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Artificial Photosynthesis

# Gating Charge Recombination Rates through Dynamic Bridges in Tetrathiafulvalene–Fullerene Architectures**

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Conversion of light into chemical energy is a process that nature has optimized over eons in photosynthetic organisms, such as bacteria, plants, and algae.[1] However, the search for non-natural systems that mimic the complex overall process of photosynthesis has remained a challenge. In particular, the key step of the initial light-induced charge separation between electron donors and acceptors is hampered by its inherent microscopic reversibility, that is, competing charge recombination.[2]

Well-defined molecular model systems typically comprise a donor (D) and an acceptor (A) covalently linked by a bridge (B). In the resulting D–B–A structures, the role of the bridge is ideally to facilitate the desired initial photoinduced charge separation, yet, to slow down the undesired charge recombination. Among the many combinations of donors and acceptors that have been explored, those consisting of proaromatic tetrathiafulvalene (TTF) and fullerene derivatives, such as $C_{60}$, have shown outstanding results. The exceptional electron donating and accepting properties originate from the aromatic stabilization of the formed TTF radical cation and from $C_{60}$'s unique three dimensional delocalized π-electron system, respectively. This last feature leads to low reorganization energies upon the reduction to the $C_{60}$ radical anion and allows for the uptake of up to six additional electrons.[2b,3] The photophysical properties of various TTF–$C_{60}$ conjugates featuring different π-conjugated molecular bridges have been investigated and charge-separated states with lifetimes ranging from a few nanoseconds up to hundreds of microseconds have been realized.[4] Of particular interest are conjugates with π-extended TTF derivatives, in which a conjugated *p*-quinoid anthracene moiety is placed between the TTF's two 1,3-dithiole rings.[4c]

Nevertheless, the design of such D–B–A architectures features inherent drawbacks. For example, even with optimized donors and acceptors, the bridge needs to play two opposing roles. On the one hand, it should enhance the coupling between D and A to facilitate the initial charge separation. On the other hand, once the charge-separated state has been formed it should prevent charge recombination by decoupling $D^{\bullet+}$ and $A^{\bullet-}$. Clearly, conventional, static bridges have to be a compromise of these two demands. However, if D and A are connected by a dynamic bridge, which can be switched between a coupled and a decoupled form, prolonged charge-separated state lifetimes could potentially be attained without compromising the initial charge separation. Such improved molecular design requires a switch entity that adopts two electronically distinct forms and allows for precise timing of the switching, that is, when the bridge is being coupled or decoupled. Dithienylethenes (DTE) are ideal candidates as switchable bridges as they reversibly interconvert between their ring-open (decoupled) and ring-closed (π-conjugated) forms upon irradiation with light of specific wavelengths.[5] Adopting this new strategy, we prepared four novel D–DTE–A structures connecting either TTF or exTTF acting as D and with $C_{60}$ functioning as A by photochromic dithienylperhydrocyclopentene or perfluorocyclopentene bridges (Scheme 1).

Some researchers have used photochromic units as light-responsive electronic traps that allow or prevent intramolecular electron transfer from D to A depending on the adopted isomeric form.[6] There are also some examples, in which the electron transfer kinetics are clearly altered by the structural modification of the bridging units by chemical inputs (chelation)[7] or, in mechanically interlocked D and A units, by topological changes.[8] However, herein, we show for the first time that in (ex)TTF–DTE–$C_{60}$ architectures, the lifetime of the charge-separated state can be significantly shortened or prolonged by performing light-induced structural changes in the bridging unit.

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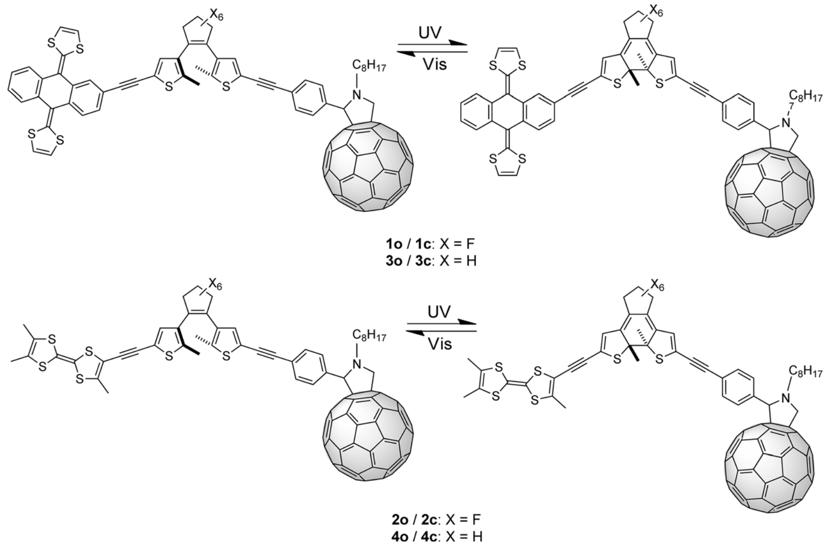
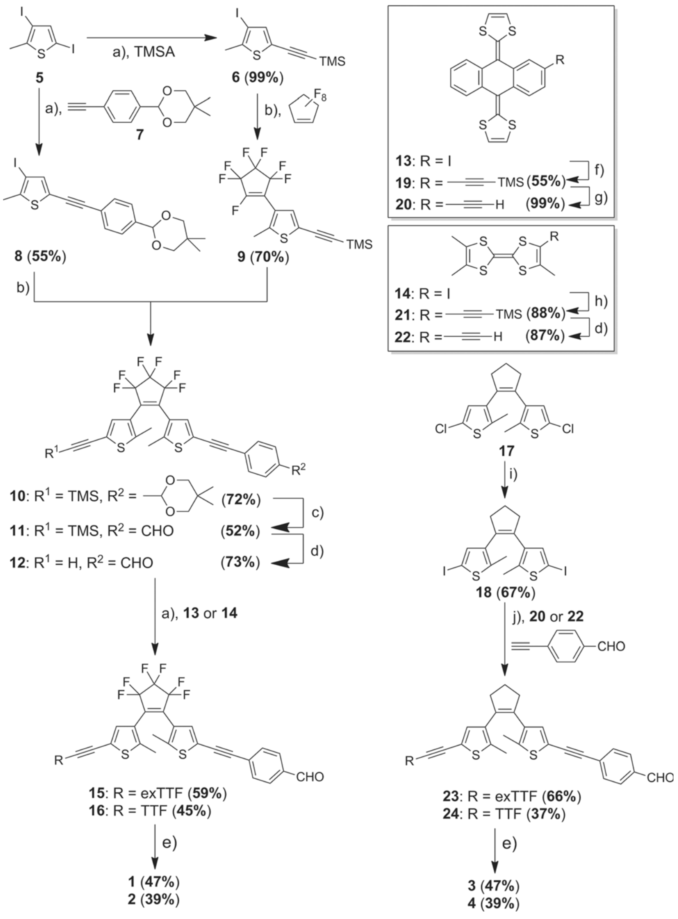


***Scheme 1.*** Open (**o**) and closed (**c**) forms of **1**–**4**.

In the four target structures **1**–**4** (Scheme 1) the electron acceptor was set to be $C_{60}$ connected to either TTF or exTTF electron donors by an electron-deficient dithienylperfluorocyclopentene bridge or an electron-rich dithienylperhydrocyclopentene bridge. Syntheses were achieved in a modular fashion, in each case attaching $C_{60}$ to an aromatic aldehyde by a Prato reaction[9] in the final step (Scheme 2). Compounds **1** and **2** were assembled by sequential nucleophilic substitution of octafluorocyclopentene with two different lithiated thienyl residues. One of them was connected to either TTF or exTTF by Sonogashira cross-coupling. The other thienyl scaffold carried an acetal-protected aldehyde function, which, after deprotection, allowed for the attachment of $C_{60}$ in the final step. Compounds **3** and **4** were obtained by stepwise Sonogashira coupling of the same functionalities to a pre-assembled diiodo-terminated dithienylcyclopentene bridge.[10] Details of the synthesis of **1**–**4**, their purification as well as all characterization data are gathered in the Supporting Information.

The photochromic properties of **1**–**4** were probed in toluene (Figure 1 and Supporting Information Figure S2 and S3). The absorption spectra of **1o**–**4o** isomers share as common features an intense band at 320–330 nm, a weak sharp peak at 434 nm, and a low-intensity broad band centered at 700 nm. The latter two are characteristics of [60]fullerene cycloadducts, as in the case of pyrrolidino-[3,4:1,2][60]fullerenes.[3d,11] Both exTTF-containing conjugates exhibited two additional maxima at 375 and 450 nm, which originate from the exTTF moieties.[12] TTFs are usually orange colored as a result of forbidden transitions in the 400



***Scheme 2.*** a) [Pd(PPh$_3$)$_2$Cl$_2$], CuI, THF/Et$_3$N; b) THF, *n*BuLi; c) TFA, THF/H$_2$O; d) K$_2$CO$_3$, MeOH/H$_2$O; e) $C_{60}$, *N*-octylglycine, toluene, Δ; f) [Pd(PPh$_3$)$_4$], CuI, *i*Pr$_2$NH, THF; g) K$_2$CO$_3$, MeOH/CH$_2$Cl$_2$; h) [Pd(PPh$_3$)$_2$Cl$_2$], CuI, TMSA, toluene/Et$_3$N; i) *n*BuLi, THF, I$_2$; j) [Pd(PPh$_3$)$_4$], CuI, toluene/*i*Pr$_2$NH.

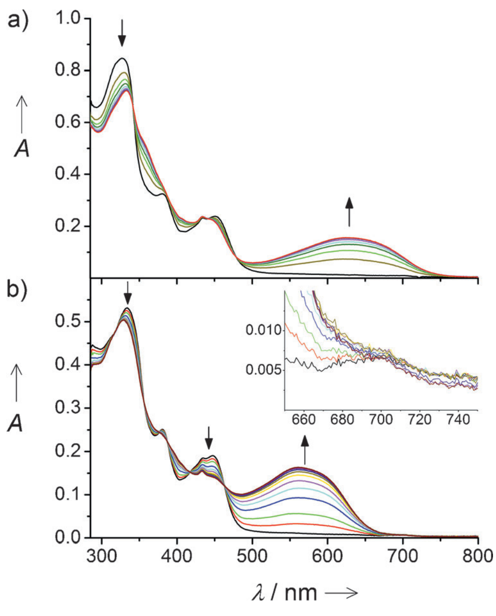


***Figure 1.*** Evolution of the absorption spectra of a) **1o** ($9.5\times10^{-6}$ M) and b) **3o** ($6.8\times10^{-6}$ M) in argon-saturated toluene at 25 °C upon exposure to UV light (325 nm, 70 s and 180 s, respectively, giving **1c** and **3c**). Inset: expansion of the $C_{60}$-cycloadduct band at 700 nm.

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to 500 nm region, although in **2** and **4** this band is masked by more intense transitions in the UV region.

In the absence of oxygen, illumination of toluene solutions of **1o**–**4o** with UV light results in the growth of a new band in the visible region accompanied by a decrease of the intense band in the UV region (Figure 1 and Supporting Information Figure S2). These changes are attributed to ring-closure to yield **1c**–**4c**, as could be confirmed by $^1$H NMR spectroscopy (shown for **1** in Supporting Information Figure S6). The signals for the aromatic protons of the thienyl units in **1o** shift drastically upfield by about 1 ppm as the conjugated octatetraene system of **1c** is formed. Ring-closure is furthermore associated with a significant downfield shift of the methyl singlets from $\delta = 1.8$ to 2.4 ppm. Note that an analogue of **1**, in which the pyrrolidinofullerene was linked to thiophene by a single bond instead of a phenylethynyl spacer (Supporting Information Scheme S1 and Figure S5) does not exhibit any photochromism. A similar inhibition of photoactivity has been reported for DTEs featuring porphyrins in the absence of long spacers.[13]

The presence of electron-withdrawing fluorine atoms in the bridge in **1o** and **2o** does not modify the absorption features relative to the perhydro analogues **3o** and **4o**. In contrast, the respective fluorinated ring-closed isomers **1c** and **2c** exhibit pronounced red-shifts of the absorption maxima when compared to their non-fluorinated counterparts **3c** and **4c**, respectively. This bathochromic shift in perfluorocyclopentene-based DTEs leads to an overlap with the $C_{60}$ centered band at 700 nm (Figure 1).

The different nature of the bridge in the DTEs strongly influences the photoconversion, that is, the ratio of closed/open isomers in the photostationary state (PSS) as determined for each compound by HPLC-UV (Supporting Information Figure S7). While close to quantitative photoinduced ring-closure was noted for non-fluorinated DTEs **3c** (95 %) and **4c** (91 %), their fluorinated counterparts **1c** and **2c** yielded only 37 and 43 %, respectively. Quantum yield values in the order of $10^{-3}$ were estimated for photochemical ring-closure, which are comparable to those reported by Osuka and Irie for related dithienylethene-bridged diporphyrin systems.[13] A likely rationale involves the superposition of $\pi\rightarrow\pi^*$ transitions, which are responsible for the photocyclization, with the absorption bands associated with donors and acceptors in the UV region. Thus, by the absorption of photons within this range of energy, vertical excitations from the ground state to inactive excited states dominate.[14]

Cycloreversion was initiated by irradiating the PSS mixture with visible light (> 500 nm) leading to a decrease of absorption in the visible region and an increase in the UV as well as in the 400–500 nm range (Supporting Information Figure S3). Full reversibility was observed for ring-opening of **1c**, while conversion of **3c** into **3o** was incomplete. We hypothesize that the perhydrocyclopentene **3** undergoes a side-reaction known for dithienylcyclopentenes that yields a rearranged byproduct.[5a]

The redox potentials of **1o**–**4o** and of their photostationary states after UV irradiation were measured by cyclic voltammetry (Table S1 and Supporting Information Figure S8). DTEs **1o**–**4o** display the electrochemical features originating from the pyrrolidino[60]fullerene moiety, that is, up to three reversible one-electron reductions at almost identical potentials ($E_{\text{red}}{}^1$ from −0.81 V to −0.84 V, $E_{\text{red}}{}^2$ from −1.21 V to −1.27 V vs. Ag/AgNO$_3$). On the contrary, their oxidations depend on the donors present in the DTE, namely **1o** and **3o** undergo one two-electron quasi-reversible oxidation ($E_{\text{ox}}{}^1 = 0.20$ V and $E_{\text{ox}}{}^1 = 0.28$ V vs. Ag/AgNO$_3$,respectively) ascribed to the formation of the exTTF dication, while **2o** and **4o** reveal two one-electron oxidations ($E_{\text{ox}}{}^1 = 0.21$ V, $E_{\text{ox}}{}^2 = 0.50$ V and $E_{\text{ox}}{}^1 = 0.21$ V, $E_{\text{ox}}{}^2 = 0.53$ V vs. Ag/AgNO$_3$, respectively) attributed to the successive formation of the radical cation and dication of TTF.

Upon irradiation with UV light (365 nm) until the photostationary state is attained, all redox potentials in DTEs **1c** and **3c** remained practically unchanged. However, in the PSS mixtures of **2** and **4** an anodic shift on the order of 60 to 100 mV was observed in both the oxidation and reduction potentials as compared to their ring-open analogues. Note that after photocyclization the perfluoro DTEs **1c** and **2c** display new irreversible reductions at −1.12 and −1.02 V and oxidations at 0.87 and 1.08 V, respectively, originating from the ring-closed form of the bridge.

The lack of changes in the reduction potentials after ring-closure can be reasoned by the presence of the pyrrolidine ring, which interrupts the conjugation between the DTE and the $C_{60,}$ thus isolating the $C_{60}$ electronically. However, an increase in the HOMO energy in **1c**–**4c** was expected as a result of the more extended conjugated π-systems as compared to **1o**–**4o**. Note that these results are not in contradiction with the observed large shifts of the absorption of **1**–**4** during ring-closure, since HOMO and LUMO may be located on the donor and acceptor units, respectively, in both open and closed isomers, whereas the molecular orbitals located on the bridge and responsible for the photocyclization can correspond to levels below (HOMO$-n$) and above (LUMO$+n$) the frontier orbitals. Thus the changes in the wavelength of the optical $\pi\rightarrow\pi^*$ transition in **1**–**4** do not originate from changes of the HOMO and LUMO levels (see Supporting Information)[14] and so the redox potentials remain unaltered upon ring-closure. Nevertheless and most importantly, the photoinduced changes in the electronic structure of the bridge proved to play a crucial role in the electron-transfer processes of **1**–**4**, as discussed below.

To shed light onto the electron transfer dynamics of these novel D–DTE–A structures, in general, and onto the influence that the ring-open or the ring-closed forms of the bridges exert on the electron transfer pathways, in particular, we turned to transient absorption measurements upon femtosecond excitation. The distinctly different absorption changes in the visible and in the near-infrared regions of **1**–**4o/c** upon light irradiation provide clear evidence for different decay mechanisms in the two isomers of each DTE (Figures 2 and 3 and Supporting Information Figures S10–13).

DTEs **1o** and **3o** were pumped with 505 nm laser pulses to avoid local excitation of the open bridge and, thus, photoconversion. Compounds **1o** and **3o** in toluene, THF, and benzonitrile instantaneously formed transient maxima at 515, 640, and 920 nm as well as transient minima at wavelengths shorter than 450 nm. In line with the corresponding reference experiments,[2b,3f,15] we assign these features to the singlet excited states of $C_{60}$, ($^{1*}C_{60}$ at 515 and 920 nm) and exTTF ($^{1*}$exTTF at 640 and at wavelengths shorter than 450 nm), respectively. Instead of, for example, slow $^{1*}C_{60}$ to $^{3*}C_{60}$ intersystem crossing, an ultrafast decay occurs simultaneously with the development of new transitions in the visible region between 550 and 700 nm that are attributed to the one-electron oxidized bridge (oDTE$^{\bullet+}$)[16] and the one-electron reduced radical anion of $C_{60}$ ($C_{60}^{\bullet-}$) in the near-infrared region at 1020 nm (Figure S10).

Therefore, the initially formed $^{1*}C_{60}$ undergoes charge separation in 3.5 ± 0.5 and 4.7 ± 0.5 ps for **1o** and **3o**, respectively, in THF, and, as such, transforms into the adjacent D–oDTE$^{\bullet+}$–A$^{\bullet-}$ (Figure 3) charge-separated states.

Multiwavelength analyses corroborated, however, the metastability of the adjacent charge-separated states. Interestingly, their lifetimes depend on the nature of the bridge, that is, perhydro (752 ± 35 ps) versus perfluoro (1150 ± 50 ps) in THF and on the polarity of the solvent, that is, toluene ($\tau_{3o} = 1045 \pm 50$ ps) versus benzonitrile ($\tau_{3o} = 505 \pm 25$ ps). The spectral features indicate a competition between charge recombination to yield the $C_{60}$ triplet excited state ($^{3*}C_{60}$ at 690 nm) and charge shift to yield the distant D$^{\bullet+}$-oDTE-A$^{\bullet-}$ (Figure 3) charge-separated states featuring the one-electron oxidized exTTF (exTFF$^{\bullet+}$ at 460/510/680 nm) and the one-electron reduced radical anion of $C_{60}$ ($C_{60}^{\bullet-}$ at 1020 nm). The lifetimes of D$^{\bullet+}$–oDTE–A$^{\bullet-}$ states exceed the time scale of our femtosecond experiments and were determined in complementary nanosecond experiments (Figure S11). In line with the competitive formation of the $C_{60}$ triplet excited state and the distant D$^{\bullet+}$–oDTE–A$^{\bullet-}$ charge-separated state, the differential absorption spectra on the nanosecond time scale are best described as the superposition of the $C_{60}$ triplet excited state ($^{3}C_{60}$* at 690 nm) and the D$^{\bullet+}$–oDTE–A$^{\bullet-}$ charge-separated state (exTFF$^{\bullet+}$ at 460/510/680 nm[17] and $C_{60}^{\bullet-}$ at 1020 nm), respectively. The kinetics described by the decays of exTTF$^{\bullet+}$ at 460/510 nm and of $C_{60}^{\bullet-}$ at 1020 nm obey clean unimolecular rate laws, implying no other competing pathways in the charge recombination, resulting in lifetimes of 59.8 ± 5.0 and 31.5 ± 3.0 ns for **1o** and **3o**, respectively, in THF.[18]

At first glance, photocyclization of DTEs **1** and **3** led to similar changes in the transient absorption measurements. Upon excitation with pulses of 387 nm, which was meant to prevent photoreversion, the ring-closed forms display, in addition to the $^{1*}C_{60}$ fingerprint at 920 nm, maxima at 485, 745, and 840 nm as well as a minimum at 610 nm for **1c** and maxima at 475, 690, 820, and 1020 nm

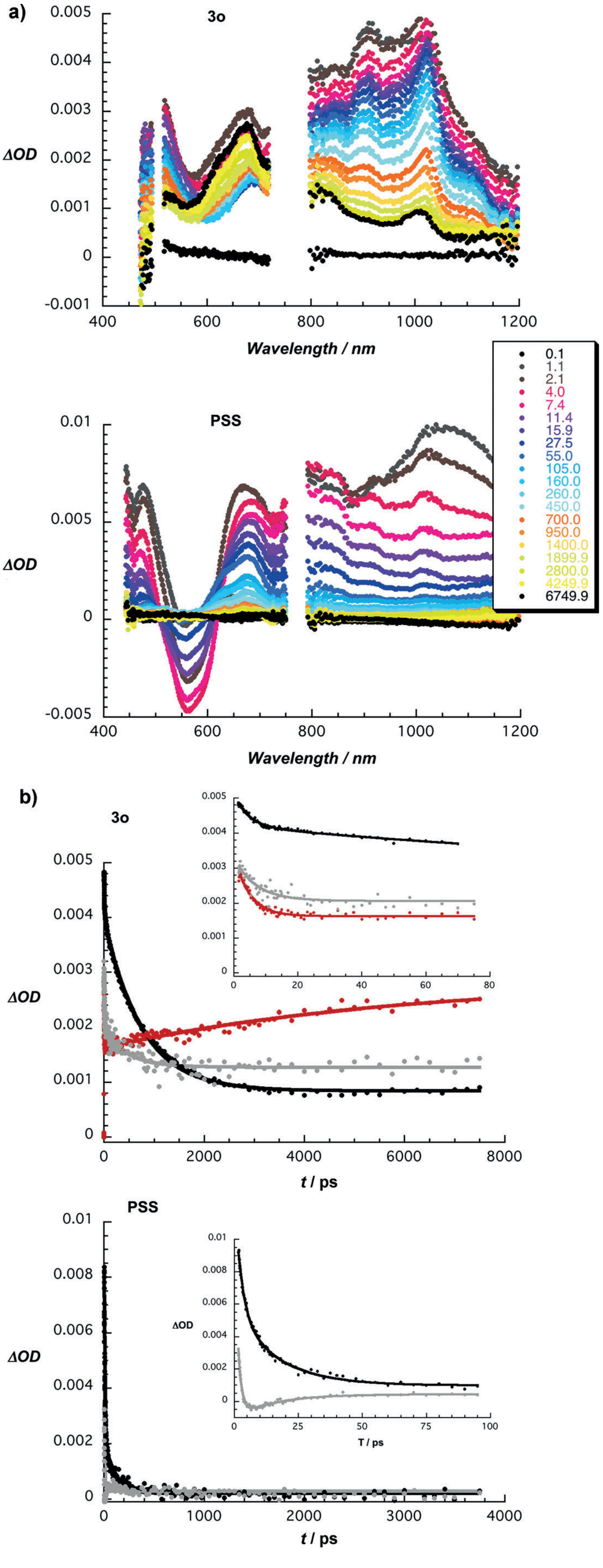

*Figure 2.* a) Transient absorption spectra of **3o** and **3o**/**3c** mixture in the photostationary state (PSS) in argon-saturated THF ($10^{-4}$ M) upon pump probe experiments (505 nm, 200 nJ for **3o** and 387 nm, 200 nJ for PSS). b) Time absorption profiles monitoring the charge-transfer dynamics at the fingerprints of exTTF$^{\bullet+}$ (510 nm, gray), $^{3*}C_{60}$ (680 nm, red), and $C_{60}^{\bullet-}$ (1020 nm, black).

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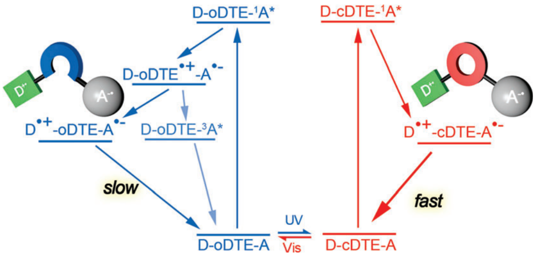

*Figure 3.* Charge separation and recombination pathways in D–B–A compounds **1–4** featuring photochromic DTE bridges for the modulation of the charge-separated states' lifetimes.

as well as a minimum at 575 nm for **3c** reflecting excited states that involve the switching unit.[19] Notably, the minima for the excited states of **1c** and **3c** mirror the maxima seen in the ground state absorption. Both of these excited states decay rather quickly (2.5 ± 0.2 ps) in THF. A closer look infers that a likely deactivation mechanism is the evolution to the distant $D^{\bullet+}$–cDTE–$A^{\bullet-}$ charge-separated states by passing the adjacent D–cDTE$^{\bullet+}$–$A^{\bullet-}$ charge-separated states, as supported by the spectral features at the end of the excited state decay with maxima of exTTF$^{\bullet+}$ at 510/680 nm and of $C_{60}^{\bullet-}$ at 1020 nm (Figure S10). The $D^{\bullet+}$–cDTE–$A^{\bullet-}$ species exhibited rather fast charge recombination and displayed shorter lifetimes in more polar benzonitrile ($\tau_{3c} = 130 \pm 5$ ps) than in less polar toluene ($\tau_{3c} = 1845 \pm 50$ ps). A qualitatively similar behavior was observed for DTEs **2c** and **4c** and their corresponding PSS mixtures, which display the TTF$^{\bullet+}$ fingerprint at 420 nm[4a] (Figure S10 and S11).[20]

Most remarkably, the recorded lifetimes ($\tau$) of the distant $D^{\bullet+}$–DTE–$A^{\bullet-}$ charge-separated states in the ring-open forms are up to two orders of magnitude longer than in the closed forms (Table 1), as deduced form the distinct kinetic traces of $D^{\bullet+}$ and $A^{\bullet-}$ in each case. We attribute the different recombination rates to the structural changes undergone by the photochromic bridge that connects $C_{60}$ and exTTF and/or TTF. The charge recombination in the open isomers, $D^{\bullet+}$–oDTE–$A^{\bullet-}$, presumably occurs by a tunneling mechanism with no participation of the non-conjugated bridging unit. On the contrary, the fast decay in the case of the $D^{\bullet+}$–cDTE–$A^{\bullet-}$ states is attributed to the extended π-conjugation throughout the ring-closed bridging unit. In other words, the lifetimes of the charge-separated states are controlled by the photochromic bridge that governs the electronic coupling between the donors and acceptors (Figure 3). Note that the presence or absence of fluorine atoms in the bridge has a rather minor effect on the charge-transfer kinetics.

*Table 1:* Lifetimes ($\tau$) of the D–DTE$^{\bullet+}$–$A^{\bullet-}$ and $D^{\bullet+}$–DTE–$A^{\bullet-}$ charge-separated states.[a]

| DTE | Compound[b] | | $\tau$ [ps]<br>D-DTE$^{\bullet+}$-A$^{\bullet-}$ | <br>D$^{\bullet+}$-DTE-A$^{\bullet-}$ | $\tau_o/\tau_c$[c] |
|---|---|---|---|---|---|
| $F_6$ | **1** (exTTF) | o | 1150 | 59800[e] | 164 |
| | | PSS[d] | – | 364 | |
| | **2** (TTF) | o | 950 | 73100[e] | 54 |
| | | PSS[d] | – | 1345 | |
| $H_6$ | **3** (exTTF) | o | 752 | 31500[e] | 94 |
| | | PSS[d] | – | 336 | |
| | **4** (TTF) | o | 810 | 54400[e] | 48 |
| | | PSS[d] | – | 1135 | |

[a] Results obtained upon photoinduced electron transfer in THF solutions of DTEs **1–4** in their open form (o) and in their photostationary state mixture (PSS) forms featuring perfluoro ($F_6$) or perhydro ($H_6$) bridges (DTE). [b] Excitation wavelengths of 505 nm (open isomer) and 387 nm (closed isomer). [c] $\tau_o$ and $\tau_c$ denote the $D^{\bullet+}$–DTE–$A^{\bullet-}$ charge-separated state lifetimes in the open and closed forms, respectively. [d] After irradiation with 313 nm light (ca. 45 min). [e] Measured on the nanosecond scale.

In summary, we have prepared new molecular constructs composed of electron-donating tetrathiafulvalene (TTF) and π-extended-TTF derivatives covalently connected to electron-accepting pyrrolidino[3,4:1,2][60]fullerene through photoswitchable dithienylethene bridges. By exposure to a light stimulus the bridge can be interconverted between a decoupled ring-open and a coupled ring-closed form and, hence, enables external control of electronic communication between the donor and acceptor units. In the resulting architectures, incoming photons give rise to efficient charge separation and, furthermore, allow modulation of the lifetimes of the charge-separated states over two orders of magnitude by variation of their wavelength. The photoresponsive, dynamic bridge provides a means for (self-)regulation through a reversible activation-deactivation mechanism for solar energy conversion in artificial photosynthetic systems.[21] Our approach thus holds promise for the design of improved systems for solar energy conversion.

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[18] For **2o** and **4o**, only the singlet excited states of $C_{60}$ ($^{1*}C_{60}$ at 515 and 920 nm) were detected because of the lack of TTF ground state absorption. These were seen to transform via the adjacent D-oDTE$^{\bullet+}$-A$^{\bullet-}$ charge-separated state to either the distant D$^{\bullet+}$-oDTE-A$^{\bullet-}$ charge-separated state (TFF$^{\bullet+}$ at 420 nm and $C_{60}^{\bullet-}$ at 1020 nm) or the $C_{60}$ triplet excited state ($^{3*}C_{60}$ at 690 nm) with 950 ± 50 and 2780 ± 140 ps for **2o**, respectively. In THF, the accordingly formed D$^{\bullet+}$-oDTE-A$^{\bullet-}$charge-separated states have lifetimes of 73.1 ± 5.0 ns for **2o** and 54.4 ± 2.0 ns for **4o**.

[19] All of these transient maxima and minima are in sound agreement with reference experiments conducted with the closed form of the switching unit, in which they were noted to deactivate rather quickly, within 10 ps (Supporting Information Figure S13).

[20] Complementary nanosecond experiments with **1c**–**4c** resulted in no detectable transients.

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