

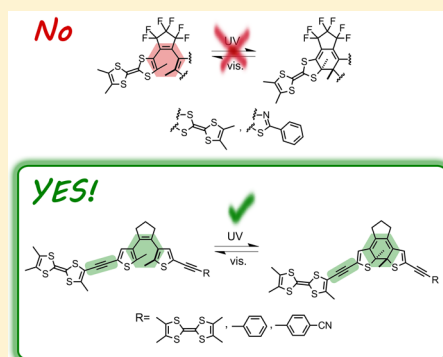
Diarylethene Photoswitches Featuring Tetrathiafulvalene-Containing Aryl Units

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S Supporting Information

ABSTRACT: The modulation of the electron-donor properties of tetrathiafulvalene (TTF) with light is attempted by two molecular designs: the integration of the TTF core as aryl unit(s) into the hexatriene system of diarylethene (DAE) derivatives and the attachment of terminal TTF unit(s) to a conventional 1,2-dithienylcyclopentene chromophore via conjugated ethynylene spacers. While photochromism is inhibited in the first approach, presumably by a twisted intramolecular charge transfer mechanism, the second approach yields photo-switchable TTF derivatives. Remarkably, the extension of the conjugated π -system upon ring closure affects the first oxidation potential values of the TTF–DAEs only slightly. Nevertheless, the electronic changes in the photochromic core are foreseen to play a crucial role in the intramolecular electron transfer process in donor–DAE–acceptor architectures.



INTRODUCTION

Organic synthesis plays a key role in the design of modern and future electronic devices since it not only provides new materials but also, in addition, can tune their advantageous properties by modification of their molecular structures. A good example of this is the vast variety of tetrathiafulvalene (TTF) derivatives reported in the literature, which have found applications in many areas of molecular electronics^{1,2} ranging from field effect transistors (OFETs)^{3–5} and optoelectronic materials⁶ to molecular switches^{7–12} and photovoltaics,^{13,14} among others. The versatility of these compounds relies on the outstanding electrochemical properties of the 2,2'-bis(1,3-dithiolyliidene) heterocyclic TTF core. In this pro-aromatic 14- π -electron system, oxidation to the cation radical and dication occurs sequentially and reversibly at relatively low potentials.^{1,15} Contrary to the neutral species, the two oxidized forms are aromatic so that both the radical cation and dication are reasonably stable, a most sought after feature in hole-transporting p-type semiconductors and photovoltaic devices.

The modulation of the TTF derivatives' unique electronic properties with a light input is an appealing challenge since it would enable controlling electron transfer efficiency by means of an external and noninvasive stimulus associated with high spatial and temporal resolution. To implement the desired reversible light response, a photochromic moiety is required. Diarylethenes (DAEs) are excellent candidates for this purpose for two reasons: (1) their open and closed isomers present well-separated absorption bands allowing for selective excitation and (2) photoinduced ring closure/opening leads to significant changes in the DAEs' HOMO and LUMO levels. With this goal in mind, two series of compounds that combine DAE and TTF units in two different molecular designs were prepared (Scheme 1).

In the first series of DAE derivatives, the 1,3-dithiole fragment of the TTF core is *integrated* into the hexatriene system of the DAE chromophore. It was anticipated that, with this approach, the changes in the π -system of the DAE upon ring closure/opening would dramatically impact the electrochemical properties of the TTF. Moreover, the nonsymmetrical substitution of the TTF–DAE could provide donor–acceptor photochromic molecules, here represented by the model DAE comprising a TTF and a thiazole unit. Although Lehn et al. reported DAE derivatives containing benzo-1,3-dithiole terminal units,^{16,17} to the best of our knowledge, the only example of a DAE featuring a TTF moiety as a part of the active photochromic hexatriene core has been reported by Uchida and Irie.¹⁸ However, in their work, the two dithiole rings of the TTF act as bridging units of two hexatriene systems, and the effect of switching on the TTF redox properties has only been briefly described.¹⁸

In a second series of compounds, one or two TTF moieties are attached as terminal units to a 1,2-dithienylcyclopentene photochromic system by means of an acetylene linker. In this fashion, the light-induced changes undergone by the photochromic fragment are expected to influence the electrochemical response of the attached TTF derivative due to the extension of the π -conjugated system throughout the ring-closed DAE. To investigate the potentially long-range electronic communication in such switchable π -systems, an electron-withdrawing benzonitrile moiety was introduced at the terminus opposite to the TTF and its influence on both the optical and the

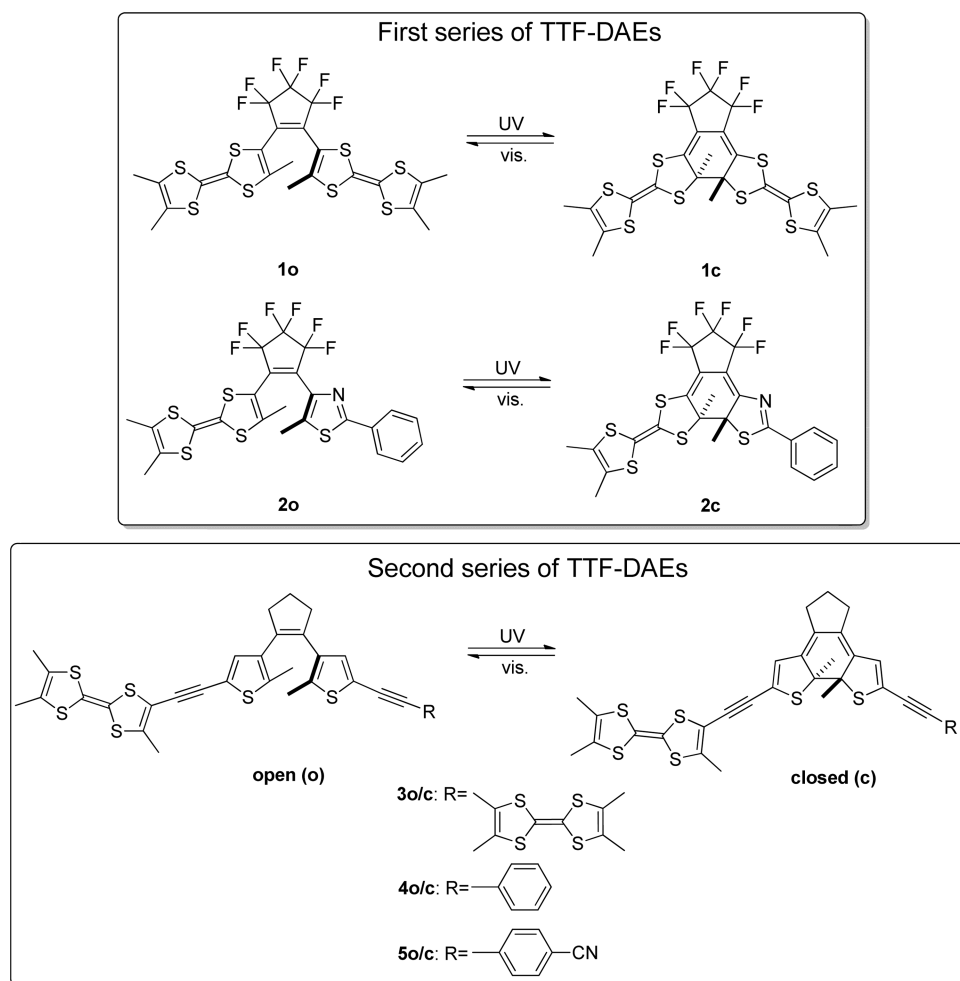
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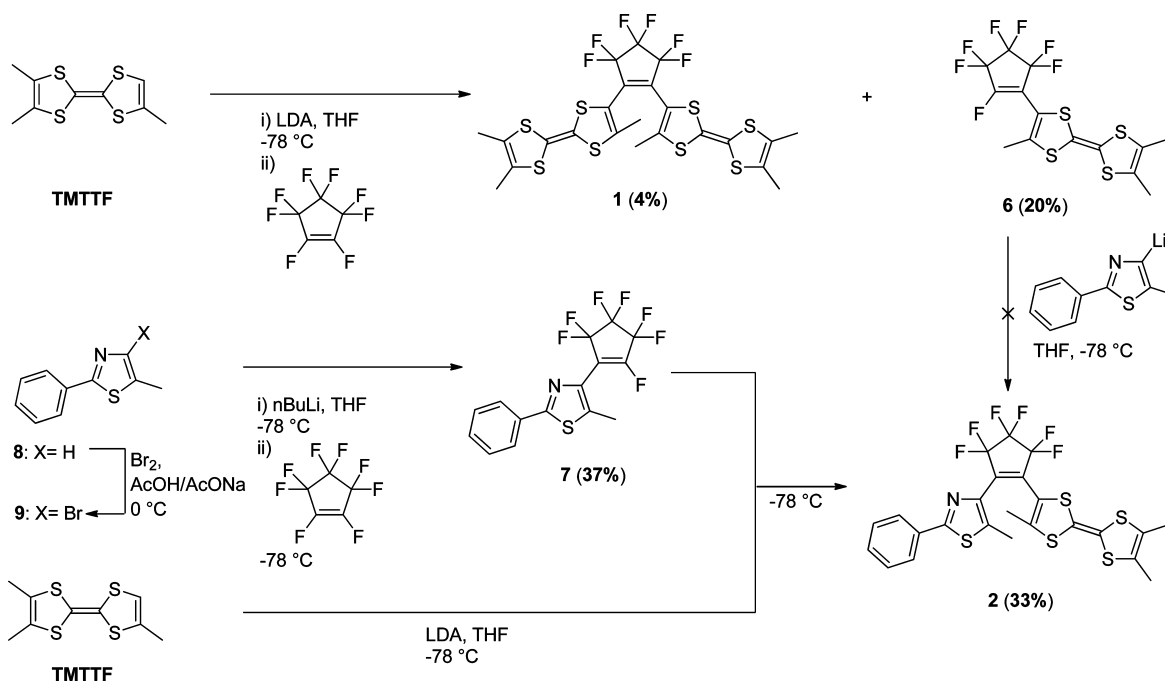
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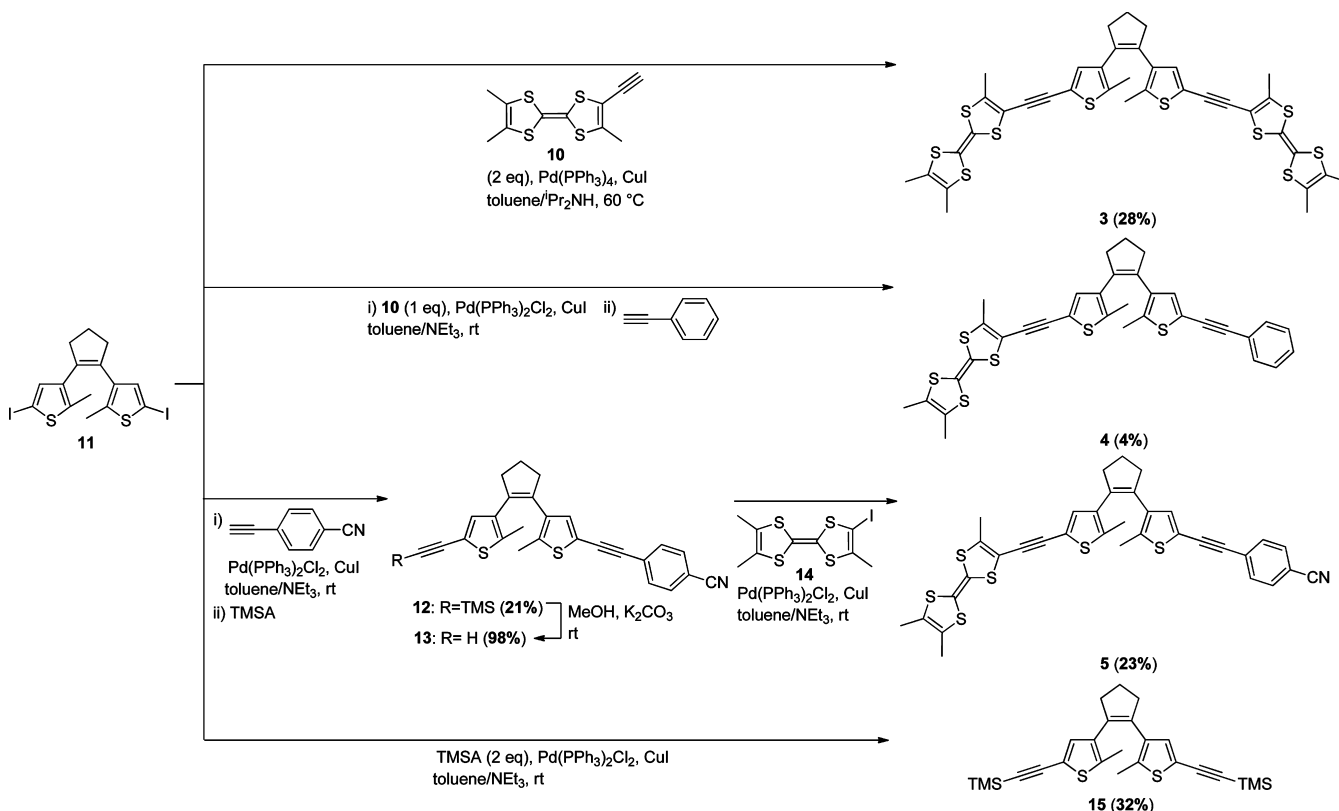
Scheme 1



Scheme 2



Scheme 3



electrochemical characteristics of the corresponding DAEs was studied.

Herein, we report the synthesis of symmetric and non-symmetric DAEs featuring the TTF entity both as part of the hexatriene core and as a terminal unit, as well as their photophysical and electrochemical properties based on experimental and theoretical characterization. Our results are relevant to the design of molecular systems that enable photocontrol over electron transfer from TTF units to a suitable electron acceptor.

RESULTS AND DISCUSSION

Synthesis. Our synthesis of the first DAE series **1** and **2** relies on the direct connection of the TTF terminal unit(s) to the hexafluorocyclopentene core (Scheme 2). Lithiation of trimethyltetrafulvalene (TMTTF)¹⁹ with lithium diisopropyl amide (LDA), followed by nucleophilic attack on octafluorocyclopentene, yielded the mono- and disubstituted compounds **1** and **6**, respectively, in moderate yields. The nonsymmetrical derivative **2** was prepared by reacting lithiated TMTTF and the intermediate compound **7**, since, for unknown reasons, the inverse order of substitution steps on the perfluorocyclopentene ring was not successful.

Although perfluorocyclopentene-based DAEs are known for their superior fatigue resistance,²⁰ our concern was that the electron-withdrawing effect of the fluorines in combination with the electron-rich nature of the TTF scaffold could lead to formation of undesired charge transfer (CT) states, possibly hampering excited-state reactivity (see below). To prevent this potential obstacle, which had been claimed to be a photochromism inhibition mechanism,^{21,22} the nonfluorinated versions of compounds **1** and **2** have also been pursued.

Unfortunately, these analogous perhydrocyclopentene TTF derivatives could not be prepared by the common synthetic paths used for 1,2-dithienylcyclopentenes.^{22,23}

Instead, a successful alternative strategy for the combination of perhydrocyclopentene-based DAEs and TTF entities was developed by the attachment of 4-ethynyl-4',5,5'-trimethyltetrafulvalene (**10**)²⁴ to the bis(5-iodo-2-methylthien-3-yl)-cyclopentene (**11**)²⁵ via Sonogashira–Hagihara cross-coupling reactions. This versatile synthetic route led to the second series of compounds, i.e., the symmetric DAE **3** displaying two terminal TTF units and the nonsymmetric DAEs **4** and **5** (Scheme 3). Desymmetrized compound **4** was prepared by a 2-fold Sonogashira–Hagihara cross-coupling in a two-step, one-pot reaction. Nonsymmetric compound **5** was synthesized through a different sequence comprising the attachment of a *p*-ethynylbenzonitrile unit and a TMS-protected acetylene unit to **11** (again in a two-step, one-pot reaction) to give compound **12**. After deprotection by removal of the terminal TMS group, a final Sonogashira cross-coupling between the resulting DAE **13** and the iodo-TTF derivative **14**²⁴ afforded **5**.

UV–vis Spectroscopy. The absorption spectrum of TMTTF (Figure 1) in toluene exhibits two main features: a broad intense band in the UV region ($\lambda_{\text{max}} = 300$ nm) and a broad low intensity band in the visible region ($\lambda_{\text{max}} = 470$ nm). The high energy band is assigned to $\pi \rightarrow \pi^*$ singlet–singlet transitions, whereas the origin of the low energy band has been controversial and the subject of several theoretical calculations. The two proposed assignments in the literature are a HOMO \rightarrow LUMO $\pi \rightarrow \sigma^*$ singlet–singlet transition, polarized along the symmetry axis perpendicular to the molecular plane, and a formally spin-forbidden single–triplet transition facilitated by spin–orbit coupling involving the sulfur atoms.^{26,27} In addition to these two main absorption peaks, compounds **1**, **2**, and **6**

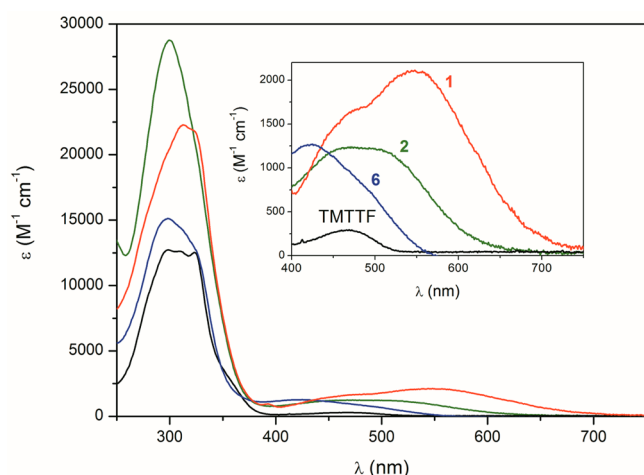


Figure 1. Absorption spectra of TMTTF (black), **1** (red), **2** (green), and **6** (blue) in toluene (10^{-5} M). Inset shows a magnification of the absorption in the visible region.

display an overlapped band at longer wavelengths in the visible range (Figure 1, inset) with a bathochromic shift increasing in the order $6 < 2 < 1$ ($\lambda_{\text{max}} = 495 < 521 < 557$ nm). We attribute this additional spectral feature to a charge transfer (CT) band from the electron-rich TTF moiety to the electron-deficient perfluorinated cyclopentene ring.²⁸ The relative shift of this CT band is clearly dependent on the nature of the neighboring substituent attached to the cyclopentene bridge, as it will be further discussed in the context of computational analyses (vide infra).

Irradiation of **1** and **2** in solution did not induce the photocyclization in any case, regardless of the employed wavelength (UV or visible). Noteworthy, the exposure to UV light in the presence of air leads to the degradation of all TMTTF derivatives, most probably caused by their photo-oxidation.²⁹

We hypothesize that the lack of photoactivity in solution might originate from the transition to a twisted intramolecular charge transfer (TICT) state upon excitation, as it had been assumed in earlier works involving an electron-donor aryl unit (thiophene or morpholino-thiazole) and an electron-poor cyclopentene ring (maleic anhydride or maleimide).^{21,22} The CT nature of the HOMO–LUMO optical transition is supported by the frontier orbital distribution predicted for **1** and **2** by DFT calculations (see the Computation section). Nevertheless, other possibilities related to the TTF core intrinsic properties could be considered, as well. For instance, a main difference between **1** and **2** and conventional diarylethenes is the nonaromatic nature of the 1,3-dithiole rings (see the Computation section). However, Branda's group proved that hexatriene backbones based on a cyclopentene featuring only one heterocycle unit can also exhibit photochromism,³⁰ which can be seen as a structure analogous to DAE **2**.

The tendency of TTF to form charge transfer salts and to aggregate by π -stacking tempted us to further speculate about two other mechanisms for photochromism inhibition: (1) the formation of a zwitterionic biradical species due to an electron transfer of the TTF to the perfluorocyclopentene bridge or (2) the stabilization of inactive conformations in solution via face-to-face⁹ or edge-to-face³¹ aromatic interactions. The first hypothesis was dismissed by EPR analyses, which revealed the presence of traces of S-centered organic radicals ($g'_1 =$

2.0069 , $g'_2 = 2.0019$)^{32,33} in the crystalline powder attributed either to point defects in the crystalline structure or to local oxidation with ambient oxygen (Figure S1 in the Supporting Information). The second hypothesis was investigated by ^1H – ^{19}F heteronuclear NOESY experiments (Figure S3 in the Supporting Information) and by low-temperature ^1H NMR (Figure S4 in the Supporting Information). However, the experiments did not allow for the discrimination of a preferred conformation for these DAEs in solution.

On the contrary, the molecular design of the second generation of TTF–DAEs **3**–**5** proved to be a successful strategy to endow TTF derivatives with a photochromic behavior. Upon irradiation of toluene solution of compounds **3**–**5** with 320 nm light, the growth of a broad band within the 500–700 nm range was registered for all three compounds, pointing to the formation of the corresponding photocyclization product. The buildup of the long wavelength band was accompanied by a decrease of the intense band centered at 320 nm and the weaker band at 420 nm, indicating conversion of the ring-opened isomer (Figure 2; see also Figure S5 in the

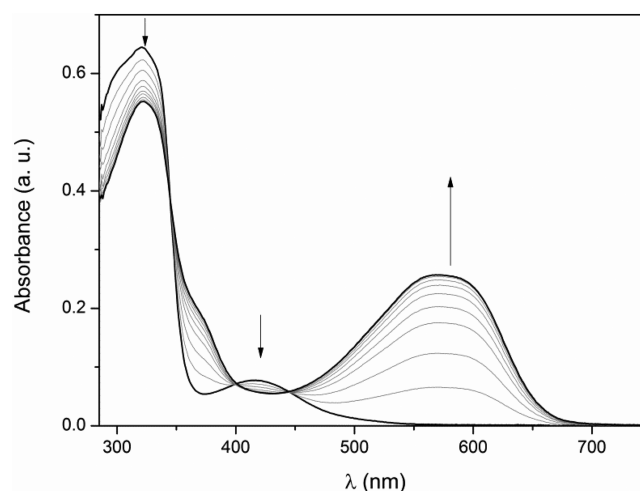


Figure 2. Evolution of the absorption spectrum of **4** in argon-saturated toluene (10^{-5} M) upon irradiation with UV light (320 nm, 90 s).

Supporting Information). The open/closed isomer ratios in the photostationary state (PSS) for **4** and **5** were estimated as 10:85 (5% of byproduct formation)³⁴ and 27:73, respectively, based on the analysis by ultraperformance liquid chromatography coupled to mass spectrometry detection (UPLC–MS). The quantum yield for the photocyclization at 334 nm was representatively measured for compound **5**, for which no side-reaction products were detected during ring closure, and gave values in the order of a few percent (see the Supporting Information). Unfortunately, suitable experimental conditions for the PSS determination by UPLC could not be found for DAE **3**, presumably due to insolubility or instability of the closed isomer. All three compounds underwent cycloreversion upon illumination with visible light > 500 nm (Figure S5 in the Supporting Information).

A bathochromic shift of ~ 20 nm was observed in spectra of **3** and **5** in relation to **4** for both the high intensity maximum in the UV region of the open isomers, assigned to a HOMO-1 \rightarrow LUMO $\pi \rightarrow \pi^*$ transition (HOMO-2 \rightarrow LUMO $\pi \rightarrow \pi^*$ for **3o**; see the Computation section), and the plateau in the red region of the closed isomer, assigned to a HOMO \rightarrow LUMO $\pi \rightarrow \pi^*$ transition. This shift is attributed to a destabilization of

the HOMO and HOMO-1 by the higher number of electron-rich TTF units, in the case of **3**, and the stabilization of the LUMO energy by the electron-withdrawing cyano group, in the case of **5**, in agreement with the complementary computational and electrochemical analysis. Please note that the low intensity band arising from the TTF fragment remains centered at 420 nm in the spectra of the open isomers of all DAEs, regardless of the substitution pattern of the TTF–DAEs.

Molecular Structure in the Solid State. The crystalline structures of **1** and **2** were investigated in order to shed light onto the conformational preferences of these inactive DAEs. X-ray diffraction studies revealed that DAE **1** (Figure 3, top)

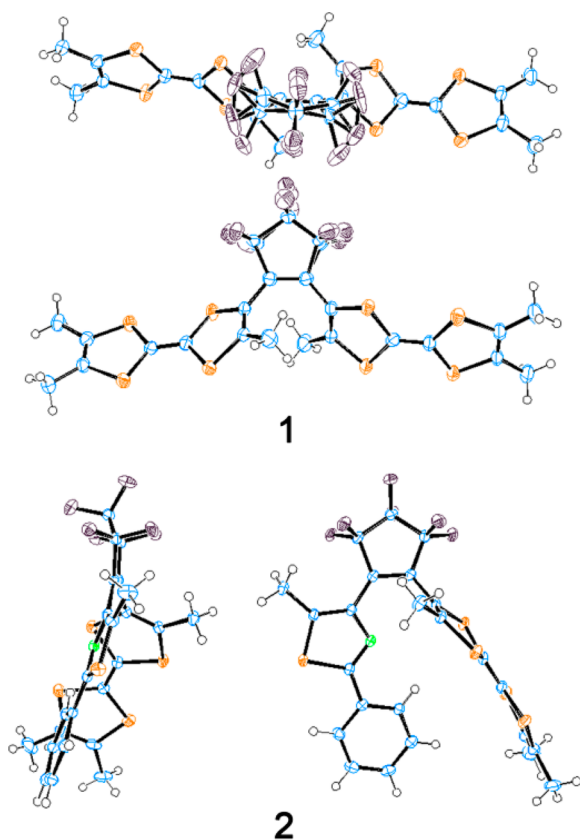


Figure 3. ORTEP diagrams of the molecular structures of **1** (top-down and front views) and **2** (side and front views) in the crystalline state. Conformational disorder of the perfluorocyclopentene ring is observed in compound **1**.

adopts an antiparallel conformation in the crystalline state with dihedral angles of 49.6° and a distance between the active carbons of 3.71 \AA , which is in the range of reported photoactive DAEs.³⁵ Still, no changes in the absorption spectrum were recorded upon irradiation of the crystalline powder. On the contrary, DAE **2** (Figure 3, bottom) displays a so-called edge-to-face relative orientation of the aryl units in which the TTF unit is placed nearly perpendicular to the cyclopentene ring (70° dihedral angle) while the phenylthiazole fragment is almost coplanar to the cyclopentene (20° dihedral angle). In addition to T-type aromatic interactions between the aryl units in such a disposition, the measured distance of 3.35 \AA suggests that a noncovalent S–N interaction between the N atom of the thiazole heterocycle and the closest S atom of the 1,3-dithiole ring could be contributing to stability as well.³⁶ An analogous conformation was found in the crystalline state of 1,2-bis(5-

methyl-2-phenyloxazol-4-yl)perfluorocyclopentene, and indeed, this DAE does not undergo photocyclization in the crystal yet proved to be photoactive in solution.³⁷

Electrochemistry. The electrochemical properties of the synthesized TTF–DAEs **1–5** (Table 1) were analyzed by cyclic voltammetry (CV). All TTF derivatives share a reversible 2-fold oxidation corresponding to the subsequent formation of the radical cation and dication of the TTF core(s) (Figure 4 and Figures S8–S10 in the Supporting Information). The lack of splitting in the first oxidation wave in the case of the TTF dimer **1** manifests that the two units do not experience Coulombic repulsions.^{24,31,38,39}

The inductive effect of the fluorine atoms of the perfluorocyclopentene ring in **1**, **2**, and **6** is denoted by both the increase of the first (E_{ox}^1) and second (E_{ox}^2) oxidation potential values regarding to reference TMTTF and the additional ability of these three novel compounds to undergo an irreversible reduction process. No electrochemically induced cyclization via the oxidation of the TTF unit was observed in any of the two DAEs **1** and **2**.

The changes in the redox potential upon the photocyclization of the photochromic TTF–DAEs **4** and **5** were detected by combining CV with UV (350 nm) irradiation (Figure 4 and Figure S9 in the Supporting Information). In addition to the two sequential oxidations originating from the TTF moiety, **4** undergoes a third irreversible oxidation ascribed to the dithienylcyclopentene core, which is most probably not observed in **5** due to the electron-withdrawing effect of the cyano group.

After UV light exposure, slight positive shifts in the range of 10–20 mV were observed for the first and second oxidation potentials. Simultaneously, the intensity of the second oxidation wave increased and a new oxidation wave around 0.56 V was recorded (Figure 4 and Figure S9 in the Supporting Information). We attribute these changes to the formation of the corresponding closed isomer, as evidenced by UPLC-MS, so that, in the closed form, the second oxidation wave originating from the TTF moiety overlaps with the first oxidation wave originating from the closed bridge unit. This assignment is supported by the cyclic voltammogram of the reference DAE 1,2-bis(5-(trimethylsilylethynyl)-2-methylthien-3-yl)cyclopentene **15** (Table 1 and Figure S9 in the Supporting Information). The effect of the largely altered DAE π -system on the TTFs' E_{ox} values is thus rather weak, and its magnitude is comparable to the effect observed in smaller TTF conjugated systems by their derivatization with different substituents.^{28,40,41} Nevertheless and most importantly, the electronic changes in the dithienylcyclopentene bridging unit can be most profitable for the gating of electron transfer to an acceptor unit in more sophisticated DAE-bridged TTF–acceptor architectures.

The low solubility of **3** in toluene and the facile formation of radical species by exposure of any halogenated solution to UV light would not allow a comparative study of the two isomeric forms' redox properties in the case of this symmetric DAE (Figure S10 in the Supporting Information).

Computation. Density functional theory (DFT) calculations were performed with Gaussian 03 (B3LYP, 6-31G(d))⁴² to assist in the understanding of the spectroscopic and electrochemical behavior of the two families of compounds.

Inspection of the electron density distribution of the frontier orbitals of **1**, **2**, and **6** (Figure 5) suggests that the HOMO \rightarrow LUMO transition has a CT character given that the HOMO is located primarily on the electron-rich TTF and the LUMO is

Table 1. Oxidation (E_{ox}) and Reduction (E_{red}) Potentials and Estimated HOMO–LUMO Gaps (E_{gap}) from the First Oxidation and Reduction Potential Values ($E_{\text{ox}}^1 - E_{\text{red}}^1$), from the Absorption Onset Wavelength (λ_{onset}), and from Theoretical Calculations (calcd) of the Prepared Compounds in the Open (o) and the Closed (c) Forms, When Applicable

compound		E_{ox} (V) ^a	E_{red} (V) ^{a,b}	E_{gap} (eV)		
				$E_{\text{ox}}^1 - E_{\text{red}}^1$	λ_{onset}	calcd ^c
1 ^d		0.05, 0.38	−1.88	1.93	1.81	2.43
2 ^d		0.01, 0.41	−1.91	1.92	2.00	2.61
6		0.04, 0.40	−2.33	2.37	2.25	2.86
3 ^e	o	−0.16, 0.33, 1.02 ^{e,f}				3.92 ^g
	c				1.83	2.08
4	o	−0.06, 0.31, 1.22 ^f				3.89 ^h
	c	−0.05, 0.32, 0.56 ^f	−2.12, −2.34	2.07	1.89	2.06
5	o	−0.10, 0.27	−2.45			3.43 ^h
	c	−0.09, 0.29, 0.57 ^f	−2.11, −2.25	1.99	1.83	1.90
TMTTF		−0.12, 0.27				
15	o					4.33
	c	0.34, 0.56	−2.17, −2.39	2.51	2.04	2.38

^aPotential values vs Fc/Fc⁺, toluene/acetonitrile 3:1 (10^{−3} M), supp. electrolyte TBAH (0.1 M), ref electrode Ag/AgNO₃, w. electrode Pt wire.

^bCathodic peak potential. ^cDFT calculations (B3LYP, 6-31G(d)). ^dOptimized from experimental X-ray geometries. ^eIn dichloromethane. ^fAnodic peak potential. ^gHOMO-2–LUMO gap. ^hHOMO-1–LUMO gaps.

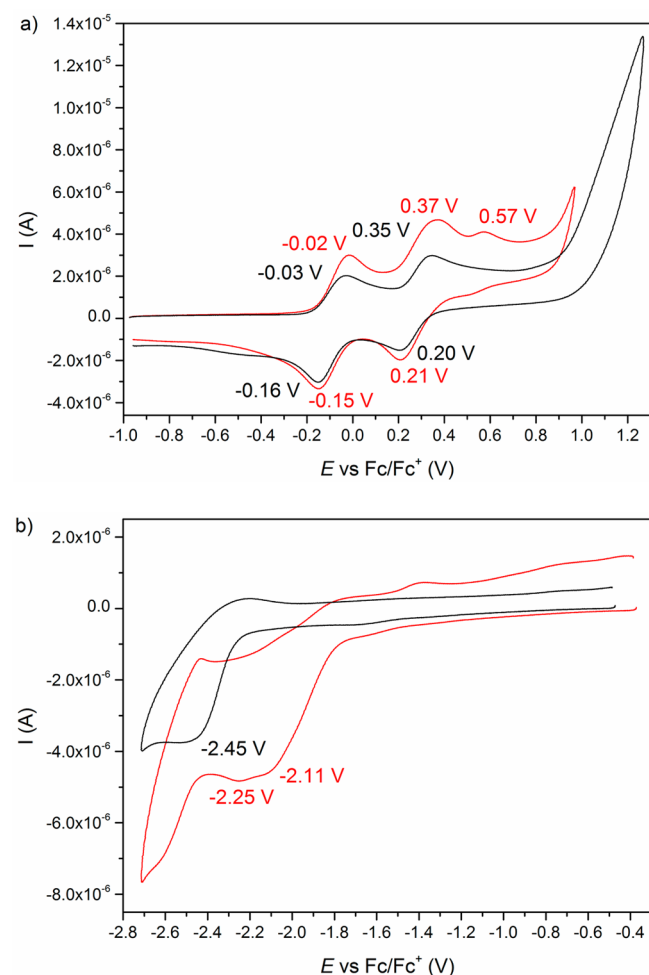


Figure 4. Cyclic voltammograms displaying (a) the oxidation and (b) the reduction processes of **5o** (black line) and of a **5o/5c** mixture (71:23, 6% byproduct, red line) generated by in situ irradiation with UV light (350 nm, 16 min) of the toluene/AN (3:1) solution (10^{−3} M); supporting electrolyte TBAH (0.1 M), reference electrode Ag/AgNO₃.

centered on the electron-poor perfluorocyclopentene bridge and to a smaller extent on the pending heterocyclic moiety. The trend in the calculated HOMO–LUMO gaps (E_{gap}) of the first series of DAEs are in line with the experimentally observed UV–vis absorption spectra; i.e., $E_{\text{gap}}(\mathbf{6}) > E_{\text{gap}}(\mathbf{2}) > E_{\text{gap}}(\mathbf{1})$ (Table 1).

The conformational and electronic aspects that can enhance or suppress photochromism in different diarylethene systems have been deeply explored by computational methods in previous works by Perrier and co-workers^{43–45} and by Staykov et al.,^{46,47} among others.^{48–50} From these investigations, it is known that many conditions must be fulfilled for a hexatriene system to undergo photocyclization. In addition to the right geometrical disposition of the open form, the promotion of an electron to an unoccupied MO with strong contribution of the reactive hexatriene carbon atoms must be allowed for photocyclization to occur; i.e., the transition to the reactive excited state should have a large enough oscillator strength. Moreover, steric hindrance can be detrimental for the stability of the closed form.⁴⁵

At a first glance, the orbital distribution of the LUMOs of **1o** and **2o** (Figure 5 and Figure S11 in the Supporting Information) as well as the calculated C–C distance for their optimized antiparallel conformations (3.67 and 3.70 Å, respectively) should fit the geometrical and electronic requirements for a ring-closure photoreaction, which is, however, experimentally not observed. Thus, photochromism efficiency in hexatriene systems cannot always be fully understood with the mere inspection of the ground-state frontier orbitals' topology.⁴⁵

Despite that the CT nature of the HOMO–LUMO transition in DAEs is not an impediment for photocyclization per se,^{45,48,51} for some open-ring DAEs based on maleic anhydride²¹ and maleimide,²² it was reasoned that relaxation of the excited state to a CT state competes with the ring-closure reaction. This was attributed to a better stabilization of a TICT state in more polar solvents. Taking these previous works into account and given the exceptional electron-donor character of the TTF aryl unit, it is tempting to conclude that UV irradiation of **1** and **2** may lead exclusively to a TICT transition state that would prevent the formation of the necessary transition-state

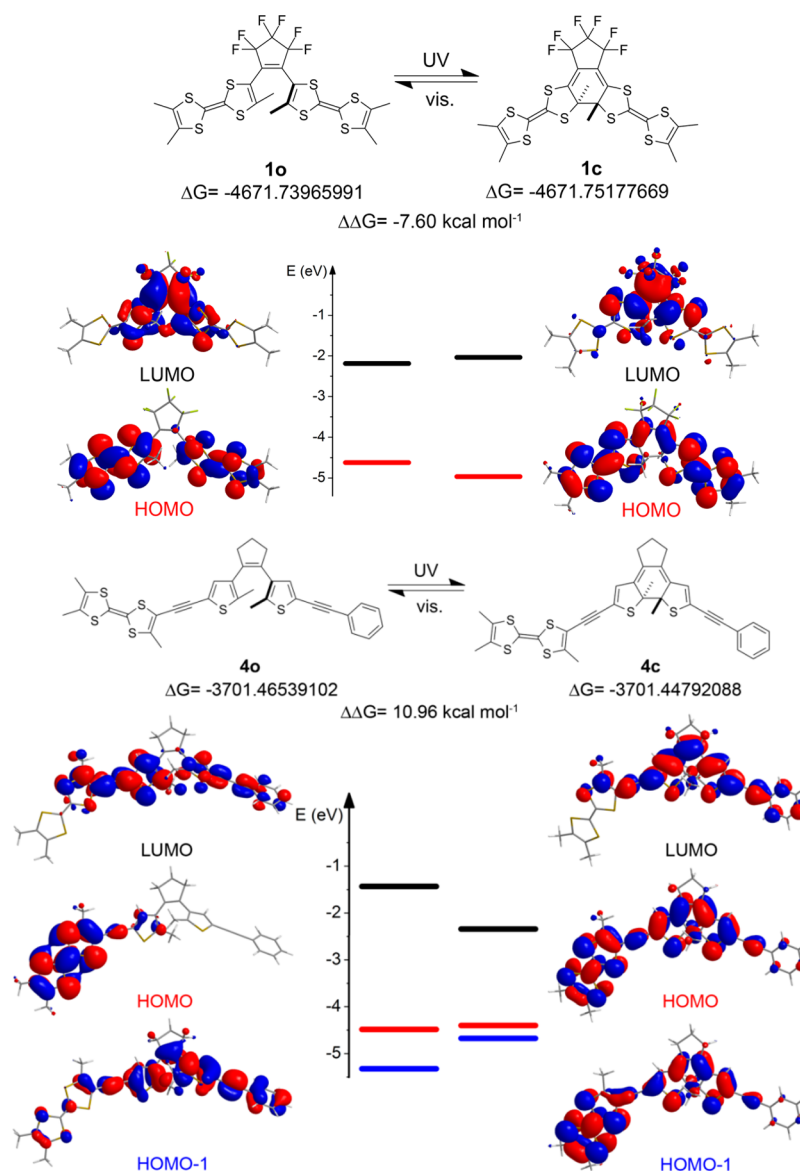


Figure 5. MO distribution and energies of **1o** and (hypothetical) **1c** (top) and **4o** and **4c** calculated by DFT/B3LYP 6-31G(d). HOMO-1, HOMO, and LUMO energies are represented with blue, red, and black lines, respectively. ΔG values are given in Hartrees. (For compounds **2**, **3**, **5**, and reference compound **15**, see Table S1 in the Supporting Information.)

geometries on the excited-state potential energy surface that yield ring closure. However, other unidentified energetic hindrances cannot be totally dismissed in the absence of detailed studies of the photoexcited states.

Calculations allow for the theoretical evaluation of electronic properties of the experimentally not accessible ring-closed isomers **1c** and **2c**, as well. Interestingly, ring closure does not render a higher HOMO energy in any case, as could be expected by referencing to related dithienylcyclopentenenes,^{46,47} but instead, the opposite trend is predicted (Figure 5 and Figure S11 and Table S1 in the Supporting Information). This surprising finding can perhaps be explained by the fact that the TTF scaffold itself is not strictly aromatic, and consequently, no aromaticity is formally lost upon cyclization.³⁴ This actually provides a better stabilization of the HOMO in the ring-closed isomer due to extension of conjugation relative to the open form, opposite to what occurs in DAEs featuring regular aromatic heterocycles.

The MO distributions and energies of the second series of TTF-DAEs, **3–5**, conversely, resemble those of the usual dithienylcyclopentenenes,^{46,47} as illustrated in Figure 5. The LUMO level is predicted to drop upon cyclization 0.91 eV for **3** and **4** and 0.58 eV for **5** (Table S1 in the Supporting Information). This prediction is qualitatively in agreement with the experimental positive shifts observed in the E_{red} after irradiation of **4** and **5**; that is, $\Delta E_{\text{red}} > 0.38$ V for **4o** \rightarrow **4c** (Table 1 and Figure S9 in the Supporting Information) and $\Delta E_{\text{red}} = 0.34$ V for **5o** \rightarrow **5c** (Table 1 and Figure 4). Notice that the solvation effects in the energy are not included in the gas phase calculations, thus contributing to the quantitative differences between the calculated and the experimentally determined shifts. It is worth to mention that, in **5o**, the LUMO extends over the thienyl ring with the benzonitrile moiety so that only one reactive carbon bears electron density. This does not prevent the system from photocyclization, similar to other examples in the literature, in which a small component

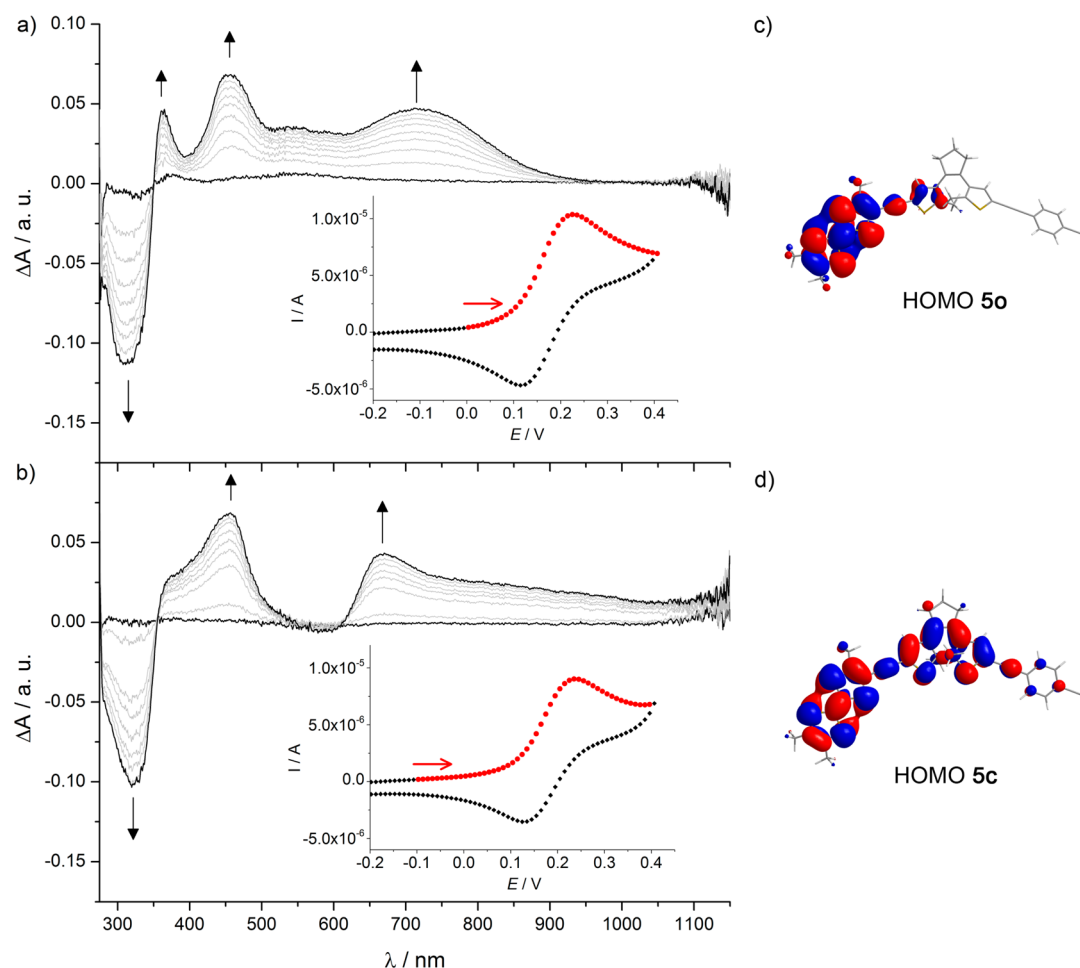


Figure 6. Differential absorption spectra of (a) **5o** (2.7×10^{-4} M) and (b) **5o/5c** (37:63, 3.0×10^{-4} M) in toluene/acetonitrile (3:1), recorded upon electrochemical oxidation to the respective radical cations. Insets show cyclic voltammograms (recorded vs Ag/AgNO₃, supporting electrolyte 0.1 M TBAH) with the red dots indicating the potential range at which the absorption spectra were recorded. On the right, the HOMO distributions for (c) **5o** and (d) **5c** from DFT calculations are shown.

on C-2 proved to be sufficient to allow photoinduced ring closure.^{48,49}

However, the photocyclization originates from the hexatriene centered HOMO-1 → LUMO transition in **4** and **5** instead of the regular HOMO → LUMO transition, whereas, in **3**, it may arise from a HOMO-2 → LUMO transition, since HOMO and HOMO-1 are almost degenerated and localized on the two TTF units.

Interestingly, the HOMO energy remains practically unchanged upon photocyclization, despite the changes in its electron density distribution (Table S1 in the Supporting Information). That is, the HOMO is located on the TTF moiety in **4o**, but it extends over the entire conjugated π -system on **4c**. Note that this optical transition assignment is in agreement with the results of the electrochemical analyses and the spectroelectrochemical studies discussed in the next section.

Spectroelectrochemistry. According to the changes in the HOMO distribution of **4** and **5** upon ring closure predicted by DFT calculations, a different stabilization of the radical cations could be expected in their open and closed forms. Notably, the absorption profiles of **5o** and of a mixture of **5o/5c** (37:63) evolved distinctly upon electrochemical oxidation to their corresponding radical cations (Figure 6). By generating **5o^{•+}**, a negative differential absorption (ΔA) peak at 310 nm was observed together with the growth of positive peaks at 362 and

454 nm, a plateau centered at 540 nm, and a broad band around 714 nm. Such a profile closely resembles the differential absorption spectrum of the TMTTF → TMTTF^{•+} oxidation process (Figure S12 in the Supporting Information). While this similarity evidences the localization of the radical cation on the TTF moiety in **5o^{•+}**, the broadening of the plateau in the 500–600 nm range and the bathochromic shift of the band in the red region (643 nm in TMTTF, 714 nm in **5o^{•+}**) indicate its further extension over the conjugated π -system⁵² comprising the triple bond and the thienyl moiety.

The differential absorption spectra recorded upon the oxidation of the **5o/5c** (37:63) mixture share with the open counterpart **5o^{•+}** and the TMTTF^{•+} reference both the negative peak (320 nm) and the positive peak (455 nm) in the UV range. However, in strong contrast to **5o^{•+}**, the longest wavelength absorption band of **5c^{•+}** is red-shifted and extends beyond the spectral range of the instrument used (>1150 nm). We attribute the absorption in the vis–NIR range to the more extended conjugation in closed **5c^{•+}** as compared to **5o^{•+}**. Complementary EPR spectra of **5o** and of the **5o/5c** mixture chemically oxidized with FeCl₃⁶ unfortunately did not display hyperfine coupling, thus not allowing us to gain any new significant insights into the degree of delocalization of the unpaired electron (see Figure S2 in the Supporting Information).

CONCLUSION

Diarylethenes containing TTF heterocyclic scaffold(s) as aryl unit(s) in two different architectures were synthesized, and their photochromic and electrochemical properties were investigated both experimentally and computationally. Integration of TTF cores in hexatriene systems featuring perfluorocyclopentene moieties resulted in nonphotoactive diarylethene. Twisted intramolecular charge transfer states deriving from the strong electron-donor character of TTF are suspected to hamper the photoinduced ring-closure processes, yet the pseudoaromatic nature of the 1,3-dithiole ring might play a role in the photoinactivity. However, the TTF entity can successfully be rendered photochromic by its attachment as a terminal unit to the 1,2-dithienylcyclopentene core through an ethynylene linker.

Interestingly, the HOMO energy and thus the oxidation potential of these photoswitchable TTF compounds undergo only minor variations upon ring closure. Nevertheless, the light-driven electronic changes in these new systems should allow for the reversible modulation of intramolecular electron transfer kinetics in TTF–DAE–acceptor architectures. Work in this direction is currently in progress in our and collaborating laboratories.

ASSOCIATED CONTENT

Supporting Information

Synthetic and analytical general methods, detailed synthetic procedures and characterization of the compounds, spectroscopic experiments, NMR studies, computational methods, and electrochemical analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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