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# The photochemistry of inverse dithienylethene switches understood

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## **ABSTRACT**

The photophysical properties of a series of dithienylethenes, free or blocked in an ideal photoactive conformation by an alkyl bridge have been investigated with stationary, ultrafast spectroscopy and state-of-the-art Time-Dependent Density Functional Theory. Thanks to clear ultrafast transient signatures corroborating NMR results, we bring strong evidences that the unreactive parallel open form conformer has been efficiently removed by the chain. For the first time, the photophysics of this species, namely an internal conversion of 120 ps is highlighted. In contradiction with the literature main spread ideas, the photocyclization mechanism is rationalized by a direct photocyclization mechanism from the Franck-Condon region passing directly through a conical intersection within  $\approx 100$  fs (not few picosecond) while a competitive mechanism occurs through the relaxed  $S_1$  state. Relaxation processes (fluorescence, internal conversion) originating from this relaxed state are sensitive to the length of the blocking chain. Both concomitant pathways are necessary to rationalize: i) the inverse relation between emission and cyclization quantum yield; ii) the non-unity value of the latter for bridged compounds.

**KEYWORDS:** • time-resolved spectroscopy • diarylethene • TD-DFT • photochromism  
• photocyclization

## INTRODUCTION

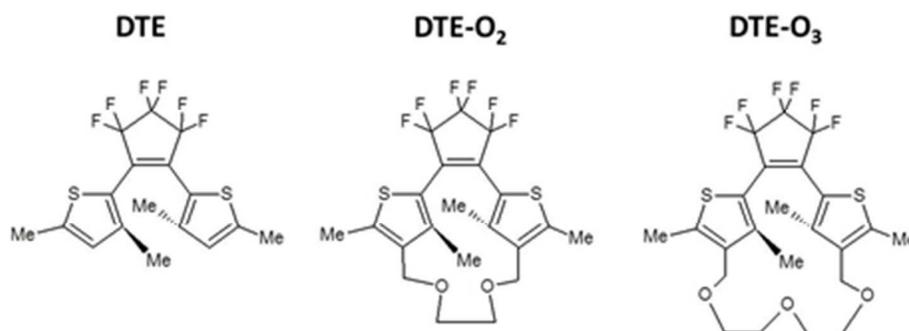
**P**hotochromism is a reversible photoinduced transformation between two chemical forms presenting different absorption spectra.<sup>[1]</sup> Photochromic compounds attract an ever-growing attention due to their potential applications in optoelectronic, e.g., they can be used as building blocks for rewritable optical memory media<sup>[2]</sup> or optical switches allowing to modulate key physical properties of both molecules and materials.<sup>[3,4]</sup> Among the photochromes reported during the last thirty years, diarylethenes and more specifically dithienylethenes (DTEs), are often viewed as the most efficient compounds due to their thermal irreversibility, high fatigue resistance and good photocyclization quantum yield between the open (OF) and closed (CF) forms.<sup>[5-7]</sup> However, this yield is strongly limited in classical diarylethenes by the existence of two OF conformers presenting anti-parallel (AP) and parallel (P) configurations, only the former being photoactive toward cyclization. In most molecules, the AP:P ratio is close to 1:1, which limits the maximal quantum yield to ca. 50%. Overcoming this inherent limitation is the focus of various research relying on a purposed-designed synthetic approach<sup>[8-11]</sup> or specific excited-state reactivity.<sup>[12-14]</sup>

Over the last two decades, our laboratories performed joint studies to probe DTEs photochemical reaction pathways by combining state-of-the-art Time-Dependent Density Functional Theory (TD-DFT) calculations with time resolved spectroscopy. Our goals were to clarify the rather large, and often inconsistent, panel of reported data, as well as to avoid improper generalization between Normal (N-type) and Inverse (I-type) DTEs. In 2010, we demonstrated that the addition of alkyl chains blocking the diarylethene in an ideal photoactive conformation induces large variations of the excited-state features, and hence of the photochemical pathways.<sup>[15]</sup> Very recently, we have compared N-type and I-type switches, aiming to ascertain the relationship between the 50% yield and the 1:1 AP:P ratio. Surprisingly, in I-type DTE, the percentage of P conformers is significantly smaller (10-25% range), but the cyclization quantum yield still does not exceed 50%.<sup>[16]</sup> A CASSCF/CASPT2 study demonstrated that the N-type and I-type DTEs follow different excited-state reaction pathways: for the former, S<sub>1</sub> and

$S_2$  excited states allow photocyclization, while for the latter, only the  $S_1$  state yields photocyclization through a Conical Intersection (CI), whereas excitation of  $S_2$  induces the formation of the P conformer.<sup>[17]</sup>

In the present contribution, we focus on one I-type DTE, bis(3,5dimethyl-2-thienyl)-perfluorocyclopentene, denoted **DTE** ( $C_{17}H_{14}F_6S_2$ ), and two analogs presenting a polyether bridge of variable length, **DTE-O2** ( $C_{21}H_{20}F_6O_2S_2$ ) and **DTE-O3** ( $C_{23}H_{24}F_6O_3S_2$ ) (see Scheme 1). These [2.n]thiophenophan-1-ene derivatives have been designed to constrain the molecule in the unique photoactive AP conformation, and, consequently to enhance the photochromic yields.<sup>[18]</sup> However, the measured cyclization quantum yields<sup>[18]</sup> are 0.40, 0.70 and 0.42 for **DTE**, **DTE-O2** and **DTE-O3** respectively and this evolution cannot be straightforwardly correlated to relevant geometrical parameters, e.g., to the distance separating the two reactive carbon atoms ( $R_{CC}$ ). In short, the reason of the unexpected better efficiency of **DTE-O2** remains unknown. As we will demonstrate, this series is relevant to unravel the complex relationship between the photocyclization quantum yield and the AP vs P photophysics.

*Scheme 1.* Inverse Dithienylethene, DTE (left), and two polyether bridged analogs DTE-O2 (center) and DTE-O3 (right).



## EXPERIMENTAL AND THEORETICAL METHODS

**Stationary techniques.** The DTE has been synthesized according to the procedure of Irie et al.<sup>[19]</sup> while the bridged molecules synthesis have been already published.<sup>[18]</sup> Hexane (HX) solvent (spectroscopic grade, Sigma-Aldrich) was used as received. All stationary absorption and fluorescence spectra were recorded using double beam CARY 100bio and Jobin Yvon Div. FluoroMax 3 spectrometers, respectively. The spectral resolution is typically 2 nm in both experiments. Emission spectra were corrected for the lamp and detector response. Measurements were performed at ambient temperature using 1 cm quartz cells with about  $10^{-5}$  -  $10^{-6}$  M solutions, keeping the maximum absorbance at less than 0.1 in order to avoid any significant reabsorption effects.

**Transient absorption experimental setup.** The femtosecond transient absorption setup had already been described elsewhere.<sup>[20, 21]</sup> Briefly, a 1-kHz Ti:sapphire laser system (Coherent oscillator and a BM Industries regenerative amplifier) delivered 100 fs (0.8 mJ) pulses at 800 nm. Pump pulses were set at 350 nm by using an OPA (Quantronix, Palitra), while probe pulses (white light continuum) were generated by focusing the fundamental beam in a CaF<sub>2</sub> rotating plate. The transient absorption measurements covered the 400-750 nm spectral range and the 0-500 ps temporal range. Sample solutions (about  $10^{-4}$  M) were circulating in a flow cell equipped with a 100  $\mu$ m thick CaF<sub>2</sub> entrance window and characterized by a 2 mm optical path length. The time-resolution of the experiment (about 200 fs) was estimated from pump-probe cross-correlation measurements.<sup>[20, 21]</sup> The characteristic times deduced from kinetics were obtained by fitting the GVD corrected data (using procedure proposed by Nakayama et al.<sup>[22]</sup>) with the result of a multiexponential function convolved with a Gaussian function which approximates the pump-probe cross-correlation one. Within this approach, global fitting were systematically performed taking into account simultaneously four or five relevant wavelengths.

**Theoretical calculations.** All the calculations have been performed using Gaussian 09 package<sup>[23]</sup> using Density Functional Theory (DFT) and Time Dependent DFT (TD-DFT) to model ground-state

(GS) and excited-state (ES) properties, respectively. We have systematically applied the 6-31+G(d) atomic basis set which is known to yield converged results for both geometrical and optical properties of a wide range of solvated dyes.<sup>[24]</sup>

The critical points corresponding to minima on the Potential Energy Surfaces (PES) of both GS and ES have been determined with the  $\omega$ B97X range-separated hybrid functional.<sup>[25, 26]</sup> Contrary to conventional hybrid functionals, range separated hybrids are known to avoid inconsistencies for ES geometries.<sup>[24, 27]</sup> The GS and ES minima have been determined with the Berny-GEDIIS algorithm<sup>[28]</sup> using a tight convergence criteria (residual RMS force smaller than 0.00001 a.u.). The geometry optimizations have been carried out in HX. In these two latter cases, the PCM model was applied to quantify the impact of the environment.<sup>[29]</sup> The (GS and) ES geometry optimization have been carried out in the equilibrium limit using the linear-response (LR) PCM scheme.<sup>[30, 31]</sup>

To determine the spectroscopic parameters, we used the hybrid PBE0 functional<sup>[32, 33]</sup> which was shown to provide fast and accurate predictions for the transition energies of conjugated molecules.<sup>[24]</sup> In fact, the only major drawback of PBE0 is its inability to describe long-range charge-transfer excited-states, but this limit is irrelevant in our case as we consider a compact molecule. For solvated systems, we selected the state-specific (SS) approximation<sup>[34]</sup> in its nonequilibrium limit to determine the total and transition energies of the ES. The SS model accounts for the variations of the polarization of the medium following the electronic density rearrangements of the solute after absorption or emission. Within this framework, we have also determined the 0-0 energies that can be compared to the absorption/emission crossing point in a physically meaningful way. We also determined the  $\lambda_{abs}^{max}$  and  $\lambda_{fluo}^{max}$  values which correspond to the longest wavelength of the vertical TD-DFT calculation computed respectively at the minimum of the GS and the ES. We redirect the interested reader to the review of Mennucci et al.<sup>[35]</sup> (and references therein) which provides a detailed discussion on the solvent models that can be used to obtain the optical properties of solvated chromophores and to

the study of Jacquemin et al.<sup>[24]</sup> which gives the protocol used to determine the absorption/fluorescence crossing point.

## RESULTS AND DISCUSSION

**AP vs P conformers.** To confirm the absence of the P conformer for the bridged DTEs, the temperature dependence of the <sup>1</sup>H-NMR signal has been investigated and compared to the free DTE features. Previously, for **DTE**, P conformer proportion has been assessed between 10 and 25% at ambient temperature through subtle comparisons between DFT calculations and temperature dependence of <sup>1</sup>H-NMR signal.<sup>[16]</sup> Focusing on the Me proton of the reactive carbons (involved in the  $\sigma$  bond formation), Figure 1 shows that the temperature effect due to the existence of the AP/P thermal equilibrium is reduced by one order of magnitude for the bridged analogs compared to **DTE**, bringing a strong evidence that the methoxy bridge efficiently disables the P conformer formation in the ground state. Nevertheless, since we evidenced in the past that conformation changes can follow a AP\* $\rightarrow$ P route,<sup>[17]</sup> the hypothesis of a non-negligible P conformer population on the excited states will not be discarded in the following.

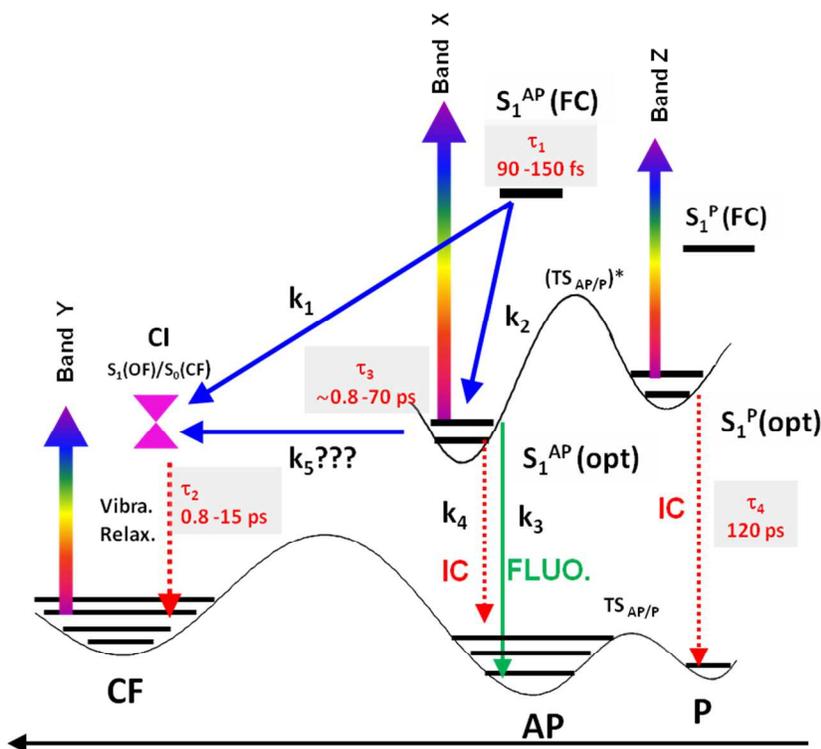
**Spectroscopic signatures of OF and CF.** In Figure 2, we present the measured and computed absorption spectra of **DTE**, **DTE-O2** and **DTE-O3** in HX still considering AP and P conformers. We observe no significant auxochromic effect (all peaks are in the 337-343 nm domain), though **DTE-O2** extinction coefficient is smaller than its **DTE** and **DTE-O3** counterparts. In line of the NMR results, the positions of the absorption maxima are better reproduced by theory considering the AP conformer rather than P one (Table 1). In addition, as seen on figure 2, by comparing the experimental extinction

coefficients of **DTE**, **DTE-O2** and **DTE-O3** (ratio 1:0.63:1.21) with TD-DFT oscillator strengths, one also obtains a much better agreement considering AP (1:0.56:1.21) than P (1:0.17:0.72) isomers. More generally, the overall absorption spectra are successfully reproduced for AP species including the shoulder near 300 nm with constant intensity within the series. These excellent agreements seem to indicate that the P conformer represents a small or very small component of the experimental conformer blend in the case of DTE, which is coherent with NMR results. From an orbital point of view, for the three molecules, the  $S_1$  state responsible for absorption can be mainly attributed to a HOMO→LUMO transition. The analysis of the frontier orbitals (see SI) shows that there is logically no electronic delocalization on the polyether bridge, thus rationalizing the absence of auxochromic effect.

For the closed form (CF), TD-DFT qualitatively reproduces the structural effect observed for the experimental absorption spectra, that is, a bathochromic shift when the bridging chain extends. This shift can be rationalized by structural considerations: the polyether bridge induces an increase of the distance between the two reactive carbon atoms  $R_{CC}$  (see Table SI-1) and thus a concomitant destabilization of the HOMO (bonding between the two reactive C) and stabilization of the LUMO (antibonding).

Experimental emission spectra of OF (see Figure 2) shows an important hypsochromic shift from DTE (507 nm) to DTE-O2 (492 nm) and DTE-O3 (426 nm). Besides, as seen on the upper part of figure 2, the hypsochromic effect induced by the bridge is perfectly reproduced by excited-state calculations (see Table 1 also) for the AP conformer while the P conformers do not follow the experimental trends. So, corroborating absorption results above and still considering the overall DTE-On series, one likely ascribes the experimental emission originating from the AP conformer rather than P conformer. Actually, considering DTE molecule alone, we published recently the inverse hypothesis based on theory-experiment comparison, i.e. the P conformer being responsible for the emission process.<sup>[16]</sup> Consequently, we face a contradiction if we follow this first idea because one would expect the extinction of the fluorescence signal for the bridged analogs, a fact not noticed experimentally. As we

will see below, transient spectroscopy will help us to definitely confirm that the emission originates from the AP conformers.



Scheme 2.

*Photophysical model displaying the two possible photocyclization pathways either from  $S_1(\text{FC})$  or  $S_1(\text{opt})$ . The extreme right of this scheme dedicated to the P conformer states holds only for (non-bridged) DTE. Transient bands are schematized as well even if one have to consider spectral overlap respective to each species contributions.*

**Post-excitation ultrafast mechanisms.** Ultrafast spectroscopic data following  $S_1$  state excitation at 350 nm, in the 370-740 nm spectral range with a temporal evolution running up to 500 ps are presented on Figure 3 for the three molecules. The transient absorption features are labeled X, Y and Table

2 lists both their growing and decaying characteristic times determined through global fitting method. We underline that the major photophysical events are very similar for all three molecules allowing analyzing those data globally.

First, just after pump laser excitation, the signal is characterized by the rapid rise of the band X peaking at ca. 610 nm, the position of the band being surprisingly conserved irrespective of the considered photochrome. In parallel, with the same apparent rising kinetics, one notices the band Y peaking at the extreme blue region. Because this band Y lies at almost the same position of the CF spectra but is broader (see in particular **DTE** spectra) it allows to tentatively ascribe it to the transient absorption of the hot CF( $v^*$ ) species following thus an ultrafast photocyclization reaction. The very small amount of negative signal between the X and Y bands is attributed to Stimulated Emission (SE) coming from the emissive state. For the bridged DTEs, the importance of the SE band, recognized as the mirror of stationary emission spectra (see Figure 2), is considerably higher which induces a modification of the shape of the band Y. As can be seen in Table 2, the respective growth kinetics of X, Y bands and of SE cannot be distinguished according to our temporal resolution, the characteristic times ranging from 90 fs for **DTE** to around 150 fs for the two bridged analogs.

Next, as can be seen in the central panels of Figure 3, one observes the decay of bands X, Y and SE, with the clear apparition of the CF spectrum for the three molecules. Two interpretations can be proposed: i) the species responsible for transient band X/SE is also one precursor of CF species, i.e., there exists a second and indirect photocyclization mechanism; or ii) the CF was already formed by direct photocyclization, subsequent decay of transient bands letting appear its spectrum. Actually, by close inspection of the transient data of **DTE** on Figure SI-1 (less influenced by negative SE bands) one clearly notices that compared to the "direct photocyclization" signal (600 fs traces) there is no additional rise of CF intensity after the decay of the transient band X/SE (500 ps traces) strongly suggesting that there is no second mechanism for photocyclization, and hence supporting the second hypothesis

An additional feature, specific of **DTE**, is the appearance of the transient Z band peaking at 570 nm. We highlight that the overall decays of the bands X and Y are monoexponential for **DTE**

( $\tau_2=0.80$  ps) but biexponential for the bridged analogs ( $\tau_2$  and  $\tau_3$  time constants in Table 2). Additionally, the decay of the band Z for **DTE** has a characteristic time  $\tau_4=120$  ps.

For the sake of clarity, all the transient band assignments and the related discussion of the photophysics of the DTE series has been summarized in Scheme 2. The band Z can be straightforwardly attributed to the excited states of the P conformer as this conformer is absent in the bridged analogues (see NMR above). To the best of our knowledge, this is the first time that a weak but clear signature of the P conformer excited state has been identified. Furthermore, the experimental transient band Z at ca. 570 nm, can be ascribed to the  $S_1 \rightarrow S_5$  absorption of  $S_1(\text{opt})$  of the P conformer according to the TD-DFT calculations (see Table SI-3). Therefore, we ascribe the decay of the band Z to an internal conversion (IC) from the  $S_1$  state of the P conformer to the ground state without emission, the stimulated emission band being related to the AP conformer. Indeed, this is a fundamental point to note. There is not even a weak SE signal accompanying the decay of the P conformer excited state (band Z) giving a solid confirmation that the AP conformer is the only emissive species even for the “free” DTE. As a consequence, we thus show that the rapid interconversion  $AP^* \leftrightarrow P^*$  is not possible for inverse type DTE, in clear contrast with the ground state situation.

Concerning the main photocyclization reaction, as already noticed for **DTE**, the transient band Y that rises with  $\tau_1=90$  fs is similar in position to the CF spectrum, the final CF spectrum being recovered after a 800 fs decay (plus the band Z contribution). This is obviously a clear manifestation of the ultrafast photoclosure reaction giving rise to hot CF structures,  $CF(v^*)$  with a broader spectrum, and the subsequent vibrational relaxations (see also Figure SI-1). For bridged molecules, by direct analogy we ascribed  $\tau_1 \approx 150$  fs to the photocyclization process. It is worth to note that the photoinduced mechanism is slower than for **DTE** most probably because bridged molecules are partially blocked in specific conformations, the chain implying that additional torsions are necessary to reach the conical intersection. Concerning the relaxation processes, among  $\tau_2$  and  $\tau_3$  the former is likely attributed to vibrational relaxation of  $CF(v^*)$  because of non-negligible signal of Band X for longest delay. Note that

the structural dependence of  $\tau_2$  (see Table 2) is tentatively ascribed to a dynamical effect related with the polyether bridge suggested by the structural effect affecting the CF species (see the rising  $R_{CC}$  in table SI-1). In addition the mono- vs bi-exponential natures of the transient signal decay for the “free” and bridged analogues, respectively, can be rationalized considering that without the bridge one cannot distinguish the two processes ( $\tau_2 \approx \tau_3$ ).

We now focus on the assignation of the intense transient bands X evolving in parallel with the negative band SE and attribution of characteristic time  $\tau_3$ . Gathering stationary and transient results together with TD-DFT calculations, this work evidences an impressive "structural effect" on the  $S_1$  relaxed excited state potential energy surface (PES) of AP conformer, noticed  $S_1(\text{opt})$ . First, the theoretical calculations indicate that the  $R_{CC}$  distance for the  $S_1(\text{opt})$  structure gradually increases in the series, with a strong ca. 0.3 Å elongation between **DTE** and **DTEO3**. We have also found a clear hypsochromic shift of the emission maxima, corroborating the increasing C-C distance of  $S_1(\text{opt})$  predicted by calculations. Note that the hypsochromic shift of emission and the increase of  $\tau_3$  are straightforwardly related with the well-known "energy gap" law. Finally, when we measure the fading process of transient band X, we notice the same trend in the series, that is an increasing characteristic time when going from **DTE** to **DTEO3** ( $\tau_3$  in Table 2). This brings evidence that the species responsible for both SE and band X is  $S_1(\text{opt})$  of AP conformer. Further confirmation of such assignation is found with the help of TD-DFT vertical transitions (see Table SI3). Comparing the  $S_1 \rightarrow S_n$  absorption in the three compounds for the  $S_1(\text{CF})$  and  $S_1(\text{opt})$  states, the former gives rise to an absorption at ca. 820 nm while the latter is located at ca. 560-670 nm in much better agreement with experimental value. As seen on table 1 and 2, the relaxation of  $S_1(\text{opt})$  accounts more for IC rather than for emission, the predominance of the former being suggested by the low emission quantum yields and the structural effect affecting  $\tau_3$  related either with the chain dynamics relaxation or some additional solute-solvent frictional effects.

At this point, the final description of the overall mechanisms has to account for additional experimental findings for the DTE series: i) the inverse relationship between photocyclization and emission quantum yields. Indeed, one observes in Table 1, the photocyclization yield is larger for DTEO<sub>2</sub>,  $\phi(\text{cycl})=0.7$ , while the emission yield is minimal,  $\phi(\text{fluo})=0.004$ ; ii) despite the absence of P conformers, a perfect photocyclization (quantum yield of 1) is not reached for bridged DTEs. To rationalize these results, one has to consider the possibilities of direct photocyclization through the CI(S<sub>1</sub>/S<sub>0</sub>) and indirect photocyclization via S<sub>1</sub>(opt) (or a combination of these two possibilities). Let consider a photophysical model including: i) a direct mechanism (k<sub>1</sub>) from S<sub>1</sub>(FC) to the CI region as already reviewed through transient band Y; ii) the internal conversion (k<sub>2</sub>) to S<sub>1</sub>(opt); iii) from the latter, the emission (k<sub>3</sub>) or the IC (k<sub>4</sub>) to ground state; and iv) a second photocyclization pathway (k<sub>5</sub>) from S<sub>1</sub>(opt). The relationship between the two quantum yields is given by (see SI) :

$$\phi(\text{cycl}) \approx 1 - \frac{k_4}{k_3} \phi(\text{fluo}) \quad (1)$$

Reversely, if one considers only the indirect mechanism, *i.e.* k<sub>1</sub>=0 and k<sub>5</sub>≠0, this equation becomes to:

$$\phi(\text{cycl}) = \frac{k_5}{k_3} \phi(\text{fluo}) \quad (2)$$

Clearly, only the first equation is compatible with the inverse relationship between the emission and cyclization quantum yields and this definitively excludes the existence of an unique photocyclization pathway passing through S<sub>1</sub>(opt). Apart transient data evidences stated above, this is the second confirmation that, unexpectedly, a direct mechanism occurs for classical I-DTE, the S<sub>1</sub> relaxed state being most likely responsible for emission and IC relaxations.

**Optimizing DTE molecules?** Therefore, to optimize the photocyclization quantum yield, we have shown that the synthetic approach consisting in proposing structural modifications to decrease the AP:P ratio, is relevant but not sufficient. For **DTEO3**, even if the population of the P conformer is negligible, the photocyclization quantum yield is comparable to the free **DTE**. The optimal quantum yield is obtained for **DTEO2** thanks to two concomitant effects : i) like in **DTEO3**, the AP population is close to 100%; and ii) the chain length is small enough to maintain the two reactive carbon atoms at an

optimal distance allowing to efficiently reach the CI. As an outlook, the optimization of a photochromic molecule should rely on an accurate knowledge of CI geometry, a feat attainable with *ab initio* calculations. We are currently attempting to enhance the direct photocyclization mechanism presented in this paper through appropriate structural modifications guided by such kind of CI calculations.

## ACKNOWLEDGMENT

D.J. acknowledges the European Research Council (ERC), and Région des Pays de La Loire for financial support in the framework of a Consolidator Grant (Marches – 278845) and a recrutement sur poste stratégique, respectively. All participants acknowledge the IRG PHoto-switchable orgaNIC molecular systems & deviceS (PHENICS) for support.

## SUPPORTINGS

Derivation of equation (1) and (2); Table SI.1: Experimental and PCM-TDDFT maximum of absorption for CF species. Calculated  $R_{cc}$  are listed as well; Table SI. 2 Maximum absorption wavelength (in nm) for transient bands X, Y and Z: TDDFT vertical excitation from either i) AP or P conformers ii) S0 or S1(opt) states; Figure SI1 Transient Absorption spectra of DTE (ACN/350 nm excitation) for 600 fs and 500 ps pump-probe delay; Figure SI2 DFT orbitals for OF and CF; Table SI3 Structural informations (Cartesian coordinates; Carbone-Carbone distances and Torsion angles) for the series including Ground and first excited states.

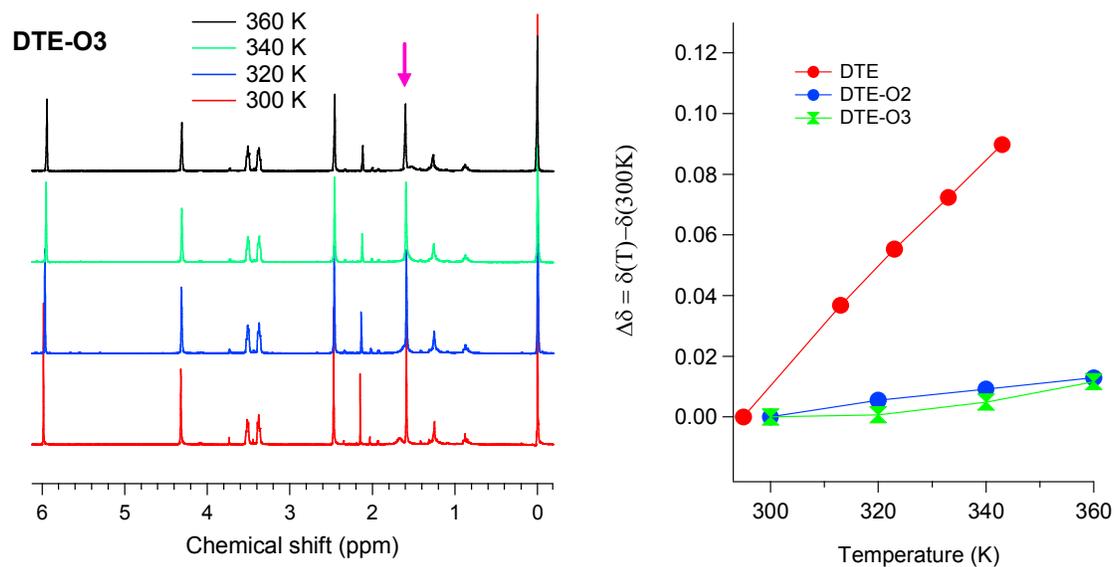


Figure 1. (Left) <sup>1</sup>H-NMR spectra in deuterated chloroform between 27 and 87°C; (Right) Evolution of the chemical shift of central Me proton (~1.6 ppm) as a function of temperature for DTE (ref 15) and the bridged analogs (this work).

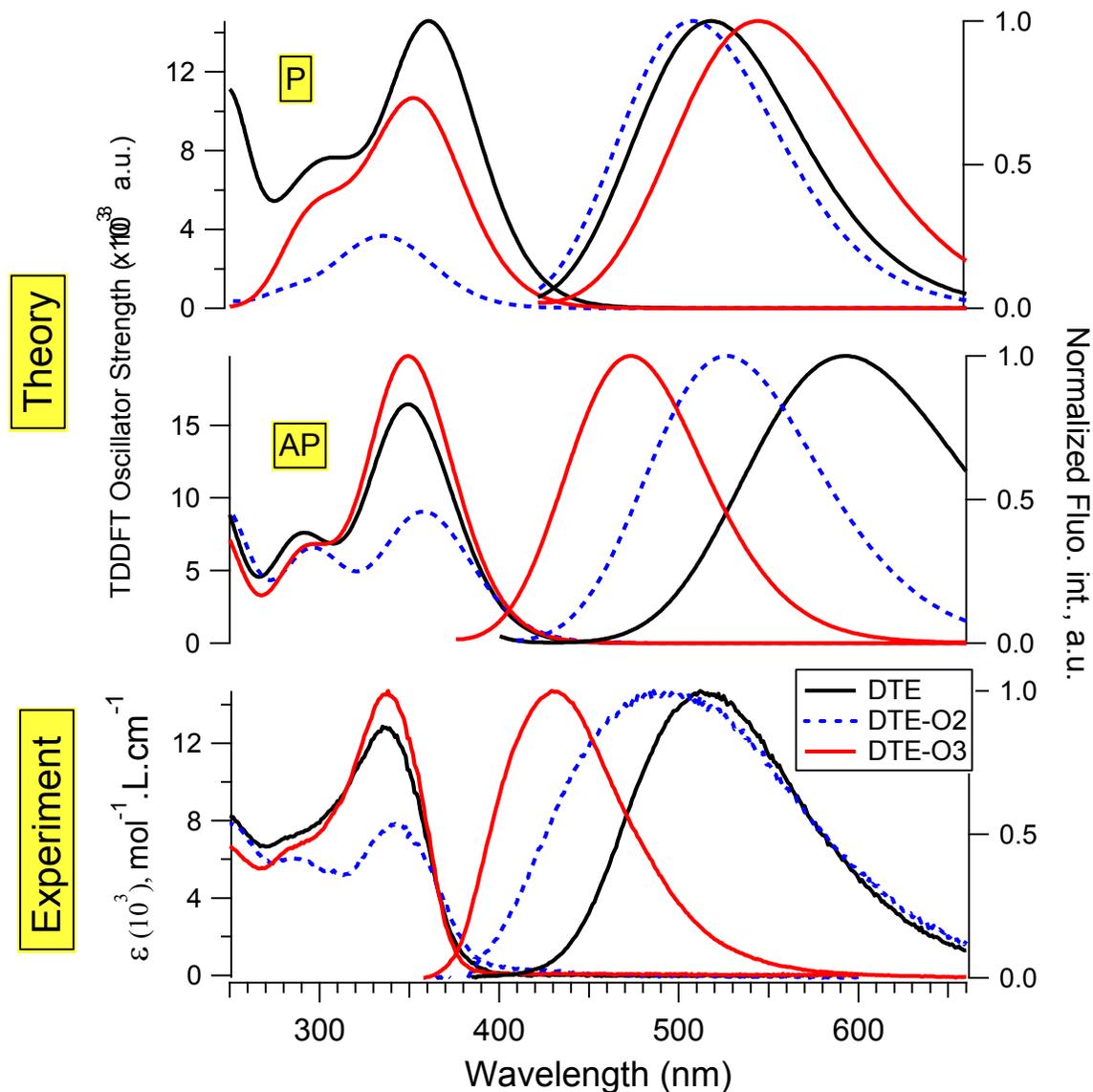


Figure 2. (down) Experimental (in HX) and (up) calculated PCM-TDDFT absorption and emission spectra for DTE, DTE-O2 and DTE-O3. Both AP and P conformers calculations have been undertaken.

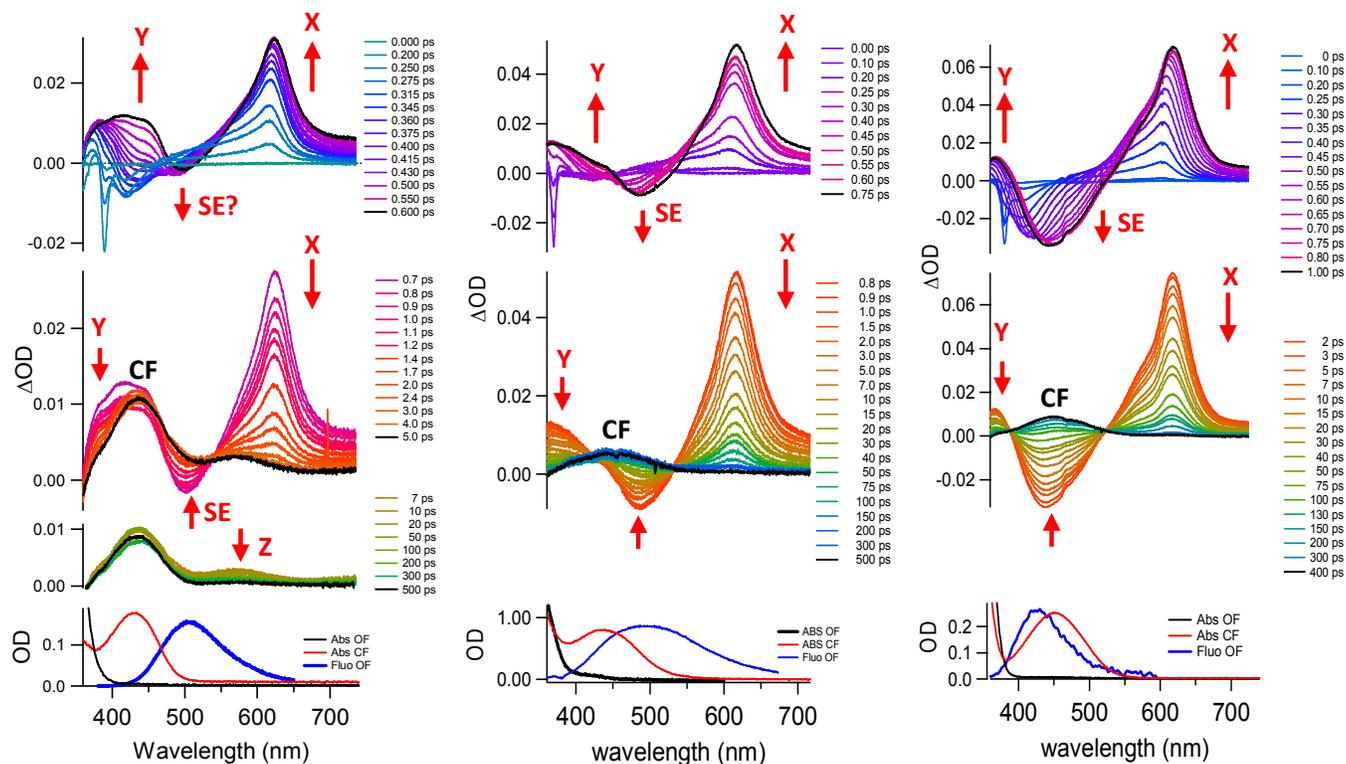


Figure 3. Time-resolved spectra of DTE (left), DTEO2 (center), and DTEO3 (right) in HX for a 350 nm excitation. Data are displayed within distinct temporal windows. To help the identification of transient bands, stationary absorption spectra of OF, CF and emission spectra of OF are given as well in the lower panel.

Table 1. Experimental quantum yields, absorption and emission parameters for OF conformers compared to PCM-TDDFT results. All data in *n*-hexane (HX).

		$\lambda_{abs}^{max}$ (nm)	$\epsilon_s(10^4)$ $\text{mol}^{-1} \text{L cm}^{-1}$ or oscillator strength	$\lambda_{fluo}^{max}$ (nm)	$\Phi(\text{fluo})$	$\Phi(\text{cycl})$
<b>DTE</b>	<b>Exp</b>	<b>337</b>	<b>1.29</b>	<b>507</b>	<b>0.008</b>	<b>0.40</b>
	<b>AP</b>	353	0.34	589	–	–
	<b>P</b>	366	0.29	508	–	–
<b>DTE O2</b>	<b>Exp</b>	<b>343</b>	<b>0.81</b>	<b>492</b>	<b>0.004</b>	<b>0.70</b>
	<b>AP</b>	365	0.19	523	–	–
	<b>P</b>	361	0.05	507	–	–
<b>DTE O3</b>	<b>Exp</b>	<b>338</b>	<b>1.56</b>	<b>426</b>	<b>0.011</b>	<b>0.42</b>
	<b>AP</b>	357	0.41	465	–	–
	<b>P</b>	369	0.21	536	–	–

Table 2.  $R_{CC}$  calculated for the OF ground and excited states. Characteristic times deduced from global fitting method of femtosecond transient data.

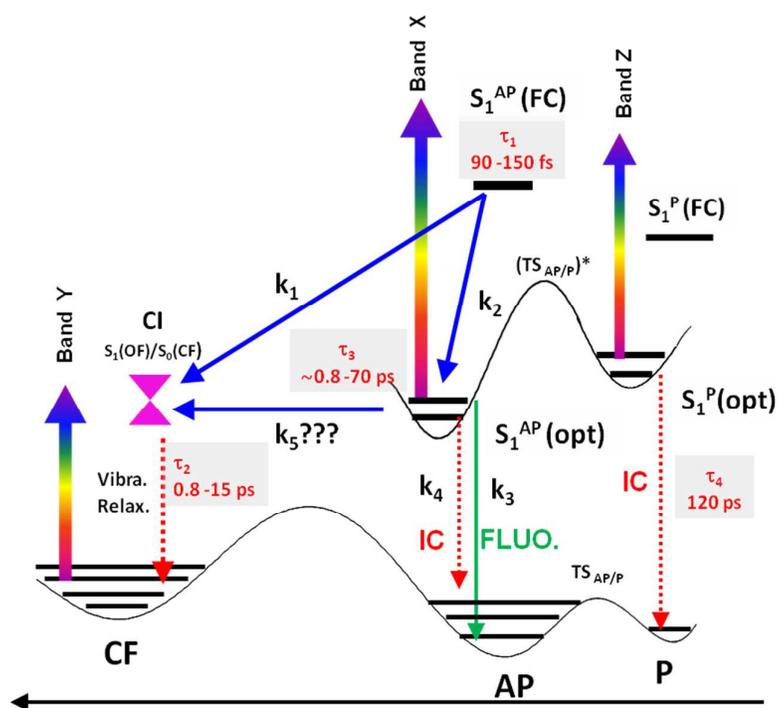
	$R_{cc}$ (Å)		Band X/Y growth	Band X Decay		Band Z decay
	Ground State $S_0$	Excited State $S_1(\text{opt})$	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ps)	$\tau_4$ (ps)
<b>DTE</b>	3.58	2.85	0.09(2)	0.8(1)		120(5)
<b>DTE-O2</b>	3.48	3.10	0.140(2)	4.7(6)	36(4)	–
<b>DTE-O3</b>	3.65	3.45	0.15(2)	15(5)	70(10)	–

## REFERENCES

- [1] H. Dürr, H. Bouas-Laurent, *Photochromism, Molecules, and Systems*, Elsevier, Amsterdam, **1990**.
- [2] J. C. Crano, R. J. Guglielmetti, *Organic Photochromic and Thermochromic Compounds, Vol. 1,2*, Plenum, New York, **1999**.
- [3] K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, *Journal of the American Chemical Society* **2011**, *133*, 13558.
- [4] M. Morimoto, M. Irie, *Journal of the American Chemical Society* **2010**, *132*, 14172.
- [5] M. Irie, *Chemical Reviews* **2000**, *100*, 1685.
- [6] M. Irie, *Chemical Reviews* **2000**, *100*, 1683.
- [7] M. Irie, *Bulletin of the Chemical Society of Japan* **2008**, *81*, 917.
- [8] S. Fukumoto, T. Nakashima, T. Kawai, *European Journal of Organic Chemistry* **2011**, 5047.
- [9] S. Fukumoto, T. Nakashima, T. Kawai, *Angewandte Chemie-International Edition* **2011**, *50*, 1565.
- [10] W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian, W. Zhu, *Angewandte Chemie* **2013**, *126*, 4691.
- [11] W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian, W. Zhu, *Angewandte Chemie International Edition* **2014**, *53*, 4603.
- [12] Y. Ishibashi, H. Miyasaka, S. Kobatake, M. Irie, Y. Yokoyama, *2007 Pacific Rim Conference on Lasers and Electro-Optics, Vols 1-4* **2007**, 1364.
- [13] Y. Ishibashi, M. Mukaida, M. Falkenstrom, H. Miyasaka, S. Kobatake, M. Irie, *Physical Chemistry Chemical Physics* **2009**, *11*, 2640.
- [14] Y. Ishibashi, K. Okuno, C. Ota, T. Umesato, T. Katayama, M. Murakami, S. Kobatake, M. Irie, H. Miyasaka, *Photochem Photobiol Sci* **2010**, *9*, 172.

- [15] S. Aloise, M. Sliwa, Z. Pawlowska, J. Rehault, J. Dubois, O. Poizat, G. Buntinx, A. Perrier, F. Maurel, S. Yamaguchi, M. Takeshita, *Journal of the American Chemical Society* **2010**, *132*, 7379.
- [16] S. Aloise, M. Sliwa, G. Buntinx, S. Delbaere, A. Perrier, F. Maurel, D. Jacquemin, M. Takeshita, *Physical Chemistry Chemical Physics* **2013**, *15*, 6226.
- [17] A. Perrier, S. Aloise, M. Olivucci, D. Jacquemin, *Journal of Physical Chemistry Letters* **2013**, *4*, 2190.
- [18] M. Takeshita, C. Tanaka, T. Miyazaki, Y. Fukushima, M. Nagai, *New Journal of Chemistry* **2009**, *33*, 1433.
- [19] K. Uchida, M. Irie, *Chemistry Letters* **1995**, 969.
- [20] G. Buntinx, R. Naskrecki, O. Poizat, *Journal of Physical Chemistry* **1996**, *100*, 19380.
- [21] B. Moine, J. Rehault, S. Aloise, J. C. Micheau, C. Moustrou, A. Samat, O. Poizat, G. Buntinx, *Journal of Physical Chemistry A* **2008**, *112*, 4719.
- [22] T. Nakayama, Y. Amijima, K. Ibuki, K. Hamanoue, *Review of Scientific Instruments* **1997**, *68*, 4364.
- [23] R. A. Gaussian 09, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.
- [24] D. Jacquemin, A. Planchat, C. Adamo, B. Mennucci, *Journal of Chemical Theory and Computation*  
*J. Chem. Theory Comput.* **2012**, *8*, 2359.
- [25] J.-D. Chai, M. Head-Gordon, *The Journal of Chemical Physics* **2008**, *128*, 084106.
- [26] N. Mardirossian, J. A. Parkhill, M. Head-Gordon, *Physical Chemistry Chemical Physics*  
*Phys. Chem. Chem. Phys.* **2011**, *13*, 19325.

- [27] D. Jacquemin, E. Perpete, I. Ciofini, C. Adamo, in *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, Vol. 128, Springer Berlin / Heidelberg, **2011**, pp. 127.
- [28] X. Li, M. J. Frisch, *Journal of Chemical Theory and Computation*  
*J. Chem. Theory Comput.* **2006**, 2, 835.
- [29] J. Tomasi, B. Mennucci, R. Cammi, *Chemical Reviews**Chem. Rev.* **2005**, 105, 2999.
- [30] M. Cossi, V. Barone, *The Journal of Chemical Physics* **2001**, 115, 4708.
- [31] R. Cammi, B. Mennucci, *The Journal of Chemical Physics* **1999**, 110, 9877.
- [32] C. Adamo, V. Barone, *The Journal of Chemical Physics* **1999**, 110, 6158.
- [33] M. Ernzerhof, G. E. Scuseria, *The Journal of Chemical Physics* **1999**, 110, 5029.
- [34] R. Improta, V. Barone, F. Santoro, *Angewandte Chemie International Edition* **2007**, 46, 405.
- [35] B. Mennucci, *The Journal of Physical Chemistry Letters* **2010**, 1, 1666.



The photophysical properties of a series of dithienylethenes, free or blocked in an ideal photoactive conformation by an alkyl bridge are investigated with stationary, ultrafast spectroscopy and state-of-the-art Time-Dependent Density Functional Theory.