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Control of triplet state generation in heavy atom-free BODIPY-anthracene dyads by media polarity and structural factors

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Abstract

A family of heavy atom-free BODIPY-anthracene dyads (BADs) exhibiting triplet excited state formation from charge-transfer states is reported. Four types of BODIPY scaffolds, different in the alkyl substitution pattern, and four anthracene derivatives have been used to access BADs. The fluorescence and intersystem crossing (ISC) in these dyads depend on donor-acceptor couplings and can be accurately controlled by the substitution or media polarity. Under conditions that do not allow charge transfer (CT), the dyads exhibit fluorescence with high quantum yields. Formation of charge-transfer states triggers ISC and the formation of long-lived triplet excited states in the dyads. The excited state properties were studied by steady-state techniques and ultrafast pump-probe spectroscopy to determine the parameters of the observed processes. Structural information for various BADs was derived from single crystal X-ray structure determinations alongside DFT molecular geometry optimization, revealing the effects of mutual orientation of subunits on the photophysical properties. The calculations showed that alkyl substituents on the BODIPY destabilize CT states in the dyads, thus controlling the charge transfer between the subunits. The effect of the dyad structure on the ISC efficiency was considered at M06-2X level of theory and a correlation between mutual orientation of the subunits and the energy gap between singlet and triplet CT states was studied using multireference CASSCF method.

Introduction

Boron dipyrromethene (BODIPY) dyes¹ represent one of the most actively studied classes of organic chromophores today. Ease of synthesis and derivatization, alongside tunability of their photophysical properties, make them attractive as materials for various applications. Most of these applications utilize the strong fluorescence of the BODIPY, e.g., for labeling of biomolecules,² as fluorescent switches,³ chemosensors,⁴ and laser dyes.⁵ Currently, attention focusses on the generation of triplet excited states in BODIPYs due to emerging applications in photodynamic therapy (PDT),⁶ photocatalysis,⁷ and triplet-triplet annihilation photon up-conversion.⁸

A general approach towards BODIPY triplet sensitizers, which involves introduction of heavy atoms (typically halogen atoms or transition metals) into the molecule, that promotes spin-orbit coupling and thus enhances intersystem crossing, was discussed in a recent review.⁹ Among the methods to facilitate triplet state formation in heavy atom-free chromophores, using a spin converter,¹⁰ exciton coupling,¹¹ doubly-substituted excited states¹² and twist-induced¹³ ISC were studied in detail. However, insufficient versatility of such methods is still a major limitation in the design of new generation triplet sensitizers.

Triplet state formation via photoinduced electron transfer (PeT) is a relatively well-known phenomenon which, however, has not been employed for the development of practical triplet sensitizers until very recently. PeT leads to the formation of charge-transfer states (CT) consisting of the donor radical-cation and the acceptor radical-anion which recombine to the ground state *via* different pathways. As has been noted in numerous works, CT state recombination may result in the formation of a local triplet excited state of either donor or acceptor, which further decays to

the ground state either *via* phosphorescence or non-radiative decay process.¹⁴ For instance, the generation of triplet excited states in heavy-atom-free donor-acceptor perylene bisimides dimers¹⁵ and dyads¹⁶ has been the subject of rigorous investigations by Wasielewski and co-workers. In these systems the triplet excited states were found to be generated *via* radical pair intersystem crossing (RP-ISC) or spin-orbit charge-transfer (SOCT-ISC) mechanisms from the CT state.

It could be expected, that, if the yield of the triplet excited states formed from a CT state is reasonably high and the resulting triplets possess long lifetimes, these systems can be applied as practical triplet sensitizers. Recently, we reported for the first time efficient triplet state generation in heavy atom-free BODIPY-anthracene dyads (BADs), mediated by PeT. BODIPY triplet states in these dyads are formed in high yields (up to 80%) and are rather long-lived (>40 μ s). Moreover, water-soluble BAD derivatives were found to generate triplet states in biological media, resulting in singlet oxygen formation and causing strong cytotoxic effects under light irradiation.¹⁷ Ease of synthesis and derivatization makes BADs promising for a wide range of applications. Subsequently, we and others reported that BADs can be employed as "Janus-faced" chromophores, showing unprecedented dual performance in triplet-triplet annihilation photon up-conversion.¹⁸

Figure 1. General structure of BODIPY-anthracene dyads studied in this work.

The key advantage of PeT-mediated triplet sensitization is the possibility of controlling the ratio between ISC efficiency and fluorescence emission of the dye. It is well-known that due to its high dipole moment the energy of CT states strongly depends on the polarity of the media. In non-polar solvents the CT energy level is usually significantly higher than the first excited state of the dyad, resulting in very low PeT efficiency and strong fluorescence. Conversely, in solvents possessing sufficient polarity, the CT state energy is reduced, making PeT and triplet state

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generation feasible. Moreover, PeT in donor-acceptor dyads can be switched on-off in response to complexation with metal ions, changes in pH, hydrogen bonding and other stimuli,¹⁹ providing a tool to control ISC.

Although many BODIPY compounds were shown to exhibit PeT when combined with appropriate electron donors or acceptors,²⁰ observations of efficient formation of long-lived triplet states in such systems are scarce. Among those are BODIPYs with appended transition metal complexes,²¹ dyads containing fullerene,²² quinone²³ or methylpyridinium²⁴ as electron acceptors and BODIPY dimers.²⁵ For instance, recently reported BODIPY dyads bearing an extended acridinium cation as an electron donor showed triplet excited state yield of up to 15%.²⁶ It is still unclear which factors govern ISC efficiency in CT states. To further advance applications of heavy atom-free PeT sensitizers, insight to their photophysical characteristics and guidelines for the design of new material systems are required. With this in mind, we investigated the relationship between molecular structure, the efficiency of triplet state generation, and $^1\text{O}_2$ formation in a family of BADs (Fig. 1), varying in substitution patterns, molecular geometries and electronic coupling between the donor and acceptor subunits.

In this study, we particularly focused on unveiling the excited-state properties of the dyads, specifically PeT and triplet state generation. For this purpose, we studied the BADs using steady-state and ultrafast transient absorption spectroscopy. Secondly, we investigated singlet oxygen generation facilitated by the dyads in polar and non-polar solvents. Structural information for various dyads was obtained by single-crystal X-ray crystallography and molecular geometry optimization. Our major finding is that both, the solvent polarity and the substitution pattern of the BODIPY subunit can control triplet state generation in BADs. We found that dyads containing alkyl substituents on the BODIPY subunit are capable of triplet state formation, however, only in polar solvents. On the other hand, unsubstituted dyads were found to undergo PeT, generate triplet states, and produce $^1\text{O}_2$ both, in polar and non-polar media. To rationalize the observed properties we employed quantum-mechanical calculations, which identify the pathways of triplet state generation from CT states in the different types of dyads. This allowed us to elucidate the role of local excited states and CT state energies, and the role of mutual electron donor to electron acceptor orientations in the ISC process.

Results and Discussion

Design of the dyads

To systematically investigate the PeT and triplet state generation processes in BADs, we synthesized various dyads in which the excited state energies of the subunits are tuned systematically over a wide range. Previous report suggested that energies of the

frontier orbitals and redox potentials of BODIPYs can be tuned by the introduction of alkyl groups.²⁷ The energies of the BODIPY HOMO orbitals increase gradually when going from unsubstituted BODIPY to hexaalkyl-substituted ones, while the HOMO-LUMO gap in this series is steadily decreasing (Fig. 2). The overall change in HOMO energies is rather considerable, suggesting that in the dyad such changes induced by alkyl groups must have a strong effect on the electron transfer process. The effect of the alkyl substituents on the electronic structure depends solely on the position and number of the substituents and is almost unaffected by the nature of the substituents. On the other hand, a variation of the anthracene substitution pattern was found to induce only slight changes in MO energies. Based on the match between HOMO energy levels of the subunits it could be expected that electron transfer occurs in these dyads.

Steady-state absorption and emission properties of the dyads

The absorption and fluorescence emission parameters of BADs in a range of solvents are given in Table 1. For all compounds the absorption spectra show transitions associated with the two subunits, indicating weak coupling of the chromophores in the ground state (Fig. 3a). Upon changing the solvent polarity, the shape and maxima of the absorption bands undergo little change. In contrast, the emission of BADs is significantly affected by the solvent polarity. The spectrum of the representative dyad **10** (Fig. 3a) in non-polar hexane ($\epsilon_r = 1.9$) shows a fluorescence emission centered at 512 nm and is characterized by a Stokes shift of 7 nm, 6.5 ns lifetime, and a very high emission quantum yield (0.91). In line with previous reports,^{1b} this emission can be attributed to a transition from the BODIPY singlet excited state (S^{BDP}) to the ground state of the molecule, or "local emission" (from LE) of the BODIPY chromophore. In polar ethanol ($\epsilon_r = 24.3$), a new broad and structureless band appears at 620 nm, accompanied by a remarkable drop in emission intensity and quantum yield to 0.005 (Fig. 3a). The relative intensity of this band with respect to the LE band becomes more pronounced in highly polar DMF ($\epsilon_r = 38.3$), accompanied by a further drop of the emission quantum yield to 0.003 (Fig. 3b). At the same time, its maximum is shifted further to the red by 20 nm, indicating that the energy of the corresponding excited state strongly depends on the solvent polarity. Quenching of the emission in polar media is usually observed upon formation of exciplexes and twisted intramolecular charge-transfer states.²⁸ Red-shifted broad emission bands reported for various donor-acceptor systems were attributed to CT states transition into the ground state of the dyad.²⁹ Such emission is commonly very weak, consistent with the low quantum yields observed for **10** in polar solvents. Thus, the emission observed for **10** in polar solvents can be interpreted as a mixture of fluorescence from the LE and CT state, which is formed due to intramolecular electron transfer.

Figure 2. Molecular orbital energies (in atomic units) corresponding to HOMO and LUMO of the BODIPY and anthracene subunits in BADs.³⁰

Table 1. Steady-state spectroscopic data for BADs in various solvents.

Compound (BAD)	Solvent ^a	λ_{abs} ^b (nm)	λ_{em} ^{b,c} (nm)	Φ_{em} ^{d,e}	Compound (BAD)	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_{em}
DMF	506	524, 738	<0.001		DMF	505	518, 615	0.011
	DCM	506	520, 706	0.002		DCM	506	517	0.072
	CH ₃ CN	502	519, 741	<0.001		CH ₃ CN	502	512, 621	0.006
	EtOH	503	520, 716	<0.001		EtOH	505	513	0.038
	toluene	508	525, 628	0.008		toluene	508	521	0.92
	hexane	505	521	0.135		hexane	504	515	0.99
DMF	506	528	0.002		DMF	506	519, 612	0.003
	DCM	506	530	0.005		DCM	506	519, 643	0.011
	CH ₃ CN	502	528	0.001		CH ₃ CN	503	518, 654	0.002
	EtOH	503	528	0.002		EtOH	504	516, 627	0.005
	toluene	508	533	0.007		toluene	509	517	0.95
	hexane	504	566	0.041		hexane	505	512	0.91
DMF	506	526, 716	0.001		DMF	507	515, 621	0.01
	DCM	506	526, 727	0.002		DCM	507	515, 602	0.024
	CH ₃ CN	502	524, 702	0.001		CH ₃ CN	503	508, 631	0.007
	EtOH	504	522, 716	0.002		EtOH	504	512, 606	0.02
	toluene	509	529, 636	0.007		toluene	509	519	0.79
	hexane	509	564	<0.001		hexane	505	514	0.90
DMF	502	520	0.002		DMF	500	510	0.13
	DCM	502	518	0.002		DCM	502	512	0.57
	CH ₃ CN	498	516	0.001		CH ₃ CN	499	508	0.11
	EtOH	500	516	0.003		EtOH	500	510	0.37
	toluene	505	524	0.036		toluene	504	515	0.65
	hexane	501	517	0.014		hexane	502	511	0.70
DMF	517	531, 671	0.003		DMF	530	541	0.705
	DCM	518	528, 637	0.009		DCM	531	543	0.799
	CH ₃ CN	514	524, 678	0.002		CH ₃ CN	527	537	0.579
	EtOH	515	524, 634	0.005		EtOH	528	539	0.778
	toluene	519	530	0.29		toluene	533	544	0.806
	hexane	515	524	0.95		hexane	530	539	0.871
DMF	517	536, 716	<0.001		DMF	530	540	0.111
	DCM	517	536, 663	0.002		DCM	531	543	0.667
	CH ₃ CN	514	535, 724	<0.001		CH ₃ CN	527	538	0.054
	EtOH	515	533, 670	0.001		EtOH	528	538	0.314
	toluene	519	534	0.052		toluene	532	544	0.863
	hexane	515	525	0.37		hexane	529	540	0.883
DMF	517	533, 676	0.004		DMF	530	539	0.648
	DCM	518	533, 651	0.007		DCM	532	543	0.833
	CH ₃ CN	514	536, 715	0.004		CH ₃ CN	528	536	0.422
	EtOH	516	528, 652	0.006		EtOH	529	538	0.804
	toluene	519	532	0.141		toluene	534	544	0.858
	hexane	516	527	0.773		hexane	531	539	0.903
DMF	512	529	0.002		DMF	526	537	0.232
	DCM	513	526	0.027		DCM	527	540	0.744
	CH ₃ CN	508	523	0.002		CH ₃ CN	523	534	0.696
	EtOH	511	526	0.037		EtOH	525	537	0.841
	toluene	516	532	0.259		toluene	529	539	0.781
	hexane	512	526	0.204		hexane	526	536	0.756

^a DMF – *N,N*-dimethylformamide, DCM – dichloromethane. ^b Absorption maxima corresponding to BODIPY chromophore are given. ^c The fluorescence was excited at the vibrational shoulder of the BODIPY absorption. Excitation wavelengths: 470 nm for dyads **1-4** and **9-12**, 480 nm for dyads **5-8**, 490 nm for dyads **13-16**. Emission spectra upon excitation in the region of anthracene absorption are given in Table S1 (ESI). ^d The fluorescence quantum yields were measured using fluorescein disodium salt as a standard ($\Phi_{\text{em}} = 0.95$ in 0.1 M NaOH). ^e Represents integral emission coming from LE and CT excited states.

Figure 3. a) Absorption and emission spectra of **10** in hexane and EtOH. b) Normalized emission spectra of **10** in a range of solvents. c) Normalized emission spectra of dyads **9**, **10**, **11** and **12** in DMF. The emission was excited at 470 nm for all dyads. d) Normalized emission spectra of dyads **2** ($\lambda_{\text{exc}} = 470$ nm), **6** ($\lambda_{\text{exc}} = 480$ nm), **10** ($\lambda_{\text{exc}} = 470$ nm) and **14** ($\lambda_{\text{exc}} = 490$ nm) in DMF.

Changing the substitution pattern in the BODIPY or anthracene subunits has a strong effect on the spectroscopic properties of the dyads. Figure 3c shows the emission spectra of dyads **9–12**, possessing the same tetramethyl-substituted BODIPY scaffold, but four different anthracene moieties, in polar DMF. Dyads **9** and **11**, based on anthracene and 9-phenylanthracene, respectively, follow the characteristics observed for **10** and show a mixture of LE and CT emission. Integral emission quantum yields were found to be 0.011 and 0.01 for **9** and **11**, respectively, indicating very efficient PeT in these dyads. In contrast, in non-polar hexane these molecules exhibit very strong fluorescence from LE states with quantum yields of up to 0.99 (Table 1).

Dyad **12**, in which the anthracene moiety is not directly linked to the BODIPY, but separated *via* a phenylene bridge, exhibited different characteristics. In DMF, CT emission is not observed in the spectrum (Fig. 3c). However, the observed LE emission is substantially weaker ($\Phi_{\text{em}} = 0.13$), than in non-polar hexane ($\Phi_{\text{em}} = 0.7$). Likewise, the excited state lifetime in DMF is shorter (0.51 ns) than in hexane (8.2 ns). This indicates, that, although PeT takes place in dyad **12**, it is less efficient compared to the dyads with directly linked subunits. The rate of PeT is known to depend on the separation of the donor and acceptor subunits;³² introduction of the phenylene spacer in **12** is likely to slow down the process.

The effect of the alkyl substitution pattern in the BODIPY on the emission properties is illustrated in Fig. 3d. Dyads **2**, **6**, **10** and **14** are composed of the same anthracenyl subunit (9-methylanthracene) and BODIPYs with different numbers (0 to 6) of alkyl-substituents, affecting the HOMO energy levels as illustrated in Figure 3. Dyads **2** and **6** show pronounced CT emission, substantially red-shifted compared to **10**, with maxima at 732 and 718 nm, respectively. Such a strong spectral shift may indicate enhanced electronic communication between the subunits, e.g., due to twisting.

On the other hand, the spectrum of **14** shows only LE emission indicating reduced PeT efficiency. The emission quantum yield of **14** in DMF and hexane was found to be 0.11 and 0.883, respectively. Thus, although PeT in **14** takes place, it is significantly less efficient compared to the other dyads and strong LE emission from the BODIPY is dominating the spectrum. This is consistent with rather low redox potentials of hexaalkyl-substituted BODIPYs,^{27a} impeding PeT from the anthracene subunit.

These observations confirm that the PeT efficiency varies to a large extent in BADs, depending on the electronic coupling between the subunits and their redox potentials. To elucidate the structure-properties relationship, transient absorption spectroscopy measurements were performed (*vide infra*).

Singlet oxygen sensitization by BADs

Trapping of the photosensitized $^1\text{O}_2$ with 1,3-diphenylisobenzofuran was applied to measure Φ_{Δ} values in polar (ethanol) and non-polar solvents (hexane). As we previously described,¹⁷ in certain cases the DPBF oxidation method overestimates the $^1\text{O}_2$ quantum yields of BADs, e.g., if chlorinated hydrocarbons are used as solvents. For instance, irradiation of oxygen-free solutions of BADs in dichloromethane results in a decrease of DPBF absorption. No reaction of DPBF with excited states of the dyads takes place under these conditions, as the absorption of BADs remains the same during the course of light irradiation. This result can be explained by photolysis of DPBF exposed to light in halogen-containing solvents in the absence of singlet oxygen, as described previously.³³ Due to this complication, quantum yields of singlet oxygen production in these solvents detected by DPBF can be significantly overestimated.

Table 2. Quantum yields of singlet oxygen photosensitization by BADs in ethanol and hexane.^a

Compound	EtOH	Hexane
1	0.11	0.39
2	0.05	0.38
3	0.12	0.43
4	0.01	0.01
5	0.47	0.07
6	0.38	0.17
7	0.46	0.18
8	0.01	0.01
9	0.53	0.01
10	0.67	0.04
11	0.59	0.04
12	0.01	0.01
13	0.11	0.02
14	0.32	0.03
15	0.15	0.03
16	0.01	0.01

^a Quantum yields were measured using DPBF as a $^1\text{O}_2$ trap and Rose Bengal as a reference photosensitizer (0.86 in ethanol).³⁴

In contrast, when ethanol or hexane was employed as solvent no such effect was observed. The absorption of DPBF showed no changes upon irradiation of oxygen-free solutions under the same conditions (concentration, light intensity, degassing procedure). Alternatively, the addition of singlet oxygen quenchers (NaN_3 or amines) to the solutions terminated DPBF oxidation, confirming selective reaction of the trap with $^1\text{O}_2$ under these conditions.

As shown in Table 2, Φ_{Δ} values of BADs largely vary depending on the solvent and subunits structure. The highest values (up to 0.67) were observed for dyads **9–11**, based on tetramethyl-substituted BODIPY scaffolds, when ethanol was used as a solvent. This correlates with the photophysical data for these compounds given in Table 1, i.e. low emission quantum yields in polar solvents due to efficient PeT. Alternatively, in hexane these dyads showed low Φ_{Δ} values and, at the same time, high quantum yields of the fluorescence (>0.9), indicating low ISC values. In line with this, dyads **13–15** exhibited strong fluorescence in polar solvents and showed decreased Φ_{Δ} values.

Series **5–7**, based on the same 3,5-dimethyl-substituted BODIPY scaffold but with different anthracenes units, showed slightly

lower Φ_A values in ethanol (0.38-0.47), while a substantial increase of $^1\text{O}_2$ sensitization ability was observed in hexane. Dyads **1-3**, lacking alkyl groups in the BODIPY showed the lowest values of Φ_A in ethanol (0.05-0.12) and, surprisingly high values in hexane (up to 0.43). Separation of the BODIPY and anthracene subunits *via* a phenylene spacer in dyads **4, 8, 12** and **16**, results in a drop of Φ_A to negligible values (0.01) in both solvents.

Femto- and nanosecond pump-probe transient absorption spectroscopy of BADs

To unravel the photophysical processes and charge transfer dynamics, two representative series of BADs were studied: 1) dyads **2, 6, 10**, and **14**, which contain the same anthracene subunit (9-methylanthracene), but with different BODIPY subunit alkyl substitution pattern (0, 2, 4 and 6 alkyl substituents) and 2) dyads **9, 10, 11**, and **12**, which are based on the same tetramethyl-substituted BODIPY, but carry different anthracene subunits. The dyads were excited at 355 nm, which selectively excites and populates the singlet state of the anthracene subunit. Based on a photophysical model established in our previous study,¹⁷ we expected to observe a series of sequential processes reflected by equations (1)-(4).

Excitation at 355 nm

Energy transfer

Electron transfer

CT recombination

CT recombination

Briefly, following excitation of anthracene at 355 nm and creation of anthracene singlet excited states (S^{Ant}), fast energy transfer (EnT) to BODIPY occurs. EnT is followed by photoinduced electron transfer (PeT), generating charge-transfer (CT) states, equivalent to radical ion-pairs composed of anthracene radical-cations ($\text{Ant}^{+\bullet}$) and BODIPY radical-anions ($\text{BDP}^{-\bullet}$). The CT states then undergo recombination and populate the triplet state of either anthracene (T^{Ant}) or BODIPY (T^{BDP}).

Figure 4. ps-ns TA spectra of **10** measured in nitrogen filled chamber at room temperature in DMF (a) and in toluene (b) upon excitation at 355 nm with 100 fs pulses at various delay times as shown in the legend. Panels (c) and (d) show kinetics of selected spectral regions, as indicated by the vertical color bars in panel (a) and (b), respectively. The inset in panel (b) represents a zoomed-in region of the PA of **10** in toluene.

In the following, we present and discuss the ps- μ s TA spectra and dynamics of compounds **2, 6, 10**, and **12** only, while we refer to the ESI for the data and analysis of the other compounds. We will start with the discussion of compound **10**. We have previously reported its spectroscopic properties¹⁷ in DMF and add a more in-depth analysis of the photophysical processes in different solvents here, before discussing the novel compounds reported in this study. For all TA measurements, the samples were either kept in a nitrogen-filled sample chamber or measured in air, as specified in the each figure captions.

Figure 4 shows room temperature picosecond-nanosecond transient absorption spectra (a-b) and corresponding kinetics (c-d) of **10** in DMF (a,c) and toluene (b,d), respectively. Figure 4a represents the spectral response of **10** in DMF at different delay times varying from 300 fs to 7 ns. Anthracene singlet excited states are created by photoexcitation at 355 nm and the associated decay of the 400 nm band and concomitant rise of the photo bleach (PB) band of BODIPY at 510 nm indicates efficient ultrafast EnT from anthracene to BODIPY,¹⁷ populating the singlet excited state of BODIPY. The population of BODIPY singlet excited states, after excitation of the anthracene at 355 nm and successive EnT, was confirmed by steady-state fluorescence experiments, which showed fluorescence mainly from the BODIPY. For UV-Vis, steady-state emission and excitation spectra, we refer to Table S1 in the electronic supporting information (ESI).

After ultrafast EnT, photo-induced absorption bands centered at 570-590 nm and 720-780 nm, originating from BODIPY radical-anions and anthracene radical-cations,³⁵ respectively, are observed; they increase until 50 ps and thereafter decay with a half-life of 3 ns. We note that, on this time scale, in addition to charges, singlet excited states still contribute to the dynamics of the entire PA region, as the singlet states live longer than 1 ns (see figure S3 for further data analysis). In addition to the emergence of the $\text{BDP}^{-\bullet}$ absorption band at 570-590 nm, another band peaking at 680 nm is observed, which shows similar kinetics. This band is assigned to anthracene radical-cations in line with assignments by earlier reports.³⁶ We note that its decay exceeds the time window of the ps-ns TA experiment shown in Figure 4. The kinetics of the 590 nm, 680 nm, and 725 nm bands (Figure 4c) are similar, indicating that they originate from the same excited state. The photoinduced absorption in the 380-420 nm region increases after several ps (not shown here), which we assign to an overlap of absorption bands of the anthracene radical-cation and anthracene triplet states, as the BODIPY triplets and charges follow very different kinetics.³⁷ Figure S9 compares the TA spectra and kinetics measured in air and nitrogen atmosphere. To better understand the generation and deactivation pathways, exponential fits to the rise of the PB at 510 nm and PA at 725 nm were used and inverse rate constants < 0.50 ps and < 1 ps for the EnT and PeT processes were observed, respectively. These rise times are in the range of previously reported values.³⁸ Kinetic traces of all PB and PA bands are shown in Figure 4c.

We further examined the ps-ns TA spectra of **10** in toluene (Figure 4b, and d) to see how the solvent medium affects the dynamics of excited states. The spectral evolution following excitation at 355 nm differs remarkably from that observed in DMF. The immediate formation of the PB band of BODIPY with an inverse rate of < 0.50 ps indicates that EnT is very efficient in this system. The PA bands evolve slower (800 ps) and decay to the ground state with negligible CT and triplet state formation. Compared to DMF as solvent, toluene has lower polarity, and thus the generated singlet states decay to the ground state without forming CT states. The poor PeT was accompanied by a high fluorescence yield of the

dyad in toluene (Table 1). Moreover, no rise of the BODIPY photo-bleach band was observed at longer delay times, only a constant decay to the ground state. A bi-exponential fit to the decay of the PB yields lifetimes of 23 ps and 6.3 ns, respectively. Time-resolved photoluminescence (TR-PL) experiments show a mono-exponential decay with a lifetime of 5.6 ns, in reasonable agreement with the long component of the PB decay from TA, indicating that the singlet states decay to the ground state mostly via fluorescence (see S1 for TR-PL spectra and kinetics of **10**). Comparing the ratio of PA and PB bands of the two samples (in DMF and toluene) shows a remarkably different yield of long-lived photo-generated states. The ratio of the band at 725 nm and corresponding PB indicates a yield of 32% in DMF solution, compared to a yield of only 5.6% in toluene. The value of the band at 590 nm compared to the PB is 50% and 5.5% for DMF and toluene solutions, respectively. These observations confirm that CT state recombination, rather than ISC from S_1 states, is responsible for triplet state formation in **10**.

Figure 5. ns- μ s TA spectra of **10** in DMF (a) and in toluene (b). Different regions in the spectra are marked with vertical color bars. The inset of figure (b) shows the zoomed-in region of the PA. Note that, clearly, before 10 μ s, most of excited states have decayed to the ground state. (c) Kinetics of the spectral region centered around 570 nm (green shaded in panel (a)) in nitrogen atmosphere (black) and in air-saturated conditions (red) of **10** in DMF, demonstrating triplet state quenching in the presence of oxygen. Panel (d) and (e) show the component spectra and kinetics of singlets (black), charges (red), and triplets (green) obtained by multivariate curve resolution of TA data from compound **10** in DMF. The red dashed line in panel (e) denotes a fitted single-exponential rise of the triplet population.

To monitor the decay dynamics of long-lived states, we also performed TA experiments covering the nanosecond to microsecond time range. Figure 5 presents ns- μ s TA spectra of **10** in DMF (a) and in toluene (b), respectively, after laser excitation at 355 nm. As observed from the ps-ns spectra, the 590 nm band blue-shifts to 570 nm and shows a rise after 1 μ s, indicating the generation of T^{BDP} as previously reported by us and others.^{17,39} We

confirmed the triplet generation by performing ns- μ s TA in air and observed substantial quenching of the 570 nm band (see Figure S9 for TA spectra) assigned to triplets. Figure 5c shows the decay dynamics of the 570 nm band in nitrogen and air as black and red lines, respectively. No rise in the dynamics is observed after 1 μ s when measured in air. The delayed generation of triplets is due to recombination of charge-transfer states after 100 ns as obvious from the component-associated spectra and dynamics (see Figure 5d and e) obtained by multivariate curve resolution (MCR) analysis of the TA data. Details of this method can be found elsewhere.⁴⁰ The singlet-induced absorption spectrum shows two peaks at 590 nm and 690 nm, respectively (black line in panel d). The charge-induced absorption spectrum (red line) spans the range from 560 nm to 680 nm and shows a weak feature in the near-infrared spectral region (>750 nm). Note that this spectrum originates from charges in both anthracene and BODIPY sub-units, in agreement with our previous observations and those from other groups.^{17,35} The triplet-induced absorption spectrum (green line in panel (d)) of **10** in DMF exhibits a broad peak covering the range from 520 – 610 nm, in line with the TA spectrum evolving after 1 μ s. A single-exponential fit to the rise of the triplet-induced absorption yields 6.1 μ s as rise time (red dashed line in panel e). Figure 5b presents the ns- μ s TA spectra of **10** in toluene. The spectral dynamics follow the ps-ns TA spectra as described above. Here, no rise was observed, indicating that triplet generation via charge recombination is much less efficient in non-polar solvents such as toluene. However, TA in air showed quenching of the band at 570 nm (see Figure S9), indicating that a small population of triplets is present in this sample. The ratio of the PA at 590 nm to PB was determined to 15.5 % and 0.8 % for DMF and toluene solutions, respectively. This ratio was calculated by considering the maximum PA at 1 μ s and the maximum PB at 1 ns of the experimentally-measured spectra. This again indicates that triplet generation in toluene solution is strongly inhibited, in excellent agreement with our photoluminescence studies (see Figure S1 for PL spectra and kinetics).

Figure 6. (a) ps-ns TA spectra of **6** in DMF measured under nitrogen atmosphere at room temperature upon excitation at 355 nm with 100 fs pulses at various delay times as indicated in the legend. (b) Nanosecond-microsecond transient absorption spectra of **6**. Panels (c) and (d) show kinetics of selected spectral regions, as indicated by vertical color bars in panels (a) and (b), respectively. For corresponding MCR analysis of nanosecond-microsecond TA, we refer to figure S20.

We now move to the discussion of the spectral features and dynamics of the other compounds and compare the results to those obtained for compound **10** to derive similarities and

differences. Figure 6 shows ps-ns transient absorption spectra and kinetics of selected spectral regions for compound **6**. While the spectral shape is identical to that of **10**, the kinetics are largely different. In Figure 6a-c, generation of BODIPY singlets is observed to be slower with an inverse rate constant of <0.7 ps. The BDP⁺ band at 570-590 nm shows a rise until 3 ps, followed by a blue shift, and peaks at 570 nm as in the case of **10**. A mono-exponential fit to the rise of the band at 590 nm gives an inverse rate constant of <1 ps, indicating effective PeT in this system. Remarkably, the spectral bands start to decay rather early with decay times of 0.92 ns, 0.83 ns, and 0.79 ns for 515 nm, 590 nm, and 725 nm, respectively. As observed for **10**, the anthracene radical-cation absorption at 680 nm also shows similar rise and decay kinetics.

Figure 6b shows ns- μ s TA spectra of **6**. A fast decay followed by a rise of the 580 nm band (see the green vertical bar in panel (b)) with a rise time of 6.5 μ s is assigned to triplet generation by charge-transfer state recombination. The presence of triplets is confirmed by measuring TA in air as done for **10**. For the complete spectra and kinetics of **6** we refer to figure S10. The ratio of the 580 nm band compared to the PB band was 14 %, which is comparable to that of **10** (in DMF). Comparable spectra and kinetics are observed for the other dyads, namely **9**, **11** and **14** as well (shown in the ESI). Table 3 compares the EnT, PeT and triplet generation rates across all four dyads. Triplet generation rates were calculated from deconvoluted kinetics of triplet states. See Figure S20 for all deconvoluted spectra and kinetics. They demonstrate spectrally similar responses upon exciting at 355 nm at room temperature. Among these four dyads, **11** shows the fastest EnT and PeT. All relevant spectral and kinetic information of the samples listed in Table 3 can be found in the ESI (Figures S10-S14). For TR-PL spectra and kinetics, we refer to figures S2-S5.

Figure 7. (a) ps-ns TA spectra of **12** in DMF, measured under nitrogen atmosphere at room temperature following excitation at 355 nm with ~ 100 fs pulses at various delay times as indicated in the legend. (b) Nanosecond-microsecond transient absorption spectra of **12** in DMF under the same conditions as in panel (a). Panels (c) and (d) show kinetics of the corresponding selected bands, as indicated by vertical color bars in panels (a) and (b), respectively.

Figure 7 illustrates transient absorption spectra and kinetics of dyad **12** in DMF. As seen from Figure 7a and c, the PB band at 510 nm exhibits first a fast rise followed by a slow growth, indicating fast EnT, but slow PeT in this molecule. The spectral characteristics are reminiscent of **10** in toluene, where PeT is suppressed due to the low polarity of the solvent. Interestingly, both PA bands (590

nm and 725 nm) show a small rise after 100 ps due to less efficient PeT. Almost 90% of the PB disappears within a few nanoseconds, demonstrating only minor population of long-lived charge-transfer states after photoexcitation. The inset of Figure 7a depicts a magnification of the PA region, showing a slow rise and subsequent decay to the ground state. Mono-exponential fits yield inverse rate constants of <0.7 ps and <0.8 ps for the PB and PA bands, respectively, indicating that the PA mostly originates from singlet states on BODIPY generated via EnT from anthracene. ns- μ s transient absorption spectroscopy results obtained on **12** are shown in Figure 7b and d. A monotonous decay of the PB up to 10 ns is observed, followed by a small growth in line with the rise of the 590 nm band, caused by the formation of triplet states. The ratio of the 590 nm band to the PB was 0.7%, far less than that of **10** in DMF, indicating very inefficient triplet generation. For the complete comparison of spectra and dynamics of **12**, we refer to Figures S15 and S16 in the ESI. Figure S6 shows complete TR-PL spectra and kinetics of **12**.

Table 3. Energy transfer time, photoinduced electron transfer time, and BDP triplet generation time for compounds **6**, **9**, **11**, and **14** in DMF.

Compound	EnT time, ps	PeT time, ps	T ^{BDP} time, μ s
6	<0.7	1	6.5 ± 0.2
9	1.06	2.4	8.0 ± 0.1
11	<0.5	1	5.7 ± 0.5
14	<0.6	5.8	4.2 ± 0.4

In Figure 8, ps-ns TA spectra and corresponding kinetics of **2** (in DMF) after 355 nm excitation are shown. Unlike for **10**, here PB and PA bands decay to the ground state within a few nanoseconds. Although the extracted inverse rate of EnT (<0.5 ps) indicates fast energy transfer, the steady-state emission spectra (see Table T1 in the ESI) show that upon excitation at 355 nm, the resulting emission originates mainly from the anthracene unit. Thus, it appears that unlike for the other dyads, upon 355 nm excitation of **2**, the population of BODIPY singlet excited states is limited. However, the CT state of **2** is short-lived compared to **10**, which in turn reduces the probability of generating triplet states. In **2**, 90% of the total excited state population decays within 0.7 ns, whereas in **10**, more than 75% are still present on this timescale. Hence, we excited **2** at 510 nm directly into the BODIPY absorption and compared the TA spectra of **2** in DMF and toluene.

Figure 8. (a) ps-ns TA spectra of **2** in DMF measured under nitrogen atmosphere at room temperature upon excitation at 355 nm with 100 fs pulses at various delay times as indicated in the legend and (b) kinetics of the corresponding bands, as indicated by vertical color bars.

Figure 9. ps-ns TA spectra of **2** in (a) toluene, (b) DMF upon excitation of the BODIPY unit at 510 nm; kinetics of the bands indicated by vertical color bars are shown in panel (c) (dotted lines: DMF, solid lines: toluene). Panels (d) and (e) show nanosecond-microsecond TA spectra of **2** (toluene) measured under nitrogen atmosphere and in air-saturated conditions, respectively. Panel (f) shows the nanosecond-microsecond kinetics in nitrogen (solid lines) and air-saturated (dotted lines) solutions of **2** for the vertical color bars indicated in panel (d) and (e).

ps-ns TA spectra of **2** in DMF and toluene after excitation at 510 nm are shown in Figure 9. The obvious difference is the presence of very long-lived states and the slow rise of the PA and PB bands of the sample measured in toluene. At 7 ns, (the longest delay we can measure with our ps-ns TA setup), 68 % of the original PB band remain. In DMF, **2** does not generate a sufficient number of long-lived states. The PA band centered at 570 nm rises until 70 ps, followed by a very slow decay (red solid line, panel c). TA measurements on solutions in air show no quenching of the long-lived states, indicating that triplets are not generated on this time scale (see Figure S17 for TA spectra in air). Surprisingly, we observe an efficient population of the T^{BDP} state in toluene. Figure 9c compares the kinetics of **2** in toluene (solid lines) and in DMF (dotted lines). In DMF, **2** shows a monotonous decay to the ground state without any signature of triplet formation, whereas in toluene, generation of long-lived BODIPY triplet states is clearly observed. Figure S7 shows TR-PL spectra and kinetics of **2**. Since the excited state population is very long-lived, we performed nanosecond-microsecond TA to monitor their decay dynamics. Panels (d) and (e) in Figure 9 show ns-μs TA spectra of **2** in toluene after exciting at 532 nm, measured in nitrogen atmosphere and in air, respectively. Three bands can be distinguished at early times from the ns-μs TA spectra, and are assigned to PB and triplet-induced absorption bands of BODIPY. Interestingly, even at 100 μs, a band around 820 nm remains, while the other bands decay monotonously. We note that the bands centered around 380-420 nm, 570-700 nm, and 780-820 nm show similar decay dynamics

and are substantially quenched upon exposure to air (Figures 9d, e and f), confirming that all bands originate from BODIPY triplets. This implies that, the excitation wavelength and solvents play a major role in the excited state dynamics of **2**. In fact, we assigned the 380-420 nm band to T^{Ant} in other dyads in DMF solution after selectively exciting the anthracene subunit. Here, we assume that exciting anthracene would not lead to T^{BDP} and a feature at 380-420 nm, but instead would generate T^{Ant} , since the T^{BDP} at 570 nm shows different dynamics. However, Zhang *et al.* reported recently that the 380 nm band can be assigned to T^{BDP} created after excitation of anthracene,⁴¹ which contradicts our results and those of others.^{17,42} We note that the 380-420 nm band and its dynamics are quenched after 100 ns upon oxygen exposure, following anthracene excitation (at 370 nm). Additionally, we note that the triplet formation in toluene upon 532 nm excitation is faster than that in DMF solution (see S11).

Elucidation of the dyad solid state structures

Single crystals of the dyads suitable for X-ray crystallography were obtained by slow evaporation of BAD solutions in DCM, chloroform or toluene. For analysis, we investigated distortions of atoms from the least-squares-planes of the BODIPY and anthracene subunits (listed in Table 4), the carbon-carbon bond lengths of C8-C15 and the rotations around the C8-C15 bond designated as ψ (Figure 10).

Additionally, in the packing arrangement, we evaluated the packing type (head-to-head or head-to-tail), solvent effects, and the formation of any halogen short contacts between fluorine and hydrogen atoms (bond lengths given with respects to H...F distance and angles are quoted for C-H...F). The previously published structures of BADs **1**⁴³ and **10**¹⁷ were included here for comparison. All structural features of interest are summarized in Table 4.

The BADs structures revealed a range of ψ rotations, as is illustrated in Figure 10. This suggests a relatively large degree of freedom of rotation is available around the C8-C15 bond. For directly-linked BODIPY-anthracene systems, the compounds studied here crystallized with an almost orthogonal (69-88°) orientation (Table 4). The introduction of additional alkyl substituents into the BODIPY core resulted in a decrease of the C8-C15 bond length: from 1.499(1) Å in alkyl-unsubstituted **2** to 1.481(1) Å for the hexaalkyl-substituted dyad **14**. Upon changing the substitution pattern of the anthracene subunit, only a small variation in the C8-C15 bond length was noted. In comparison, the structure of **1**, with unsubstituted BODIPY and anthracene moieties, exhibited the largest C8-C15 bond length (1.501 Å).⁴³ Two major forms of crystal packing were found for the BAD systems. The first is the head-to-head arrangement, as for **2** (Figure S29). This is strongly favored due to the formation of a dimer *via* two C-H...F halogen bonds, C5_1-H5_1...F13 (2.181(1) Å and 145.0(1)°) and C5_2-H5_2...F14 (2.498(8) Å and 154.1(1)°). Dyads **7** (Figure S30) and **14** (Figure S31) feature a predominantly head-to-head overlapped structure, aided by short contacts between the fluorine atoms of the BODIPY and anthracene subunit. In **14**, a C-H...F short contact is seen between C26-H26...F14 (2.479(1) Å and 157.2(1)°). This is commonly referred to as the 2-position of the anthracene subunit and preserves the head-to-head structure in the crystal packing. Dyad **7** displays a similar packing to **14**; however, in this case, the short C-H...F contact is present between C17-H17...F13 (2.309(1) Å and 167.9(1)°), which is commonly referred to as the 1-position of the anthracene subunit.

Figure 10. Structural features of the dyads under investigation. Orange denotes the bond used to C8–C15 bond length. ψ -angle rotations were determined by measuring the dihedral angle between the anthracene (green) and BODIPY (purple) least-squares-plane. Thermal ellipsoids displacement show 50 % probability, hydrogen atoms have been omitted for clarity.

Table 4. Selected structural details of twist angle, bond length and deviations from planarity in the dyads studied.

Compound	ψ (°) ^a	C8–C15 (Å)	ΔB (Å) ^b	$\Delta A/P$ (Å) ^c
1 ^d	81.5(1)	1.501(2)	0.035	0.041
2 ^e	77.5(1)	1.499(1)	0.036	0.016
	73.9(1)	1.499(1)	0.126	0.074
5 ^e	75.3(4)	1.505(1)	0.020	0.025
	81.2(6)	1.493(1)	0.014	0.012
6	69.2(3)	1.494(1)	0.026	0.057
7	86.7(2)	1.496(1)	0.041	0.015
8	42.0(1)	5.804(1) ^f	0.067	0.026
	53.0(1)	5.798(1) ^f	0.071	0.043
10	78.3(5)	1.492(1)	0.066	0.028
10-T ^g	85.4(6)	1.492(1)	0.070	0.011
14	87.8(3)	1.481(1)	0.015	0.030

^a Dihedral angle between the mean planes of the BODIPY and 8-substituent (anthracene or phenylene). ^b Deviation of atoms from the mean plane of the BODIPY. ^c Deviation of atoms from the mean plane of the anthracene. ^d Described in reference 43. ^e Two independent molecules in the asymmetric unit and both structural factors are reported. ^f Separation between the anthracene and BODIPY moieties was measured by taking the distance between C8 and C21 due to the presence of a phenyl spacer unit. ^g Isostructural to **10**, however, includes toluene molecules of solvation.

The crystal structures **10** and **10-T** are isostructural, varying only by the inclusion of a toluene molecule that resulted in ~ 1 Å increase in the *a*-axis of the unit cell for **10-T**. The inclusion of toluene prevents formation of a head-to-head dimer, observed in the previously published structure of **10**, and favors a head-to-head overlap. This is aided by a short contact between the C24–H24...F14 (2.579(2) Å, 125.7(1)°) and C25–H25...F14 (2.639(1) Å, 122.5(1)°) for **10-T**. C25 is commonly referred to as the 4-position of the anthracene unit. Similarly, in compound **10**, the presence of a short contact between C26–H26...F14 (2.329(1) Å and 132.1(1)°), which is considered the 2-position of anthracene, is observed.

Additionally, **10** shows a short contact between C31–H31C...F14 (2.517(1) Å and 121.1(1)°), which forms the head-to-head dimer. Due to the presence of toluene in **10-T**, this feature is removed as the major packing motif due to the toluene molecule occupying the space previously occupied by the anthracene subunit.

The second type of packing is a head-to-tail arrangement within the unit cell. This is the main feature observed for **5** (Fig. S33), **6** (Fig. S34) and **10** (Fig. S35–36). The packing of **5** displays a highly

ordered fluorine...hydrogen short contact network within the packing of molecules in the unit cell. This results in two close contacts between C22_1–H22_1...F13_1 and its symmetry equivalent C22_1–H22_1...F13_1 (2.491(2) Å and 152.8(3)°), forming a bifurcated interaction between the BODIPY and the 10-position of the anthracene unit. This feature is singular to compounds **5** and **1**, due to the presence of methyl or phenyl moieties on the 10-position of the remaining anthracene units within this set. When compared to the published structure of **1**, we can see this type of H...F interaction is favored, provided the anthracene subunit is unhindered. Additionally, the presence of a close contact between C23_1–H23_1...F13_2 (2.418(2) Å and 172.9(1)°) facilitates a H...F close contact system between neighboring molecules related by an almost orthogonal rotation. Dyad **6** shows a packing independent of close contacts between H...F, in which the BAD units are in a head-to-tail orientation. This is due to the presence of a methyl group which shields the fluorine atoms from forming close contacts with the methyl-substituted anthracene unit, as compared to the other BAD systems shown (Fig. S34).

Figure 11. Structural features in the molecular structure of **8**. Separation between the anthracene and BODIPY moieties was measured by taking the distance between C8 and C21. ψ -angle refers to the dihedral angle between the anthracene (green) and BODIPY (purple) least squares plane. Thermal ellipsoids displacement show 50% probability, hydrogen have been omitted for clarity.

The structure of dyad **8**, (Fig. 11) in which a phenylene spacer is positioned between the BODIPY core and anthracene subunit, displays a significantly decreased ψ -angle of 42.0(1) and 53.0(1)° in comparison to the BAD systems outlined above. It features one of the shortest C8–C15 bond lengths with 1.484(2) and 1.486(2) Å for both independent molecules. However, it should be noted that due to the phenylene spacer, **8** displays the largest distance between the BODIPY core (C8) and the anthracene subunit (C21) of 5.798(1) and 5.804(1) Å. It features a predominantly head-to-head overlapping crystal structure (Fig. S32) aided by short contacts between the fluorine atoms of the BODIPY and anthracene or terminal phenyl subunit. The structure of **8** shows a

similar head-to-head overlap as seen in **7** with C33_1–H33_1...F14_1 (2.602(3) Å and 142.5(1)°), with both compounds **7** and **8** interacting with the 1-position of the anthracene moiety. However, as two independent molecules are present in the asymmetric unit, a second C–H...F is present between the BODIPY and the terminal phenyl, C39_2–H39_2...F14_2 (2.405(4) Å and 167.4(2)°), Fig. S32.

In conclusion, the ψ -angle in the solid state depends on the environment (i.e. the substitution pattern) around both the BODIPY and the 8 ('meso')-residue. The introduction of methyl groups at the anthracene 10-position facilitates head-to-head dimer formation, while the introduction of methyl groups at the C3 and C5 positions make this interaction less favorable. The inclusion of solvents, while not always having the largest effect on the overall packing (changing head-to-head to head-to-tail, or *vice-versa*) leads to inclusion of solvent molecules in pockets that would have been previously been occupied by the meso-substituent as in the case of **10** and **10-T**. Throughout these systems, compounds containing C3- and C5-substituents always presented H...F intramolecular contacts with the methyl substitutions and fluorine atoms.

Effect of alkyl substituents and solvent polarity on charge transfer

In order to understand the effect of alkyl substituents in controlling the properties of BODIPYs, a comparative computational study was performed.

The first excited state S^{BDP} in the studied molecules arises from local $\pi_{\text{BDP}} \rightarrow \pi^*_{\text{BDP}}$ excitation on the BODIPY fragment. This excitation was characterized by the TDDFT/M06-2X method to possess an oscillator strength of 0.5. Feasibility of the PeT processes from the anthracene (π_{Ant}) to the BODIPY (π_{BDP}) fragments after $S_0 \rightarrow S^{\text{BDP}}$ excitation is evidenced by the population of natural orbitals (NO) obtained using CASSCF(4/4) method. NOs are the eigenvectors of one-electron density matrix, and their occupation numbers (i.e. eigenvalues of NOs) are helpful in recognizing the electronic state structure. Figure 12 schematically demonstrates the transitions of electrons between three active orbitals (fourth one π^*_{ant} is not involved in these processes) which take place upon $S_0 \rightarrow S^{\text{BDP}}$ and $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ excitations and the resulting NOs occupations (n) in S^{CT} state.

Figure 12. Scheme of electronic transitions corresponding to $S_0 \rightarrow S^{\text{BDP}}$ and $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ interconversions. Surfaces correspond to CASSCF(4/4) natural orbitals involved in these processes with their occupation numbers (n) in S^{CT} state are depicted.

Two main factors govern the excitation energy of S^{CT} . First, the effect of alkyl substituents on E_{HOMO} and E_{LUMO} of both subunits and the CT state. The data shown in Fig. 2 demonstrate the effect of alkyl substituents on the HOMO and LUMO energies of the subunits. In the S^{CT} state the BODIPY fragment accepts an electron to form the $\text{BDP}^{\cdot-}$ species and thus, the addition of electron donating alkyl groups inevitably increases the energy of the S^{CT} state. Consequently, this hinders the electron transfer from anthracene to the BODIPY subunit. The data in Table 5 include the

energies of S^{CT} states for a series of substituted systems and fully confirm the conclusion given above.

Table 5. DFT-SCF computed excitation energies of the dyad's S^{CT} states and the energy gap between the S^{BDP} and S^{CT} states, $E[S^{\text{CT}} - S^{\text{BDP}}]$, in vacuum and ethanol (see ESI for details). All data are given in eV.

Dyad	$E(S^{\text{CT}})$	$E(S^{\text{CT}})$	$E(S^{\text{CT}}) - E(S^{\text{BDP}})$	$E(S^{\text{CT}}) - E(S^{\text{BDP}})$
	Vacuum	EtOH	Vacuum	EtOH
1	2.86	2.18	0.43	−0.24
2	2.75	2.07	0.32	−0.35
5	3.03	2.38	0.70	0.06
6	2.92	2.27	0.59	−0.05
9	3.23	2.57	0.85	0.19
10	3.11	2.46	0.73	0.08
13	3.26	2.62	0.98	0.33
14	3.15	2.52	0.86	0.24

The second factor influencing the excitation energy of S^{CT} is the dielectric susceptibility of a medium or, in other words, the solvent polarity. In the CT state two separated electrons are located on the anthracene and BODIPY subunits, thus leading to a very large dipole moment that is computed to be $\mu = 17\text{--}19$ D *in vacuo*, which is much larger than that for the valence S^{BDP} state (5 D). It is well known that in non-polar media CT cannot be stabilized *via* electrostatic interactions with solvent molecules, resulting in its energy being far above that of S^{BDP} . This makes PeT between the subunits inefficient and results in the dyad becoming a strong fluorophore. Interactions with polar solvent molecules strongly stabilize the CT state by about 0.7 eV (Table 5). Thus, the stabilized S^{CT} state is close in its energy to S^{BDP} , with an energy gap between the states of around 0.1–0.4 eV. In polar solvents the $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ transition can be observed even for dyads with alkyl substituents, which destabilize the S^{CT} state. Note, that the probability of such a transition in polar solvents is subtly reduced for dyad **2** due to an increase in the separation energy gap (more than 0.3 eV, in reverse order) between the S^{BDP} and S^{CT} states (the latter is more significantly decreased in energy). Therefore, the $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ transition for alkyl-substituted dyads can efficiently take place only in highly polar solvents, but in the case of alkyl-unsubstituted systems, the apolar environment allows such a process. This conclusion is fully supported by the energy separation gaps observed between these two states presented in Table 5. Thus, the probability of the $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ transition reduces upon increasing the energy gap between LE and CT states ($E[S^{\text{CT}}] - E[S^{\text{BDP}}]$).

Figure 13. Dependence of Φ_A measured for BADs on the computed $E[S^{\text{CT}}] - E[S^{\text{BDP}}]$ values in EtOH.

Singlet oxygen quantum yield values of BADs are in full agreement with these conclusions given above. The dependence of the

measured Φ_A on the computed difference between S^{CT} and S^{BDP} states energies is given in Figure 13. Two branches are observed: one corresponding to $E[S^{CT}] > E[S^{BDP}]$ (right branch), while the other relates to the $E[S^{CT}] < E[S^{BDP}]$ situation (left branch). Clearly, increasing the $E[S^{CT}] / E[S^{BDP}]$ gap leads to a subtle decrease of Φ_A , indicating the reduced probability of the $S^{CT} \rightarrow T^{CT}$ ISC process.

Tentative intersystem crossing pathway in BADs

The calculations based on the M06-2X functional showed that the BODIPY and anthracene fragments are nearly orthogonal in all studied systems. According to the study of a potential energy surface along the dihedral angle between the fragments, at standard room temperature conditions can vary only in a limited range. For instance, in dyads **1-3**, based on unsubstituted BODIPY, the maximum achievable twist at room temperature is 60-65° (this corresponds to ~3-4 kcal/mol vibrational energy). Variable temperature 1H NMR studies support that mutual rotation between the subunits is taking place in these dyads. A singlet at 6.38 ppm, corresponding to the pyrrolic protons in position 1 and 7 of the BODIPY core, was observed to split into a multiplet at lower temperatures (Fig. S39), while other pyrrolic protons are affected. In line with previous reports on BODIPY molecular rotors⁴⁴ such splitting is due to the restriction of rotation of anthracene rings. Additionally, substantially red-shifted CT emission of dyads lacking alkyl substituents in positions 1 and 7 of the BODIPY (Fig. 3d) evidences increased conjugation between the subunits which is achieved due to twisting.

Figure 14. Frozen scan energy curves of PES for S^{BDP} , S^{CT} and T^{CT} states along the twist angle.

The presence of alkyl substituents in the BODIPY restricts the maximal twisting angle to 80°. The geometries with lower angles possess substantially higher energies. Thus, it appears likely that the most favorable geometry of the dyads **9-11** and **13-15** (bearing alkyl substituents in positions 1 and 7) in solution is close to orthogonal, as was shown by XRD analysis (see above). For dyads **1-3** and **5-7** (no alkyl substituents in positions 1 and 7), with a larger degree of rotational freedom along the C8-C15 bond, a range of conformations in solution can be expected. In the case of dyads **4, 8, 12** and **16**, containing phenylene bridges between the subunits, an almost free rotation with an angle of 55° corresponding to its lowest energy configuration can be expected. It has been noted in a number of previous works that an orthogonal arrangement of the subunits in multichromophoric systems results in increased ISC. Particularly, orthogonal BODIPY dimers and trimers were reported by Akkaya *et al.* as efficient triplet sensitizers.^{12a} However, the effect of orthogonal chromophore arrangement on ISC was attributed to a prevention of mixing of the π -systems of the two subunits, keeping HOMO and LUMO of the subunits essentially unperturbed. The present quantum chemical investigation, in conjunction with experimental

photophysical data for BADs, shows that the orthogonal geometry is responsible for reducing the S-T energy gap in the CT state. Similar effects have recently been reported for donor-orthogonal-acceptor conjugated polymers⁴⁵ and OLED emitters exhibiting thermally-activated delayed fluorescence.⁴⁶

The frozen scan for the simplest dyad **1** along the twist dihedral angle at CASSCF(4/4) level of theory is given in Fig. 14. Energies of singlet and triplet CT states strongly depend on the relative orientation of the donor and acceptor subunits, with the ΔE_{S-T} energy varying from 0.1 eV for a conformation with 70° twist between the subunits, to less than 0.03 eV for a dihedral angle larger than 80°. The near-orthogonality of the D-A units is thus key to achieving almost degenerate singlet and triplet levels. The closeness of S^{CT} and T^{CT} energies (they are almost degenerate) on the potential energy surface in the vicinity of orthogonal geometries (~70-100 cm⁻¹ by M06-2X level) opens the possibility for ISC to take place.

Two general mechanisms for ISC in the studied dyads can be considered: spin orbit coupling (SOC) and hyperfine coupling (HFC). However, if the dihedral angle between the subunits is close to 90°, SOC is not operative due to a very low ferromagnetic exchange coupling integral caused by negligible overlapping of singly occupied orbitals π_{ant} and π_{BDP}^* , located in mutually orthogonal molecular moieties, and thus the matrix element for the $S^{CT} \rightarrow T^{CT}$ transition approaches zero. Hence, no change in orbital angular momentum, as required for a spin flip, can occur.⁴⁷ The orthogonal geometry of the dyad subunits allows for efficient crossing between the S^{CT} state and an energetically close local triplet state – the T^{BDP} or T^{Ant} state in this case – via a spin orbit charge transfer ISC process, (SOCT), as this spin flip transition couples to a change in orbital angular momentum.⁴⁸ On the other hand, the process can take place due to the electronuclear hyperfine coupling in the two radical-ion fragments. Populated S^{CT} states may lead to ISC, thus producing the triplet T^{CT} electronic states, which then undergo spin-selective intersystem charge recombination to the S_0 ground state or pass through the triplet valence states T^{BDP} and T^{Ant} . Both HFC and SOCT have been proposed to be operative in donor-acceptor dyads.^{15,16} However, this is still an open question and further investigations are needed to evaluate the role of HFC in BADs.

Thus, while the electronic coupling between the local singlet excited state of the BODIPY (S^{BDP}) and the charge-transfer singlet state (S^{CT}) are responsible for the efficiency of PeT, ISC in the BADs is controlled by the molecular geometry. In order to minimize the singlet-triplet energy gap the dyad's geometry has to be dynamically fluctuating about orthogonality. When the molecule is rigidly constrained in the orthogonal geometry (e.g., due to the presence of alkyl substituents on the BODIPY), the singlet-triplet gap in the CT state is minimized. In dyads **9-11**, efficient electron transfer provides high yields of CT, which, in conjunction with a near orthogonal geometry, results in efficient ISC and triplet state formation as evidenced by the TA studies and high Φ_A values. In contrast, while an orthogonal geometry is conserved for dyads **13-15**, the larger number of destabilizing alkyl groups lowers the efficiency of PeT and CT state yield resulting in a decrease of ISC and Φ_A values. In the absence of methyl substituents in positions 1 and 7 of the BODIPY, molecular vibrations allow a deviation from orthogonality for dyads **5-7**. Despite the high efficiency of PeT due to low $E(S^{CT})-E(S^{BDP})$ values, deviations from orthogonality lead to reduced triplet state yields in these dyads. A similar effect can be considered, if the subunits are separated by phenylene spacers, as in dyads **4, 8, 12** and **16**. Finally, for alkyl-unsubstituted dyads **1-4**, the geometry can relax towards non-orthogonality and as a result the singlet-triplet energy gap in CT state increases, preventing

efficient ISC and the formation of local BODIPY triplet states becomes inefficient, consistent with reduced Φ_{Δ} values. The processes described are schematically depicted in Figure 15.

Figure 15. General schematic mechanism of the ISC process in BADs involving $S^{\text{BDP}} \rightarrow S^{\text{CT}}$ transition.

Restriction of molecular rotation in a viscous solvent could be expected to decrease ISC in dyads **1-3** due to reduced probability of adopting an orthogonal conformation. The effect of viscosity-controlled twisting on the photophysical properties has been studied in details for porphyrin dimers and BODIPY molecular rotors.⁴⁹ A large difference in triplet excited state yields between polar (ethanol, DMF) and non-polar (hexane, toluene) solvents, observed for these dyads by transient absorption and $^1\text{O}_2$ trapping experiments could be in part associated with this effect. Under standard conditions, the viscosities of ethanol and hexane are 1.14 and 0.33 mPa, respectively. When measured in more viscous cyclohexane ($\eta = 1.0$ at 20°), the Φ_{Δ} value of dyad **2** dropped to 0.28, compared to hexane (0.38, Table 2) which possesses similar polarity and, consequently, comparable PeT rates. Likewise, in methanol ($\eta = 0.59$ at 20°) Φ_{Δ} increased to 0.15, compared to ethanol (0.05, Table 2).

Conclusions

Overall, in the BAD systems rapid light-induced charge transfer is observed to compete with local fluorescence of the BODIPY's local excited state. Structural factors and media polarity determine the dominant decay pathway. Alkyl substituents effectively attenuate the HOMO energy level of the BODIPY subunit and CT state, making PeT feasible for these dyads in polar solvents. Depending on the energy gap between the S^{BDP} and CT state, the latter species can be formed in high yields. The lifetimes of the CT states are reasonably long, allowing ISC process to take place. This leads to the formation of a local T^{BDP} and T^{Ant} state, as was evidenced by transient absorption studies. The resulting triplets can be used for selective generation of singlet oxygen, depending on the polarity of the medium.

Intersystem crossing in the CT state is promoted by the orthogonal orientation of the subunits in the BADs. Many examples of efficient ISC in orthogonal dyads have been reported, however the nature of this effect had not been clearly identified so far. The present computational study suggests that ISC in such dyads is driven by a reduced S-T energy gap and may take place *via* hyperfine coupling. In order for the $S^{\text{CT}} \rightarrow T^{\text{CT}}$ transition to be possible, the molecule should stay on the potential energy surface near orthogonal geometry, thereby bringing the S^{CT} and T^{CT} states together. For example, the presence of a separating phenylene unit will lead to free rotation between the BODIPY and anthracene fragments, thus reducing the probability of adopting an

orthogonal conformation. As a result, negligible ISC is observed in such dyads.

A particular point of interest in the BADs family discussed here concerns the generation of triplet states and singlet oxygen by dyads **1-3**. We suggest that the observed generation of triplet excited states in non-polar solvents is due to lower CT state energies, with respect to BADs with alkyl substituents, which were shown to destabilize CT states. Lower energy gap between S^{BDP} and S^{CT} makes the PeT process feasible, which is consistent with steady-state emission and transient absorption data. In addition, solvent viscosity is likely to affect triplet state formation, as indicated by comparing the Φ_{Δ} values in solvents of similar polarity but largely different viscosities. This result suggests the possibility of tuning ISC in these dyads by changing solvent viscosity and/or temperature.

Looking forward, we anticipate that the scope of donor-acceptor dyads capable of triplet sensitization mediated by intramolecular charge-transfer is very broad and not limited to systems containing anthracene as an electron donor or BODIPY as an acceptor. Efficient PeT has been reported by Nagano *et al.* in BODIPYs with electron donor phenyl (mono-, di- and trimethoxyphenyl) and naphthalenyl groups.⁵⁰ Although ISC in these molecules has not been studied, the observed photophysical properties are consistent with the idea of triplet state formation from CT states. Similar donor-acceptor couplings, resulting in a pronounced solvatochromism were reported by Murgia *et al.* for BODIPY-pyrene dyads.⁵¹ Very recently, Zhao and others studied photoinduced charge transfer in BODIPY dimers²⁵ and confirmed that triplet excited state generation takes place through the mechanism presented here, rather than through SO-ISC as previously claimed for such systems.¹² Finally, when this paper was in preparation, Majima *et al.* reported $^1\text{O}_2$ sensitization in aggregates formed by electron donor-acceptor fluorescein-anthracene dyads in an aqueous environment,⁵² confirming that PeT-mediated triplet state sensitization is not limited to BODIPY derivatives.

Triplet sensitizers based on such dyads possess significant potential for many applications, particularly related to biomedical applications due to the unique polarity-dependent generation of triplet excited states and singlet oxygen. Exploration of these applications requires efficient PeT sensitizers based on synthetically readily accessible dyad molecules and their biocompatible derivatives. Our previously described synthetic approach towards BADs bearing water-solubilizing groups¹⁷ allowed us to elaborate corresponding derivatives of dyads **1-16** for *in vitro* and *in vivo* investigation. The results of these studies will be reported elsewhere.

Conflicts of interest

There are no conflicts to declare.

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[†] Electronic supplementary information (ESI) available: Analytical data for new compounds, spectroscopic data, crystallographic data and calculations details.

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38 In reference 17, please read the sentence, ‘fitting of the PB decays at 380 and 400 nm and the rise of BDP⁺ and Ant⁺ bands (Figure 1b) yields time constants of 1.15 and 0.54 ps for the EnT and PeT processes, respectively’ in page 6283 as ‘fitting of the PB decays at 380 and 400 nm and the rise of BDP⁺ and Ant⁺ bands (Figure 1b) yields time constants of 0.54 and 1.15 ps for the EnT and PeT processes, respectively’.

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Heavy atom-free BODIPY-anthracene dyads show triplet excited state formation via PeT, controlled by molecular rotation and environmental polarity.

39x23mm (300 x 300 DPI)