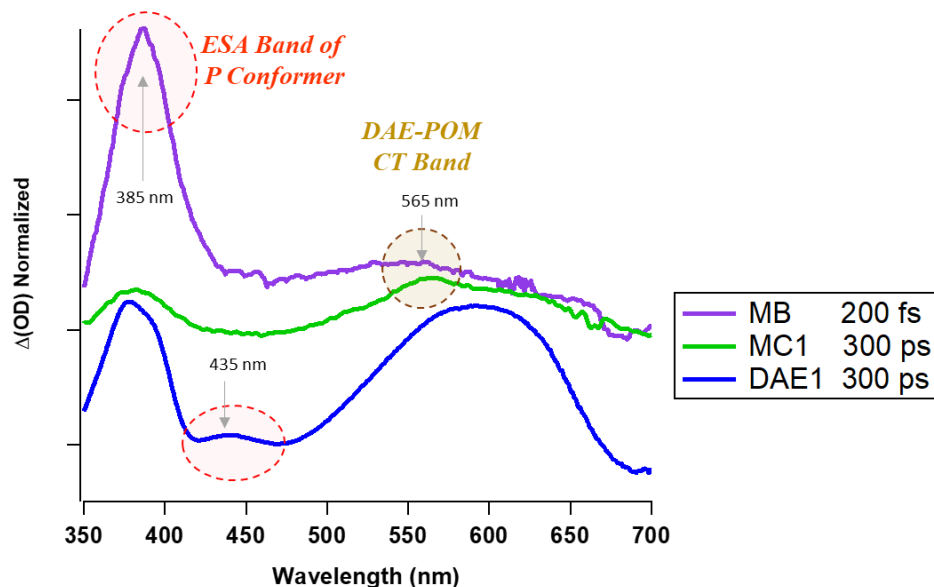


Figure 4.9. Comparison of the CT spectral features of MB and MC1.

In the second TW [0.2 - 6000 ps], the assignation of the processes is straightforward. The fastest decay of the CT band is attributed to BCT from the POM to the DAE with a characteristic time of $\tau_3 \approx 13$ ps. Two relaxation channels are possible: (i) BCT repopulates the local excited state $S_1^P(min)$, prolonging its lifetime before subsequent decay, (ii) BCT proceeds directly to the electronic ground state (S_0), bypassing the local excited manifold. Finally, the slowest ESA band decay with $\tau_4 \approx 1100$ ps is assigned to the expected IC from $S_1^P(min)$ back to the ground state, S_0 . Note that this characteristic time is close to that of free DAE1 ($\approx 880/960$ ps).

An energy diagram summarizing these relaxation pathways is presented in **Figure 4.10**. The scheme highlights the sequential relaxation of MB: $P(FC) \rightarrow P(min) \rightarrow S_0$, with an additional charge-transfer channel. As expected from the enforced P geometry, no photocyclization is observed. This early charge-transfer behavior is unexpected for MB, as in MC1 previously reported (34), the CT process occurs only after photocyclization. In contrast, in MB, CT takes place directly from the excited state, despite the enforced P geometry in which no photocyclization is observed.

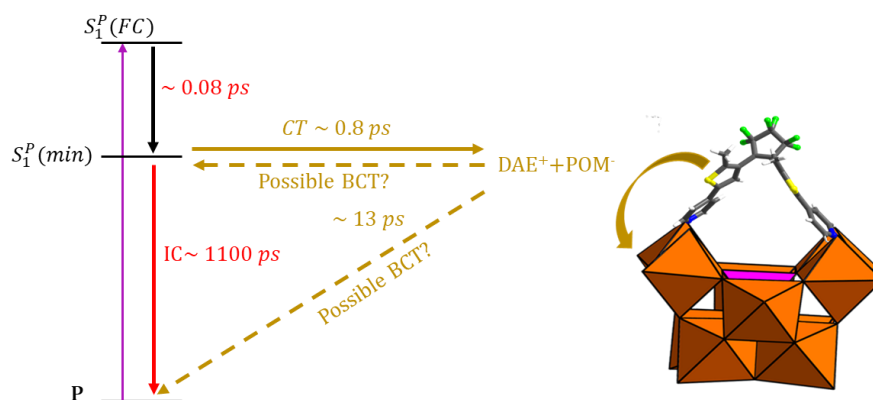


Figure 4.10. Energy diagram for the P conformers as a function of the reactive coordinate (Rcc) of MB, highlighting the main relaxation pathways and characteristic times.

Table 4.3. Global fit lifetimes (τ_1 to τ_5 , in ps) obtained from multi-exponential analysis of fs-TA data for DTE 1 and DTE 2, measured at different excitation powers and in various solvent environments (ACN, DCE).

Molecules	Solvents	Power (μ J)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)	τ_5 (ps)
MB	ACN	0.10	0.08(0.004)	0.8(0.04)	13.0(0.2)	-	1100(80)
MC 1	ACN	0.12	0.20(0.02)	0.33(0.03)	35(5)	-	2600(400)
MC 1	ACN	1.60	0.32(0.02)	2.00(0.02)	95(10)	-	1600(300)
MC 2	ACN	0.75	0.130(0.008)	1.3(0.2)	2.4(0.3)	18(2)	1270(150)

4.5. Photocyclization dynamics of MC1

After establishing the excited-state dynamics of the free DAE1 molecule in Chapter 3, we now investigate its encapsulated analogue, MC1, to examine how confinement within the POM-based capsule impacts the photocyclization mechanism, the competing relaxation pathways, and the CT process previously reported for this system. Compare to this seminal paper, fs-TAS experiments were performed using a novel upgraded setup at the LASIRE laboratory, covering a broad spectral range from the UV-visible to the NIR. As for DAE1, the influence of excitation power was systematically investigated to evaluate possible multiphoton contributions and to determine whether confinement or the presence of multiple DAE units alters the pathways.

This section begins with TD-DFT calculations that provide insight into the electronic transitions accessed upon 330 nm excitation, followed by a detailed analysis of the fs-TAS results at low and high excitation powers.

4.5.1 Electronic Excited States Involved (TDDFT)

The electronic structure of MC1 in its OF has already been characterized in detail in Chemical Science (34). The calculated spectrum (**Figure 3.4**) reproduces the experimental UV band and resolves three transitions in the 265- 271 and 280 nm. The most intense excitation is found at 280 nm, accompanied by weaker transitions at 271 nm and 265 nm. Molecular orbital analysis (**Figure 3.4**) shows that the three main excitations are delocalized over the diarylethene units, as already observed for free DAE1. However, in MC1, this delocalization clearly extends toward the POM cluster, giving rise to a pronounced CT character. The observed delocalization and POM involvement provide the basis for discussing possible CT pathways in the following sections.

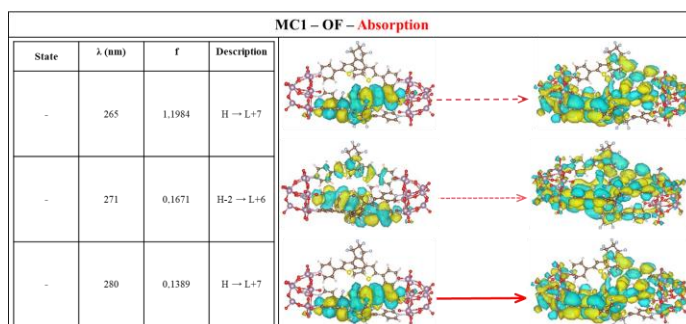


Figure 4.11. Theoretical Absorption Transitions with Orbital Contributions for MC1.

4.5.2 fs-TAS of MC1

Fs-TAS measurements of MC1 in dry ACN were carried out at both low (0.12 μJ) and high (1.6 μJ) excitation powers using 330 nm pump pulses. In both cases, the spectra reveal the same sequence of relaxation pathways, but with a bit of differences in the characteristic timescales. Therefore, we focus on the low-power dynamics only (**Figure 4.13**). The corresponding high-power data are shown in Appendix chapter 4, section S.4.2.

The resulting spectra are dominated by broad ESA bands spanning the region. For clarity, the data are grouped into four temporal windows: [-1 to 0.22 ps], [0.22 to 5.2 ps], [5.2 to 300 ps], and [300 to 6000 ps]. The perfect global fitting of representative kinetics at 385, 550, and 1000 nm yielded four characteristic time constants: $\tau_1 = 0.20 \pm 0.02$ ps, $\tau_2 = 0.33 \pm 0.03$ ps, and $\tau_3 = 35 \pm 5$ ps, $\tau_4 = 2600 \pm 400$ ps (**Figure 4.12**). The dynamics and their assignments are summarized in the energy diagram **Figure 4.16**.

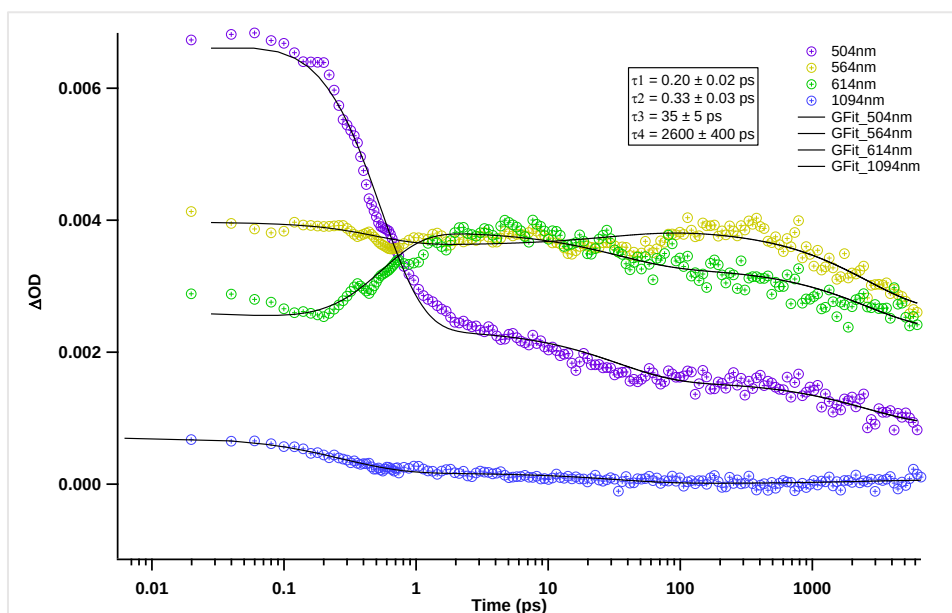


Figure 4.12. Global fitting of transient absorption kinetics of MC1 at four selected wavelengths.

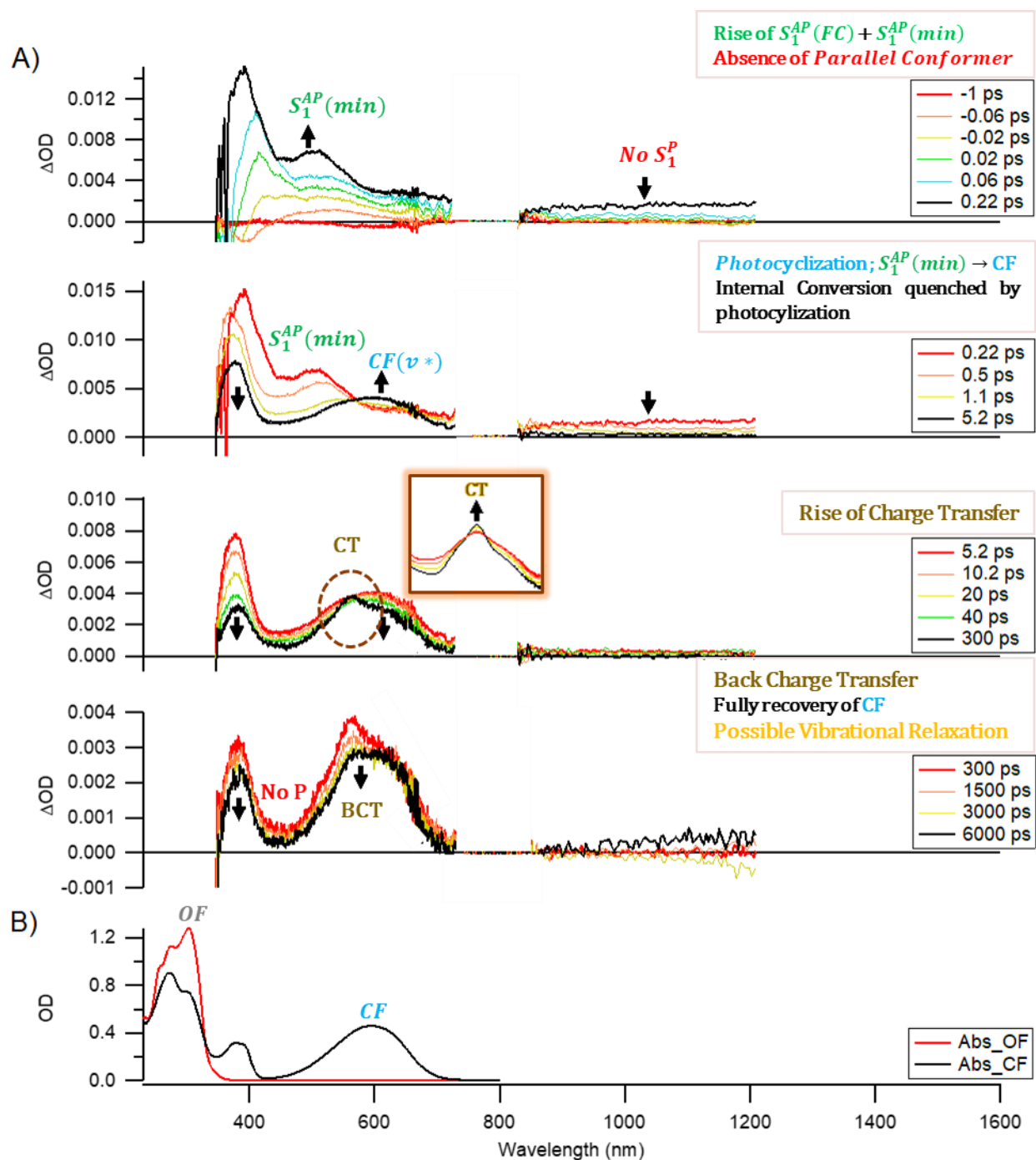


Figure 4.13. (A) fs-TAS of MC1 in dry ACN (20 μM), recorded upon 330 nm laser excitation with a power of 0.12 μJ . The color gradient from red to black represents the spectral evolution over time, grouped into four temporal windows: top panel [-1 ps to 0.22 ps], upper middle panel [0.22 ps to 5.2 ps], lower middle panel [5.2 ps to 300 ps], and bottom panel [300 ps to 6000 ps]. (B) Steady-state UV-Vis absorption spectra of MC1 in its open (red) and closed (black) forms, shown for reference.

In the earliest window [-1 to 0.22 ps], a transient ESA band emerges near 510 nm. In line with TDDFT results and considering the absence of the P conformer, this feature reflects the relaxation of the population from the FC region of the S_1 state of the AP conformer, $S_1^{AP}(FC)$, toward its minimum, $S_1^{AP}(min)$, within $\tau_1 \approx 0.2$ ps.

A very important observation is the absence of the characteristic ESA band associated with the P conformer, which is clearly visible in MB and coexists with the AP-related band in free DAE1 (**Figure 4.14**). The complete lack of this spectral feature in MC1 confirms that no DAE1 unit adopts the P configuration inside the capsule. This spectral evidence fully supports the X-ray crystallographic structure, which established that all three DAE1 units in MC1 are fixed in the AP geometry.

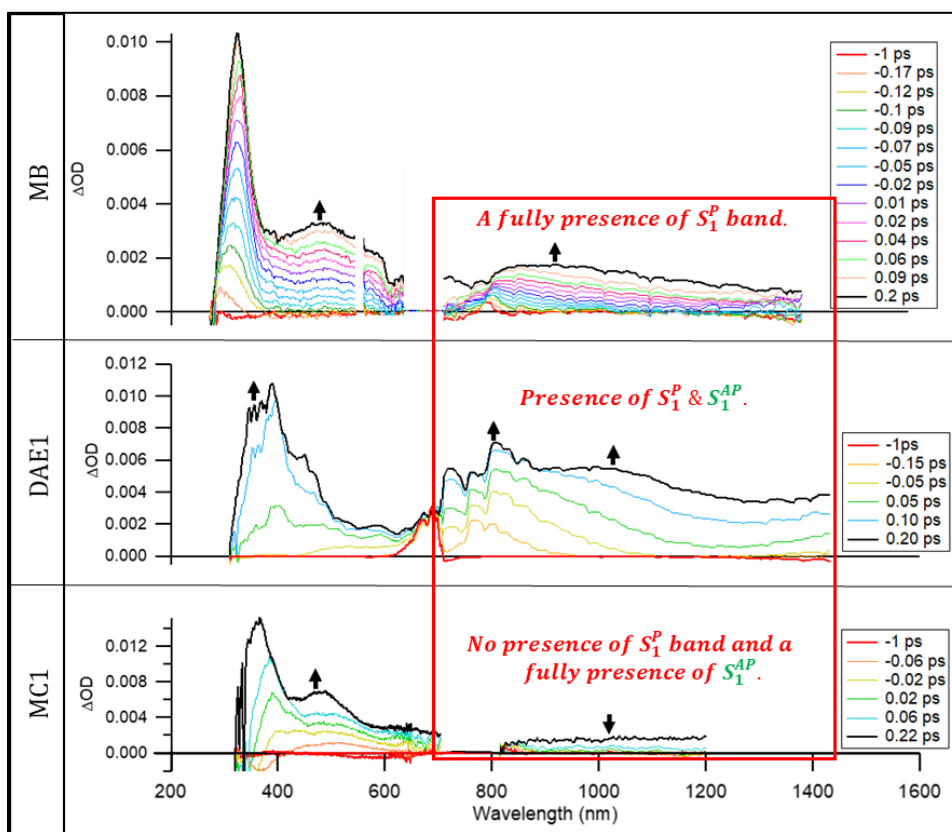


Figure 4.14. Comparison of Early-Time ESA Signatures Emphasizing the Absence of the P Conformer in MC1.

In the second window [0.22-5.2 ps], the 510 nm ESA band related to $S_1^{AP}(min)$ species decays while a new feature emerges at ~ 600 nm, corresponding to the CF. The rise ($\tau_2 \approx 0.33$ ps) is accompanied by two isosbestic points at 568 and 660 nm, indicating a direct and efficient spectral conversion. The ultrafast photocyclization channel from $S_1^{AP}(min)$ efficiently funnels the excited population toward CF formation with a characteristic lifetime of 0.33 ps, consistent with a conical-intersection-mediated process that effectively suppresses internal conversion. For MC1, these results provide clear evidence of a sequential photocyclization mechanism, in contrast to the direct pathway observed for DAE1 under low excitation power. A detailed comparison between the two systems will be addressed in the following section.

The third window [5.2-300 ps] reveals the emergence of a distinct absorption band at ~ 558 nm, which we assign to a CT process from the CF of DAE1 to the POM cluster, that is, from $POM-CF \rightarrow POM^- - CF^+$. This assignment is consistent with the preliminary results reported in 2022 (34), where complementary ultrafast spectroscopy, electrochemistry, and TD-DFT calculations confirmed the same CT process. The band reflects genuine electronic coupling between the encapsulated DAE and the POM, and its growth on a timescale of $\tau_3 \approx 35$ ps highlights the efficiency of this intermolecular delocalization. Confinement within the capsule thus enables a relaxation pathway inaccessible to the free molecule, emphasizing the active photophysical role of the POM environment.

Finally, in the **long-time regime [300-6000 ps]**, the CF absorption band stabilizes while the CT signature gradually decays through BCT, with a lifetime of ~ 2600 ps. The system thus relaxes to the ground state with complete recovery of the CF spectrum.

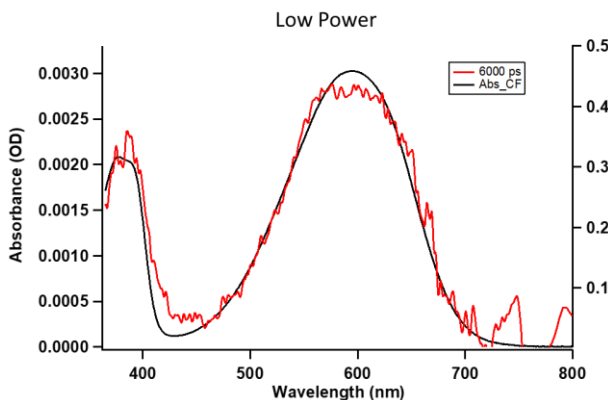


Figure 4.15. Spectral overlap between the transient absorption spectrum at 6000 ps (red) and the steady-state CF absorption spectrum (black) for MC1 under low power laser excitation, confirming complete formation of the CF photoproduct.

4.5.3 DAE1 vs MC1: Confinement effect on photocyclization route

A direct comparison between free DAE1 and encapsulated MC1 highlights the profound influence of confinement on the photocyclization mechanism (**Figure 4.16**). The most immediate differences are the complete absence of the P-conformer signatures in the near-infrared region and the appearance of a new CT band in MC1, centered around 565 nm.

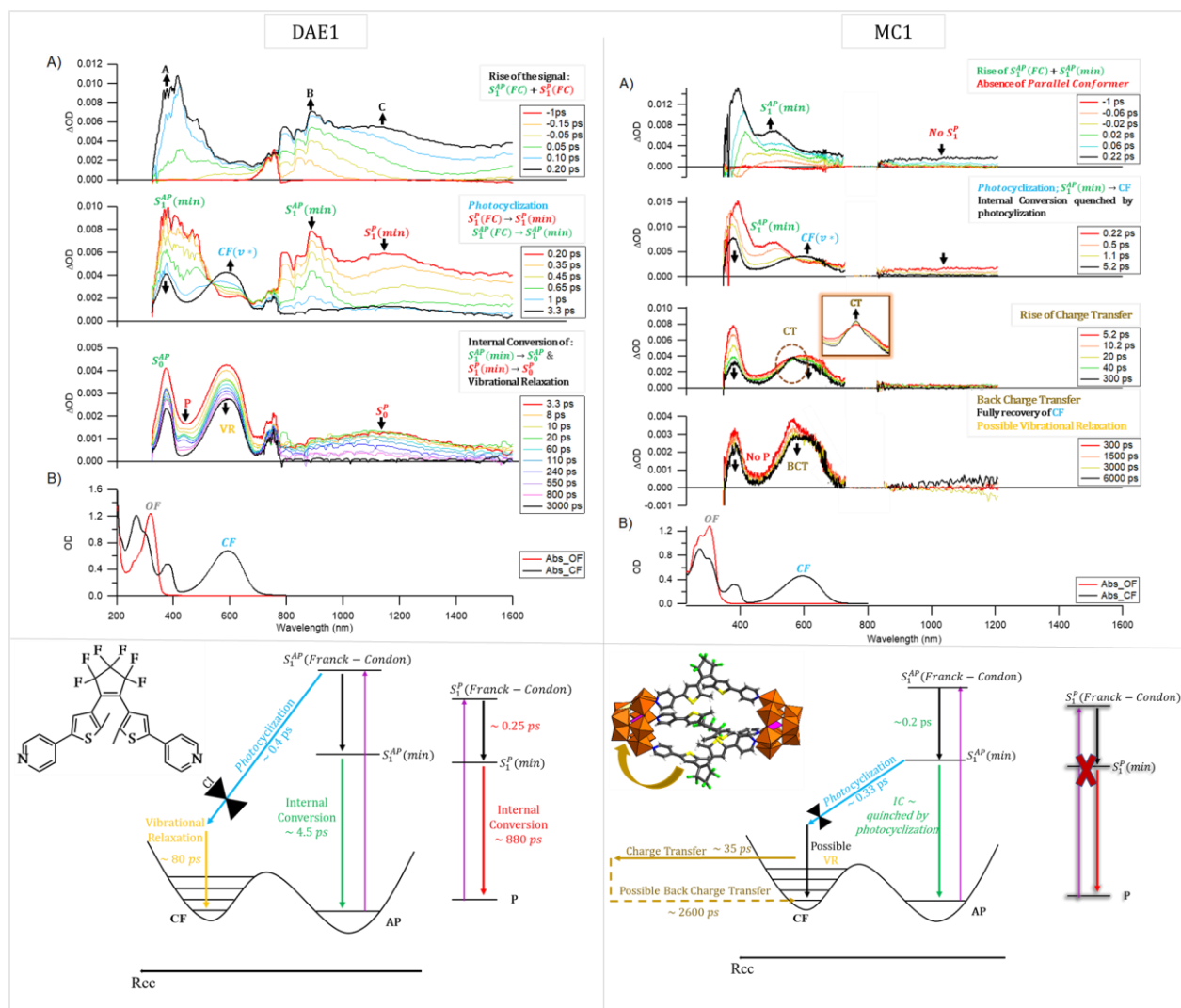


Figure 4.16. DAE1 vs. MC1: fs-TAS spectra and energy diagrams.

A very unexpected result concerns the photocyclization characteristic times. At first glance, one would expect the POM capsule to slow down the ring-closure reaction. Instead, a slight acceleration is observed, with $\tau \approx 0.33$ ps for MC1 compared to 0.4 ps for DAE1. In the same vein, the prominent P-conformer channel in free DAE1 contributes strongly to the long-lived dynamics, with clear spectral features also confirmed in the MB reference system (**Figure 4.8**), which isolates the P conformer. By contrast, in MC1 no such signatures are observed and encapsulation locks the diarylethene into the AP geometry, eliminating the P pathway altogether and reducing the dynamics to a purely AP driven response.

Once the P channel is suppressed, the observed dynamics in MC1 arise solely from the reactive AP conformer, allowing its photocyclization mechanism. In DAE1, the origin of CF formation depends on excitation power: under low power, CF arises directly from the $S_1^{AP}(FC)$, direct mechanism, while at high power it proceeds via the relaxed minimum $S_1^{AP}(min)$, sequential mechanism. In the literature, excitation-energy-dependent switching between S_1 and higher-lying states has been reported by Miyasaka et al. (42), who demonstrated that photoexcitation into S_n levels can open alternative photocyclization routes in diarylethenes. Likewise, Aloïse and co-workers (23) later showed that structural constraints in bridged diarylethenes can lead to two distinct photocyclization channels, a direct pathway from the FC region and a sequential one via a relaxed S_1 min, findings later reflecting how geometric confinement can reshape the topology of the S_1 potential energy surface (46). By contrast, MC1 consistently follows the sequential $S_1^{AP}(min) \rightarrow CF$ route, independent of power (the high-power case sees section S.4.2). This behavior agrees with earlier observations that both excitation energy and molecular rigidity can dictate the active photocyclization pathways, with structural confinement favoring a single, oriented pathways.

This confinement-controlled mechanism not only removes the P contribution but also explains the markedly lower photocyclization QY of MC1 (0.09) compared to free DAE1 (0.5). The inorganic POM cage effectively suppresses the direct FC photocyclization pathway, enforcing instead a slower route through the $S_1^{AP}(min)$ geometry. A likely explanation is that the specific molecular vibrations required to reach the CI geometry are partially frozen by the rigid cage environment. Future quantum molecular dynamics simulations will be required to confirm this

hypothesis. While the presence of a true CI cannot be definitively established here, the results suggest that the intersection point leading to CF formation becomes less accessible in MC1 than in DAE1.

Another defining feature of MC1 is the emergence of a CT channel, manifested by the growth of a 558 nm band. This pathway, absent in DAE1, reflects electronic delocalization from the DAE units into the POM cluster, giving birth to DAE^+ and POM^- species. While previous studies reported only the forward CT process, the BCT (BCT, ~ 2600 ps) now governs the long-time behavior

Altogether, the comparison shows that MC1 behaves as a clean AP only system, free from P conformer interference, while confinement simultaneously enforces a sequential photocyclization pathway only and introduces a unique CT channel inaccessible to free DAE1.

4.6. Photocyclization Dynamics of MC2

After discussing MC1, which enforces an AP geometry and removes the P contribution, we now turn to MC2, a bridged system where three DAE2 linkers connect two similar POM clusters. Unlike MC1, MC2 accommodates both AP and P conformers, as evidenced by the NMR data presented above (Section 2.3, **Figure 4.5**), allowing us to directly probe how these two pathways coexist and interact under confinement. Recent DFT optimization further supports this coexistence, revealing a stable configuration containing one P and two AP units within the capsule (although these calculations are still ongoing at the time of completing this manuscript). Furthermore, as discussed in the previous chapter, DAE2 exhibited a novel transient feature, the so-called X feature, along with an unexpected emission. Altogether, these observations raise several key questions: does the coexistence of both AP and P conformers alter the photocyclization kinetics? Will the charge-transfer process observed for MC1 after photocyclization also occur in MC2? And will the transient X feature identified for DAE2 reappear in MC2? In the next section, we present steady-state and fs-TAS results to elucidate how the mixed conformer distribution in MC2 reshapes its photoresponse compared to free DAE2.

4.6.1 Unexpected Emission in MC2: a new Chromophore?

Absorption. The TDDFT results obtained for MC2 (at the same level of theory as for the previous systems) are quite unexpected. The calculated OF absorption peak (**Figure 4.17**) appears at ~293 nm and is mainly attributed to a H $\rightarrow$ L excitation localized on the pyridyl-phenylthiophene (PPT) lateral moieties. In contrast, the transitions centered on the photochromic core are found to be very weak.

Emission. In MC2, the OF also displays a fluorescence band centered around 412 nm (**Figure 4.18**), closely matching the emission observed for free DAE2. This suggests that the origin of the emission is the same lateral chromophoric unit, rather than the central photochromic core, that is, this similarity in spectral position strongly indicates that the encapsulation does not significantly alter the intrinsic emissive behavior of this fragment.

In the following discussion, we will consider that UV irradiation can excite either the PPT chromophore, responsible for the emission near 412 nm, or the photochromic core, as illustrated in diagram **Figure 4.19**, which distinguishes the two chromophoric regions.

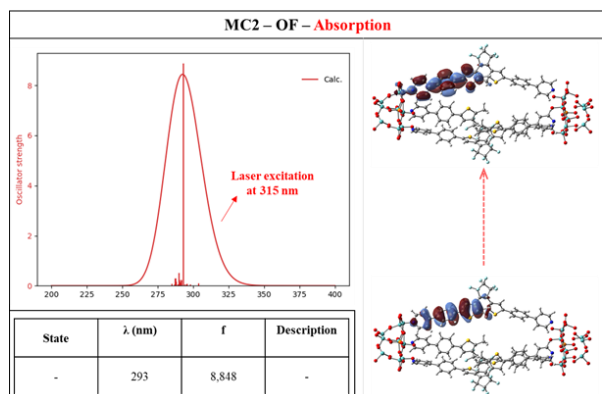


Figure 4.17. Theoretical Absorption Transitions with Orbital Contributions for MC2-OF.

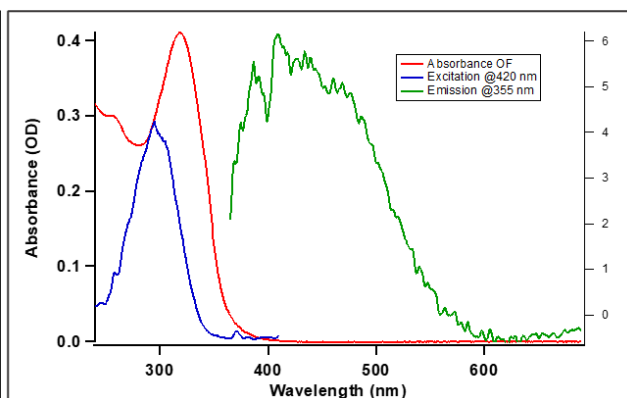


Figure 4.18. Steady-state emission (green) and excitation (blue, $\lambda_{em} = 420$ nm) spectra of MC2 (OF) in ACN under 355 nm excitation, shown with the absorption spectrum (red) for comparison.

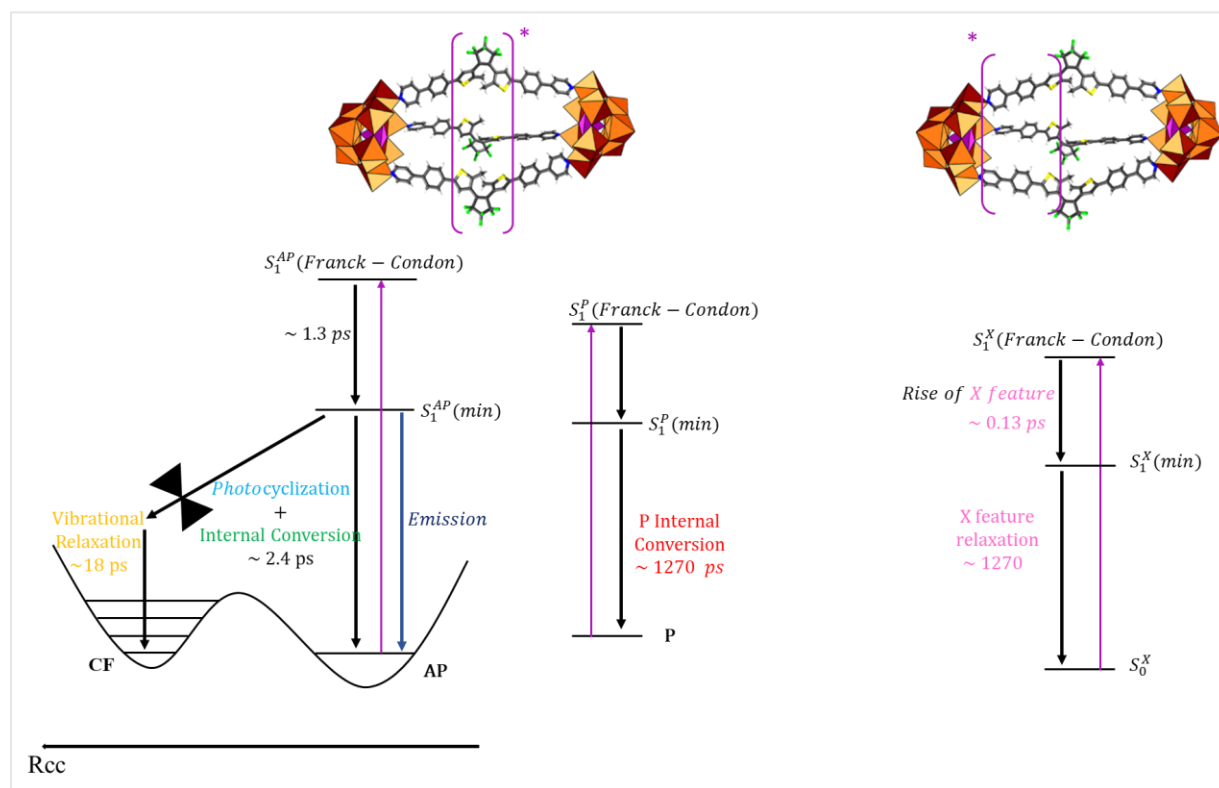


Figure 4.19. Energy diagram for the AP/P conformers, X feature and CF species as a function of the reactive coordinate (Rcc) of MC2 at low power, highlighting the main relaxation pathways and characteristic times.

4.6.2 fs-TAS of MC2

The fs-TAS response of MC2 is organized into four temporal windows: [-1 to 0.14 ps], [0.14 to 0.8 ps], [1 to 45 ps], [0.8 to 30 ps] and [30 to 6000 ps] (**Figure 3.13** and **Figure 3.15**). Global fits at representative probe wavelengths (390- 460 590- 870- 1304- 1590nm) yield the time constants $\tau_1 = 0.130 \pm 0.008$ ps, $\tau_2 = 1.3 \pm 0.2$ ps, $\tau_3 = 2.4 \pm 0.3$ ps, $\tau_4 = 18 \pm 2$ ps and $\tau_5 = 1270 \pm 150$ ps (Figure S.4.5). Those times are gathered together into **Table 4.3** above). The high power MC1 shown in appendix, Figure S.4.6.

At first glance, the overall transient evolution seems resemble to that of MC1; however, beyond these apparent similarities, notable differences arise. The photocyclization step is immediately recognized (detailed later), but an additional absorption feature appears near ~588 nm, corresponding to the X feature previously identified for DAE2. As will be discussed later, this band is not related to the CT process observed for MC1 but instead to the newly introduced PPT chromophore.

In the earliest window [-1 to 0.14 ps], the spectra display broad ESA bands associated with the $S_1^{AP}(FC)$ and $S_1^P(FC)$ states, closely resembling those previously observed for DAE2 along with the same X feature as well appearing at 588 nm, rising within ~0.13 ps. Note that the X signature appears instantaneously.

In the second window [0.14 to 0.8 ps], an ESA band peaking at 460 nm (notably at 0.14 ps trace) decays with a minor contribution persisting in the NIR region. As this band diminishes, a new feature emerges at 530 nm, accompanied by the persistent X band. This ultrafast evolution reflects the relaxation of the AP conformer relaxes from $S_1^{AP}(FC)$ to its minimum geometry $S_1^{AP}(min)$ with $\tau_2 \approx 1.3$ ps.

The third window [0.8 to 30 ps] is dominated by the decay of $S_1^{AP}(min)$ ESA band leading to CF band formation, still exhibiting the X feature superimposed on it. This dynamics corresponds to the photocyclization process, characterized by a time constant of $\tau_3 \approx 2.4$ ps. The kinetics are comparable with a time slower to those observed for DAE2, suggesting that MC2 follows a similar relaxation pathway. Rather than proceeding directly from the FC region to the CI, the system appears to relax first to $S_1^{AP}(min)$ before bond closure. It is therefore reasonable to assume that the photocyclization proceeds through a CI, as the 2.4 ps timescale is consistent with an ultrafast reaction. However, it remains unclear whether this crossing is identical to that of DAE2

or corresponds to a distinct, confinement-modified CI. Further ab initio calculations will be necessary to resolve this question.

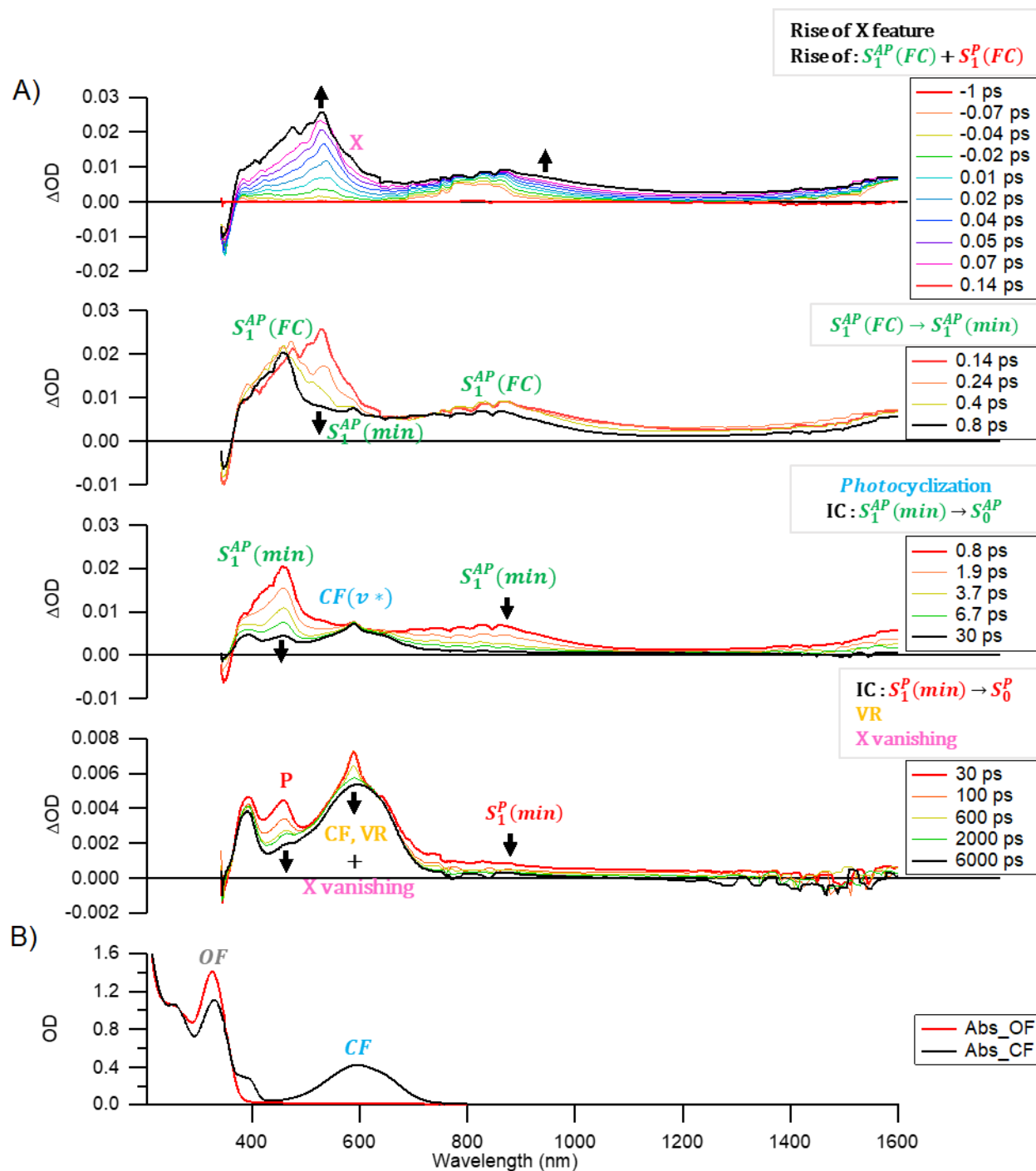


Figure 4.20. (A) fs-TAS of MC2 in dry ACN (40 μM), recorded upon 315 nm laser excitation with a power of 0.75 μJ. The color gradient from red to black traces the spectral evolution over time, grouped into five distinct temporal windows: top panel [-1 ps to 0.14 ps], second panel [0.14 to 0.8 ps], third panel [0.8 to 30 ps], fourth panel [30 to 6000 ps]; (B) Steady-state UV-Vis absorption spectra of MC2 in its open (red) and closed (black) forms, included for reference.

In the long time regime [30-6000 ps], two main processes dominate. First, the CF absorption band undergoes vibrational relaxation with $\tau_4 \approx 18$ ps, noticeably faster than in free DAE2 (~ 70 ps). Second, the characteristic long lived signatures from the P conformer and the X feature decay with $\tau_5 \approx 1270$ ps, shorter than in DAE2 (3090 ps), confirming the complete formation and full recovery of the CF photoproduct (**Figure 4.21**). Notably, the P contribution is more pronounced in MC2 than in DAE2, making the parallel channel more visible in the femtosecond spectra than DAE2. This enhanced parallel contribution aligns with the NMR observation of two distinct conformer signals in MC2 (AP and P), in contrast to the single signal in free DAE2. Unlike the latter, where the P conformer contribution is hidden, MC2 shows a more pronounced P conformer due to its conformational locking, which prevents rapid AP $\leftrightarrow$ P interconversion. This difference arises because MC2 incorporates three DAE2 units within the capsule, whereas the free system contains only one. As a result, the effective P population is substantially higher in MC2 (estimated $\sim 30\%$) compared to free DAE2 ($\sim 10\%$).

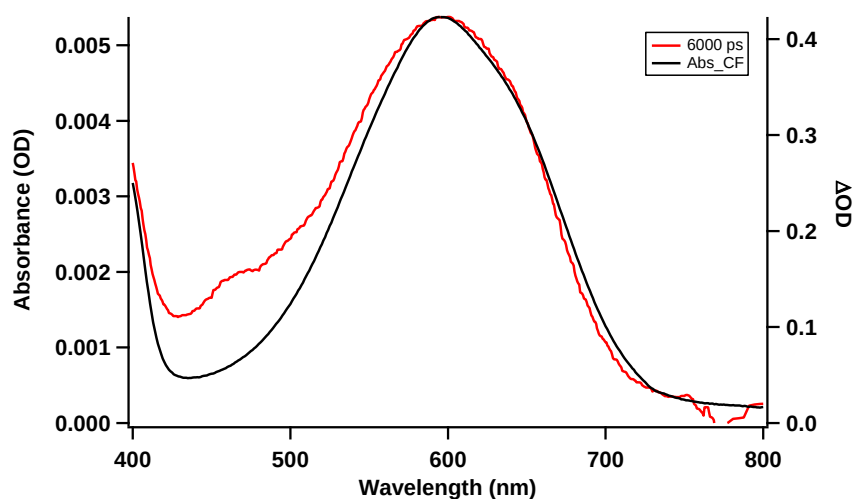


Figure 4.21. Spectral overlap between the ESA spectrum at 6000 ps (red) and the steady-state CF absorption spectrum (black) for MC2 under low power laser excitation, confirming complete formation of CF (photoproduct) except some weak remaining P conformer contribution.

Overall, MC2 reproduces the same sequence of relaxation channels observed in DAE2 (**Figure 4.22**). FC excitation of AP and P, relaxation to $S_1^{AP}(min)$, partial photocyclization, and slow decay of P and X. Yet, all dynamics proceed on a bit accelerated timescales, with stronger visibility of the parallel channel. Compared with MC1, which suppresses the P pathway entirely, MC2 clearly retains and even reinforces it, showing how confinement can either eliminate or amplify conformer specific dynamics depending on the molecular architecture.

Hypothesis #1 - Charge Transfer. A first hypothesis is that the X band could correspond to a CT state. Indeed, direct comparison between the CT band observed in MC1 (560 nm) and the X feature in MC2 (588 nm) reveals close position values with similar sharp and well localized band characteristics. However, unlike MC1, where CT occurs from the DAE to the POM cluster, DAE2 lacks any POM acceptor, making such a process unlikely. Moreover, the solvent-dependent behavior of the X band does not support this assignment. Between DAE2 in ACN (more polar) vs in DCN (less polar), the X band shifts only slightly, from ~588 nm in ACN to ~598 nm in DCE (Appendix 3, Figure S.3.4). CT states are generally more strongly stabilized in polar solvents, often showing pronounced red shifts and intensity variations, which are not observed in our case (56).

Hypothesis #2 - Stacking or Excitonic Effects. A second hypothesis is that the X feature could originate from an **exciplex formed between stacked molecules**. The X-ray structure of DAE2 indeed reveals a stacking arrangement that could suggest such an origin (**Figure 4.25.a**). To test this possibility, theoretical calculations of the S_1 state were performed for a DAE2 dimer. In the case of exciplex formation, one would expect orbital delocalization extending over both monomers. However, our results show that the hole and electron densities remain confined to a single monomer (**Figure 4.25.b**), with no evidence of intermolecular delocalization. This finding suggests that exciplex formation is unlikely to account for the X feature. In parallel, we considered the possibility of an **intermolecular ground-state exciton**. In such cases, excitonic coupling between molecules typically leads to concentration-dependent changes in the ground-state UV-Vis spectra, such as band shifts or altered line shapes. In our case, however, no concentration-dependent effect was observed in the UV-Vis spectra recorded at different concentrations (**Figure 4.25.c**), ruling out the presence of ground-state intermolecular excitons (57). Even in the absence of a ground-state exciton, one could envisage an **excited-state intermolecular exciton** formed transiently through molecular encounters. This mechanism could, in principle, appear directly after excitation. However, literature studies show that such excitons relax very rapidly, typically within tens to hundreds of femtoseconds (58). In contrast, the X band in our case persists up to several nanoseconds. This discrepancy in lifetimes makes the excited-state intermolecular exciton an unlikely explanation, although a minor contribution cannot be entirely excluded.

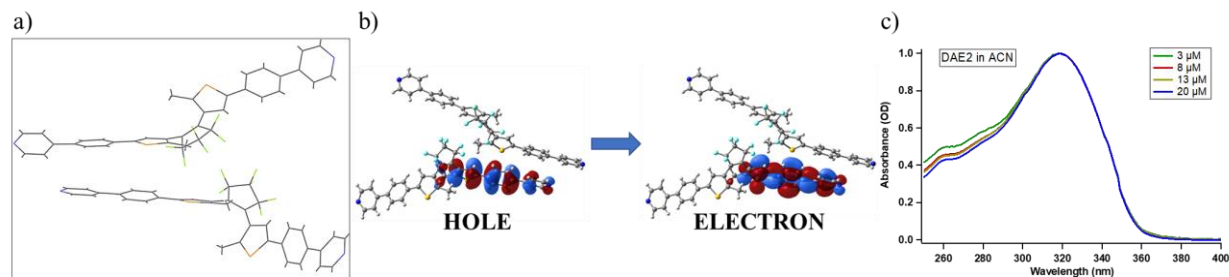


Figure 4.25. a) X-ray crystal structure of DAE2 (solid) highlighting the stacking; Hole (left) and electron (right) density distributions of the S_1 state in the DAE2 dimer, showing orbital delocalization on a single fragment with no intermolecular delocalization. c) Effect of concentration on UV-vis spectra of DAE2 in OF (Normalized Spectra).

Hypothesis #3 - PPT Chromophore. Finally, the most probable hypothesis relies on the fact that both the X transient feature and the specific emission of the OF appear in parallel. The latter process has been identified by TDDFT calculations as originating from a chromophore localized on the PPT moiety. During laser excitation, part of the population is expected to be localized on the DAE core, while another part involves localized transitions associated with this moiety. This substituent possesses its own π -system, as confirmed by its independent emission, and can stabilize a localized excited-state minimum responsible for the X band through its own excited-state absorption. In other words, considering the lowest excited state of the PPT chromophore, denoted PPT (S_1), the emission corresponds to the PPT (S_1) $\rightarrow$ PPT (S_0) transition, whereas the transient X feature is assigned to the PPT (S_1) $\rightarrow$ PPT (S_n) transition. This interpretation is consistent with previous reports describing a visible ESA band attributed to a localized S_1 minimum, long-lived and only weakly sensitive to solvent polarity (56).

It is also worth noting that excitation of the PPT chromophore constitutes a competitive process relative to photocyclization, diverting part of the excited population away from the ring-closure pathway.

4.7. Photoreversion dynamics of MC1 and MC2

We now turn to the description of the photoreversion process induced by visible light, keeping in mind the results previously discussed for DAE1 and DAE2 in the preceding chapter. It is worth recalling that the corresponding photoreversion QYs are summarized in **Table 4.1**.

4.7.1 Electronic Excited States Involved (TD-DFT)

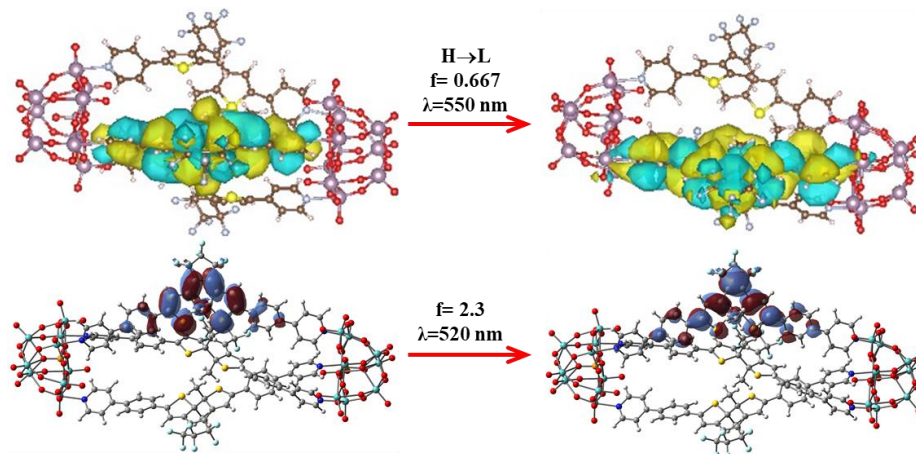


Figure 4.26. Theoretical Absorption Transitions for MC1-CF (34)(top) and MC2-CF (bottom).

TD-DFT calculations performed on the closed forms of MC1 and MC2 (**Figure 4.26**) reveal that both systems preserve the general electronic structure of their DAE-based chromophores, yet with spectral shifts arising from coordination to the POM framework. For comparison, the main absorption transition in the closed forms of free DAE1 and DAE2 occurs at 606 and 614 nm, respectively, corresponding to a strong HOMO $\rightarrow$ LUMO excitation delocalized across the diarylethene core. In contrast, in the confined assemblies, these transitions are blue-shifted, appearing at 550 nm for MC1 ($f = 0.67$) and 520 nm for MC2 ($f = 2.3$), evidencing a moderate increase in transition energy upon encapsulation. This effect can be attributed to the electronic influence of the POM nodes, which slightly modify the π - π^* interaction within the DAE framework while maintaining the same transition character. In both capsules, the frontier orbitals remain primarily localized on the diarylethene units, with only minor extension toward the inorganic clusters, confirming that ground-state coupling between the organic and inorganic components is limited.

Experimentally, neither MC1 nor MC2 closed forms exhibits detectable steady-state emission, in contrast to the free DAE2 molecule, which showed fluorescence near 500 nm and a weak low-energy channel around 970 nm. The complete absence of emission in the capsules indicates that confinement introduces efficient non-radiative relaxation pathways.

Overall, the encapsulation of the DAE units within the polyoxometalate environment preserves their principal absorption features but strongly alters their excited-state relaxation landscape. The confined geometry suppresses emissive decay channels and favors non-radiative, reflecting the decisive role of the POM clusters in reshaping the photophysics of these hybrid assemblies.

4.7.2 Photoreversion Ultrafast Dynamics of MC1 and MC2

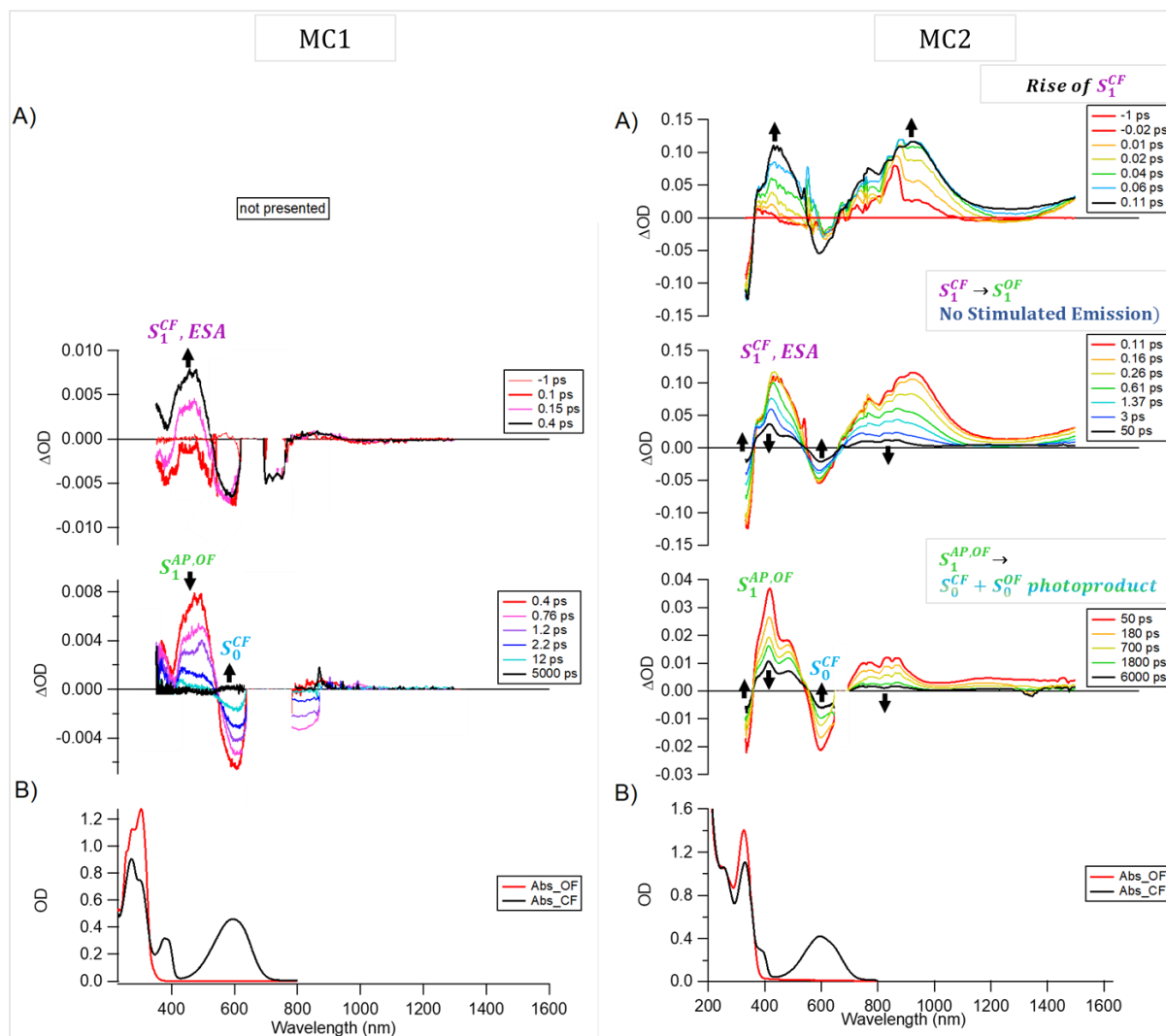


Figure 4.27. (A) fs-TA spectra of MC1 (left, 0.2 μJ) and DAE2 (right, 2.5 μJ) in dry ACN, recorded upon 660 nm excitation. The color gradient from red to black represents the spectral evolution over time, segmented into multiple temporal windows. (B) Corresponding steady-state UV-Vis absorption spectra of the open (red) and closed (black) forms are shown for reference.

The photoreversion (ring-opening) dynamics of the CF of MC1 and MC2 were investigated by fs-TAS following excitation at 660 nm, corresponding to the absorption band of the reactive CF conformer (**Figure 4.27** and **Figure 4.28**). The observed evolution therefore describes the CF $\rightarrow$ OF conversion occurring within the POM-confined environment. **Table 4.4**, summarize the kinetic components.

Table 4.4. Characteristic time constants associated with the photoreversion process of the four molecules.

Molecules	Solvents	Power (μ J)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
DAE 1	ACN	5	0.100(3)	0.900(3)	15(1)
MC1	ACN	0.2	0.12(2)	1.00(4)	32(5)
DAE 2	ACN	2.5	0.3(1)	1.00(5)	10 (3)
MC2	ACN	2.5	0.22(1)	2.00(4)	210(10)

Although both systems exhibit transient behaviors similar to their molecular analogues DAE1 and DAE2, the confinement within the POM framework introduces distinct kinetic and spectral modifications. The early rise of the signal is not clearly resolved in MC1, while in MC2 a clear rise of the transient features is observed, indicating population relaxation from the FC region $S_1^{CF}(FC)$ to its local minimum $S_1^{CF}(min)$, with $\tau_1 = 0.12$ ps for MC1 and $\tau_1 = 0.22$ ps for MC2. The corresponding global kinetic fittings for both systems are shown in supplementary Figure S.4.7 and S.4.8.

During the subsequent temporal windows, both systems display broad ESA bands. In contrast to the free molecules, the characteristic negative band in the NIR region is absent. The complete lack of any negative feature confirms the full quenching of the emissive $S_1 \rightarrow S_0$ transition previously observed near 970 nm in free DAE1/2, indicating that the emissive S_1 state is entirely suppressed under confinement. Consequently, relaxation proceeds mainly through ESA transitions associated with $S_1^{CF}(min) \rightarrow S_1^{OF}$ internal conversion (IC). The global analysis yields $\tau_2 = 1$ ps for MC1 and $\tau_2 = 2$ ps for MC2.

The near-IR ESA component is extremely weak in MC1 but clearly visible in MC2 as the behavior of free DAE1 and DAE2. This difference most likely arises from the lower excitation power used

for MC1 (0.2 μJ) compared with MC2 (2.5 μJ), which limits the population of long-lived excited states while still maintaining a weak transient indication of their presence.

At longer delays, ESA bands persist together with a distinct ground-state bleach near 600 nm, describing the relaxation $S_1^{OF} \rightarrow S_0^{CF} + S_0^{OF}$ probably passing through CI. The global fits yield $\tau_3 = 32$ ps for MC1 and $\tau_3 = 210$ ps for MC2. Notably, the late-time trace of MC1 (5000 ps) kind of full recovery of the OF, whereas MC2 does not, likely due to the lower excitation power used for MC1, which may limit the extent or visibility of the photoproduct formation.

Altogether, both MC1 and MC2 follow the same general photoreversion scheme as their free DAE1/2 analogues.

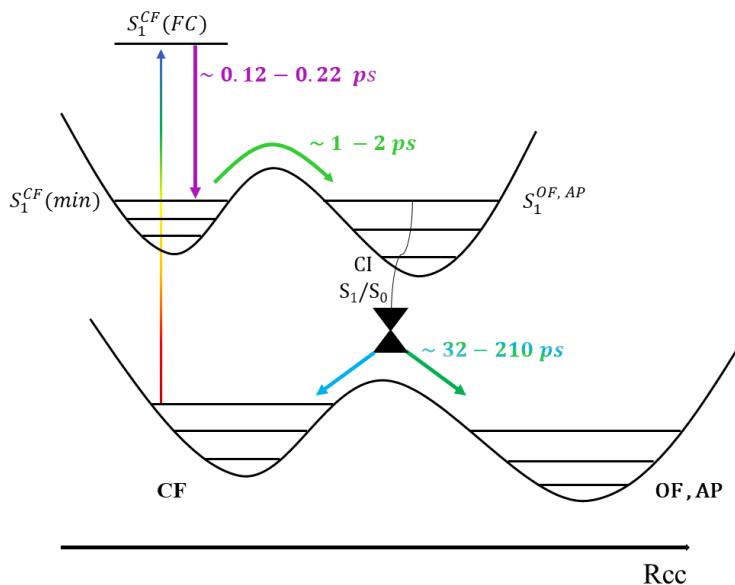


Figure 4.28. Schematic energy level diagram illustrating the ultrafast excited-state dynamics during the photoreversion of MC1 and MC2.

4.8. Conclusion

This chapter has explored the ultrafast photoinduced mechanisms of three diarylethene-based molecular capsules: MB, MC1, and MC2, each incorporating either DAE1 or DAE2 units within structurally distinct polyoxometalate architectures. By combining steady-state spectroscopy, fs-TAS, and TD-DFT calculations, together with a comparison to the results discussed in the previous chapter, we have gained detailed insight into how confinement, geometry, and molecular design affect photocyclization, photoreversion pathways. The key photoinduced processes identified for 5 different systems are summarized in **Table 4.5**.

Table 4.5. Summary of the main photoinduced processes observed in DAE1, DAE2, and POM-based assemblies MB, MC1, MC2.

Molecules	Photocyclization	CT	Emission lateral moiety
DAE1	Yes	No	No
DAE2	Yes	No	Yes
MB	No	Yes	No
MC1	Yes	Yes	No
MC2	Yes	No	Yes

The MB system, which forces the DAE1 unit into a P geometry, served as a reference for the photophysically active but photochemically inactive conformer. In this configuration, the photophysics of the P conformer is isolated from the photochemistry of the AP conformer, displaying an $S_1 \rightarrow S_0$, IC characteristic time of approximately 1100 ps. Furthermore, this system enabled the confirmation of the transient characteristic ESA bands of the P conformer, observed at 385 nm and predominantly in the NIR region at 995 nm, as previously reported in Chapter 3. In addition to these expected results, some unexpected features were also identified. Fs-TAS revealed characteristic relaxation dynamics involving CT to the POM cluster with no evidence of ring-closure, as anticipated from the conformational constraint. All these results have not been previously reported in the literature, and a scientific paper is currently being prepared for submission.

In contrast, MC1, which contains three DAE1 units locked exclusively in the AP conformation, displayed clean and efficient photocyclization dynamics. TAS measurements

resolved a full photocyclization sequence ($FC \rightarrow (S_1(AP) \rightarrow CF)$ (~ 0.33 ps), followed by the emergence of a POM-localized CT (~ 35 ps) state and BCT (~ 2600 ps). Compared to free DAE1, confinement in MC1 suppresses the P-conformer ($\tau \approx 880$ ps) and internal conversion ($\tau \approx 4.5$ ps) channels observed in the unconfined molecule. But the most notable difference is the influence on the photocyclization process that was direct in the case of DAE1 (≈ 0.6 ps). These comparisons highlight how confinement not only simplifies the photocyclization mechanism by enforcing a purely AP pathway but also introduces new relaxation processes through capsule interactions.

The case of MC2 was not straightforward to rationalize due to the appearance of a new transient X feature, previously reported for DAE2. As confirmed by NMR, MC2 incorporates three DAE2 units per capsule and retains both AP and P conformers. While the same overall relaxation sequence was observed, the dynamics occurred on faster timescales. Importantly, the "X feature", absent in MC1, was clearly resolved in MC2 and linked to PPT chromophore, which is decoupled from the photochromic core, based on combined experimental and theoretical analyses. Notably, the absence of CT in MC2 is attributed to the quenching of this process by the fluorescence of the PPT chromophore.

The comparison between MC1 and MC2 clearly indicates that the POM clusters far from being inert scaffolds, play an active role in modulating excited-state behavior. Their ability to mediate CT and impose conformational control stems from their polyanionic, redox-active nature and well-defined geometry. Altogether, these findings provide deeper insight into the role of confinement and electronic coupling in influence the photoreactivity of diarylethene-POM hybrid systems. In the future, it would be interesting to design new pyridyl-DAE-POM cages that allow controlled photoinduced CT and can trap small molecules, with the aim of developing light-driven photocatalytic systems.

Chapter 5. Ultrafast Spectroscopy of Porphyrin-DAE Polymers.

This chapter study the ultrafast photodynamics of two diarylethene-porphyrin electropolymers, P1 (poly-DAE1-ZnT₂isoP[•]) and P2 (poly-DAE2-ZnT₂isoP[•]), derived from the DAE1 and DAE2 units presented in Chapter 3 and incorporating porphyrin moieties. The objective is to understand how coupling DAE switches to a porphyrinic backbone reshapes photocyclization and photoreversion pathways. Guided by spectroelectrochemical fingerprints (IsoP[•] → IsoP⁺ oxidation, Py⁺ → Py[•] reduction), and CF growth, we employ femtosecond transient absorption spectroscopy in solution (dimethylformamide) and as thin films on ITO slide to follow key events like photoinduced electron transfer, internal conversion, back-electron transfer, and their possible interplay with ring-closure. By selectively exciting the UV region (315 nm), as well as the porphyrin Soret (420 nm) and Q bands (570 nm), we benchmark polymer dynamics against the isoporphyrin reference and uncover how environment and linker effects determine whether photocyclization pathways are expressed, suppressed, or only weakly hinted at, while also drawing parallels with the behavior of the free DAE units to highlight how their incorporation into the porphyrinic backbone reshapes switching dynamics. The integrated analysis of steady-state spectra, red-shifted porphyrinic bands in the polymers, and global-fit time constants provides a comparative map of how polymer architecture and medium govern excited-state energy flow and reactivity.

5.1. Introduction

Following the molecular-level studies of the free DAEs derivatives presented in Chapter 3, this chapter examines their integration into porphyrin-based copolymers and the resulting impact on their photophysics and ultrafast dynamics. The two polymers investigated, (poly-DAE(Py)₂-ZnT₂isoP[•]) (P1) and (poly-DAE(Ph-Py)₂-ZnT₂isoP[•]) (P2), were synthesized through the electropolymerization of zinc tetratolylporphyrin (ZnT₂P) in the presence of pyridine-substituted DAE, as shown in **Figure 5.1**. The synthesis protocols for both P1 and P2 were described in Chapter 2. These diarylethene units correspond directly to DAE1 and DAE2, respectively, thus providing a clear structural and mechanistic link between the molecular and polymeric systems. A central question addressed here is whether DAEs, once incorporated into the main chain of the copolymer through their pyridyl substituents, can still undergo their characteristic photoisomerization between OF and CF. Importantly, this question is investigated under two different physical states: in solution, where polymer chains are individually solvated, and in the solid state, where intermolecular interactions and packing effects may strongly influence the switching behavior.

The redox properties of the polymers were studied by electrochemistry, and their spectroelectrochemical signatures provide an essential reference for interpreting the electronic processes investigated by ultrafast spectroscopy. Indeed, fs-TAS was then employed to resolve the ultrafast dynamics, offering direct insight into the excited-state pathways. The results highlight how integration within porphyrin affects diarylethene photoswitching process, and whether structural modifications, particularly the additional phenyl group in P2, affect their relaxation pathways. Moreover, the comparison between solution and solid-state measurements reveals the critical role of the environment in dictating the efficiency and dynamics of the switching process.

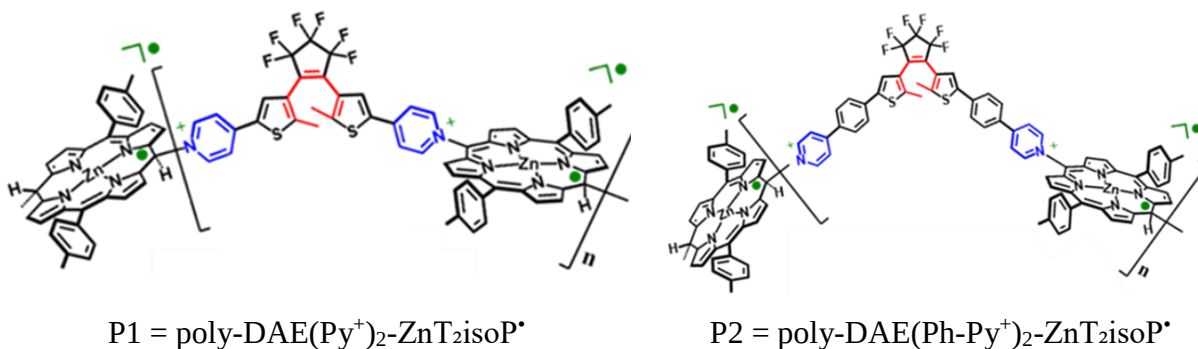


Figure 5.1. Chemical structures of P1 and P2.

5.2. General Photochromic Properties of P1 and P2

5.2.1 Porphyrin Characteristics in UV-Vis Spectroscopy

The absorption spectra of porphyrins are dominated by two characteristic features: a strong Soret band and weaker Q bands. These bands are highly sensitive to the structure of the macrocycle. As shown in **Figure 5.2** (left), the green trace (metalloporphyrin) displays a typical Soret band in the 390-450 nm range together with Q bands between 450 and 800 nm. In contrast, the purple trace (isoporphyrin) exhibits a weaker, red-shifted Soret band at ~430 nm and Q bands displaced into the near-infrared (750-900 nm) (59).

In our case, the polymers P1 and P2 include porphyrin units derived from ZnT₂P, which are integrated through electropolymerization together with diarylethene switches. To establish a baseline, **Figure 5.2** (right) shows the UV-Vis spectrum of the ZnT₂P porphyrin alone. The spectrum displays a Soret band at 415 nm and two Q bands at 547 and 584 nm. These specific features serve as a reference point for identifying porphyrinic contributions within the polymer spectra as well as in the fs-TA measurements discussed later. Within the electronic structure framework of porphyrins, the intense Soret transition corresponds to excitation into the higher singlet state (S_2), while the weaker Q bands originate from transitions into the lower singlet manifold (S_1). According to the Gouterman four-orbital model (60), both Q_1 and Q_2 bands arise from the same electronic state (S_1), split into two distinct features by orbital mixing and symmetry effects. Thus, excitation into either Q-band directly populates S_1 , whereas excitation of the Soret band initially prepares S_2 . This distinction is central for the interpretation of the transient absorption dynamics of isoporphyrin-diarylethene copolymers.

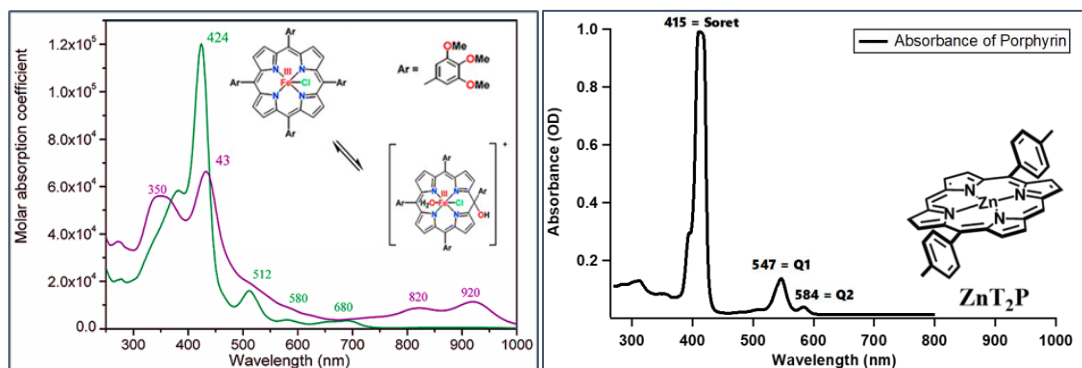


Figure 5.2. UV-Vis spectra of metalloporphyrin (green) and isoporphyrin (violet) (left) in DCM, and ZnT₂P used in this work (right) in DMF.

5.2.2 Photochromic Behavior of Polymers in Solution

Before discussing the optical measurements, it is worth recalling that the polymer films electropolymerized on ITO slides were dissolved in DMF to obtain clear molecular solutions, as described in Chapter 2 (Section 2.3.3). The resulting solutions were degassed with nitrogen to remove dissolved oxygen prior to the spectroscopic measurements. As shown in **Figure 5.3** below, both polymers display a visible color change under UV/Vis irradiation. In the OF, the solutions already appear slightly yellow because of the intrinsic absorption of the porphyrin units, while in the CF they turn into a darker yellow. This color shift reflects the underlying spectral changes that will be detailed in the following UV-Vis analysis.

Upon UV excitation at 313 nm, both systems exhibit characteristic spectral variations involving the Soret and Q regions, consistent with the gradual conversion from OF to CF. The absorption around 300 nm decreases, while new features emerge near 380 nm and 600 nm, crossing well-defined isoabsorptive points ($\sim 325 - 340$ nm). The differential spectra confirm this behavior by showing the progressive loss of OF and growth of CF bands.

Photocyclization proceeds slowly, requiring several minutes to reach the PSS (≈ 600 s for P1 and ≈ 1260 s for P2). Under visible irradiation at 435 nm, the process reverses completely, with recovery of the OF band and decay of the CF features, occurring more rapidly (~ 300 -1200 s). Multiple irradiation cycles demonstrated that both polymers undergo highly reversible photoisomerization in solution without thermal recovery in the dark. P2 behaves analogously to P1 but displays slightly slower forward kinetics, likely due to its additional phenyl linker that subtly alters electronic conjugation within the polymer backbone.

P1/P2 in DMF-solution. The UV-Vis spectra of P1 and P2 in DMF clearly demonstrate its photochromic response under alternating UV and visible irradiation. Upon excitation at 313 nm, characteristic spectral changes for both systems appear, involving the Soret and Q regions, reflecting the gradual conversion from the OF to the CF. A new absorption band emerges around 600 nm, together with an intermediate feature near 365-380 nm, while the intensity of the ~ 300 -310 nm band decreases (**Figure 5.3**, top). These variations cross isobestic points at ~ 325 nm for P1 and 340 nm for P2. Altogether, these changes clearly map the spectral pathway from OF to CF.

The differential spectra, obtained by subtracting successive spectra from the initial one, provide a clearer view of the CF growth by highlighting the loss of the OF features and the rise of the CF contributions, confirming the progressive build-up of the CF state. The photocyclization proceeds requiring approximately ~600 s to reach the PSS for P1 and about requiring ~1260 s for P2.

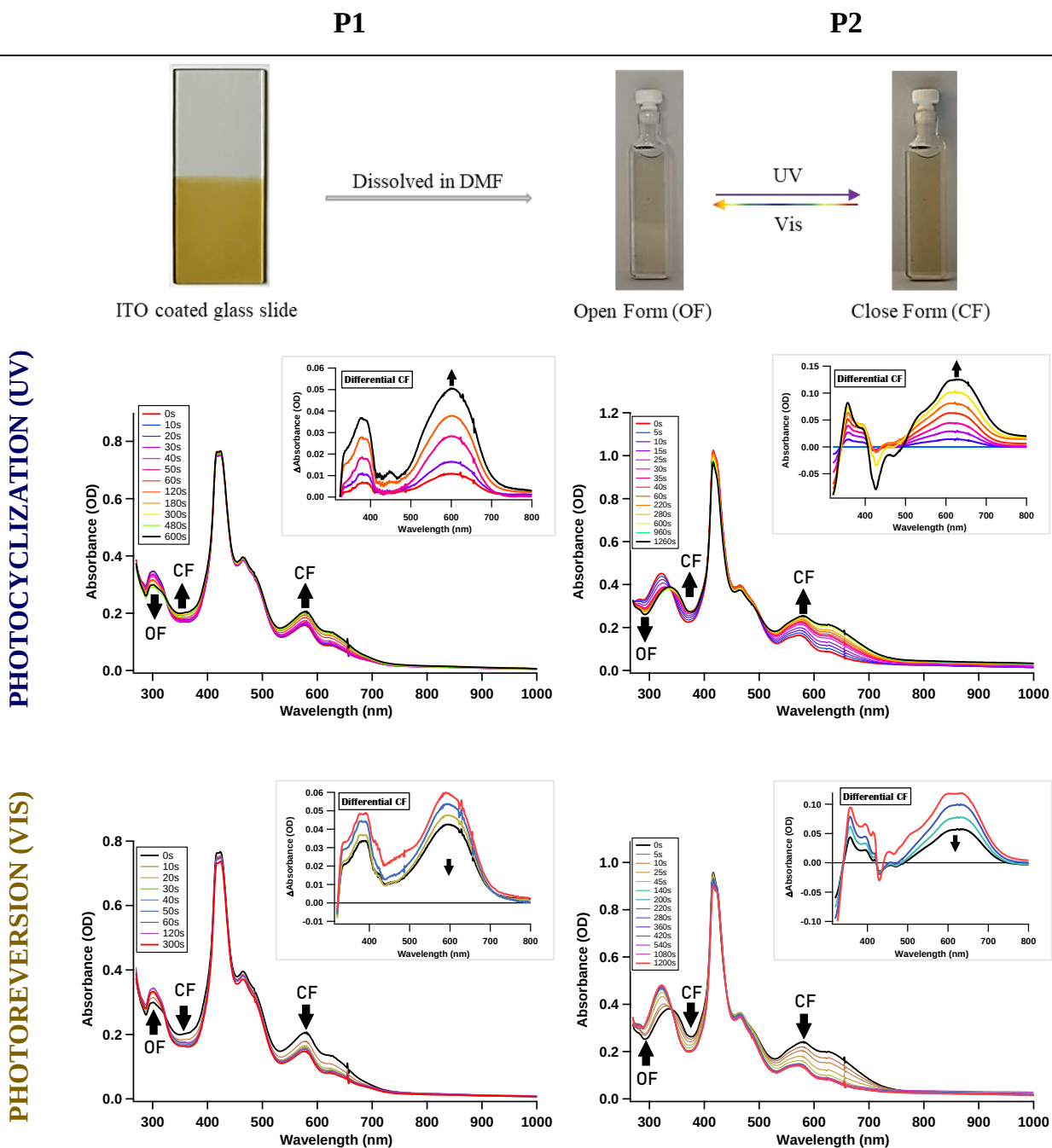


Figure 5.3. UV-Vis absorption changes of P1 and P2 in DMF (degassed solution) during photocyclization and photoreversion.

When irradiated with visible light (435 nm), the spectral evolution is reversed (**Figure 5.3**, bottom). The CF bands at 600 and 365-380 nm gradually diminish, while the OF absorption around 300 nm recovers, again near the same isobestic points (~325 nm for P1 and ~340 nm for P2). The differential spectra confirm the decay of the CF contribution and the reappearance of the OF signal. In contrast to the forward process, the reversion occurs more rapidly, likely due to the higher lamp power, stabilizing within ~300 s for P1 and 1200 s for P2. Multiple irradiation cycles (UV/Vis) were performed, revealing that both polymers can be repeatedly switched with high reversibility and without any spontaneous recovery in the dark at room temperature. Overall, both systems exhibit efficient and reversible photoisomerization in solution, with P2 behaving comparably to P1 but displaying slower kinetics.

5.2.3 Lack of Photochromic Behavior of Polymers in Solid State

In sharp contrast to the clear spectral changes observed in solution, both P1 and P2 tend to show only very weak photochromism when directly used as thin films deposited on ITO glass. Under standard UV/Vis irradiation, no appreciable modifications of the absorption spectra are detected within practical timescales. Only after prolonged exposure do slight differences emerge, corresponding to a low degree of CF formation. These weak signals suggest that, in the solid state, structural constraints and the coiled arrangement of the electropolymers strongly limit the flexibility required for the diarylethene cyclization process. This point will be further addressed in the discussion of fs transient absorption measurements, which provide complementary evidence of restricted switching in the thin-film state.

5.3. Spectroelectrochemistry of P1 and P2

5.3.1 Spectral Features of Redox Processes

To provide a framework for the fs studies, we first established the spectroelectrochemical fingerprints of the polymers in thin films. Spectra were recorded under oxidative and reductive conditions, with oxidation shown at the top and reduction at the bottom of each **Figure 5.5**. These measurements were taken from the thesis of Dr. Ning JIANG (36), who performed the spectroelectrochemical experiments on the polymer films in Strasbourg University.

Oxidation (grey + orange + blue features). Applying positive potentials leads to a decrease in the Soret band ($\sim 430\text{-}470\text{ nm}$) and Q bands ($\sim 560\text{-}640\text{ nm}$), together with the growth of broad new absorption extending across the visible and into the NIR ($\sim 700\text{-}1100\text{ nm}$). A shoulder near $\sim 375\text{ nm}$ develops while the $\sim 325\text{ nm}$ band decreases. These changes correspond to the oxidation of isoporphyrin radicals (IsoP $^{\bullet}$) into their cationic form (IsoP $^{+}$), as illustrated in **Figure 5.4**. This process reduces the electronic conjugation of the porphyrin core (grey feature ①) and is accompanied by broad NIR absorptions that are characteristic of the delocalized IsoP $^{+}$ cation (orange feature ②). The red traces correspond to the neutral isoporphyrin radical (IsoP $^{\bullet}$) before oxidation, while the green trace represent the fully oxidized state (IsoP $^{+}$). The spectral evolution from red to green therefore reflects the conversion of IsoP $^{\bullet}$ to IsoP $^{+}$, evidenced by the rise of the broad NIR band and the attenuation of the porphyrinic Soret and Q bands. In addition, both polymers display changes in region assigned to the growth of the DAE closed-form band (blue feature ③), which, as observed, evolves together with the oxidation/reduction process and therefore does not correspond to a normal photocyclization. This point will be discussed in detail in the following section. The intensity of the orange feature NIR contribution is stronger in P1, while in P2 it is less pronounced, showing weaker stabilization of the delocalized IsoP $^{+}$ state in the phenyl-substituted copolymer.

Reduction (green feature). Under negative potentials, both polymers exhibit a decrease in the Soret and Q bands, while new bands appear near $\sim 500\text{ nm}$ and $\sim 680\text{ nm}$. These signals originate from the stepwise reduction of the pyridinium substituents into pyridyl radicals, which then delocalize across the conjugated scaffold (green feature ④). In this case, the green curve corresponds to the spectrum recorded at the reduction potential, while the red curve represents the neutral reference prior to reduction. The difference between the two shows the characteristic positive bands associated with Py $^{+} \rightarrow \text{Py}^{\bullet}$ conversion. In P1, this delocalization extends further into the NIR with a broad contribution up to $\sim 1100\text{ nm}$, whereas in P2 the spectral changes remain confined to the visible region ($\sim 520\text{-}700\text{ nm}$), indicating a more localized radical distribution.

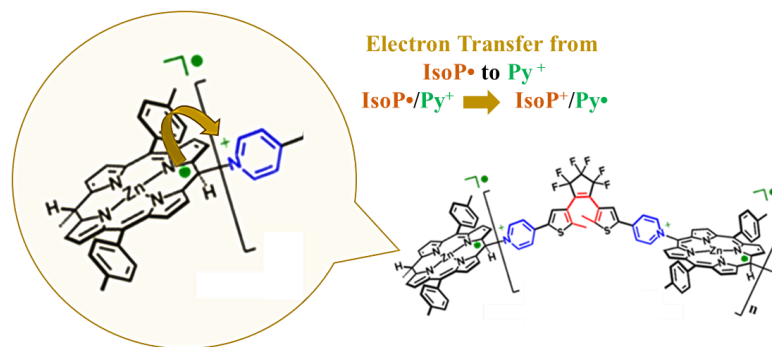


Figure 5.4. Illustration of the electron transfer mechanism between the isoporphyrin unit and the pyridinium substituents.

Taken together, these four-color coded features define the spectroscopic signatures of the key redox-active species in P1 and P2. They serve as benchmarks for assigning the transient signals observed in the femtosecond experiments discussed in the next section.

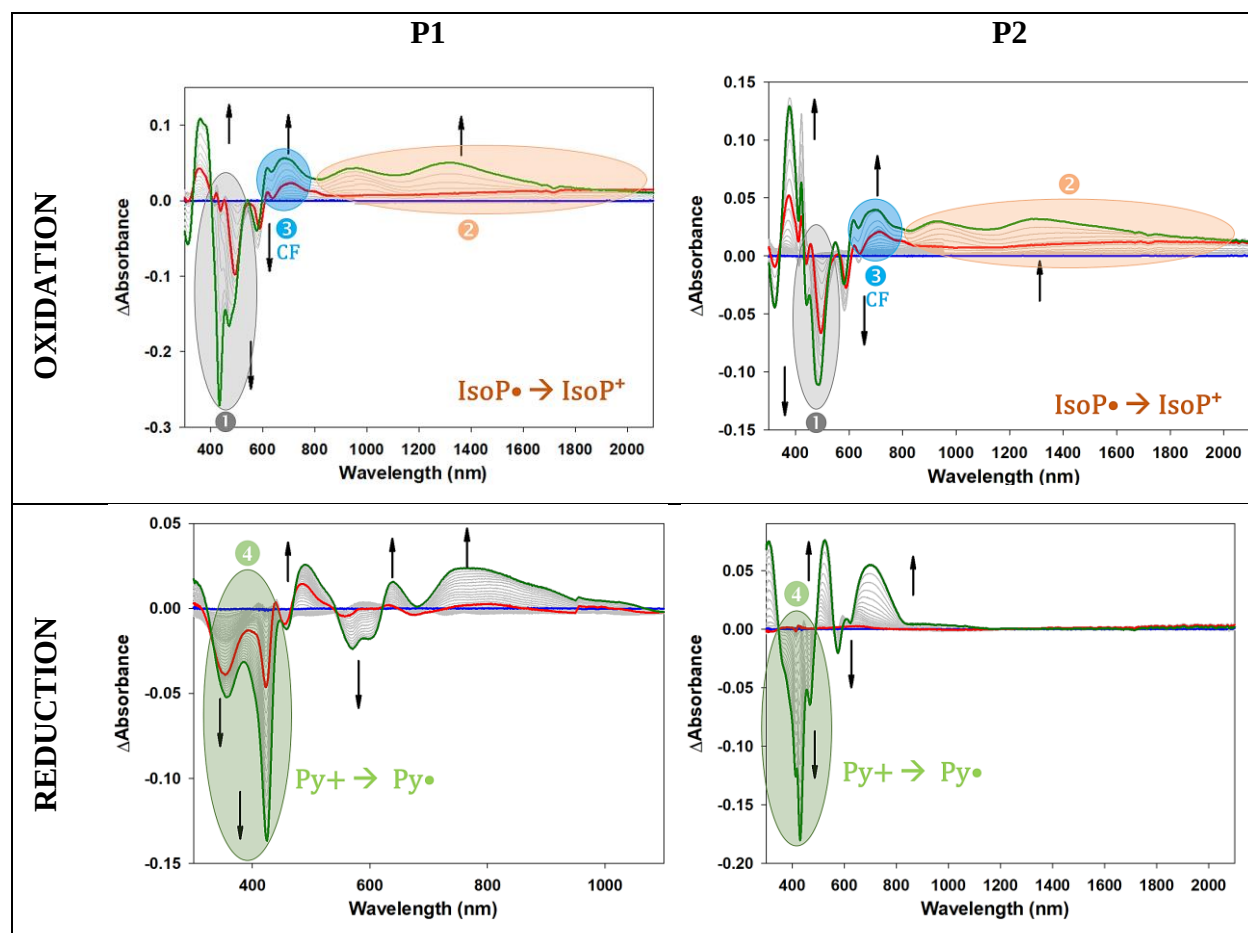


Figure 5.5. Differential Uv-vis-NIR spectroelectrochemical responses of P1 and P2 under oxidation (top) and reduction (bottom).

5.3.2 Indirect Unexpected Electrocyclization Mechanism

Beyond the signature rising at the CF position (blue feature) described above, this process clearly arises under applied electrochemical potential, revealing an electrochemically assisted ring closure, that is, an electrocyclization of oxydo-reductive nature. This mechanism does not correspond to a conventional light-driven photocyclization but instead results from charge redistribution following the oxidation of the isoporphyrin radical ($\text{IsoP}^{\bullet} \rightarrow \text{IsoP}^+$) and the reduction of the pyridinium units ($\text{Py}^+ \rightarrow \text{Py}^{\bullet}$). In this reduced state, the radicals generated on both pyridinium sites can delocalize through the $\text{Py}^{\bullet}$ -DAE- $\text{Py}^{\bullet}$ bridge, and their coupling promotes C-C bond formation, giving rise to an electrochemically induced ring closure of the DAE.

As illustrated in **Figure 5.6**, once this species is generated, electron density on the adjacent pyridyl radicals appears to become delocalized across the DAE bridge. This redistribution likely enforces a more planar geometry of the thiophene arms, ultimately favouring C-C bond formation and driving the DAE units toward their closed form. In this sense, the ring closure is triggered indirectly through electron transfer rather than direct photoexcitation, highlighting the interplay between porphyrinic redox events and DAE structural reorganization.

In P1, the delocalization extends more strongly to the isoporphyrin unit, while in P2 it remains localized due to the phenyl spacer, explaining the less intense NIR component.

Such electrocyclization may account for the appearance of the band assigned to the DAE closed form in the spectroelectrochemical data, evolving in redox activity. This redox-driven closure pathway will be further addressed in the fs-TA studies, where its photochemical analogue can be examined in more detail.

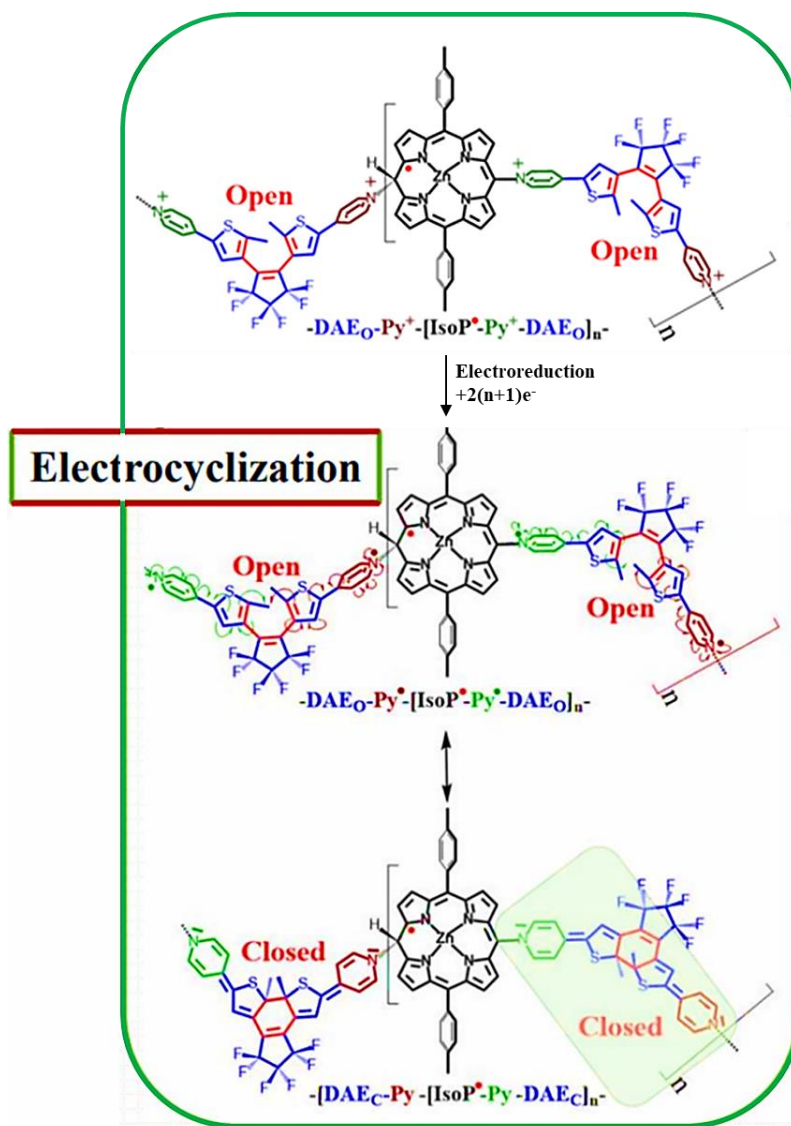


Figure 5.6. Proposed electrochemically induced DAE ring-closure (electrocyclization) mechanism of P1.

5.4. fs-TAS of porphyrin in DMF

Excitation of isoporphyrin (ZnT₂P) at 420 nm in DMF reveals a transient spectrum (**Figure 5.7**) characterized by the typical signatures of its Soret and Q bands. This measurement serves as a reference background for interpreting the polymer dynamics discussed later. Global fitting with three exponential function (Figure S.5.1.) at selected wavelengths (449, 480, 545, 568, 613, and 648 nm) yields three characteristic time constants: $\tau_1 \approx 0.3$ ps, $\tau_2 \approx 8$ ps, and $\tau_3 \approx 8800$ ps. **Table 5.1** compiles all characteristic time constants (τ_1, τ_2, τ_3) extracted from the global fitting of transient absorption data for P1 and P2 under different excitation conditions, in both solution and solid state. The transient data naturally separate into three temporal windows that can be readily assigned.

In the first TW, upon excitation into the Soret band, the system is promoted to the S₂ state, as already discussed above. The immediate appearance of the bleach band (545 nm) indicates that population has already been transferred to S₂. Along with this, two ESA bands appear, one around 450 nm and another in the IR range. These features are assigned to the ultrafast vibrational decay of the S₂(FC) state toward the minimum potential well, S₂(min) associated within $\tau_1 \approx 0.3$ ps, Subsequently, in the second TW, the spectrum evolves with the growth of a well-defined ESA maximum at 447 nm, a slight contribution from the bleach at 545 nm, and the emergence of a negative stimulated emission band around 645 nm, in agreement with the steady-state emission spectrum from S₁ emissive state (**Figure 5.7.B**, green curve). The SE signal subsequently decays, and the ESA band stabilizes. This stage is thus assigned to the expected internal conversion, S₂ → S₁ within a characteristic time $\tau_2 \sim 8$ ps, confirming that this ps-scale cooling of S₁ is a general feature of porphyrin photophysics (a point that will be important for later comparison).

At longer times, in the third TW, the transient spectra reveal a decay of the ESA band in the visible region together with the emergence of new signatures characteristic of the triplet state (61,62), most prominently near 485 nm. These spectral changes are accompanied by clear isosbestic points at 437 and 463 nm, evidencing a clean conversion between electronic states. This evolution reflects the growth of the triplet manifold through intersystem crossing. In parallel, the apparent reduction in bleach band amplitude can be rationalized by overlap between the negative ground-state bleach and the positive triplet absorption. The associated timescale ($\tau_3 \sim 8800$ ps) is

characteristic of $S_1 \rightarrow T_1$ intersystem crossing in porphyrins, consistent with the values reported in the literature (61,62). **Figure 5.8** summarizes these relaxation pathways and characteristic times in a simplified energy-level scheme.

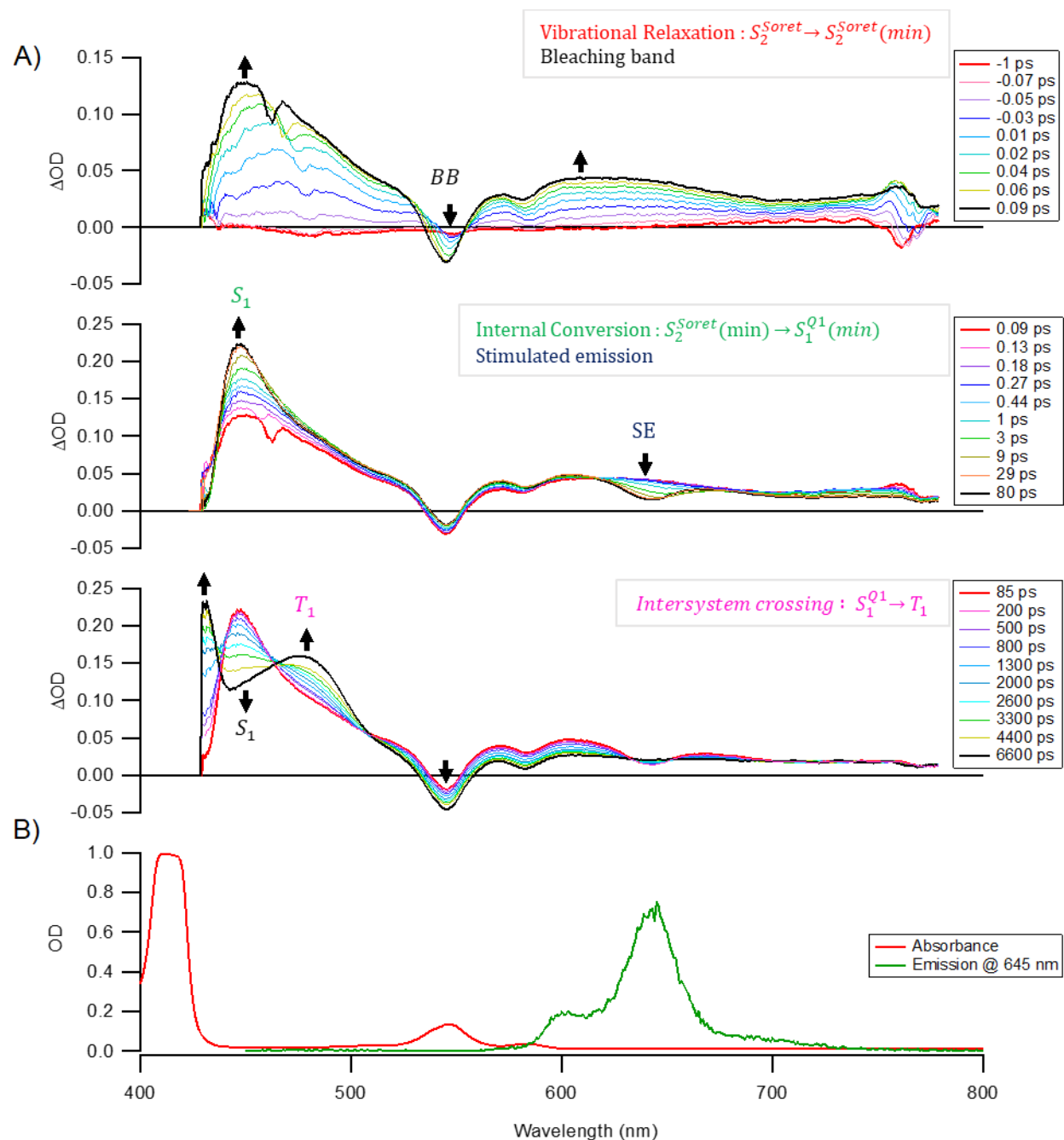


Figure 5.7. (A) fs-TA spectra of porphyrin in DMF, recorded upon 420 nm laser excitation with a power of 0.2 μ J. The color gradient from red to black represents the spectral evolution over time, grouped into three temporal windows: top panel [-1 ps to 0.09 ps], middle panel [0.09 ps to 80 ps] and bottom panel [85 ps to 6600 ps]. (B) Steady-state UV-Vis absorption spectra of porphyrin (red) and emission (green), shown for reference.

Altogether, the data establish a sequential relaxation pathway under Soret excitation: Ultrafast vibrational relaxation within S_2 , picosecond internal conversion to S_1 , and nanosecond intersystem crossing to T_1 . The well-resolved isosbestic points confirm the clean progression between these electronic states.

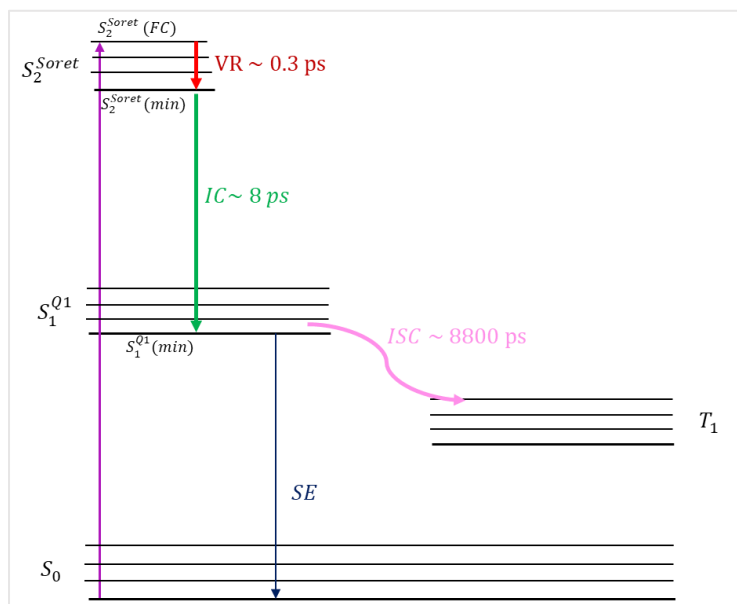


Figure 5.8. Energy diagram showing the main relaxation pathways and characteristic times of isoporphyrin.

Table 5.1. Characteristic Time Constants of P1 and P2 under Different Excitation Conditions in the UV region (315 nm) and to the porphyrin S band (420nm) or Q band (~570 nm) , measured in solution (DMF) and in the solid state (ITO).

Molecules	Medium	$\lambda_{exc.}(nm)$	Power (μJ)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
Isoporphyrin	DMF	420 (S)	0.2	0.30(1)	10 (2)	8800(500)	-
P1	DMF	315	0.2	0.080(1)	1.8(2)	15(1)	530(70)
P1	DMF	420 (S)	0.3	0.060(5)	13(6)	310(35)	-
P1	ITO	315	0.2	0.55(1)	10(3)	380(40)	-
P1	ITO	570 (Q)	0.2	0.10(6)	1.5(5)	40(2)	-
P2	DMF	315	0.2	0.080(1)	0.30(2)	9(1)	200(20)
P2	DMF	420 (S)	0.2	0.04(4)	12(1)	930(110)	-
P2	ITO	315	0.2	0.80(2)	14(4)	920(55)	-
P2	ITO	570 (Q)	0.2	0.13(7)	2.5(1)	95(4)	-

5.5. Solid-State Photodynamics: Lack of Photocyclization

The fs-TAS results of P1 and P2 in the solid state (on ITO substrates) are discussed below, considering the non-photochromic character of the system and taking into account both the spectroelectrochemical data and the previous transient studies on the isoporphyrin reference.

5.5.1 fs-TAS of P1 onto ITO slide (315 nm Excitation)

The transient spectra of P1 recorded directly in the solid state on the ITO slide are grouped into three temporal windows: TW1 [-1 to 0.11 ps], TW2 [0.11 to 16 ps], and TW3 [16 to 6000 ps] (**Figure 5.9**). Using a three-exponential model, which provided the best fit, global fits at selected wavelengths (365, 427, 453, 480, 530, 576, 614, 674, and 923 nm) results three characteristic times: $\tau_1 = 0.55$ ps, $\tau_2 = 10$ ps, and $\tau_3 = 380$ ps (Figure S.5.2.).

At first glance, the interpretation of the transient data is complicated by the strong ground-state bleaching associated with the Soret and Q absorption bands. Roughly, the three temporal windows can be defined as follows: (i) the initial rise of the transient signal, featuring prominent bleaching in the visible region and broad absorption in the NIR; (ii) a subtle spectral shift of the transient bands in the visible range accompanied by the appearance of a new band in the NIR; and (iii) a final decay phase, during which no further visible shifts are observed and the NIR band gradually vanishes.

By combining these transient features with the spectroelectrochemical fingerprints, each of the three processes can be confidently assigned in the following discussion. The assignment relies on a careful comparison between the fs-TAS and spectroelectrochemical data, which provide complementary information on the $\text{IsoP}^\bullet \rightarrow \text{IsoP}^+$ and $\text{Py}^+ \rightarrow \text{Py}^\bullet$ transitions, aiding the identification of the corresponding features within the femtosecond spectra. In particular, the main spectroelectrochemical signatures: feature ① (grey), oxidation of the isoporphyrin radical ($\text{IsoP}^\bullet \rightarrow \text{IsoP}^+$); feature ② (orange), growth of the NIR band associated with the delocalized cation IsoP^+ ; and feature ④ (green), reduction of the pyridinium spacers ($\text{Py}^+ \rightarrow \text{Py}^\bullet$).

In TW1, the spectra display a prompt rise of the transient signal followed by an ultrafast decay of the ESA bands spanning the visible and NIR regions. This behavior is consistent with a very fast internal conversion from an initially populated higher singlet state $S_n(\text{FC})$ region toward

the $S_1(\text{min})$ manifold, with a characteristic time below 130 fs. Ongoing TD-DFT calculations are expected to further clarify in the future the exact nature of the excited states involved.

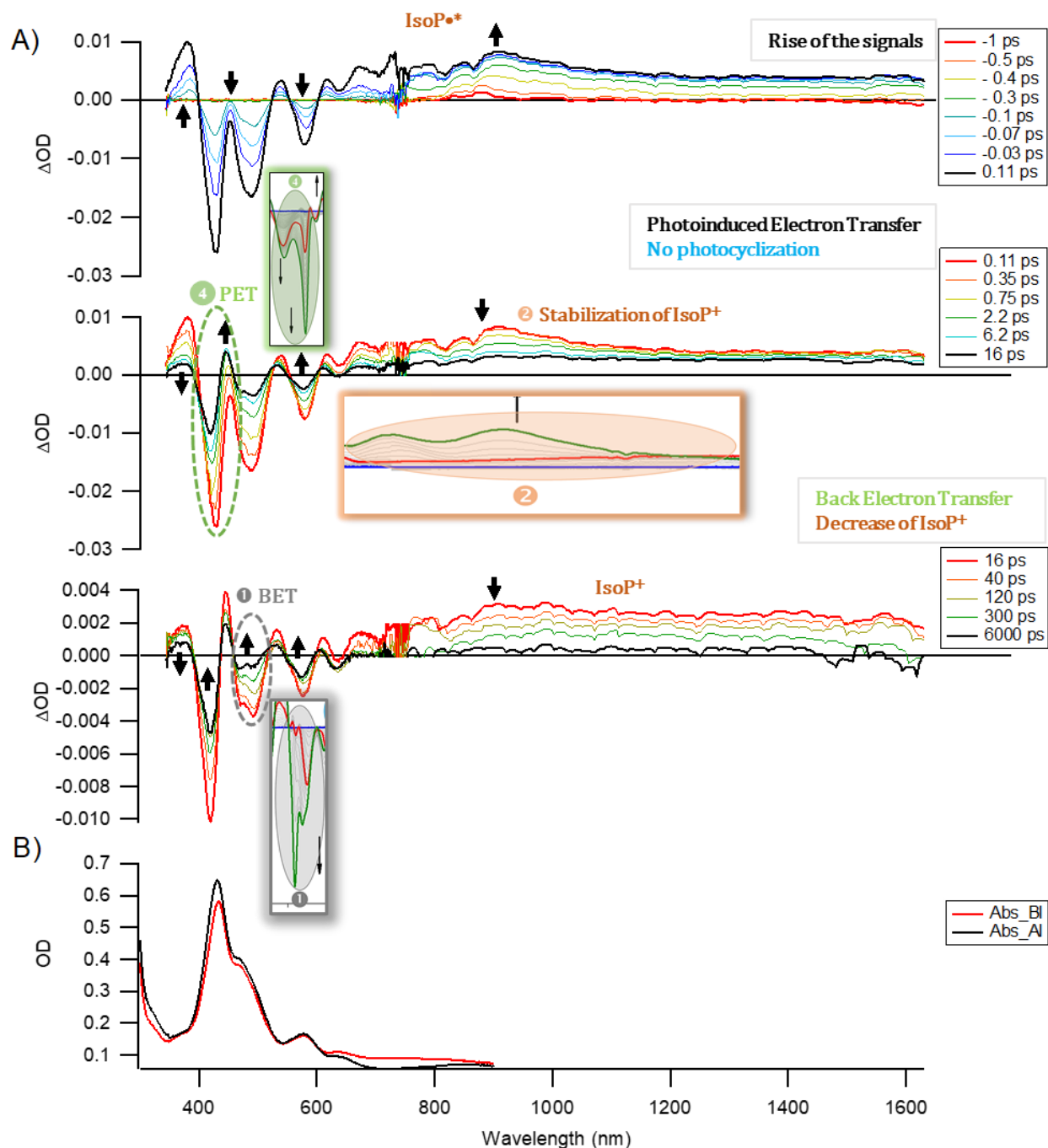


Figure 5.9. (A) fs-TA spectra of P1 in solid, recorded upon 315 nm laser excitation with a power of 0.2 μJ . The color gradient from red to black represents the spectral evolution over time, grouped into three temporal windows: top panel [-1 ps to 0.11 ps], middle panel [0.11 ps to 16 ps] and bottom panel [16 ps to 6000 ps]. (B) Steady-state UV-Vis absorption spectra of P1 before (red) and after (black) irradiation, shown for reference.

In TW2, the spectral evolution becomes more complex. A concomitant decay of two ESA features (indicated by black arrows pointing down) occurs alongside the rise of new ESA bands that partially overlap the bleaching dips. A closer inspection reveals an apparent spectral shift of the Soret band bleaching around 425 nm. This shift is most likely attributed to a photoinduced electron transfer (PET) from the excited isoporphyrin radical (IsoP•) toward the pyridinium substituents ($\text{Py}^+ \rightarrow \text{Py}^*$) (green feature ④), observed electrochemically at the same wavelength (425 nm). A zoomed-in spectroelectrochemical comparison of feature ④, highlighting the Py^* signature, is displayed in the same window to facilitate direct correlation. The PET step occurs on an ultrafast timescale of $\tau_1 \approx 0.55$ ps. Moreover, in contrast to the solution case that will be discussed later, the formation here of IsoP^+ is clearly stabilized and evidenced by the growth of a new absorption band in the IR region feature ② also presented in the same window for direct comparison.

Following this electron-transfer process, a residual contribution reflecting relaxation within the IsoP^* manifold. This stage likely corresponds to internal conversion from $\text{S}_1(\text{min})$ to S_0 . The relaxation represents the classical porphyrinic decay pathway found ($\tau \approx 8$ ps) and is described by the second kinetic component ($\tau_2 \approx 10$ ps). Since the PET QY is not expected to reach unity, this relaxation channel probably proceeds concurrently with the charge-separation process.

In TW3, a concomitant decay of the negative bleaching band at 470 nm occurs together with the decays to zero of the NIR band, while some ESA features remain persistent in the visible range. This behavior is consistent with the formation of a photoproduct unrelated to photocyclization. Because the decay of the bleaching feature at 470 nm corresponds to the spectral position of feature ①, it is likely associated with back-electron transfer (BET). This process is described by the third kinetic component ($\tau_3 \approx 380$ ps), corresponding to back electron transfer from the reduced pyridyl radical back to IsoP^+ , thereby regenerating the $\text{Py}^+/\text{IsoP}^*$ ground-state pair, probably with slight photodegradation indicating incomplete BET recovery.

5.5.2 Fs-TAS of P2 onto ITO slide (315 nm Excitation)

The transient dynamics of P2 in the solid state (Appendix 5, Section S.5.1.) follow the same sequence of processes as P1; PET, internal conversion, and BET, without any evidence of photocyclization. The only distinction lies in the characteristic times (**Figure 5.10**): all three

dynamics are longer in P2, with the most notable difference observed for $\tau_3 \approx 920$ ps, which extends beyond that of P1 (≈ 380 ps). This slowdown is attributed to the phenyl substituent in P2, which increases the spatial separation between the IsoP⁺ and pyridinium units, thereby delaying both PET and BET. Aside from these kinetic differences, the mechanistic picture remains unchanged, with stabilization of IsoP⁺ preventing CF formation in both polymers.

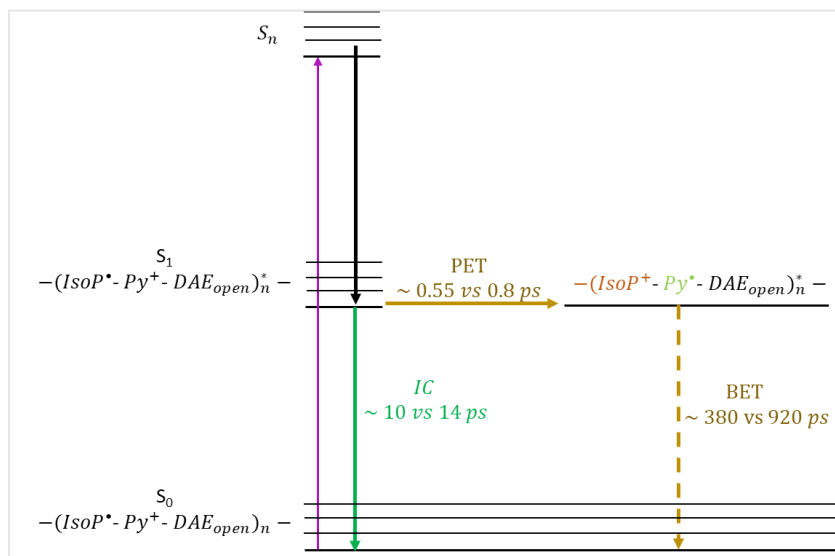


Figure 5.10. Energy diagram showing the main relaxation pathways and characteristic times of P1 vs P2 solid.

5.6. fs-TAS of P1 and P2 with Q-Band Excitation

Excitation of P1 and P2 films at 570 nm directly populates the Q band (**Figure 5.11**), a weaker absorption feature corresponding to the S₁ manifold. Pumping at this band bypasses the ultrafast relaxation observed at higher energies and places the system directly in S₁. As expected from the absence of photocyclization at 315 nm excitation, the dynamics observed here closely mirror those results. Both polymers follow the same sequence of processes: an ultrafast PET ($\tau_1 \approx 0.1$ ps), followed by internal conversion within S₁ (τ_2), and finally BET (τ_3) with negligible photodegradation. Crucially, no CF production is detected, confirming that photocyclization is suppressed in the solid state. For P1 at 570 nm, τ_2 (1.5 ps) and τ_3 (40 ps) are markedly shorter than at 315 nm ($\tau_2 = 10$ ps, $\tau_3 = 380$ ps), showing that relaxation and BET are strongly accelerated when S₁ is accessed directly. P2 at 570 nm exhibits slightly longer times ($\tau_2 = 2.5$ ps, $\tau_3 = 95$ ps) compared to P1, consistent with the additional phenyl spacer imposing slower reorganization, but

both remain much faster than their 315 nm counterparts. Altogether, the comparison demonstrates that while the mechanistic sequence (PET $\rightarrow$ IC $\rightarrow$ BET) is unchanged, excitation of the Q band drastically shortens the IC relaxation time relative to 315 nm, consistent with the energy gap law: starting from a lower-energy state (S_1) enables more efficient and faster decay.

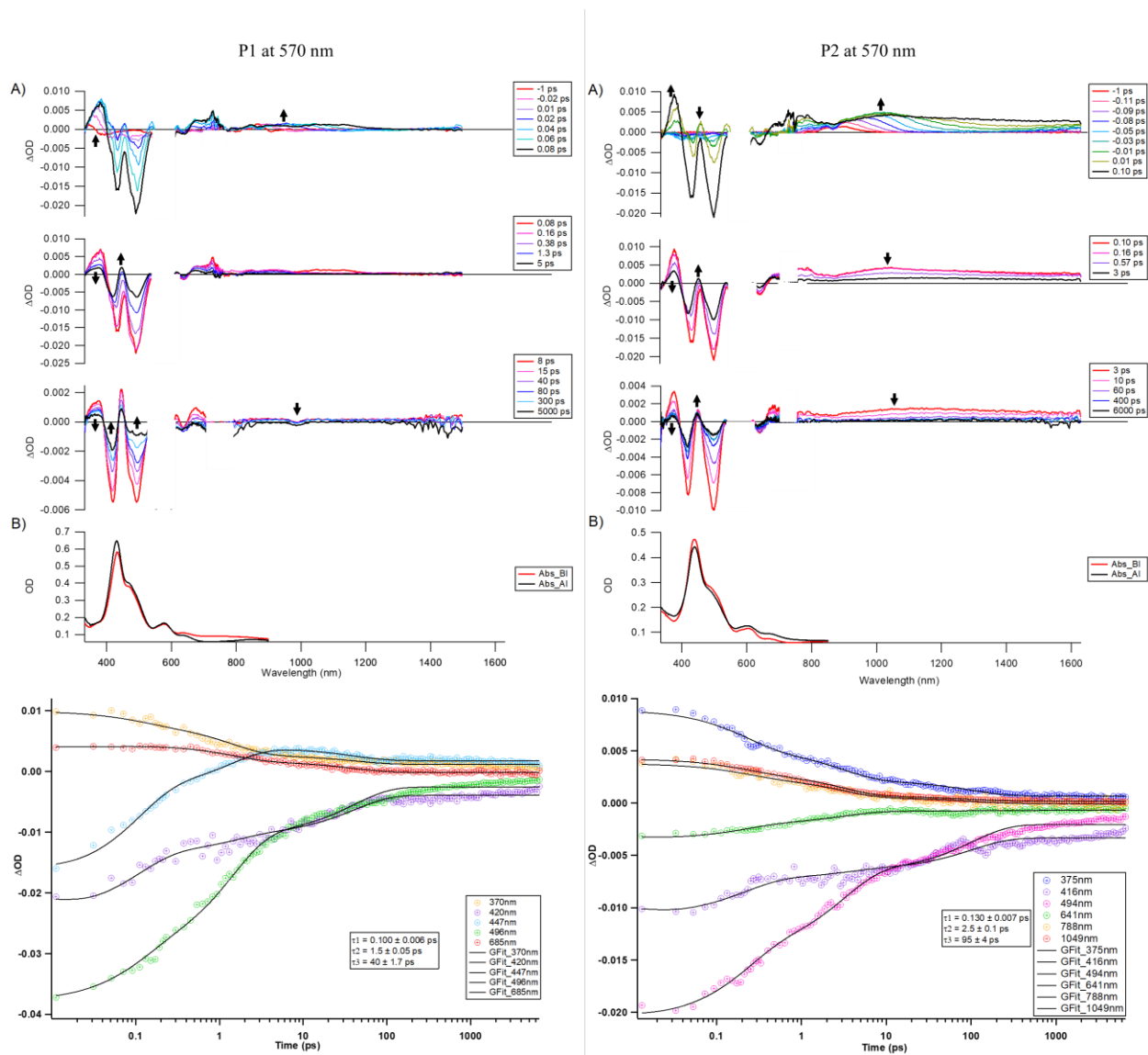


Figure 5.11. Comparative fs-TA spectra and global fitting analysis of P1 (left) and P2 (right) thin films excited at 570 nm.

5.7. Femtosecond Photodynamics of P1 and P2 in Solution

Compared to the solid state, the solution case is more complex to rationalize, as both photoswitching mechanisms and photoinduced electron transfer are expected to occur concurrently.

5.7.1 Dual Photocyclization Pathways of P1 and P2 in DMF

In this section, excitation at 315 nm was employed, a wavelength that simultaneously addresses both chromophores in the polymers: the DAE moiety and the isoporphyrin unit. This dual excitation provides access to the excited states of both components, allowing us to probe their coupled dynamics within the polymer framework. The assignment of the ESA bands is based on spectroelectrochemical results and comparison with the fs-TAS data of pure isoporphyrin. Additional insight is drawn from the DAE1 and DAE2 results presented in Chapter 3 to refine the interpretation of the transient features.

Since P1 and P2 exhibit analogous dynamical behavior under these excitation conditions, only the representative data of P1 are shown here, while the corresponding spectra and global fits for P2 are provided in the Supplementary Information while all times are provided in **Table 5.1**. For clarity, the characteristic times extracted for P2 are nonetheless included in the comparative diagram alongside those of P1.

The transient spectra are grouped into three temporal windows: TW1 [-1 to 0.77 ps], TW2 [0.77 to 30 ps], and TW3 [30 to 5000 ps] (**Figure 5.12**). Global fits at selected wavelengths (366, 414, 445, 487, 529, 578, 607, 1200 nm) yield three characteristic times: $\tau_1 = 0.10$ ps, $\tau_2 = 18$, and $\tau_3 = 465$ ps (Figure S.5.5). These components correspond directly to the spectroelectrochemical fingerprints identified previously in the case of solid.

In TW1, the spectra exhibit a prompt rise of the transient signal followed by an ultrafast decay of the ESA bands $S_n(\text{FC})$ toward the $S_1(\text{min})$ manifold consistent with solid-state case. While the observed decay is consistent with internal conversion, it cannot yet be established whether both chromophores contribute equally to this relaxation process, an important uncertainty that gives rise to two possible relaxation scenarios, which will be further discussed in the following.

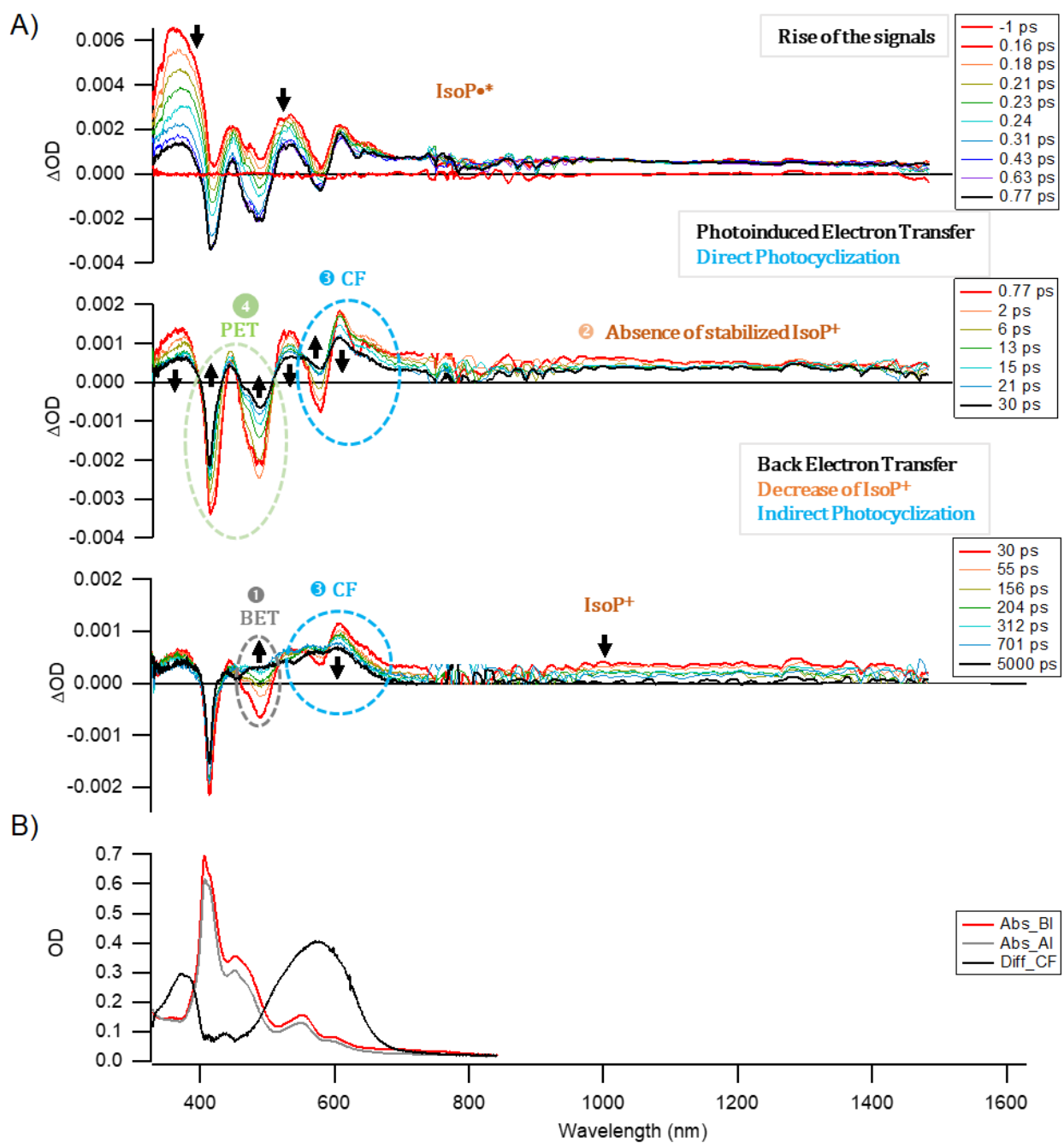


Figure 5.12. (A) fs-TA spectra of P1 in DMF, recorded upon 315 nm laser excitation with a power of 0.2 μ J. The color gradient from red to black represents the spectral evolution over time, grouped into three temporal windows: top panel [-1 ps to 0.77 ps], middle panel [0.77 ps to 30 ps] and bottom panel [30 ps to 5000 ps]. (B) Steady-state UV-Vis absorption spectra of P1 before (red) and after (black) irradiation, shown for reference.

In TW2, the spectral evolution becomes more complex. A subtle shift of the Soret band bleaching around 425 nm is observed, attributed to PET from the excited isoporphyrin radical (IsoP[•]) toward the pyridinium substituents (Py⁺ → Py[•], green feature ④) (**Figure 5.5**), as evidenced previously in the solid-state spectra. In contrast to the solid-state behavior seen before, a rising signal appears near the CF band position (~570 nm), accompanied by a shallow negative contribution from the overlapping bleach. This feature is characteristic of a direct photocyclization process. Altogether, the PET step occurs on an ultrafast timescale of about 0.08 ps, while the direct photocyclization develops more slowly, with a characteristic time of approximately 1.8 ps. Given this timescale and the confinement effects deduced from MC1, the process is more likely to correspond to sequential photocyclization mechanism rather than a direct closure from the FC region.

In TW3 [30 ps to 5 ns], three main features can be identified: (i) a narrow negative band remains persistent, (ii) no distinct NIR signal is detected, and (iii) a concomitant decay of the negative bleaching band at 490 nm occurs together with the decay of the positive ESA band, revealing the spectral signature of the CF. This evolution is governed by the third kinetic component ($\tau_3 \approx 15$ ps), which reflects an indirect photocyclization process, followed by a slower component ($\tau_4 \approx 530$ ps) associated with BET.

How can we justify this apparent second photocyclization signal together with the absence of the broad NIR band associated with the IsoP⁺ species? A possible explanation can be proposed based on the spectroelectrochemical results discussed above concerning the electrochemically induced DAE ring closure. Indeed, in the third temporal window, the continuous rise of the CF band suggests the presence of a secondary photocyclization mechanism. Mechanistically, the two Py[•] radicals generated after PET delocalize across the DAE bridge, enforcing coplanarity of the thiophene arms and driving C-C bond formation (63). This constitutes an indirect cyclization mechanism, in which PET not only initiates electron redistribution but also promotes the geometry required for ring closure as illustrated in bottom panel of **Figure 5.13**. The absence of stabilized IsoP⁺ (feature ②) is consistent with CF formation driven by the radical pyridyls, which prevents IsoP⁺ stabilization. The narrowing of the ~420 nm band further reflects radical delocalization and redistribution during cyclization. In parallel, BET occurs as Py[•] radicals donate electrons back to IsoP⁺, thereby restoring Py⁺/ IsoP[•] ground-state species while the CF band established. It is worth noting that identifying a possible internal conversion from the S₁ state to S₀ proved extremely

challenging maybe due to the strong spectral overlap and the difficulty in disentangling their respective dynamic and characteristic time.

In summary, the photodynamics of P1 in solution at 315 nm proceed through four main steps:

- an ultrafast PET process ($\tau_1 \sim 0.1$ ps) that generates $\text{IsoP}^{*\bullet}/\text{Py}^\bullet$ pairs;
- a slower component ($\tau_2 \sim 1.7$ ps) associated with classical photocyclization probably along sequential mechanism;
- a longer indirect photocyclization process ($\tau_3 \sim 15$ ps) driven by radical delocalization across the DAE bridge;
- a BET ($\tau_4 = 530$ ps) that restores charge balance. The absence of stabilized IsoP^+ in the solution spectra remains the defining feature of this indirect pathway.

Polymer P2 (Section S.5.3.) exhibits a strictly similar photochemical sequence, following the same direct photocyclization and PET $\rightarrow$ indirect photocyclization $\rightarrow$ BET framework. This indicates that both mechanisms remain unaffected by the presence of the additional phenyl linker, which primarily modulates the kinetics rather than the overall reaction topology. The detailed transient absorption results for P2 are provided in the Annex, while its characteristic times are included alongside those of P1 in the comparative energy-level diagram **Figure 5.14**.

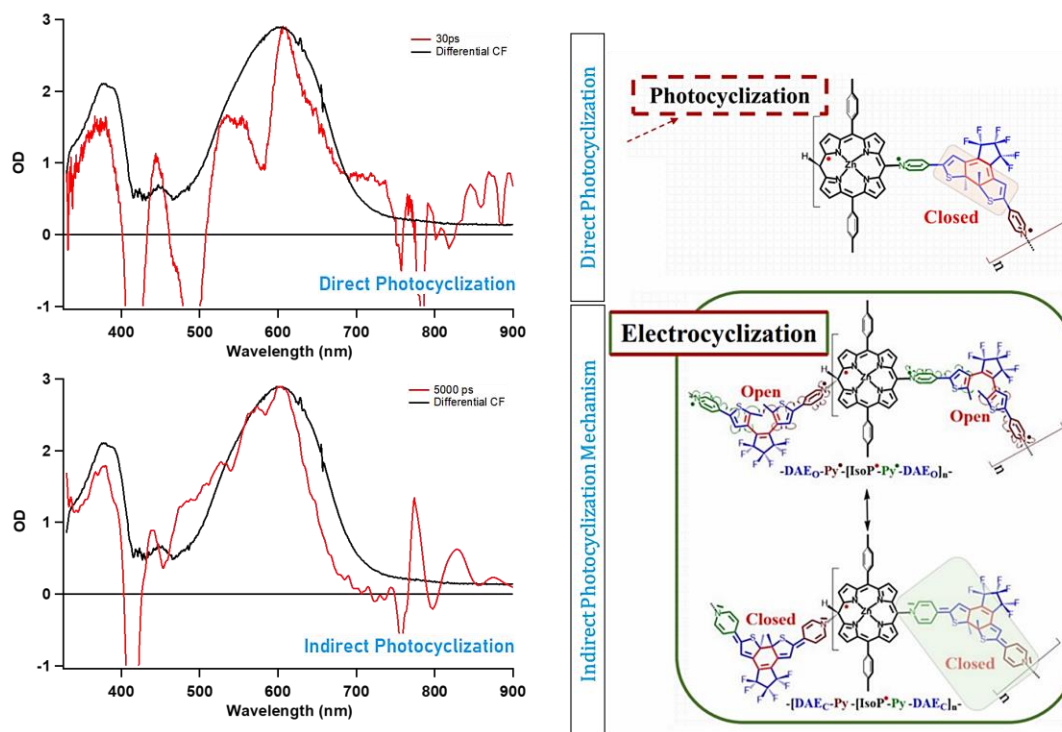


Figure 5.13. Direct (top) vs. indirect (bottom) cyclization of P1: transient spectral signatures and proposed mechanisms.

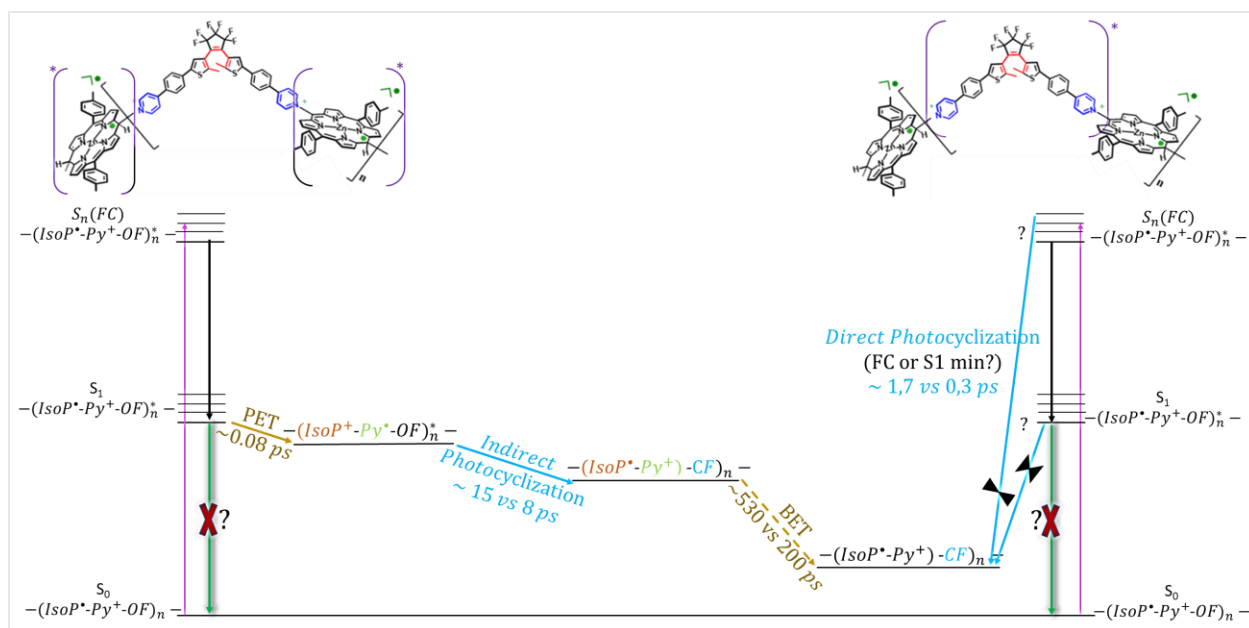


Figure 5.14. Energy diagram showing the main relaxation pathways and characteristic times of P1 vs P2 in DMF.

5.7.2 Direct comparison: Solid vs Solution

In the solid state, both polymers show no contribution from direct or indirect photocyclization. This behavior can be directly attributed to the stabilization of the oxidized isoporphyrin species (IsoP^+), which prevents the formation of the closed form (CF) and thereby blocks the cyclization pathway. Moreover, the solid-state morphology reinforces this suppression: the rigidity and limited conformational flexibility of the polymer coils immobilized on the ITO surface hinder the structural rearrangements required for DAE closure.

In contrast, in solution, the transient pyridyl radicals ($\text{Py}^\bullet$) generated upon PET efficiently promote both direct and indirect ring-closure pathways, thereby suppressing IsoP^+ stabilization. This difference highlights the decisive role of environmental constraints: while the flexible solvated chains allow charge delocalization and conformational reorganization leading to CF formation, the solid-state rigidity traps the system in the charge-separated $\text{IsoP}^+/\text{Py}^\bullet$ configuration.

Overall, the comparison reveals that IsoP^+ stabilization and restricted structural freedom are the key factors that suppress photocyclization in the solid phase, whereas in solution, radical delocalization across the DAE bridge restores the photochromic reactivity characteristic of the open-to-closed form transformation.

5.8. Photoreversion of Polymers in Solution under Soret Excitation

In this section, we investigate the photoreversion dynamics of P1 and P2 in solution by pumping at 420 nm, targeting the Soret band, in direct analogy to the isoporphyrin reference discussed earlier. The Soret band is the most intense feature in porphyrin UV-Vis spectra and corresponds to excitation into the higher singlet state (S_2). As established for the isoporphyrins reference under the same 420 nm excitation, population injected into $S_2(\text{FC})$ undergoes ultrafast internal conversion to S_1 with ($\text{VR} \approx 0.3$ ps). The excited system then relaxes within the S_1 manifold through ($\text{IC} \approx 8$ ps), before finally decaying via intersystem crossing to the triplet manifold on the nanosecond timescale ($\text{ISC} \approx 8800$ ps). This porphyrinic relaxation sequence serves as the framework for analyzing the polymer transient absorption dynamics under Soret excitation.

5.8.1 DAE Photoreversion and Porphyrinic Relaxation pathways of P1 vs P2

Exciting at 420 nm into the Soret band, both P1 and P2 exhibit the same sequence of relaxation steps characteristic of porphyrinic systems, but with dynamics reshaped by the presence of the DAE units (**Figure 5.15**). The absorption spectra already reveal a key structural consequence: in both polymers the Soret and Q bands are red-shifted relative to the isoporphyrin reference, reflecting the altered electronic distribution within the polymer backbone.

The initial ultrafast step (P1 vs P2 is $\tau_1 \sim 0.05$ ps vs ~ 0.04 ps; Figures S.5.9 and S.5.10 respectively) corresponds to VR within the $S_2(\text{FC})$ level, leading to population of the $S_2(\text{min})$ state, identical to free porphyrin where VR proceeds on the sub-ps timescale. The second component ($\tau_2 \sim 13$ ps vs ~ 12 ps) combines internal conversion of the $S_2(\text{min})$ state to S_1 with the photoreversion of the diarylethene, as indicated by the concurrent recovery of the CF bleach. This timescale is again consistent with porphyrin reference values (~ 8 ps), showing that the polymers retain almost the same vibrational relaxation kinetics while coupling them to DAE ring-opening. It was difficult, however, to disentangle the CF recovery from the internal conversion, given their similar temporal profiles.

The divergence between P1 and P2 arises in the long-lived component. For P1, intersystem crossing into the triplet manifold occurs on the order of ~ 315 ps, while for P2 the process is

substantially slower (~ 930 ps). Compared with the isoporphyrin reference ($\tau_3 \sim 8800$ ps), both polymers exhibit a drastic acceleration of ISC, reflecting the role of the DAE-isoporphyrin framework in facilitating nonradiative decay. The longer τ_3 in P2 relative to P1 highlights the stabilizing effect of its phenyl substituent, which prolongs the S_1 lifetime before ISC.

In summary, excitation into the Soret band drives both polymers through the porphyrinic sequence, VR, IC, and ISC; but with two clear distinctions: (i) the ps relaxation step is coupled to DAE photoreversion, and (ii) ISC is dramatically accelerated compared to free isoporphyrin, with subtle but systematic differences between P1 and P2 due to linker substitution.

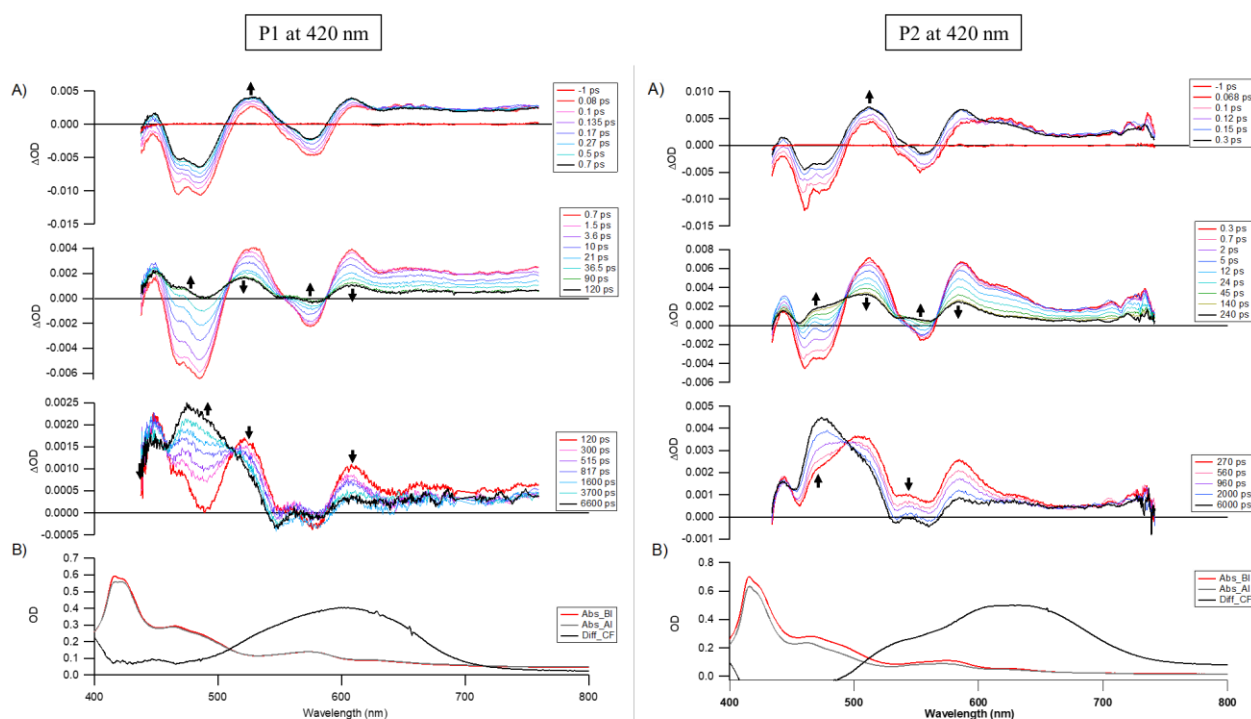


Figure 5.15. (A) Comparative fs-TA spectra of P1 (left) and P2 (right) in DMF solution, recorded upon 420 nm excitation of the Soret band. The color gradient from red to black represents spectral evolution over time, grouped into three temporal windows. (B) Steady-state UV-Vis absorption spectra before (red) and after (black) irradiation are shown below for reference.

5.9. Conclusion

Focusing on the electropolymers P1 and P2, fs-TAS, guided by spectroelectrochemical fingerprints, provides a coherent picture of how the diarylethenes DAE1 and DAE2 behave once integrated into a porphyrinic polymer backbone.

Under UV excitation at 315 nm, which simultaneously addresses both chromophores the DAE core and the isoporphyrin moieties, the resulting dynamics strongly depend on the environment.

In the solid state, both polymers are not photochromic under normal illumination conditions. This lack of photochromic activity is rationalized by the ultrafast spectroscopic results: instead of inducing photocyclization, UV excitation triggers electron transfer from IsoP^{*} to the neighboring Py⁺ units. The resulting oxidized isoporphyrin species (IsoP⁺) is stabilized, while the rigidity of the immobilized polymer chains on the ITO surface further restricts the conformational rearrangements required for DAE closure.

In solution, UV excitation triggers both the classical photocyclization mechanism and the same IsoP^{*}/Py⁺ electron transfer observed in the solid state. In addition, a new indirect photocyclization pathway is uncovered, in which two photoinduced electrons become delocalized and subsequently recombine within the photochromic core, inducing an electrocyclization-like ring closure. Thus, both direct and indirect DAE ring-closure processes lead to CF formation, followed by BET. Compared with the solid state, the absence of IsoP⁺ stabilization and the enhanced flexibility of the solvated polymer chains partially restore the photochromic response of the system.

Upon Soret-band excitation (420 nm), the characteristic porphyrinic sequence (S₂(FC) → S₂(min) VR → S₁(IC) → ISC) is preserved, but the ps relaxation step becomes coupled to DAE ring-opening, while ISC is markedly accelerated compared to the free isoporphyrin reference. Q-band excitation (570 nm), which directly populates S₁, yields the same PET → IC → BET mechanism but with significantly faster kinetics, consistent with an energy-gap-controlled relaxation.

Across all conditions, P2 exhibits systematically slower dynamics than P1, both in solution and in the solid state, reflecting the influence of its additional phenyl linker, which reduces electronic coupling and increases reorganization energy.

Overall, these results establish a unified framework in which IsoP⁺ stabilization, medium flexibility, and linker-induced coupling collectively dictate the competition between CT and photoisomerization in porphyrin-DAE polymers. Looking ahead, these findings provide valuable guidelines for the design of next-generation DAE-porphyrin systems tailored for photocatalytic applications.

General Conclusion and Perspectives

This manuscript is dedicated to the study of a series of systems derived from two pyridyl-substituted photochromic diarylethenes. These two molecules were either combined with polyoxomolybdate clusters or co-electropolymerized with isoporphyrin moieties. The aim of our study was to explore how structural confinement, molecular coupling, and electronic communication reshape the ultrafast photoswitching dynamics of these complex systems across multiple levels of organization. Through a combination of steady-state spectroscopy, femtosecond transient absorption spectroscopy, spectroelectrochemistry, and quantum-chemical calculations, this study provides a unified framework that links molecular design to function, revealing how photoinduced electron transfer, back electron transfer, and photoswitching pathways evolve with increasing structural complexity.

At the molecular level, Chapter 3 investigated two closely related diarylethenes, DAE1 and DAE2, whose structures differ by the insertion of a phenyl spacer. This seemingly modest modification profoundly impacts their photophysics and photochemistry. DAE1 displays classical behavior typical of well-known DAEs from the literature, undergoing ultrafast reversible photocyclization and photoreversion between open and closed forms with high fatigue resistance. In contrast, DAE2 exhibits enhanced photocyclization QY and faster ring-closure dynamics, together with an unexpected emission localized on its pyridyl-phenyl-thiophene moiety, violating Kasha's rule. Femtosecond transient absorption spectroscopy measurements revealed that DAE1 can cyclize via two parallel channels depending on the excitation power: a direct route from the FC region (0.4 ps) and a sequential route involving relaxation to the anti-parallel S_1 (minimum) (0.6 ps). DAE2, however, follows exclusively the sequential pathway, with its relaxation sequence strongly influenced by the extended conjugation of the PPT chromophore. These results demonstrated how even subtle structural changes modify the energetic pathway, shifting the balance between reactive and non-reactive conformers and opening new emissive channels. The discovery of the sharp transient "X feature" around 588 nm in DAE2, assigned later to a localized excitation on the pyridyl-phenyl-thiophene moiety, introduced a new type of chromophoric interaction in the family of diarylethenes.

In Chapter 4, the same DAE cores were incorporated within redox-active POM cages to form hybrid molecular assemblies: MB (one DAE1 unit in the photoinactive parallel form), MC1 (three DAE1 units locked in antiparallel form), and MC2 (three DAE2 units combining both AP and P conformers). This step toward molecular confinement, enabled a systematic examination of how spatial restriction and electronic coupling affect photoinduced processes. The comparison between free and encapsulated DAEs revealed three major effects of confinement: (i) the suppression of conformational interconversion, (ii) the stabilization of charge-transfer states, and (iii) the modulation of relaxation kinetics through confinement effects.

In the MB system, confinement imposed the photochemically inactive P geometry, isolating its photophysical response, a result that has never been reported before in the literature. As expected, fs-TAS measurements revealed no ring-closure but, unexpectedly, an ultrafast DAE $\rightarrow$ POM charge transfer (0.8 ps) has been discovered, confirming that the POM cage actively participates in excited-state processes rather than serving as a passive scaffold.

In MC1, containing three DAE1 units locked in the reactive AP form, restored photocyclization activity but through a modified relaxation chain: the cyclization became sequential (0.2 ps $\rightarrow$ 0.33 ps) rather than direct, and a secondary DAE $\rightarrow$ POM charge-transfer step appeared, followed by back charge transfer on the nanosecond scale. The confinement thus not only simplified the photocyclization pathway but also introduced new charge-transfer dynamics mediated by the POM cluster.

MC2, which combined DAE2 units with mixed conformations (probably two anti-parallel and one parallel conformations), revealed the coexistence of several channels. Its dynamics were faster overall and marked by the reappearance of the “X feature,” again linked to the PPT chromophore, while charge transfer to the POM was suppressed due to emission competition. These results highlighted that the POM cluster, far from being an inert architecture, acts as an active environment that can stabilize excited states (CT) depending on coupling group and conformational flexibility. Together, the results from MB, MC1, and MC2 established the concept of confinement-controlled reactivity, in which molecular motion, electronic communication, and redox balance dictate the efficiency and outcome of photochromic transformations.

In Chapter 5, attention turned to the macromolecular scale, where DAE units were wired into conjugated porphyrinic backbones through electropolymerization, giving rise to poly-DAE1-ZnT₂isoP[•] (P1) and poly-DAE2-ZnT₂isoP[•] (P2). These polymers bridge molecular and solid-state systems, providing a unique platform to probe how DAE photoactivity behaves when electronically coupled to an isoporphyrin radical network. Here, fs-TAS guided by spectroelectrochemical fingerprints uncovered a rich interplay between photoinduced electron transfer and photochromism. Under UV excitation (315 nm), both polymers exhibited ultrafast PET from the isoporphyrin donor (IsoP^{•*}) to the pyridinium acceptors (Py⁺), followed either by direct photocyclization or by an unexpected a slower PET-assisted indirect closure, resembling an electrochemical ring-formation process. In solution, both mechanisms coexist, leading to efficient closed-form generation and back-electron transfer. In contrast, in the solid state, photocyclization was fully suppressed: the IsoP⁺ species was stabilized, and the rigidity of the immobilized polymer chains prevented the structural rearrangements required for DAE closure.

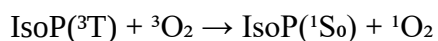
Excitation into the Soret (420 nm) and Q bands (570 nm) further revealed the coupling between porphyrinic relaxation sequences (S₂→S₁→T₁) and DAE ring-opening. Across all conditions, P2 displayed slower dynamics than P1, reflecting weaker electronic coupling and greater reorganization energy introduced by its phenyl spacer. These results showed how polymerization extends the DAE-POM concept into π -conjugated materials, where electron-transfer mediation, rigidity, and energy-gap control together govern the competition between isomerization and recombination.

Altogether, the progression from isolated molecules to confined assemblies and finally to extended conjugated polymers paints a coherent picture of structure-dynamics relationships in photochromic systems. The findings demonstrate that diarylethenes are not passive photoactive switches, but dynamic platforms whose reactivity and relaxation can be tuned by chemical environment, confinement, and coupling. Confinement simplifies dynamics by removing competing conformations but introduces new electron-transfer pathways. Coupling to redox-active frameworks allows control over charge migration, cover the way for functional molecular devices.

Perspectives. Beyond fundamental understanding, this work provides valuable design guidelines for the next generation of photoresponsive hybrid materials, particularly with regard to photocatalytic applications.

For the capsule systems, a promising direction is to take advantage of the free internal cavity to host suitable guest molecules, transforming the cage into a photocatalytically active reactor at molecular level. The objective would be to initiate the degradation or activation of the encapsulated guest through a charge generated in the DAE/POM catalytic cycle. To ensure effective light control, it is important to avoid spontaneous charge transfer as observed in the MB system and to prevent interference from additional photoactive moieties, such as the porphyrin units in MC2.

On the polymer side, and based on the good performance obtained in solution, optimizing the rigidity and solid-state organization of the DAE/IsoP frameworks could lead to efficient photocatalytic films. To take advantage of the photosensitization ability of IsoP toward molecular oxygen:



a promising strategy would be to modify the DAE so that the absorption spectrum of its closed form strongly overlaps (i.e., has a high ϵ) with the Q band of IsoP, thereby introducing photo-switchable control over singlet oxygen generation.

The insights gained here on the interplay between structure, confinement, and ultrafast dynamics thus pave the way for the design of advanced diarylethene-based materials with tunable and controllable photochemical functions.

References

1. Irie M, Mohri M. Thermally irreversible photochromic systems. Reversible photocyclization of diarylethene derivatives. *J Org Chem*. 1988 Feb;53(4):803–8.
2. Eaton DF. International union of pure and applied chemistry organic chemistry division commission on photochemistry. *Journal of Photochemistry and Photobiology B: Biology*. 1988 Dec;2(4):523–31.
3. Hirsberg, Y. Photochromie Dans La Série de La Bianthone. *Compte rendu* 1950, No. 7, 116–117.
4. Crano JC, Guglielmetti RJ. *Organic Photochromic and Thermochromic Compounds: Volume 1: Main Photochromic Families*. Boston, MA: Kluwer Academic Publishers; 2002. (Topics in Applied Chemistry).
5. Hoffmann R, Woodward RB. Selection Rules for Concerted Cycloaddition Reactions. *J Am Chem Soc*. 1965 May;87(9):2046–8.
6. Irie M, Sakemura K, Okinaka M, Uchida K. Photochromism of Dithienylethenes with Electron-Donating Substituents. *J Org Chem*. 1995 Dec;60(25):8305–9.
7. Kobatake S, Yamada M, Yamada T, Irie M. Photochromism of 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene in a Single-Crystalline Phase: Dichroism of the Closed-Ring Form Isomer. *J Am Chem Soc*. 1999 Sept 1;121(37):8450–6.
8. Shibata K, Muto K, Kobatake S, Irie M. Photocyclization/Cycloreversion Quantum Yields of Diarylethenes in Single Crystals. *J Phys Chem A*. 2002 Jan 1;106(1):209–14.
9. Kobatake S, Kuratani H. Photochromism of Diarylethene-functionalized Polystyrene with High Conversion in a Solid-state Polymer Film. *Chemistry Letters*. 2006 June 1;35(6):628–9.
10. Sumi T, Takagi Y, Yagi A, Morimoto M, Irie M. Photoirradiation wavelength dependence of cycloreversion quantum yields of diarylethenes. *Chem Commun*. 2014;50(30):3928.
11. Irie M, Fukaminato T, Matsuda K, Kobatake S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem Rev*. 2014 Dec 24;114(24):12174–277.
12. Nakamura S, Irie M. Thermally irreversible photochromic systems. A theoretical study. *J Org Chem*. 1988 Dec;53(26):6136–8.
13. Ern J, Bens A, Martin HD, Mukamel S, Schmid D, Tretiak S, et al. Femtosecond reaction dynamics of a photochromic dithienylethene derivative. *Journal of Luminescence*. 2000 May;87–89:742–4.

14. Ern J, Bens AT, Martin HD, Kuldova K, Trommsdorff HP, Kryschi C. Ring-Opening and -Closure Reaction Dynamics of a Photochromic Dithienylethene Derivative. *J Phys Chem A*. 2002 Mar 1;106(9):1654–60.
15. Boggio-Pasqua M, Ravaglia M, Bearpark MJ, Garavelli M, Robb MA. Can Diarylethene Photochromism Be Explained by a Reaction Path Alone? A CASSCF Study with Model MMVB Dynamics. *J Phys Chem A*. 2003 Dec 1;107(50):11139–52.
16. Garavelli M, Page CS, Celani P, Olivucci M, Schmid WE, Trushin SA, et al. Reaction Path of a sub-200 fs Photochemical Electrocyclic Reaction. *J Phys Chem A*. 2001 May 1;105(18):4458–69.
17. Garavelli M, Celani P, Fato M, Bearpark MJ, Smith BR, Olivucci M, et al. Relaxation Paths from a Conical Intersection: The Mechanism of Product Formation in the Cyclohexadiene/Hexatriene Photochemical Interconversion. *J Phys Chem A*. 1997 Mar 1;101(11):2023–32.
18. Boggio-Pasqua M, Bearpark MJ, Hunt PA, Robb MA. Dihydroazulene/Vinylheptafulvene Photochromism: A Model for One-Way Photochemistry via a Conical Intersection. *J Am Chem Soc*. 2002 Feb 1;124(7):1456–70.
19. Olivucci M, Bernardi F, Celani P, Ragazos I, Robb MA. Excited-state cis-trans isomerization of cis-hexatriene. A CAS-SCF computational study. *J Am Chem Soc*. 1994 Feb;116(3):1077–85.
20. Pontecorvo E, Ferrante C, Elles CG, Scopigno T. Structural Rearrangement Accompanying the Ultrafast Electrocyclization Reaction of a Photochromic Molecular Switch. *J Phys Chem B*. 2014 June 19;118(24):6915–21.
21. Ishibashi Y, Mukaida M, Falkenström M, Miyasaka H, Kobatake S, Irie M. One- and multi-photon cycloreversion reaction dynamics of diarylethene derivative with asymmetrical structure, as revealed by ultrafast laser spectroscopy. *Phys Chem Chem Phys*. 2009;11(15):2640.
22. Hamdi I, Buntinx G, Tiwari AK, Delbaere S, Takeshita M, Aloïse S. Cyclization Dynamics and Competitive Processes of Photochromic Perfluorocyclopentene Dithienylethylene in Solution. *ChemPhysChem*. 2020 Oct 2;21(19):2223–9.
23. Aloïse S, Sliwa M, Pawlowska Z, Réhault J, Dubois J, Poizat O, et al. Bridged Photochromic Diarylethenes Investigated by Ultrafast Absorption Spectroscopy: Evidence for Two Distinct Photocyclization Pathways. *J Am Chem Soc*. 2010 June 2;132(21):7379–90.
24. Jean-Ruel H, Gao M, Kochman MA, Lu C, Liu LC, Cooney RR, et al. Ring-Closing Reaction in Diarylethene Captured by Femtosecond Electron Crystallography. *J Phys Chem B*. 2013 Dec 12;117(49):15894–902.

25. Ishibashi Y, Tani K, Miyasaka H, Kobatake S, Irie M. Picosecond laser photolysis study of cycloreversion reaction of a diarylethene derivative in polycrystals: Multiphoton-gated reaction. *Chemical Physics Letters*. 2007 Apr;437(4–6):243–7.
26. Ern J, Bens AT, Bock A, Martin HD, Kryschi C. Femtosecond transient absorption studies on photochromism of dithienylethene derivatives. *Journal of Luminescence*. 1998 Feb;76–77:90–4.
27. Hania PR, Telesca R, Lucas LN, Pugzlys A, Van Esch J, Feringa BL, et al. An Optical and Theoretical Investigation of the Ultrafast Dynamics of a Bisthienylethene-Based Photochromic Switch. *J Phys Chem A*. 2002 Sept 1;106(37):8498–507.
28. Aloïse S, Yibin R, Hamdi I, Buntinx G, Perrier A, Maurel F, et al. The photochemistry of inverse dithienylethene switches understood. *Phys Chem Chem Phys*. 2014;16(48):26762–8.
29. Ishibashi Y, Fujiwara M, Umesato T, Saito H, Kobatake S, Irie M, et al. Cyclization Reaction Dynamics of a Photochromic Diarylethene Derivative as Revealed by Femtosecond to Microsecond Time-Resolved Spectroscopy. *J Phys Chem C*. 2011 Mar 17;115(10):4265–72.
30. Hamdi I. Photoréactivité de dithiényléthènes fonctionnalisés pour l'assemblage supramoléculaire : de la solution jusqu'au film opto-activable.
31. Ward CL, Elles CG. Cycloreversion Dynamics of a Photochromic Molecular Switch via One-Photon and Sequential Two-Photon Excitation. *J Phys Chem A*. 2014 Oct 30;118(43):10011–9.
32. Presa A, Vázquez G, Barrios LA, Roubeau O, Korrodi-Gregório L, Pérez-Tomás R, et al. Photoactivation of the Cytotoxic Properties of Platinum(II) Complexes through Ligand Photoswitching. *Inorg Chem*. 2018 Apr 2;57(7):4009–22.
33. Han M, Luo Y, Damaschke B, Gómez L, Ribas X, Jose A, et al. Light-Controlled Interconversion between a Self-Assembled Triangle and a Rhombicuboctahedral Sphere. *Angew Chem Int Ed*. 2016 Jan 4;55(1):445–9.
34. Choudhari M, Xu J, McKay AI, Guerrin C, Forsyth C, Ma HZ, et al. A Photo-Switchable Molecular Capsule: Sequential Photoinduced Processes. *Chem Sci*. 2022;13:13732–40.
35. Choudhari M. Synthesis and Characterization of Polyoxometalate-Organic Architectures as Potential Photochromes and Mediators for Noncovalent Interactions [PhD thesis]. Monash University; 2023.
36. Jiang N. Formation d'électropolymères à base d'isoporphyrines, de diaryléthènes ou de polyoxométallates : génération de photocourant ou de l'oxygène singulet et électrochromisme. [PhD thesis]. Université de Strasbourg; 2023.
37. Perkampus HH. *UV-VIS Spectroscopy and Its Applications*. Springer Science & Business Media; 2013. 252 p.

38. Agilent Technologies. Cary 100/300/4000/5000/6000i/7000 Spectrophotometers [Internet]. 2021 [cited 2025 Apr 26]. Available from: https://www.agilent.com/cs/library/usermanuals/public/1972_7000.pdf
39. Khokrale S, Lulla J, Borse A. A review of the UV-visible spectroscopy's method development and validation. 2024;2(6):527–38.
40. Agilent Technologies. Agilent Cary Eclipse Fluorescence Spectrophotometer [Internet]. 2019.
41. Spangenberg A, Métivier R, Gonzalez J, Nakatani K, Yu P, Giraud M, et al. Multiscale Approach of Photochromism: Synthesis and Photochromic Properties of a Diarylethene in Solution, in Nanoparticles, and in Bulk Crystals. *Advanced Materials*. 2009 Jan 19;21(3):309–13.
42. Tamai N, Miyasaka H. Ultrafast Dynamics of Photochromic Systems. *Chem Rev*. 2000 May 1;100(5):1875–90.
43. Aloïse S, Sliwa M, Buntinx G, Delbaere S, Perrier A, Maurel F, et al. Do inverse dithienylethenes behave as normal ones? A joint spectroscopic and theoretical investigation. *Phys Chem Chem Phys*. 2013;15(17):6226.
44. Hamdi I, Buntinx G, Perrier A, Devos O, Jaïdane N, Delbaere S, et al. New insights into the photoswitching mechanisms of normal dithienylethenes. *Phys Chem Chem Phys*. 2016;18(40):28091–100.
45. Hamdi I, Buntinx G, Poizat O, Perrier A, Le Bras L, Delbaere S, et al. Excited-State Dynamics of Dithienylethenes Functionalized for Self-Supramolecular Assembly. *J Phys Chem A*. 2018 Apr 12;122(14):3572–82.
46. Hamdi I, Buntinx G, Poizat O, Delbaere S, Perrier A, Yamashita R, et al. Unraveling ultrafast dynamics of the photoswitchable bridged dithienylethenes under structural constraints. *Phys Chem Chem Phys*. 2019;21(12):6407–14.
47. Hamburger R, Rumble C, Young ER. An Introduction to Processing, Fitting, and Interpreting Transient Absorption Data. *J Vis Exp*. 2024 Feb 16;(204).
48. Maiuri M, Garavelli M, Cerullo G. Ultrafast Spectroscopy: State of the Art and Open Challenges. *J Am Chem Soc*. 2020 Jan 8;142(1):3–15.
49. Ziólek M, Lorenc M, Naskrecki R. Determination of the temporal response function in femtosecond pump-probe systems. *Appl Phys B*. 2001 May 1;72(7):843–7.
50. Tamai Y, Murata Y, Natsuda S ichiro, Sakamoto Y. How to Interpret Transient Absorption Data?: An Overview of Case Studies for Application to Organic Solar Cells. *Advanced Energy Materials*. 2024;14(7):2301890.

51. Nakayama T, Amijima Y, Ibuki K, Hamanoue K. Construction of a subpicosecond double-beam laser photolysis system utilizing a femtosecond Ti:sapphire oscillator and three Ti:sapphire amplifiers (a regenerative amplifier and two double passed linear amplifiers), and measurements of the transient absorption spectra by a pump-probe method. *Review of Scientific Instruments*. 1997 Dec 1;68(12):4364–71.
52. Orio M, Pantazis DA, Neese F. Density functional theory. *Photosynth Res*. 2009;102(2–3):443–53.
53. Irie M, Miyatake O, Uchida K. Blocked photochromism of diarylethenes. *J Am Chem Soc*. 1992 Oct;114(22):8715–6.
54. Perrier A, Aloise S, Olivucci M, Jacquemin D. Inverse versus Normal Dithienylethenes: Computational Investigation of the Photocyclization Reaction. *J Phys Chem Lett*. 2013 July 3;4(13):2190–6.
55. Turro NJ, Ramamurthy V, Scaiano JC. *Modern Molecular Photochemistry of Organic Molecules*. Photochem & Photobiology. 2012 July;88(4):1033–1033.
56. Kochman MA, Durbeej B, Kubas A. Simulation and Analysis of the Transient Absorption Spectrum of 4-(*N,N*-Dimethylamino)benzonitrile (DMABN) in Acetonitrile. *J Phys Chem A*. 2021 Oct 7;125(39):8635–48.
57. Horng ML, Quitevis EL. Visible Absorption Spectroscopy and Structure W of Cyanine Dimers in Aqueous Solution.
58. Lemaistre JP. Intraband relaxation and dephasing of Frenkel exciton states in one-dimensional J-aggregates. *Journal of Luminescence*. 2004 May;107(1–4):332–8.
59. Abhilash GJ, Bhuyan J, Singh P, Maji S, Pal K, Sarkar S. • NO₂ -Mediated *meso* -Hydroxylation of Iron(III) Porphyrin. *Inorg Chem*. 2009 Mar 2;48(5):1790–2.
60. Spectra of Porphyrins*.
61. Baskin JS, Yu HZ, Zewail AH. Ultrafast Dynamics of Porphyrins in the Condensed Phase: I. Free Base Tetraphenylporphyrin. *J Phys Chem A*. 2002 Oct 1;106(42):9837–44.
62. Abraham B, Nieto-Pescador J, Gundlach L. Ultrafast Relaxation Dynamics of Photoexcited Zinc-Porphyrin: Electronic-Vibrational Coupling. *J Phys Chem Lett*. 2016 Aug 18;7(16):3151–6.
63. Léaustic A, Anxolabéhère-Mallart E, Maurel F, Midelton S, Guillot R, Métivier R, et al. Photochromic and Reductive Electrochemical Switching of a Dithiazolylethene with Large Redox Modulation. *Chemistry A European J*. 2011 Feb 11;17(7):2246–55.

Appendices

Appendix of Chapter 3

S.3.1. Photocyclization Dynamics of DAE2 at high excitation power

To facilitate understanding, we first examine the fs-TA response of DAE2 under high excitation power, in contrast to DAE1 where the low power case was discussed first. Measurements were performed in dry ACN (207 μM) using 325 nm excitation at 1.2 μJ . The data are presented in four temporal windows: [-1 to 0.20 ps], [0.20 to 1 ps], [1 to 45 ps], and [45 to 6000 ps] (Figure S.3.1.A). The corresponding steady-state UV-Vis spectra of the OF and CF forms are shown in Figure S.3.1.B. Global fitting (Figure S.3.4.) at selected probe wavelengths (360-387-451-520-590-895 nm) yielded the characteristic time constants $\tau_1 = 0.180 \pm 0.005$ ps, $\tau_2 = 1.00 \pm 0.01$ ps, $\tau_3 = 2.30 \pm 0.02$ ps, $\tau_4 = 20 \pm 0.02$ ps and $\tau_5 = 1640 \pm 0.02$ ps.

For clarity, the main relaxation pathways and characteristic times extracted from these measurements are summarized in the energy diagram shown in Figure S.3.2.

Early time dynamics [-1 to 0.14 ps]: Immediately following photoexcitation of the OF, a broad ESA profile emerges across the spectral range, with distinct peaks in UV, visible and near-IR regions. This early response corresponds to the formation of FC states of the coexisting AP and P conformers, $S_1^{AP}(FC)$ and $S_1^P(FC)$.

Second time window [0.14 to 0.38 ps]: This a newly resolved time window enabled by high excitation power. During this stage, the decay of $S_1^P(FC)$ toward $S_1^P(min)$ becomes evident, while the $S_1^{AP}(FC)$ features remain largely unchanged. Notably, no CF absorption band appears in this window, but instead arises in the subsequent stage. This enables the identification of a weak feature at ~ 590 nm (X). Its presence raises the question of whether the X feature and the P conformer are connected, an issue that will be further addressed in the section 3.6.4. The rise of this feature occurs within $\tau_1 = 0.20$ ps. This window therefore represents the completion of the fastest relaxation pathway of the P conformer, with the AP population still confined to its FC region. An isosbestic point is observed at 495 nm.

Intermediate dynamics [0.38 to 1.13 ps]: In this window, $S_1^{AP}(FC)$ relaxes to $S_1^{AP}(min)$ with $\tau_2 = 1.00$ ps. (This value found to be identical to that obtained for DAE2 under low power excitation, indicating that this relaxation pathway is unaffected by excitation fluence).

[1.13 to 45 ps]: This stage marks the decrease of $S_1^{AP}(min)$ decay, accompanied by the rise of the CF absorption band. In parallel, part of the $S_1^{AP}(min)$ population probably undergoes internal conversion

to the ground state. The measured CF formation and AP internal conversion time, $\tau_3 = 10.0$ ps, is significantly longer than in the low power case. The spectral evolution is characterized by two isosbestic points at 557 nm and 664 nm, confirming a clean conversion process. This finding is particularly significant, as it demonstrates that photocyclization under high excitation power does not proceed directly from the FC region, but instead occurs via the relaxed minimum geometry $S_1^{AP}(min)$.

Late time processes ([45 to 6000 ps]): Two relaxation pathways dominate this final stage. First, the CF band undergoes vibrational relaxation with $\tau_4 = 70$ ps. Second, the P conformer decays via internal conversion from $S_1^P(min)$ to S_0^P , with a time constant of $\tau_5 = 3090$ ps (obtained using basic fitting). This slow decay also coincides with the disappearance of the X feature hump within 1800 ps. By the end of this time window, the spectra stabilize and perfectly overlap with the steady-state CF spectrum, confirming complete photoproduct formation, Figure S.3.3.

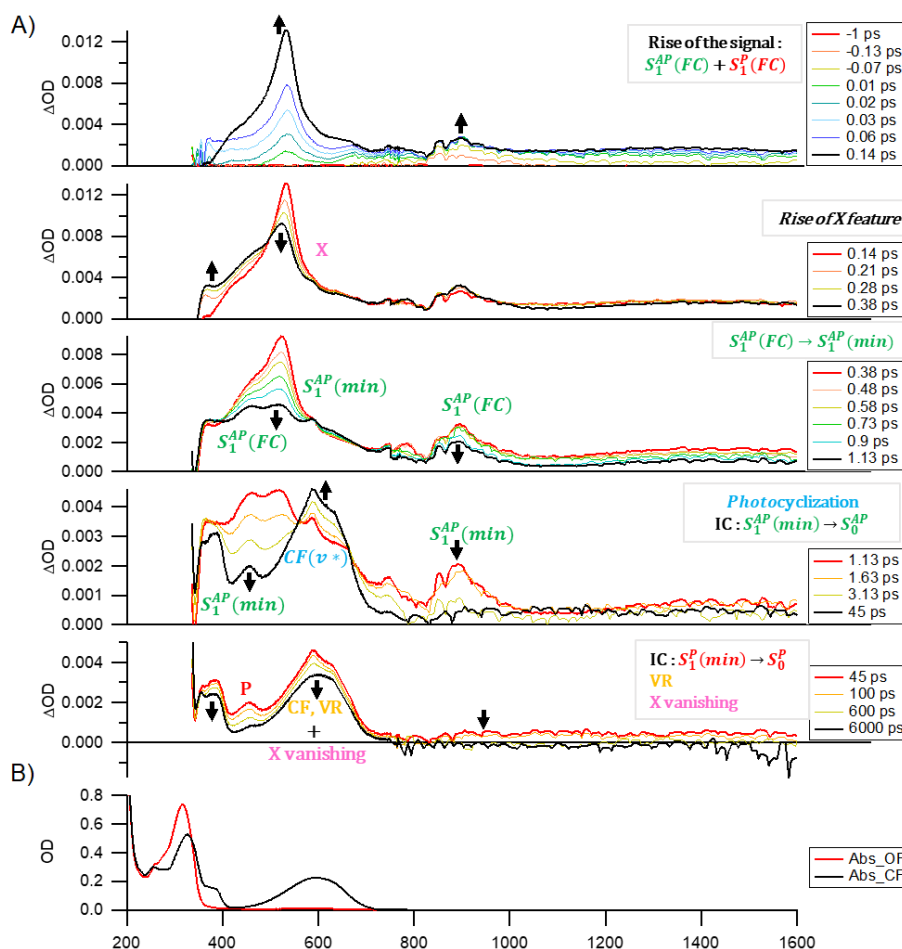


Figure S.3.1. (A) fs-TA spectra of DAE2 in dry ACN (207 μ M), recorded upon 325 nm laser excitation with a power of 1.2 μ J. The color gradient from red to black illustrates the spectral evolution over four segmented temporal windows: top panel [-1 ps to 0.2 ps], second panel [0.2 ps to 1 ps], third panel [1 ps to 45 ps], and bottom panel [45 ps to 6000 ps]. (B) Steady-state UV-Vis absorption spectra of DTE2 in its open (red) and closed (black) forms, included for reference.

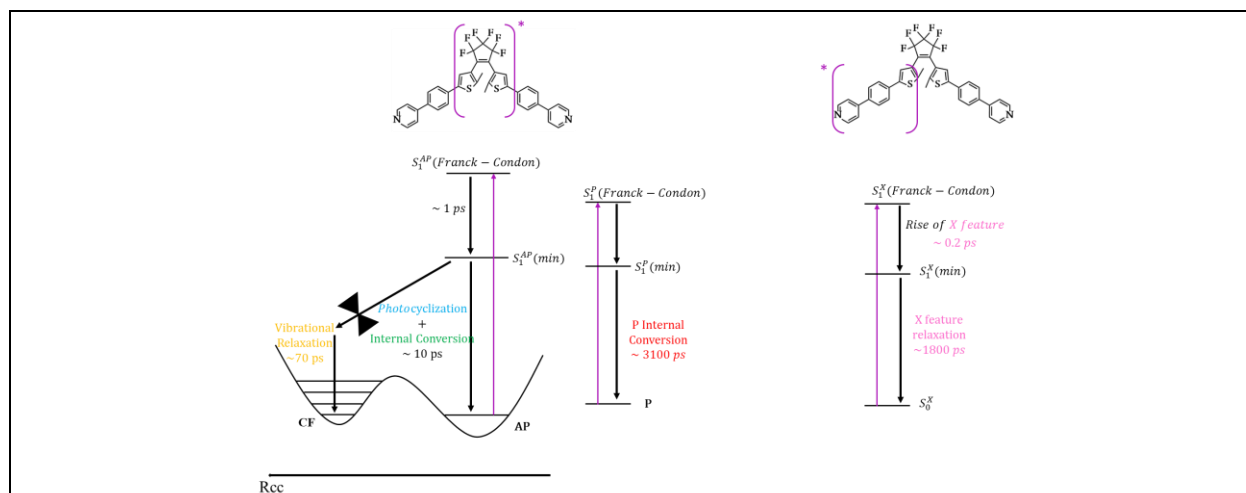


Figure S.3.2. Energy diagram for the AP/P conformers, X feature and CF species as a function of the reactive coordinate (Rcc) of DAE2 at high power, highlighting the main relaxation pathways and characteristic times.

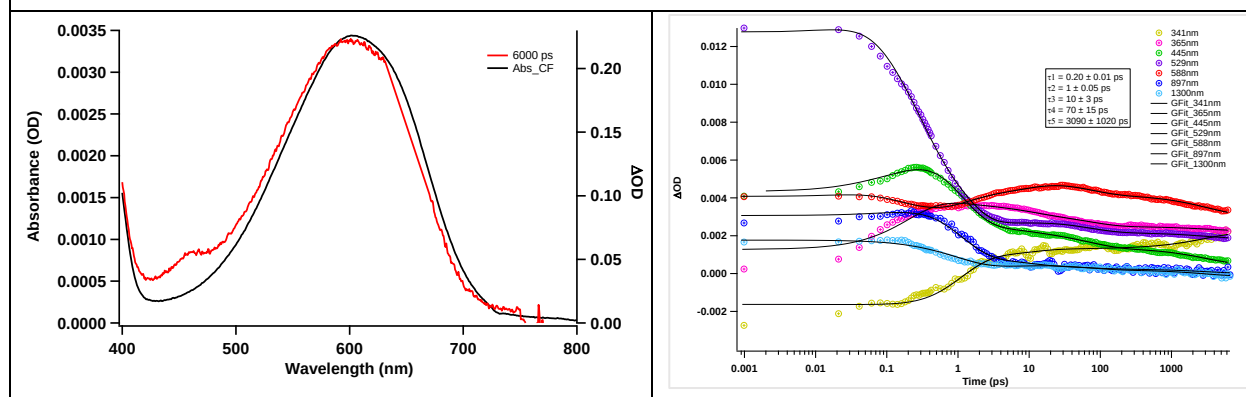


Figure S.3.3. Spectral overlap between the transient absorption spectrum at 6000 ps (red) and the steady-state CF absorption spectrum (black) for DAE2 under low power laser excitation, confirming complete formation of the closed form photoproduct.

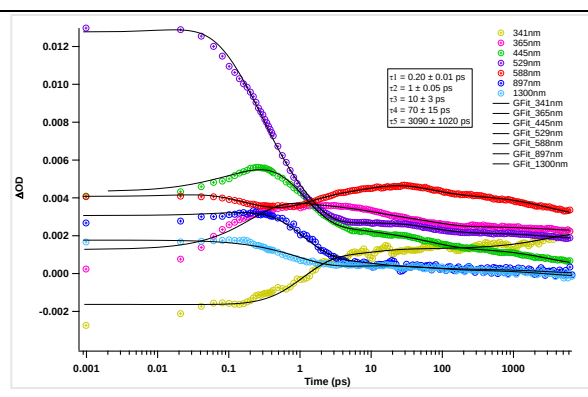


Figure S.3.4. Global fitting of transient absorption kinetics of DAE2 (high power) at six selected wavelengths.

S.3.2. Photocyclization Dynamics of DAE2 in Dry DCE

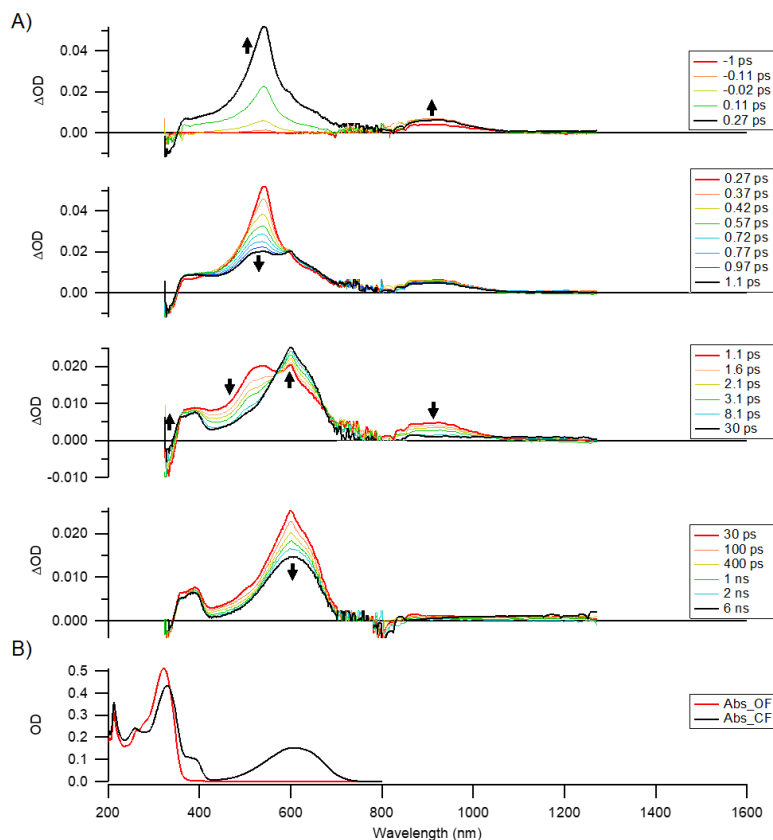


Figure S.3.5. (A) fs-TA spectra of DAE2 in dry DCE, recorded upon 325 nm laser excitation with a power of 0.02 μ J. The color gradient from red to black represents the spectral evolution over time, segmented into five temporal windows: top panel [-1 ps to 0.27 ps], second panel [0.27 ps to 1.1 ps], third panel [1.1 ps to 30 ps], fourth panel [30 ps to 6 ns]; (B) Steady-state UV-Vis absorption spectra of DAE2 in its open (red) and closed (black) forms, included for reference.

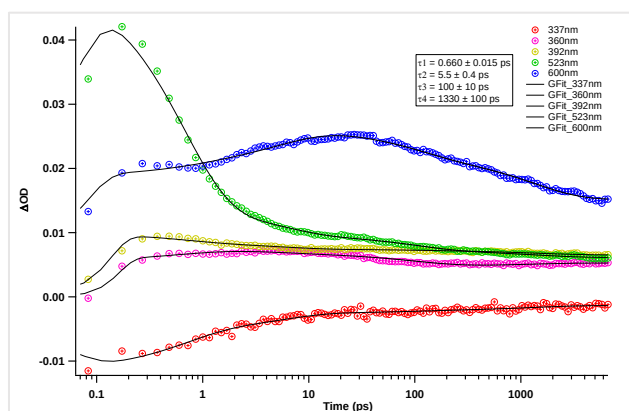


Figure S.3.6. Global fitting of transient absorption kinetics of DAE2 in dry DCE at six selected wavelengths.

Appendix of Chapter 4:

S.4.1. Photocyclization of MB

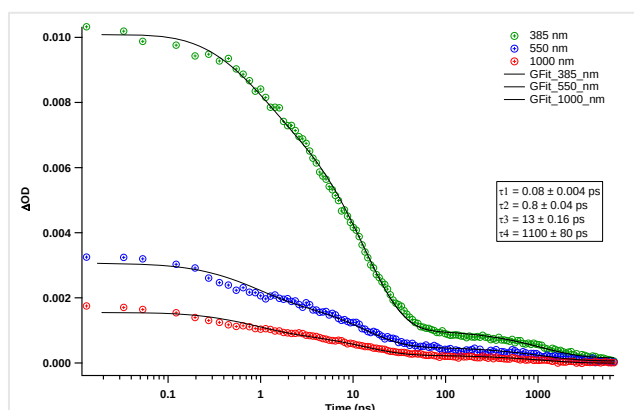


Figure S.4.1. Global fitting of four exponential of transient absorption kinetics of MB at three selected wavelengths.

S.4.2. Photocyclization of MC1 at high power

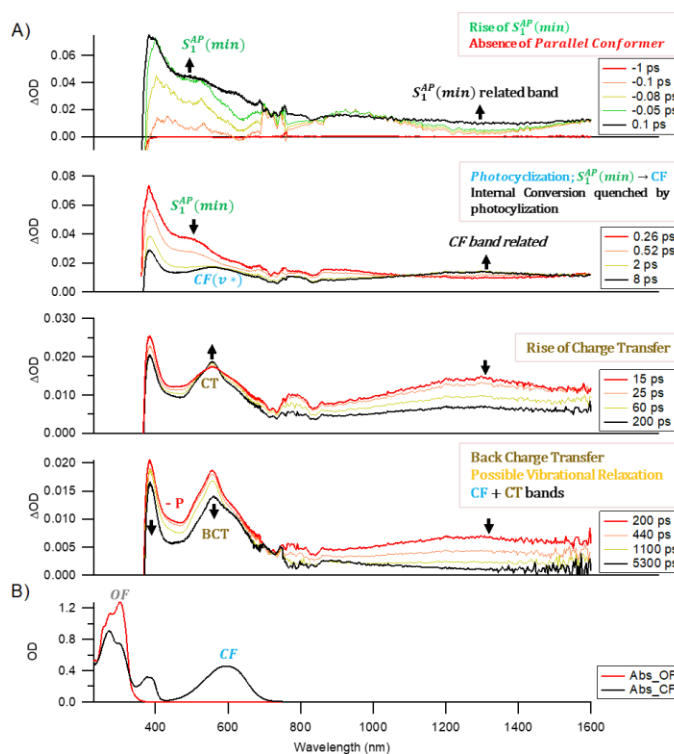


Figure S.4.2. (A) Fs-TAS of MC1 in dry ACN (75 μ M), recorded upon 330 nm laser excitation with a power of 1.6 μ J. The color gradient from red to black represents the spectral evolution across four temporal windows: top panel [-1 ps to 0.1 ps], second panel [0.26 ps to 8 ps], third panel [15 ps to 200 ps], and bottom panel [200 ps to 5300 ps]. (B) Steady-state UV-Vis absorption spectra of MC1 in its open (red) and closed (black) forms, shown for reference.

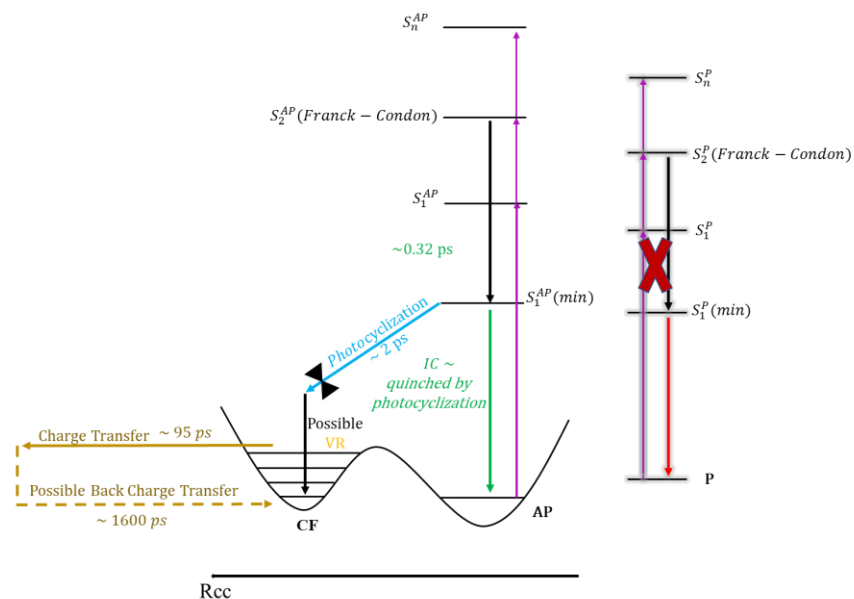


Figure S.4.3. Energy diagram for the AP/P conformers and CF species as a function of the reactive coordinate (R_{cc}) of DAE1 at high power, highlighting the main relaxation pathways and characteristic times.

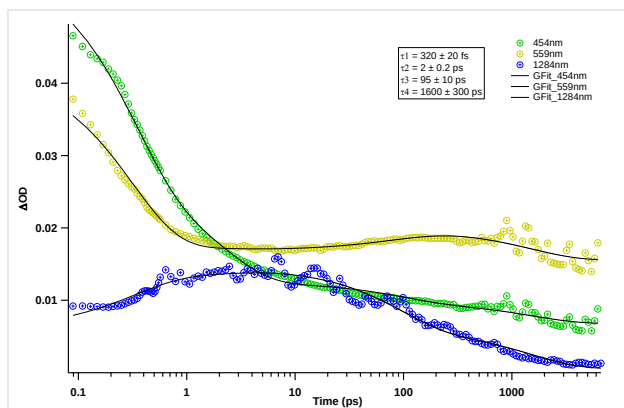


Figure S.4.4. Global fitting of transient absorption kinetics of MC1 (high power) at three selected wavelengths.

S.4.3. Photocyclization of MC2

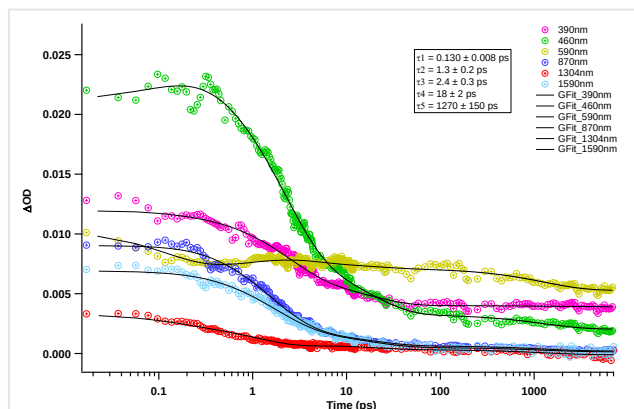


Figure S.4.5. Global fitting of transient absorption kinetics of MC2 at six selected wavelengths.

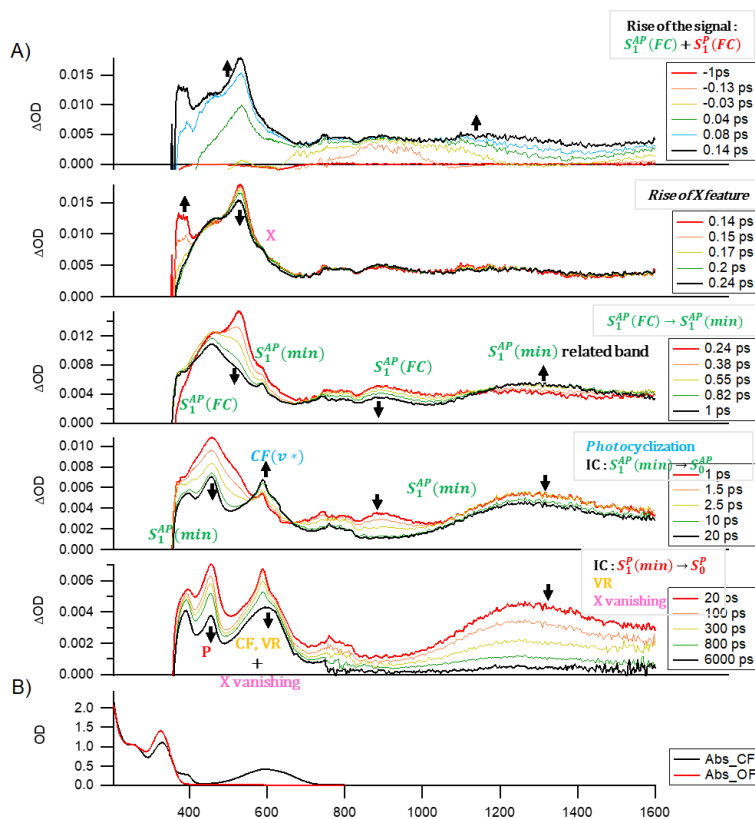


Figure S.4.6. (A) Fs-TAS of MC2 in dry ACN (35 μ M), recorded upon 325 nm laser excitation with a power of 1.8 μ J. The color gradient from red to black illustrates the spectral evolution, grouped into five temporal windows: **top panel** [−1 ps to 0.14 ps], **second panel** [0.14–0.24 ps], **third panel** [0.24–1 ps], **fourth panel** [1–20 ps], and **bottom panel** [20–6000 ps]; (B) Steady-state UV-Vis absorption spectra of MC2 in its open (red) and closed (black) forms, included for reference.

S.4.4. Photoreversion of MC1 and MC2

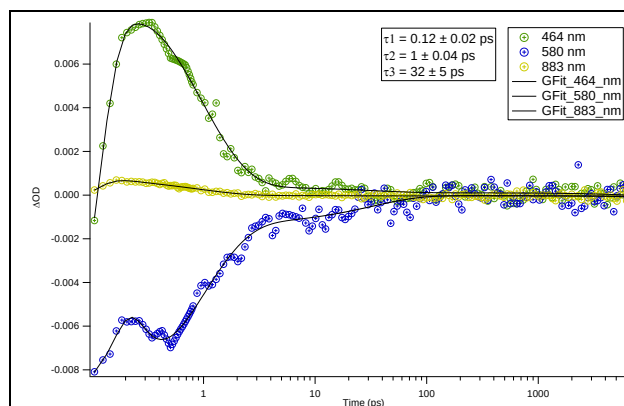


Figure S.4.7. Global fitting of transient absorption kinetics of MC1 at three selected wavelengths.

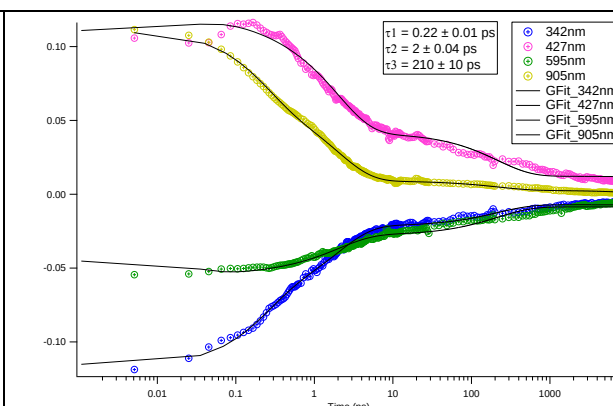
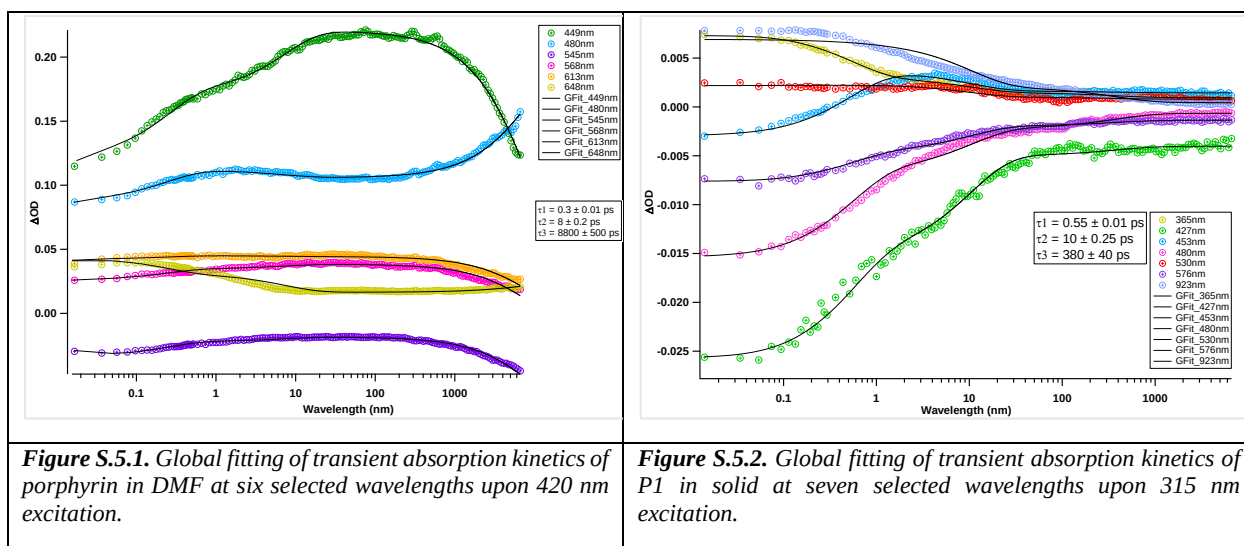


Figure S.4.80. Global fitting of transient absorption kinetics of MC2 at four selected wavelengths.

Appendix of Chapter 5:



S.5.1. P2 in the solid state

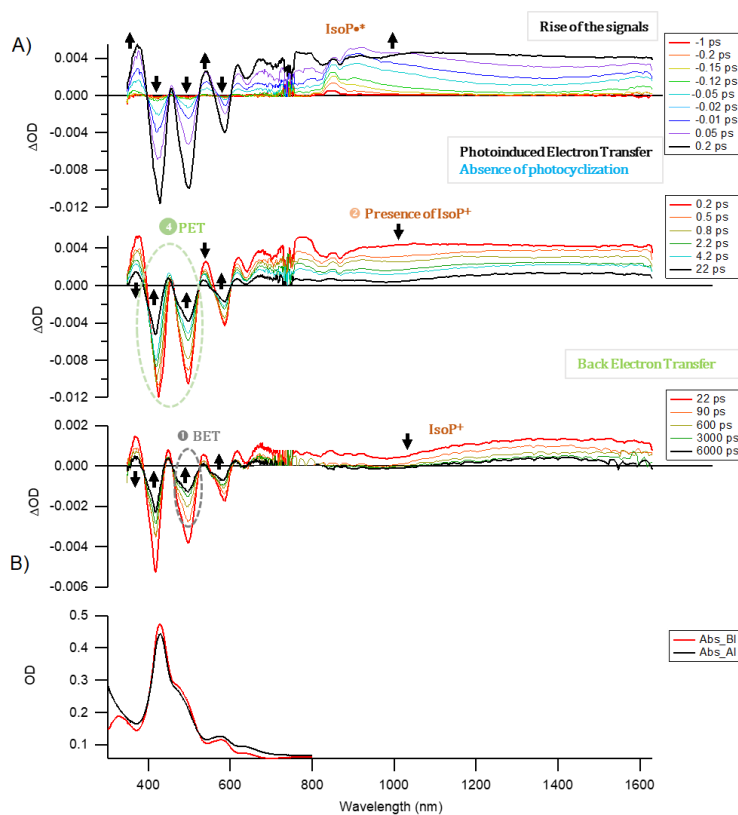


Figure S.5.3. (A) fs-TA spectra of P2 in solid, recorded upon 315 nm laser excitation with a power of 0.2 μJ . The color gradient from red to black represents the spectral evolution over time, grouped into two temporal windows: top panel [-1 ps to 0.2 ps] middle [0.2 ps to 22 ps] and bottom panel [22 ps to 6000 ps]. (B) Steady-state UV-Vis absorption spectra of P2 before (red) and after (black) irradiation, shown for reference.

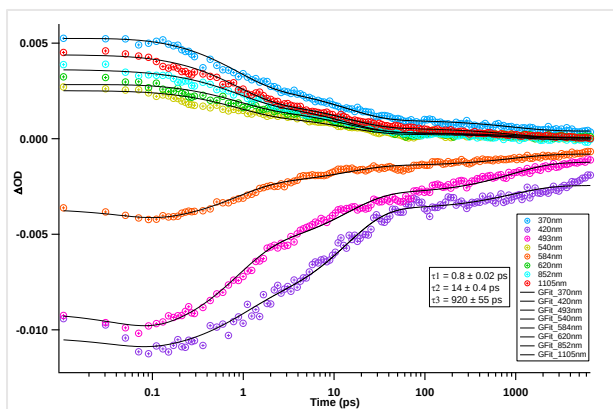


Figure S.5.4. Global fitting of transient absorption kinetics of P2 in solid at eight selected wavelengths upon 315 nm excitation.

S.5.2. Photocyclization of P1 in DMF

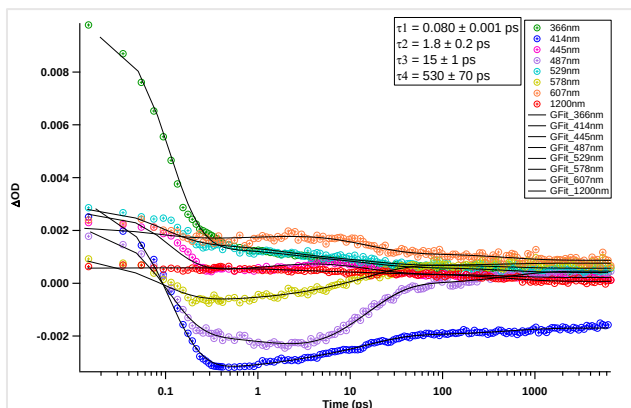


Figure S.5.5. Global fitting of transient absorption kinetics of P1 in DMF at eight selected wavelengths upon 315 nm excitation.

S.5.3. Photocyclization of P2 in DMF

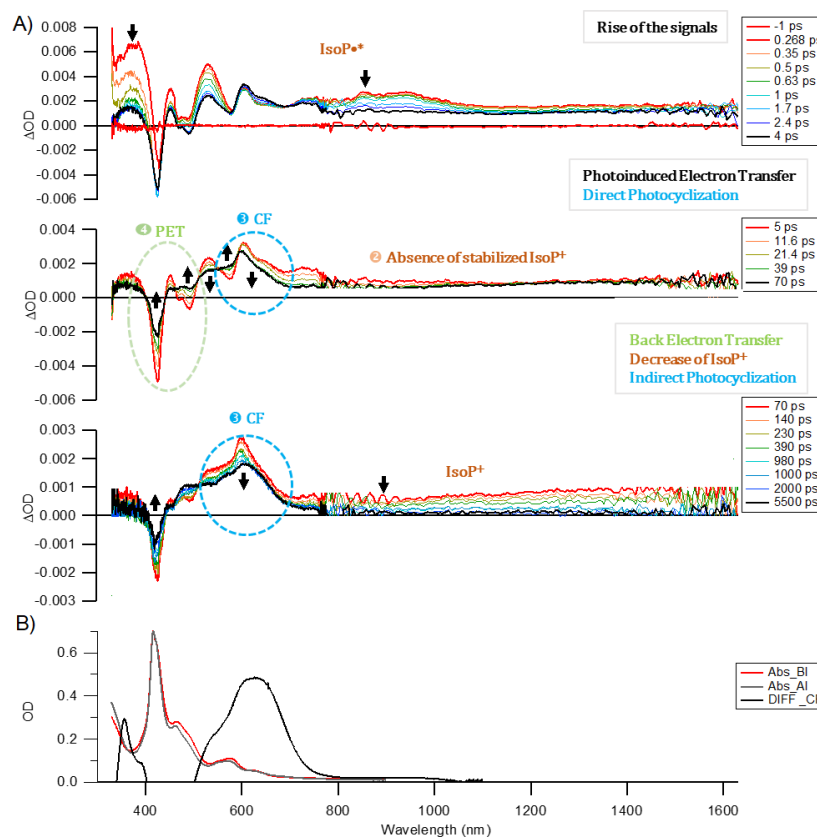


Figure S.5.6. (A) fs-TA spectra of P2 in DMF, recorded upon 315 nm laser excitation with a power of 0.2 μ J. The color gradient from red to black represents the spectral evolution over time, grouped into three temporal windows: top panel [-1 ps to 4 ps], middle panel [5 ps to 70 ps] and bottom panel [70 ps to 5500 ps]. (B) Steady-state UV-Vis absorption spectra of P2 before (red) and after (black) irradiation, shown for reference.

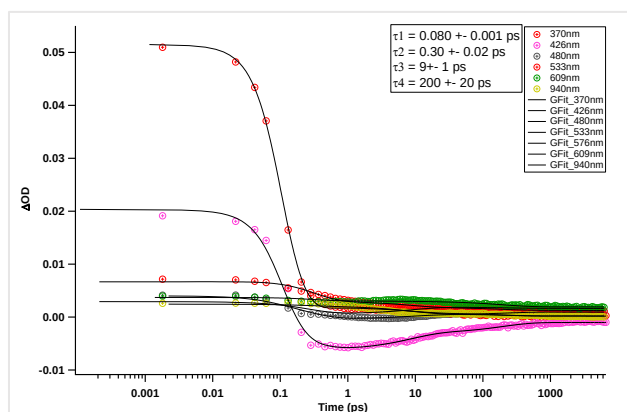


Figure S.5.7. Global fitting of transient absorption kinetics of P2 in DMF at six selected wavelengths upon 315 nm excitation.

The transient spectra of P2 are grouped into three temporal windows (TW1: -1 to 4 ps; TW2: 4 to 70 ps; TW3: 70 to 5500 ps) (Figure S.5.6). Global fits at selected wavelengths (370, 426, 452, 472, 490, 533, 576, 609, 739, 940, and 1261 nm) yield four characteristic times: $\tau_1 \sim 0.08$ ps, $\tau_2 \sim 0.3$ ps, $\tau_3 \sim 9$ ps and $\tau_4 \sim 200$ ps (S.5.7).

The first component ($\tau_1 \sim 0.08$ ps) mirrors that of P1, corresponding to an ultrafast PET process from the excited IsoP• to the pyridinium substituents ($\text{Py}^+ \rightarrow \text{Py}^\bullet$). The second component ($\tau_2 \sim 0.3$ ps) is attributed to a direct photocyclization pathway, while the third ($\tau_3 \sim 9$ ps) reflects a slower indirect photocyclization process mediated by radical delocalization across the DAE bridge. Finally, the $\tau_4 \sim 200$ ps component corresponds to BET, restoring the ground-state $\text{Py}^+/\text{IsoP}^\bullet$ configuration.

Both direct and indirect photocyclization, as well as BET, occur more rapidly in P2 than in P1. This overall acceleration is attributed to the additional phenyl linker, which provides enhanced structural flexibility and facilitates the C-C bond formation within the polymer (Figure S.5.8).

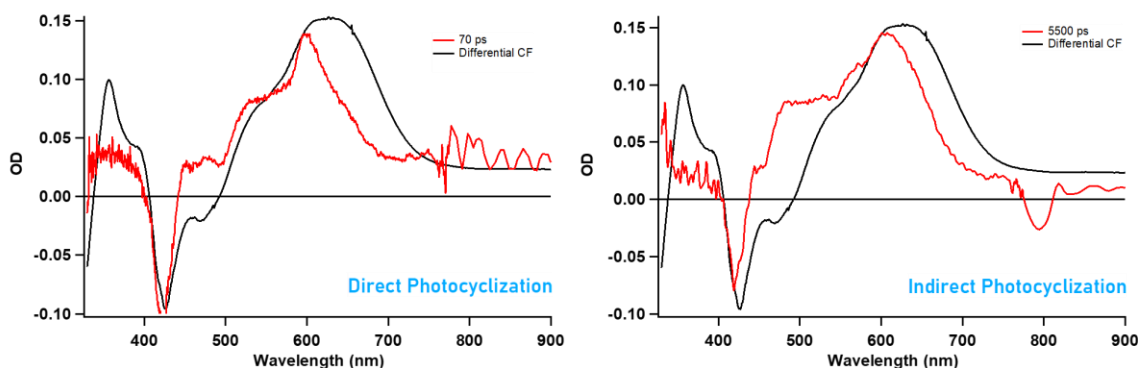


Figure S.5.8. Direct vs. indirect cyclization of P2: transient spectral signatures and proposed mechanisms.

S.5.2. Photocyclization of P1 and P2 in DMF at 420 nm

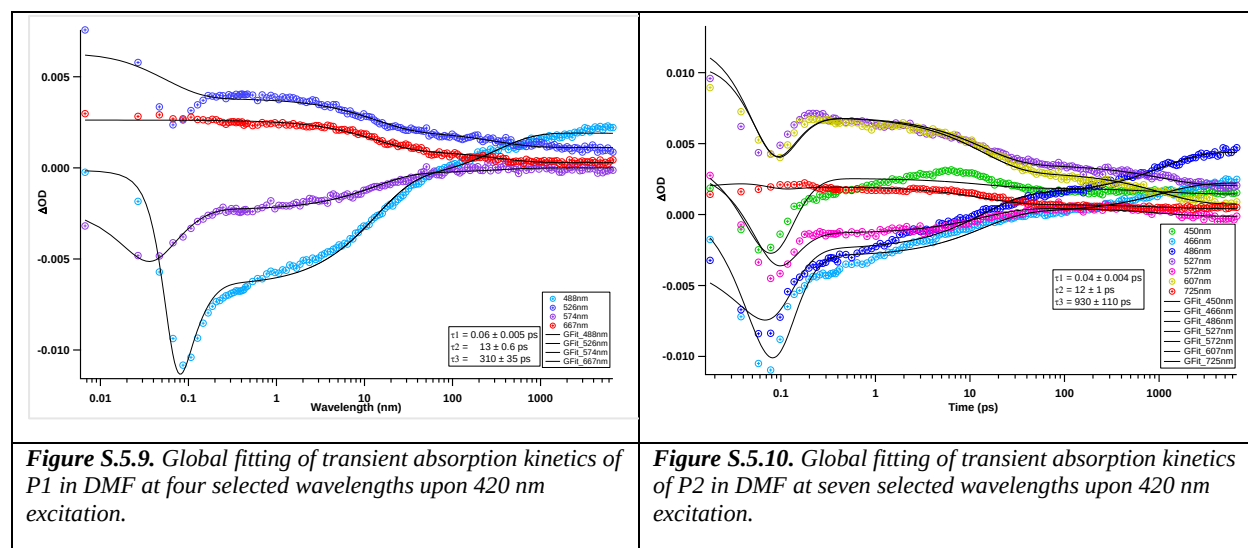


Figure S.5.9. Global fitting of transient absorption kinetics of P1 in DMF at four selected wavelengths upon 420 nm excitation.

Figure S.5.10. Global fitting of transient absorption kinetics of P2 in DMF at seven selected wavelengths upon 420 nm excitation.