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Marie Barale, Muriel Escadeillas, Gregory Taupier, Yann Molard, Clément Orione, et al.. Nondestructive All-Optical Readout through Photoswitching of Intramolecular Excimer Emission. *Journal of Physical Chemistry Letters*, 2022, 13 (47), pp.10936-10942. 10.1021/acs.jpcclett.2c02960 . hal-03886880

HAL Id: hal-03886880

<https://hal.science/hal-03886880>

Submitted on 30 Mar 2023

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Non-Destructive All-Optical Readout Through Photoswitching of Intramolecular Excimer Emission

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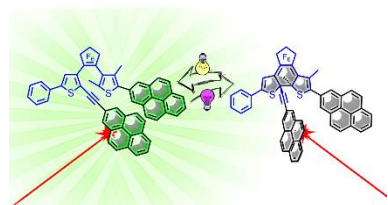
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ABSTRACT

We report the first intramolecular excimer photoswitching induced by molecular motion within a dithienylethene (DTE) molecule, without destructive readout. The photochromic compounds DTE

bears two pyrene chromophores, judiciously positioned to face each other in the DTE's open form. The close proximity of the pyrenes in the open form is confirmed by NMR experiments and geometry optimization. Intense pyrene excimer luminescence is recorded, both upon one- and two-photon excitation (OPE and TPE). The photocyclization reaction of the DTE core induces a molecular motion of one pyrene moiety which thus prevents the possibility of formation of an excimer. Our DTE-based pyrene is stable upon TPE irradiation and shows a high photo-cyclization quantum yield. Such properties specifications, allow us to report the original non-destructive readout fluorescence by alternative exposure to OPE and TPE.

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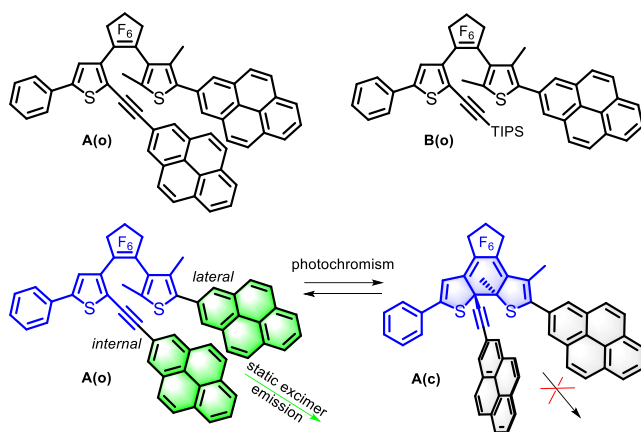


KEYWORDS

Photochromism, Dithienylethene, Luminescence, Pyrene, Two-photon excitation

As chemists, we are all impressed by the ingenuity and efficiency of the actuators that pave every Nature's machinery.¹⁻³ Inspired by, but far from the smart life's molecular designs, chemists have gathered experience over the past decades in preparing efficient activatable molecular systems, in a wide range of purposes and scales.⁴⁻⁸ Among them, employing light as actuator offers the advantages of simple and contactless modulation of the intensity and space resolution, and can be used orthogonally to electronic processes. Controlling and understanding the dynamics of externally light-triggered molecular motion is one fascinating topic that spawned groundbreaking

successes, ranging from biomedicine to smart molecular materials.⁹⁻¹¹ Photochromic molecules stand as efficient molecular light-switches since they are able to undergo reversible photo-reactions by absorbing photons of suitable frequencies, which promotes different deactivation paths such as the formation of new chemical bonds and/or transforming their configuration leading to modulation of properties like electronic gap, polarity, or geometry. As far as molecular motion is concerned, the targeted photochrome must undergo photo-modulation of geometrical changes. Azobenzene derivatives are the most studied due to their large geometrical changes upon light irradiation but suffer from low thermal stability.¹² We learned during the journey of photo-activatable molecules that the specifications of reversibility, fatigue-resistance and non-destructive readout are crucial toward operating photo-responsive molecular systems, particularly in the fields of bio-imaging or molecular data storage.¹³⁻¹⁵ Besides, the choice of an optical output signal appears both beneficial and challenging.^{12,16,17} Among the all-optical molecular systems reported to date for the photo-control of linear or nonlinear¹⁸ optical output, a common design combines photochromic and fluorescent units, where the fluorescence emission is modulated by the photochromic reaction. Among the various photochromic compounds known to date, the dithienylethenes (DTE) are the most suitable for fluorescence photoswitching owing to their excellent thermal stability and fatigue resistance.^{17, 19-22} The “ON”/“OFF” readout process is usually based on the contrast between the observed fluorescence of the open form of the DTE system (DTE_o) and the fluorescence quenching of the closed DTE compound (DTE_c). In the latter systems, the quenching of the excited dye by the DTE_c core is usually due to energy or electron transfers such as, FRET (Förster Resonance Energy Transfer) or PET (Photo-induced Electron Transfer).²³



Scheme 1. Representations of **A(o)** and **B(o)** (*top*), and the photo-modulation of the static excimer emission in **A** (*bottom*).

Such energy-transfer-based systems have drawbacks for non-destructive fluorescence readout. Depending on the nature, the structure and the environment of the dyad, the usually observed destructive fluorescence readout can be due to, *i*) the fluorescence quenching process by excitation energy transfer which can trigger the cycloreversion reaction of the DTE unit, *ii*) the contribution of the triplet state in the photocyclization reaction or *iii*) the competition between fluorescence emission and photocyclization reaction.^{18,24,25}

To overcome this issue, several strategies have been proposed, such as readouts using the changes of the refractive index or IR absorption at the wavelengths out of the switching unit,²⁵ stabilized signals by means of acid or base reactions,²⁷ switching by photoinduced electron transfer,²⁰ molecular polarity, or supramolecular conformational changes. While efforts have been made to reduce competitive processes to luminescence photoswitching, it is still very challenging to completely suppress the destructive readout in DTE-based systems.

We report herein an efficient approach combining photo-triggered geometrical change and alternative one- and two-photon excitations (OPE and TPE).

The photo-modulation of molecular motions have already been investigated with overcrowded-alkene-based systems,^{11,28,29} azobenzenes³⁰ and diarylethenes,³¹ as examples. Herein, inspired by the elegant work of Hashimoto *et al.*,³¹ on the photo-modulation of the excimeric emission of pyrene, we report the new pyrene-based DTE **A(o)** (Scheme 1). In **A(o)**, the two pyrenes can face each other in the open's DTE form, thus leading to static excimer emission. Upon ring-closure reaction, the pyrene introduced on the inner position will be moved apart from the lateral pyrene, thus avoiding the possibility of excimer. To benefit from a large molecular movement upon photocyclization the DTE must be functionalized at the lateral and internal positions, as the changes in distance between the two lateral positions upon photochromism is only 1 Å. However, reports on DTEs functionalized at the lateral and internal positions are rare due to the synthetic challenge that represents such an unsymmetrical functionalization.^{31,32} Thus, design of **A(o)** is expected to give higher propensity of excimer emission in comparison to a symmetrically substituted DTE.³³

Nonlinear optical processes such as stepwise and simultaneous TPE have been reported to enhanced the cyclo-reversion reaction of DTE.^{34,35} However, for both TPE processes, the photocyclization reaction is known to be ineffective. Knowing that TPE produces specific one-photon forbidden excited states, the combination of one- and two-photon excitations can allow to selectively trigger the photochromism and collect the excimer emission in **A(o)**, respectively. This opens the way of an unprecedented non-destructive fluorescence readout with orthogonal light stimuli i.e.; one-photon irradiation (UV and visible) employed to control the photochromic reaction and two-photon excitation (730 nm) used to probe the fluorescence. Besides, TPE can provide precise three-dimensional visualization deep within the samples using low-energy photons.

The targeted DTE **A(o)** and the reference **B(o)** (Scheme 1) are obtained via a convergent synthesis strategy, allowing their early functionalization at will (see ESI).^{27,36} The two thiophenic sides of the DTE **B(o)** are firstly prepared separately through classical cross-coupling reactions. Finally, the two thiophene derivatives are bridged by the perfluorocyclopentene via stepwise nucleophilic substitutions. From **B(o)**, the deprotection of the acetylenic arm followed by a Sonogashira cross-coupling with the 1-bromopyrene yields the bis-pyrene DTE **A(o)**.

The geometry optimization of compound **A(o)** was performed using the B3LYP hybrid functional with the D3BJ model to describe weak interactions, and the 6-31G(d,p) basis set, using the Gaussian 16 software (Figure 1).³⁷ The anti-parallel conformation of **A(o)** was found to be the most stable, confirming a majority of anti-parallel conformations in solution. In this conformation, the two pyrenes are facing each-other, at a distance of 3.5 Å, evidencing their possible interaction in the ground state and their capacity to form an excimer in the excited state.

Scan calculations performed at the B3LYPGD3BJ / 6-31G level of theory allowed us to estimate the rotational energy barrier around the thiophene – perfluorocyclopentene bridge. It was estimated at 75 kJ.mol⁻¹ for the C10-C3' bond and 161 kJ.mol⁻¹ for the C6-C3 bond (Figure 1). The latter being superior than 100 kJ.mol⁻¹, the rotation around the bond is indeed blocked at room-temperature, agreeing the observed experimental behavior.³⁸ Interestingly, the interchromophoric distance of 3.5 Å found between the two pyrenes in **A(o)** leads to ground state interactions, whereas similar distances calculated in PDI dimers exhibit monomer-like absorption feature likely due to higher rigidity and slip stacks.³⁹ One can notice that in **A(o)**, the two differently branched pyrenes allow an optimized overlap with very short slip stacks of 1.4 Å and 0.73 Å along the short and long pyrene axes respectively.

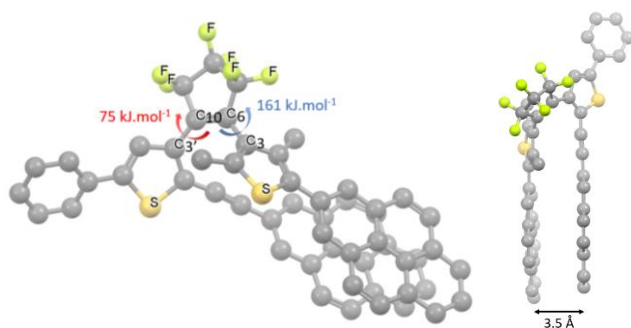
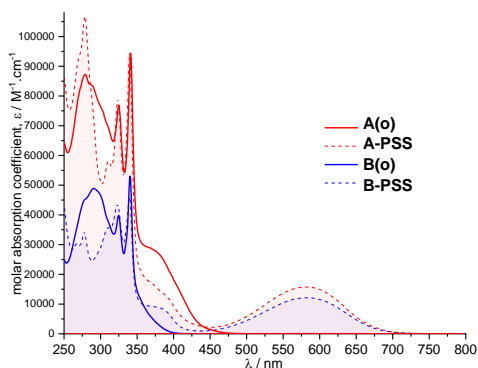


Figure 1. side (left) and top (right) view of the calculated structure of compound **A(o)**.

The electronic absorption spectra of the bis- and monopylene-based DTEs (**A** and **B**) in their open and closed (photo-stationary state: PSS, at $\lambda_{\text{ex}} = 350$ nm) forms are presented in Figure 2 and the related data are summarized in Table 1. The absorption spectrum of reference compound **B(o)** is characterized by two sets of bands in the UV region gathering π - π^* transitions on the DTE core and on the pyrene moiety *i.e.*, from 250 to 300 nm (S_0 - S_3 for pyrene) and from 300 to 400 nm (S_0 - S_2 for pyrene).⁴⁰ The S_0 - S_2 excitation in 2-substituted pyrene was described as “pyrene-like”, regardless of the electronic nature of the substituent, due to a node in the HOMO and LUMO orbitals at the 2-position.⁴¹ As a matter of fact, the S_0 - S_2 transition of **B(o)** exhibits structuration with characteristic vibrational spacing of 1400 cm^{-1} (Figure 2). The vibrational structure of the S_0 - S_3 transition cannot be seen due to the overlapping with transitions belonging to the DTE core.



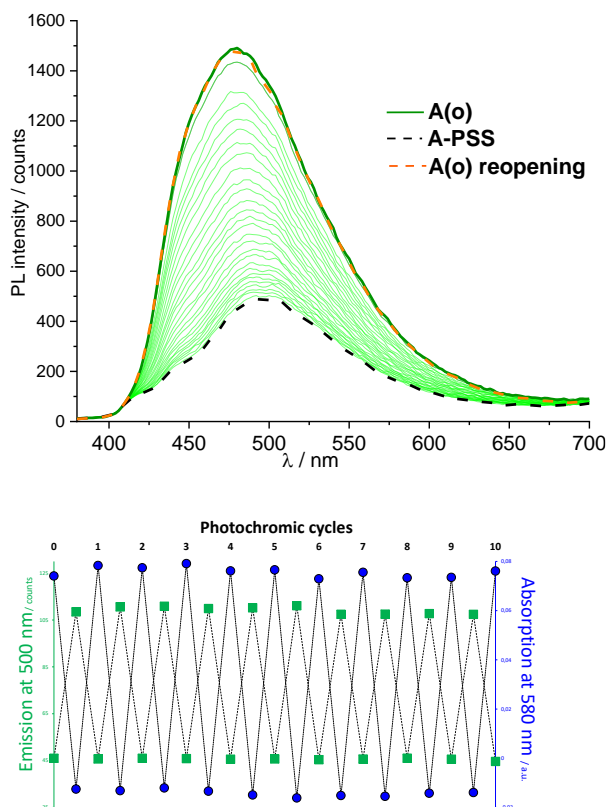


Figure 2. *top*: Absorption spectra of **A** and **B** in their open and at the photostationary state (PSS) (under irradiation at 365 nm). *middle*: emission spectra of **A** in its open form (green line), at the PSS (dotted black line, $\lambda_{\text{ex}} = 365$ nm) and after reopening (dotted orange line, $\lambda_{\text{ex}} = 580$ nm). In a dichloromethane solution ($c \approx 10^{-6}$ M) at 298 K. *bottom*: follow-up of the emission at 500 nm (in green) and the absorption at 580 nm (in blue) during several photochromic cycles consisting of alternate irradiations at 365 and 580 nm for ≈ 2 h.

The absorption spectrum of the bis-pyrene DTE **A(o)** shows similar absorption maxima and shapes in the UV region, with the expected increase in absorptivity centered at 300 nm, corresponding to the second pyrene moiety. An additional lower-lying absorption band from approximately 360 to 465 nm is attributed to the $[\pi \cdots \pi]$ stacking of the two pyrene moieties, in agreement with the structural characterization (*vide infra*).

Complete ^{13}C , ^{19}F and ^1H NMR assignments have been established, and through space interactions observed for **A(o)** (Figure S22) support this $[\pi\cdots\pi]$ interaction between the pyrene as well as TD-DFT calculations (*vide infra*). For **A(o)**, ^1H - ^{19}F -correlation experiments gave clear signals of through space interactions between protons located on the thiophenes and fluorine of the bridge (Figure S23). The protons of methyl groups at the 4- or 2-position of the thiophene ring (4Me or 2Me) show through space interaction with the fluorine 7a (F7a) or 7b (F7b) respectively, thus indicating a blocked configuration of the thiophene group around the C6-C3 bound. The proton H4' of the second thiophene group shows through space correlations with both F9a (weak) and F9b (strong), consistent with a rotation around the C10-C3' bound (fast in NMR timescale), but with a preferential anti-parallel conformation. This is corroborated by ^1H NOESY experiments revealing spatial proximity of H4' with both 4Me and 2Me but also clear correlations between the protons of 4Me and the protons at the ortho positions of both pyrenes (Figure S24).

The latter result evidences that the two pyrenes point in the same direction and are thus facing each-other. Similar $^1\text{H}/^{19}\text{F}$ NMR correlations are monitored between fluorine F7 and protons 2-4CH₃ for **B(o)** (Figure S25) indicating a hindered rotation around the C6-C3 bound.

Table 1. Absorption and emission data for **A** and **B**.

	Open form		PSS ($\lambda_{\text{irr}} = 365 \text{ nm}$)		$\Phi_{\text{c}\rightarrow\text{o}}(365\text{nm})$, $\Phi_{\text{c}\rightarrow\text{o}}(365\text{nm})$, $\Phi_{\text{c}\rightarrow\text{o}}(575\text{nm})^{\text{d}}$
	$\lambda_{\text{abs}}^{\text{a}}$ [nm] ($\epsilon \times 10^3$ [$\text{M}^{-1}\text{cm}^{-1}$])	$\lambda_{\text{em}}^{\text{a,b}}$ [nm] (Φ_{em} [%], τ [ns])	$\lambda_{\text{abs}}^{\text{a}}$ [nm]	Conversion ^c [%]	
A	278 (86.9), 291 (82.8), 325 (76.7), 340 (94.4), 378 (27.9)	490 (5, 3)	270sh, 278, 310, 323, 340, 581	75	0.68±0.09 0.40±0.04 0.033±0.002
B	277 (45.6), 291 (48.6), 324 (39.5), 340, (53.2)	/	267, 278, 310, 322, 340, 383, 582	90	1.00±0.08 0.11±0.03 0.040±0.002

^a In dichloromethane solution ($C \approx 10^{-6} \text{ M}$) at 298 K. ^b $\lambda_{\text{ex}} = 365 \text{ nm}$. ^c Estimated from ^1H -NMR experiments. ^d Photochromic quantum yields determined under irradiation at 365 and 575 nm (error intervals estimated from 5% uncertainty on power and epsilon measurements).

The photochromic activity of the DTE **A** and **B** have been investigated by means of UV-visible absorption and NMR experiments. Interconversions between the open and closed forms are triggered by 365 and 575 nm light irradiations, respectively.

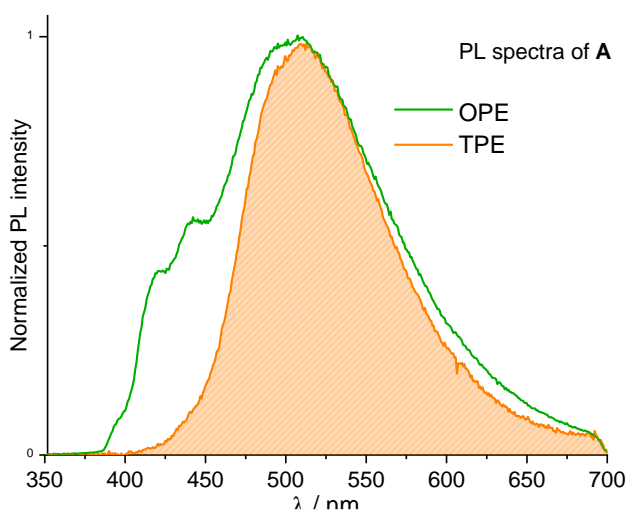
The initial colourless solution of **B(o)** turns dark blue upon irradiation at 365 nm with the emergence of two characteristic absorption bands in the visible, *i.e.*: a large band centered at 582 nm and a shoulder at 383 nm, respectively attributed to the S₀-S₁ and S₀-S₂ transitions on the closed DTE unit (Figure 2).¹⁷ These features attest the formation of the closed isomer **B(c)**. One can notice that the energies and shapes of the broad bands in the visible are identical for **A(c)** and **B(c)**. This is explained by the formation of a sp³ carbon at the central position upon ring-closure reaction, which prevents any electronic communication with the closed DTE core.

Monitoring the ring-closure reaction by ¹H NMR spectroscopy gives access to the percentage of conversion at the photostationary state (PSS under irradiation at 350 nm), that are 75 % and 90 % for **A** and **B**, respectively.

The ring-closure and ring-opening photokinetics were recorded by means of a UV-visible spectroscopy set-up. The resulting absorption time-profiles under continuous irradiation at 365 and 575 nm respectively were analyzed numerically, providing the photochromic quantum yields $\Phi_{o \rightarrow c}$ and $\Phi_{c \rightarrow o}$ for **A** and **B**, as listed in Table 1. The photocyclization quantum yields $\Phi_{o \rightarrow c}$ were found at 0.68±0.09 and 1.00±0.08 for **A(o)** and **B(o)**. Such high values of $\Phi_{o \rightarrow c}$ are likely due to the hampered thiophene's rotation that favored the anti-parallel form ratio.⁴² The quantum yields corresponding to the cycloreversion reaction ($\Phi_{c \rightarrow o}$) induced at 575 nm are much lower and very similar for both **A** and **B** (0.033±0.002 for **A(c)** and 0.040±0.002 for **B(c)**), as commonly observed for such DTE derivatives. The introduction of substituents (Me, ^tBu) in the 4-positions of the

thiophene rings has shown to be effective in increasing photocyclization quantum yields close to unity.⁴³

The fluorescence properties of the DTE-based pyrene derivatives **A** and **B** were investigated in solution at room temperature with a concentration of c.a. 10^{-6} M, diluted enough to exclude intermolecular excimer (Figure S30). The monopyrene compound **B** is non-emissive due to rapid competitive ring-closure reaction triggered by irradiation of UV light, which agrees with the photocyclization quantum yield determined at almost unity (Figure 3, *bottom*). However, the DTE-based bispyrene **A** exhibits excimeric emission (Figure 2, Table 1). The emission spectrum of **A(0)** shows a broad band centered at 490 nm attributed to the intramolecular excimer and corresponding to 5 % of photoluminescence quantum yield.⁴⁴



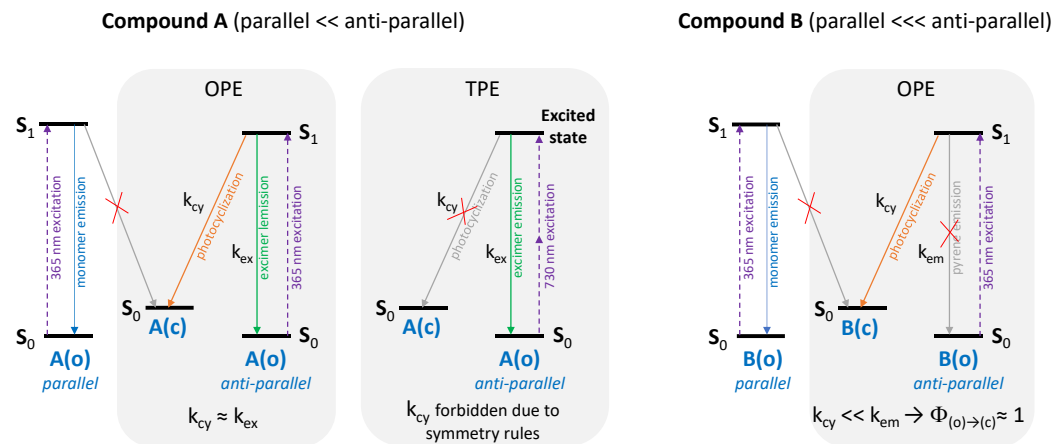


Figure 3. *top*: Normalized fluorescence spectra of **A** by OPE or TPE at 365 and 730 nm, respectively, by femtosecond-pulsed laser. *bottom*: Diagram of the photochemical processes (illustrations) of compound **A** (left part) upon OPE and TPE, and **B** (right part) upon OPE.

Upon irradiation at 350 nm and reaching the PSS, the solution of **A** shows a decrease of the excimer emission intensity of about 70 % (Figure 1 and Figure 3, *bottom*). The observed emission profile is likely an admixture of several radiative deactivation processes, accounting for: i) remaining amount of the anti-parallel conformer, ii) various plausible parallel conformers with both centered pyrene (structured) and charge transfer (broad) emission profiles. One can notice that because the pyrenes are functionalized at 2-positions (thiophenyl and alkynyl-thiophene groups), their emission energies appear at lower energy than a non-functionalized pyrene.⁴⁵ Moreover, this pyrene's emission cannot originate from **A(c)** because; i) it is expected to be quenched by the closed DTE core, ii) a concomitant increase of the pyrene's emission is not observed upon the photocyclization process. The remaining excimer emission ($\approx 30\%$) at the PSS is due to the presence of residual open isomers, as the photoconversion is not quantitative ($\approx 75\%$). Upon irradiation at 580 nm the initial emission spectra is fully recovered.

The excimer emission of **A(o)** is recorded upon two photon excitations with the same solution (TPE: $700 \text{ nm} < \lambda_{\text{ex}} < 800 \text{ nm}$). One can notice that no TPE emission signal was observed for **B** in same conditions. Remarkably, the TPE spectra of **A** exhibits an emission band at the same energy as the excimer emission recorded upon OPE, without any residual structured emission of monomeric pyrene (Figure 3). In this system, the TPE measurement selectively probes the excimer, likely due to symmetry rules (Figure 3, *bottom*).⁴⁶ The output intensity of two-photon excited fluorescence (TPEF) was linearly dependent on the square of the input laser intensity, confirming the nonlinearity of the absorption process. **A** shows a modest two-photon absorption cross section of 90 GM, typical for pyrene systems (Figure S33 and Table S1). Interestingly, while the emission intensity of OPE decreases upon consecutive emission spectra acquisitions due to the competition with the ring-closure reaction (Figure S31), the emission recorded on two-photon excitation remains stable (Figure S32). The robustness of **A** toward TPE allowed us to perform an all-optical switching experiment where OPE was employed to trigger the photochromic reaction and TPE was used to record the “ON” or “OFF” signal, over 10 cycles without any loss of readout (Figure S35).

To conclude, we report herein the synthesis of original unsymmetrical DTE-based pyrenes, with a complete characterization and assignment of their composition. We also confirmed the face-to-face arrangement of the pyrenes in **A(o)** prior to the photo-physical investigation. The close proximity of the pyrenes in **A(o)** gives rise to the excimeric luminescence, both upon OPE and TPE. As we expect, upon ring-closure reaction the internal arm undergoes a movement that brings pyrene moieties apart, inhibiting the excimer luminescence. Also, we discovered that the additional methyl at position 4 of the thiophene (right side) advantages the extremely effective photochromic behavior and promotes the pyrenes stacking. Finally, the efficient photo-modulation of the

excimeric luminescence combined with the selective and stable response to TPE, allows us to record the non-destructive readout fluorescence by alternative exposure to OPE and TPE. We believe that our original approach of preparing such unsymmetrical DTE-based chromophores demonstrates an alternative and promising way to design fluorescent molecular photoswitches with non-destructive read-out behavior, by taking advantage of the molecular motion that takes place in the internal position. This work may open new perspectives in photo-triggered sensing, super-resolution bio-imaging, and light-fueled molecular machines.

ASSOCIATED CONTENT

Supporting Information.

General information, synthesis way and characterization, NMR and emission experiments.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by financial supports from the CNRS and the University of Rennes 1. The PhD grant of the first author has been provided by the University of Rennes 1. This work was granted access to the computing resources of CINES (Montpellier, allocations 2020-AP010811752, 2021-A0100805032). Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1- Campus de Villejean- 35043 RENNES Cedex, FRANCE

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