Photoswitches

Reversible Photomodulation of Electronic Communication in a π -Conjugated Photoswitch-Fluorophore Molecular Dyad

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Abstract: The extent of electronic coupling between a boron dipyrromethene (BODIPY) fluorophore and a diarylethene (DAE) photoswitch has been modulated in a covalently linked molecular dyad by irradiation with either UV or visible light. In the open isomer, both moieties can be regarded as individual chromophores, while in the closed form the lowest electronic $(S_0 \rightarrow S_1)$ transition of the dyad is slightly

Introduction

Molecular switches, which upon irradiation with light efficiently and reversibly interconvert between two stable isomers, have been widely studied in the past and continuously improved.^[1-5] Nowadays their accurate and on-demand implementation in complex molecular systems is possible with applications for such nanoengineered constructs ranging from optoelectronic devices to stimuli-responsive materials.^[6,7] Diarylethenes (DAEs)^[8] experience a dramatic increase in conjugation upon photoinduced isomerization with UV light, and some of their derivatives possess a high fatigue resistance.^[5,8] These attributes can be exploited to modulate or even unlock secondary functions at the molecular or supramolecular level by using light as a remote control with high spatial and temporal resolution.^[9] Among the many chemical and physical properties of molecular switches, fluorescence emission is of particular importance since fluorescent molecules can be used as probes for intracellular processes^[10-12] as well as for optical recording materials with fluorescence readout.[13-16] Furthermore, stable photoswitchable fluorophores are specifically required in novel super-resolution techniques capable of overcoming the diffraction limit of light.[17-19]

Several approaches have been followed to modulate the emission of fluorophores in compounds bearing an attached photochromic DAE derivative. In most of these fluorophore– shifted, enabling photomodulation of its fluorescence. Transient spectroscopy confirms that the dyad behaves dramatically different in the two switching states: while in the open isomer it resembles an undisturbed BODIPY fluorophore, in the closed isomer no fluorescence occurs and instead a redshifted DAE behavior prevails.

photoswitch dyads, either electron or energy transfer is responsible for the fluorescence modulation,^[20-23] whereas the initial open isomer is strongly emissive while the photochemically generated closed isomer exhibits a diminished fluorescence emission. If, for example, energy transfer is responsible for fluorescence quenching (demanding spectral overlap of the fluorophore emission with the closed photoswitch absorption),^[24,25] the excitation energy of the fluorophore is funneled to the closed isomer. This leads to formation of the open isomer, causing a destructive read-out, which is a typical phenomenon encountered in these so called turn-off fluorescence switches.

Linking the fluorophore and the DAE via a π -conjugated bridge enables direct electronic coupling and therefore lightinduced formation of the closed isomer is efficiently transduced to the fluorophore. The associated increased conjugation throughout the entire (bi)chromophore system will lead to a bathochromic shift of the lowest-energy electronic $(S_0 \rightarrow S_1)$ transition (Figure 1). Importantly, if the fluorophore is chosen in such a way that its emission does not overlap with the DAE absorption, it can be anticipated that no cycloreversion would occur during read-out. In fact, a molecule designed following this working principle could be fluorescent in both the initial and the other photoswitched state, enabling true reversible photomodulation of its emission on demand. Considering the stringent molecular design outlined above, a potent fluorophore with an absorption band red-shifted from the closed DAE isomer has to be employed. We therefore chose a benzofused boron dipyrromethene (BODIPY) dye and attached it to a DAE photoswitch via a modular phenylene ethynylene spacer to be able modulate the strength of the coupling between the two components while maintaining photochromism.^[26] The specific benzothiophene derived DAE was selected due to its relatively blue-shifted absorption band in the closed isomer as well as outstanding fatigue resistance.^[7]

Herein, we report the novel BODIPY-DAE dyad 1, including its synthesis and photophysical and photochemical properties,

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Figure 1. Concept of photomodulation of fluorescence in π -conjugated DAE-BODIPY dyad 1: Chemical structures and photochromism and associated representation of the envisioned bathochromically shifted $S_0 \rightarrow S_1$ transition of the BODIPY fluorophore, in principle enabling dual fluorescence and non-destructive readout.

including both stationary and transient spectroscopic characterization. Our results are relevant for the design of molecular systems that enable photocontrol of fluorescence without involving energy transfer while at the same time providing a deeper understanding of electronic coupling in photochromic molecular dyads.^[20, 27]

Results and Discussion

Synthesis

The synthesis of target DAE-BODIPY dyad 1 (Scheme 1) was accomplished in a modular convergent fashion, coupling BODIPY 6 to DAE 4 in the final step following a sequence of desilylation, lithiation, stannylation, and Pd-catalyzed Stille alkynylation reactions. On the one hand, the non-symmetrical DAE 4 was obtained by a sequential nucleophilic substitution of octafluorocyclopentene with two different lithiated hetaryl, that is, thiophene and benzothiophene, residues. The preparation of building block 2 from 2,4-dibromo-5-methylthiophene via Suzuki cross-coupling with a suitable phenylethynylene was straightforward. The synthesis of benzothiophene 3 was vastly optimized when compared to previous reports where at least three equivalents of the rather expensive and volatile octafluorocyclopentane had to be employed.[28] In our own initial work related to the synthesis of symmetrical DAE precursors, we observed that employing Et₂O instead of THF as the solvent had a dramatic effect on the reaction, leading to isolation of exclusively the mono-coupled product despite the use of a two-fold excess of lithiated benzothiophene. This important observation was adapted in our new method, which now uses only an equimolar amount of octafluorocyclopentene and lithitated methylbenzothiophene. Indeed, lithiation of 3-bromomethyl-benzo[b]thiophene in anhydrous Et₂O at -78°C with n-BuLi, and subsequent addition of one equivalent of octafluorocyclopentene led to quantitative formation of 3 and an excellent 92% yield after purification by column chromatography. Our optimized reaction conditions are generally applicable for the cost-efficient preparation of new non-symmetrical DAEs with exceptional fatigue resistance. On the other hand, synthesis of the precursor BODIPY fragment 6 was accomplished by an initial reduction of phthalimide with AICl₃ under superacidic conditions and high pressure in cyclohexane to yield isoindoline,^[29,30] which was subsequently chloroformylated under modified Vilsmeier-Haack conditions,^[31] yielding compound 5. Final treatment with POCl₃ under basic conditions accompanied by addition of kryptopyrrole and after complexation with BF₃·OEt₂ yielded BODIPY 6. Model compound Ph-bdp was ob-



Scheme 1. Synthesis of DAE-BODIPY dyad 1 and reference compound Ph-bdp.

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tained by Stille alkynylation of **6** with tributyl(phenylethynyl)stannane. Further details of the synthesis of all compounds, their purification, and all characterization data are collected in the Supporting Information.

UV/Vis spectroscopy

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After their successful preparation, the photochromic behavior of DAE-BODIPY dyad 1 and also the DAE moiety 4 was investigated. The absorption spectrum of the open DAE isomer 4-o in CH_2Cl_2 (Figure 2, top right) exhibits a broad intense band in



Figure 2. UV/Vis absorption spectra and photoinduced ring-closure of DAE-BODIPY dyad 1 (left) and DAE unit 4 (right). Top: absorption spectra of the open isomer (——), the PSS (-----), and the calculated pure closed isomer (-----) in CH₂Cl₂ at 25 °C are shown. Bottom: evolution of the absorption spectra during the course of ring-closure induced by irradiation with UV light (λ_{irr} = 313 nm) in CH₂Cl₂ at 25 °C.

the UV region, which is attributed to the $\pi \rightarrow \pi^*$ singlet-singlet transition. Upon irradiation with 313 nm UV light, the growth of an intense band within the 460-650 nm range and another yet less intense broad band between 370-460 nm was observed (Figure 2, bottom right). The buildup of the long wavelength band indicating formation of the closed isomer 4-c was accompanied by a simultaneous decrease of the intense-band UV absorption centered at 318 nm. The ratio of the open and closed isomers in the photostationary state (PSS) 4-o:4-c of DAE 4 was estimated as 15:85 based on the analysis of the ¹H NMR spectrum of the PSS mixture. The isomerization quantum yield for the cyclization at 313 nm was determined as $arPsi_{
m o
ightarrow}$ $_{\rm c}$ = 0.63. This value is relatively high and is most likely due to a preferential population of the photoactive anti-parallel conformation in solution. Upon irradiation of the closed isomer (PSS mixture) with visible light at 546 nm, cycloreversion was initiated with the concomitant rise of the 318 nm absorption maximum and decrease of the broad visible bands. The determined cycloreversion yield of $\varPhi_{\rm c\to o}{=}\,0.02$ is in the common range for phenyl substituted DAEs.^{[7]}

Inspection of the absorption spectrum of the DAE-BODIPY dyad 1-o (Figure 2, top left) shows a broad intense band in the UV region, which is ascribed to the $\pi \rightarrow \pi^*$ singlet-singlet transition of the DAE moiety. Note that the shape is significantly broadened in comparison to 4-o since in the same spectral region the $S_0 \rightarrow S_2$ transition of the BODIPY fluorophore is located. Furthermore, a comparison of the spectral characteristics of 1-o and 1-c in the UV region (Figure 2, bottom left) leads to the conclusion that the band originally corresponding to the $\pi \rightarrow \pi^*$ transition in the parent DAE **4-o** is bathochromically shifted and centered at 378 nm. The same effect is observed for the previously mentioned $S_0 \rightarrow S_2$ transition assigned to the BODIPY, which is red-shifted from 322 nm in model compound Ph-bdp (Supporting Information, Figure S1) to 333 nm in 1-o. The same red-shift is observed for the main $S_0 \rightarrow S_1$ transition of the BODIPY band centered at 624 nm in Ph-bdp and at 636 nm in 1-o. These spectral shifts are attributed to the electronic ground state coupling associated with an elongated π conjugated system in the dyad, established between the BODIPY system and the DAE photoswitch in its open isomer. Upon irradiation with 313 nm (Figure 2, bottom left), the intense $S_0 \rightarrow S_1$ transition centered at 636 nm associated with the BODIPY fluorophore markedly decreases accompanied by formation of a strong red-shifted shoulder owing to the build-up of an intense new band assigned to the BODIPY unit in the ring-closed dyad 1-c. Furthermore, ring-closure is associated with the growth of a less intense band in the 400-600 nm range as well as the decrease of the $\pi \rightarrow \pi^*$ transition at 378 nm assigned to the DAE unit.

The extent of photoconversion was measured by ultrahighperformance liquid chromatography coupled to mass spectrometry detection (UPLC-MS) and provided the isomer ratios 1-o:1-c in the PSS as 74:26 in acetonitrile and 56:44 in CH₂Cl₂, respectively. The quantum yield for the cyclization induced at 313 nm irradiation was determined as $\Phi_{o\rightarrow c}$ =0.004, which is common for fluorophore-photoswitch molecular dyads, since a large spectral overlap in the UV region imposes a low efficiency to address the electronic transition responsible for photochemical ring-closure.^[24] Upon visible-light irradiation at 546 nm, the cycloreversion was initiated with the concomitant raise of the 378 nm band and decrease of the broad visible bands. The determined cycloreversion quantum yield $\Phi_{c \rightarrow o} =$ 0.004 is relatively high for a DAE having such an elongated π system. Although the PSS attained by irradiation of 1-o with 313 nm is rather low, an emerging new band can be distinguished, which is significantly red-shifted to the fluorophore absorption maximum (636 nm). Performing a singular value decomposition (SVD) analysis, it was possible to obtain the simulated absorption spectrum of pure 1-c, which is in good agreement with the spectra obtained from the UPLC-traces and the ones calculated by differential subtraction (Supporting Information, Figure S3). Importantly, the absorption spectra of neither the open nor the closed isomer of the dyad are simply the sum of the spectra of reference BODIPY Ph-bdp and DAE 4, indicating an electronic coupling between both individual ChemPubSoc Europe

components. Importantly, the appearance of a new red-shifted absorption band upon photoisomerization validates the effect of increased electronic conjugation in the dyad upon cyclization.

Fluorescence spectroscopy

To investigate the change of electronic communication beyond the ground state, stationary fluorescence spectra of the dyad (Figure 3) and also the reference BODIPY **Ph-bdp** (Supporting Information, Figure S1) were also obtained and the key emission parameters determined (Table 1). As observed



Figure 3. Left: Corrected normalized fluorescence emission spectra of 1-o (——) and in the PSS (----) obtained in CH₂Cl₂ ($\lambda_{esc} = 600$ nm, $c \approx 10^{-6}$ M). Right: Relative fluorescence emission intensity upon alternating 313 nm (gray bar) and 690 nm irradiations (white bar) to carry out successive switching cycles of 1.

Table 1. Molar absorptivities, absorption maxima, emission maxima, Stokes shifts, and relative fluorescence quantum yields of 1-o and Ph-bdp in CH_2CI_2 .					
Compound	ϵ [10 ⁴ L mol ⁻¹ cm ⁻¹]	λ _{max} [nm]	$\lambda_{ m em}$ [nm]	Stokes shift [cm ⁻¹]	$\Phi_{\rm f}$
1-o Ph-bdp	10.8 9.5	636 624	644 631	195.3 177.8	0.63 0.66

for the absorption spectra, the maximum of the emission of 1-o is bathochromically shifted by 13 nm when compared to Ph-bdp. This red-shift can be explained with the increased length of the π -system in the dyad as compared to the parent BODIPY, in agreement with an electronic coupling between both moieties in the open form of the dyad. The relative fluorescence quantum yield determined for **Ph-bdp** was $\Phi_{\rm f}$ =0.66, which is in line with related BODIPY fluorophores.[32] Interestingly, the relative fluorescence quantum yield of 1-o was slightly lower ($\Phi_{\rm f}$ =0.63), which may be attributed to a fast intramolecular charge transfer process (ICT) from the electronrich thiophene to the BODIPY acceptor similar to those previously described previously.[33] On the contrary, the emission intensity of the PSS mixture (1-PSS), obtained after irradiation of 1-o with UV light, was significantly reduced (Figure 3, left). The associated degree of fluorescence guenching was determined to be of 44% in CH₂Cl₂ and of 26% in acetonitrile, corresponding to the actual amount of closed isomer (1-c) in the PSS mixture (Supporting Information, Figure S2). Importantly, upon cycloreversion with visible light the fluorescence emission could be completely restored, enabling several switching cycles to be performed without noticeable fatigue (Figure 3, right).

Transient absorption spectroscopy

To elucidate the origin of the fluorescence quenching in the closed form, ultrafast transient absorption (TA) spectroscopy was performed. Excitation of the PSS mixture of the reference DAE (**4-PSS**) at 600 nm (black circles in Figure 4, bottom) shows a fast relaxation (ca. 4 ps) to the ground state as known for other DAE derivatives^[34,35] (Supporting Information, Figure 56). In the case of the dyad **1-o** (gray squares in Figure 4, bottom) the BODIPY moiety is excited at 600 nm resulting in a very long-lived excited state with a life time of several nanoseconds (Figure 4, top). The signal consists of an excited state absorption (ESA) between 450 and 600 nm and a combination of ground state bleach (GSB) and stimulated emission (SE) at



Figure 4. TA data of **1-o** (top) and single transient traces (bottom) of GSB and ESA of **1-o** ($\lambda_{probe} = 642 \text{ nm}$, 503 nm, respectively) and **4-PSS** ($\lambda_{probe} = 572 \text{ nm}$ (with background subtracted), 465 nm, respectively) excited at 600 nm (gray \Box , black \bigcirc , respectively), and **1-PSS** ($\lambda_{probe} = 673 \text{ nm}$, 489 nm, respectively) excited at 685 nm (red \triangle).

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 λ > 600 nm. In the PSS mixture of the dyad (1-PSS), also the closed isomer (1-c) is excited at this wavelength owing to the overlap of the absorption bands. Therefore, this initially recorded data set contained the dynamics of both open and closed isomers. For this reason, measurements were performed using $\lambda_{exc} = 685$ nm to allow for rather selective excitation of the redshifted absorption band of the closed isomer (1-c, red triangles in Figure 4, bottom).

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In these TA measurements on 1-PSS, a much faster decay of the excited state is observed (Figure 5, top). The ESA ($\lambda_{probe} =$ 450-570 nm) is narrower than in the open isomer and the GSB signal is broader, now ranging from 580 nm to 700 nm. The main decay associated with 1-c in the PSS mixture occurs within the first 10 ps (see transient traces in Figure 5, bottom). Upon increasing the delay times, the decay associated spectra (DAS) shift to shorter wavelengths and show the same spectral characteristics as the excited open isomer in the λ_{exc} = 600 nm measurement (Supporting Information, Figure S4, right). Note that TA measurements with λ_{exc} = 685 nm on pure **1-o** (Supporting Information, Figure S7) show only a very small amount



Figure 5. TA data of 1-PSS (top) excited at λ_{exc} = 685 nm and associated DAS of 1-PSS (bottom).

of excited open isomer. Therefore, the presence of excited 1-o in the PSS mixture upon excitation at $\lambda_{exc} = 685$ nm is attributed to ring-opening of excited 1-c rather than direct excitation of 1-o.

In a global lifetime analysis,^[36] four time constants were necessary to describe the obtained data satisfactorily. The first decay with $\tau_1 = 180$ fs was required to describe a fast process immediately following photoexcitation. This process lies within the time resolution of the experiment (ca. 100 fs) and essentially describes an ultrafast relaxation in the excited state. The time constant τ_4 , which is larger than the time range of the experiment, was fixed to a value of 2.6 ns. This value was obtained from the measurements of the open isomer excited at 600 nm and describes the decay of the small amount of open isomer within the PSS. Spectra at fixed delay times and the DAS of these two time constants look very similar for both data sets (Figure 5, bottom; Supporting Information, Figure S4), an observation that consolidates this assignment. The decay of the main signal is associated with $\tau_2 = 2.6$ ps. It contributes with large negative amplitudes in the range of the broad GSB signal. The spectral characteristics of this DAS (Figure 5, bottom) fit well with the (negative) steady state absorption spectrum of the pure closed isomer (Figure 2, top left). Therefore, this time constant is assigned to the repopulation of the ground state of the closed dyad (1-c). Finally, the DAS at $\tau_3 = 19$ ps with its derivative-like shape can be attributed to a cooling process of the closed isomer after relaxation to the electronic ground state. This behavior is already known for other dithienylethene-BODIPY conjugates^[34] as well as for individual DAEs.[35]

All of these observations lead to the conclusion that in the closed dyad (1-c) the BODIPY and the DAE are electronically coupled. Owing to this coupling, they behave as one chromophore with relaxation dynamics comparable to the ones of the pure DAE (see Figure 4, bottom). The fast non-radiative relaxation proceeds through at least one conical intersection as widely discussed for various DAE derivatives.^[37] Importantly, an energy transfer from BODIPY to DAE as another alternative relaxation pathway can be ruled out owing to the absence of any signals of excited pure DAE. Upon irradiation at λ_{exc} = 685 nm, predominantly 1-c could be excited. Once 1-c is in its excited state, the excitation energy is employed either in the non-radiative deactivation to the ground state or in the photoisomerization to 1-o. This process takes place without any fluorescence emission. Indeed, steady-state experiments using irradiation of the PSS mixture at 690 nm demonstrated the generation of the open similarly to direct excitation of the DAE-band centered at 546 nm. The associated quantum yield for ringopening following 690 nm irradiation ($\Phi_{\rm c
ightarrow o} =$ 0.004) equals that when performing the irradiation at 546 nm (or 565 nm) as expected by Kasha's rule, which predicts ring-opening to occur from the lowest excited state.^[38] This finding seemingly contradicts a recent report of a wavelength dependency for the cycloreversion quantum yield of two other DAE derivatives, which was explained by a thermal barrier in the photoreactive excited state.^[39] However, in our case, merging of the DAE and the BODIPY fragments creates one new chromophore with an

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intense and broad absorption band, where excitation at the blue shoulder (546 nm or 565 nm) as well as the red shoulder (690 nm) populates one and the same excited state. Importantly, the ability of this lowest excited state to undergo ring opening is maintained. This is in contrast with the general observation that in DAEs featuring extended π -conjugated systems or push-pull substitution and therefore red-shifted absorption bands, the cycloreversion process is utterly suppressed.^[40]

Conclusion

In summary, we have prepared a new covalent bichromophoric construct, dyad 1, composed of a far-red emitting BODIPY fluorophore directly π -conjugated to a DAE photoswitch. In the open isomer (1-o) both individual subunits retain their intrinsic functions, that is, fluorescence emission and photoisomerization, as shown by comparison with related reference compounds. However, in the closed form (1-c) strong electronic coupling is established and results in one new chromophore system, which combines the features of both individual subunits, that is, the ring-opening capability of a DAE and the intense red-shifted absorption of the BODIPY. Time-resolved spectral data show that upon excitation of the closed isomer (1-c) in the red (λ_{exc} = 685 nm) the typical BODIPY fluorescence is lost and instead DAE cycloreversion is taking place. Hence, our system allows on the one hand for modulation of BODIPY fluorescence and on the other hand represents a DAE, in which ring opening can be triggered by visible light in the farred with reasonable efficiency. Current efforts in our laboratories are focusing on improving the ring closing efficiency to allow for quantitative switching and enhanced fluorescence modulation.

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