LETTERS

Bodipy–Anthracene Dyads as Triplet Photosensitizers: Effect of Chromophore Orientation on Triplet-State Formation Efficiency and Application in Triplet–Triplet Annihilation Upconversion

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Supporting Information

ABSTRACT: Bodipy–anthracene dyads with two chromophores assuming orthogonal geometry to enhance the spin-orbital charge-transfer intersystem crossing (SOCT-ISC) were prepared. The photosensitizers show strong absorption of visible light, efficient triplet-state formation (quantum yield 90%), and a long-lived triplet state (85 μ s). The dipole moment orientation exerts significant effect on the ISC efficiency. It is also the first time that photosensitizers based on SOCT-ISC were used for triplet–triplet annihilation upconversion. The upconversion quantum yield is up to 15.8%.

H ighly efficient triplet photosensitizers (PSs) are important for photocatalysis,¹ photodynamic therapy (PDT),² and more recently, triplet—triplet annihilation upconversion (TTA UC).³ Efficient intersystem crossing (ISC) is pivotal for triplet PSs.⁴ Normally a heavy atom effect is used to enhance the ISC.⁴ As such, most typical triplet PSs contain Pt, Ru, Ir, I, or Br, etc.⁵ Heavy atom-free triplet PSs have been rarely reported but are highly desired in terms of cost efficiency, toxicity, and fundamental photochemistry.^{4,6} However, it is still a major challenge to develop efficient heavy atom-free triplet PSs.

Some strategies have been developed to enhance the ISC of heavy atom-free compounds, for instance, exciton coupling, double excited state,⁸ spin converter,^{9a} thermally activated reverse ISC,^{9b-d} and singlet fission.¹⁰ Although these approaches are promising, drawbacks do exist. For instance, for most of these methods, a synthetically demanding bichromophore molecular structure is required.⁷⁻¹⁰ New methods to enhance ISC in organic chromophores with simple molecular structures are desired. Recently, it was shown that spin-orbital charge transfer (SOCT) is effective to enhance the ISC in organic chromophores.^{10,11} For instance, julolidineanthracene dyads show ISC ability.¹⁰ Recently Bodipyanthracene dyads were shown to show ISC.¹¹ The key molecular structural design strategy is the orthogonal orientation between the electron donor and the electron acceptor, so that the change of molecular orbital angular momentum can compensate for the change of electron-spin angular momentum during ISC. As a result, the ISC can be enhanced because the conservation of the angular momentum is achieved.

SOCT-ISC is particularly interesting in terms of ISC since only one *major* chromophore is required and a structurally simple electron donor or acceptor can be used, thus making the synthesis easier. Moreover, introducing an electron donor or



acceptor into the molecule will offer additional functionality; for instance, the triplet PSs can be responsive to external redox stimuli, which is important for biological systems.¹² However, some critical problems still remain in this new area: the molecular structure–ISC efficiency relationship is unclear, the molecular structures that have been investigated are very limited, and the chromophores studied until now are limited to those showing weak absorption of visible light. Moreover, no application has been demonstrated for this ISC strategy.

To address the above challenges, herein we designed Bodipy—anthracene dyads to probe the relationship between the molecular structure, mainly the chromophore orientation, and the ISC efficiency (Figure 1). This relationship is crucial to elucidate the SOCT-ISC mechanism and it is useful for future molecular structural design.

Owing to the versatile derivatization of Bodipy chromophore, we prepared new dyads **BDP-AN-3** and **BDP-AN-4**. The dipole moment orientation of the anthracene and Bodipy of **BDP-AN-3** is different from that of **BDP-AN-1** and **BDP-AN-**2, although the energy-minimized geometry is orthogonal for all three dyads (the dihedral angle between Bodipy and anthracene are 90°, 90°, and 93° for **BDP-AN-1**, **BDP-AN-2**, and **BDP-AN-3**, respectively). Conversely, **BDP-AN-4** has a 52° dihedral angle between Bodipy and the anthracene moiety. The restriction on the rotation of the anthranyl moiety is on the order of **BDP-AN-3** > **BDP-An-1** \approx **BDP-An-2** > **BDP-AN-4** due to the presence of the methyl groups.

The UV-vis absorption of the compounds was studied (Figure 2). The absorption profiles are the sum of the Bodipy monomer and anthracene; thus, the electronic coupling







Figure 1. Molecular structures of BDP-AN-1, BDP-AN-2, BDP-AN-3, and BDP-AN-4 and reference compounds BDP and IBDP.



Figure 2. Normalized UV-vis absorption and fluorescence emission spectra of BDP-AN-1 in (a) *n*-hexane and (b) acetonitrile at 20 °C.

between the anthracene and the Bodipy moiety is very weak at the ground state. A lack of charge-transfer band in the UV–vis absorption spectra is evidence of the decoupling of the anthracene and the Bodipy moieties. This is reasonable since the anthracene and the Bodipy moiety take the most stable *orthogonal* geometry at the ground state.

The fluorescence emission spectrum in hexane (Figure 2a) is the mirror of the absorption spectrum. However, a new redshifted emission band at 600–800 nm was observed in acetonitrile (Figure 2b), which is attributed to the chargeseparated state (CSS) emission.¹¹ Similar results were observed for **BDP-AN-2**, **BDP-AN-3**, and **BDP-AN-4** (Figure S13) The fluorescence intensity was significantly quenched in polar solvents (Figure S12). Charge separation and emission from charge separated state is favored in polar solvents due to the larger driving force for charge transfer (CT) and the stabilized CSS.¹³ Observation of the CSS emission is an indication for possible SOCT-ISC.

In order to confirm the production of the triplet state upon photoexcitation, the nanosecond transient absorption spectra (ns TA) of the compounds were studied (for **BDP-AN-1**, see Figure 3). Upon nanosecond pulsed laser excitation, an excitedstate absorption (ESA) band at 420 nm was observed, as well as a weak absorption band in 560 nm -630 nm. This is the typical transient absorption feature of the triplet excited state of Bodipy.¹⁴ A triplet-state lifetime of 85 μ s was observed. The triplet state quantum yield was determined as 90% (Table 1). Similar results were observed for other dyads (Figures S14– S16). Using a singlet-state depletion method, the triplet-state quantum yields ($\Phi_{\rm T}$) of the dyads in different solvent were determined (Table 1).



Figure 3. Nanosecond transient absorption spectra of **BDP-AN-1**: (a) **BDP-AN-1** upon ns pulsed laser excitation ($\lambda_{ex} = 502$ nm) and (b) decay trace of **BDP-AN-1** at 505 nm. $c = 1.0 \times 10^{-5}$ M in deaerated dichloromethane, 20 °C.

The results show that the triplet state quantum yields are highly dependent on the chromophore orientations, as well as the dipole moment orientation, in the dyads (Table 1). This is a new finding.¹¹ For instance, with the anthracene moiety attached at the *meso*-position (i.e., **BDP-AN-1** and **BDP-AN-2**), the triplet states yields are much higher (up to 96%) than the dyads with the anthracene moiety attached at the 2-position of the Bodipy core (**BDP-AN-3**, <31%). Note in both cases that the orientation of the chromophores is "orthogonal", but the *dipole moments* alignments are different. For **BDP-AN-2**, the dipole moment vectors of anthracene part and the Bodipy part are antiparallel, while for **BDP-AN-3** they are approximately orthogonal (Figure S25).

This result indicates that the previously proposed concept of orthogonal geometry for the chromophores in the dyads is insufficient to attain high ISC yield. An additional description of the geometry of the components of the PSs should be used, i.e., vectorial dipole moment orientations of the chromophores. We tentatively propose that the parallel/antiparallel dipole moment orientation of the CT donor and acceptor maybe more beneficial to SOCT-ISC rather than orthogonal dipole moment alignment. Moreover, the restriction of the rotation of the anthracene moiety also exerts a non-negligible effect on the ISC yields, as such BDP-AN-3 shows a higher triplet-state quantum yield (16-31%) than BDP-AN-4 (6-21%). BDP-AN-4 has larger rotational freedom, and the dihedral angle of the donor and acceptor (52°) deviates greatly from 90°, which is detrimental to the SOCT-ISC. Moreover, compared with BDP-AN-1 and BDP-AN-2, the red-shifted absorption and emission wavelength of BDP-AN-3 and BDP-AN-4 indicated a relatively larger π -conjugation (thus a relatively stronger coupling) between bodipy and anthracene units, which also contributes to a less efficient SOCT-ISC for BDP-AN-3 and BDP-AN-4.

We found that the triplet quantum yields of the dyads are highly dependent on the solvent polarity. In nonpolar solvents such as toluene, the triplet-state quantum yields are very low, whereas in high polar solvents (such as DCM) the triplet-state quantum yields become much higher. This is in agreement with the CT character of the ISC pathway. This charge-transfer-induced ISC mechanism was illustrated with an energy diagram (Scheme 1).¹⁵ The energy level of the CSS is highly dependent on the solvent polarity, and generally, the energy level becomes lower in polar solvents. It should be pointed out that the CSS energy level in polar solvents should be higher than the T₁ state of the chromophore; otherwise, the charge recombination (CR) will not give triplet state or the triplet state will be quenched.¹⁵

Table 1. Photophysical Properties of the Compounds

	solvent	λ_{abs}^{a}	ε^{b}	$\lambda_{ m em}$	$\Phi_{\mathrm{F}}{}^{c}$	$\tau_{\rm F}^{\ d}$ (ns)	$\tau_{\mathrm{T}}^{e}(\mu \mathrm{s})$	Φ_{Δ}^{f}	$\Phi_{\mathrm{T}}^{\ g}$	$\Phi_{\mathrm{UC}}^{ h}(\%)$
BDP-AN-1	toluene	508/373	9.0/1.7	521	0.81	5.8	317	0.10	0.06	
	dichloromethane	506/373	8.6/1.7	518/595	0.01/0.02	$5.0^{i}/4.8^{j}$	85	0.95	0.90	15.8
	acetonitrile	503/373	8.0/1.7	512/641	0.002/0.007	$4.2^{i}/2.9^{j}$	68	0.84	0.92	3.2
BDP-AN-2	toluene	508/366	9.9/1.5	521	0.84	5.5	345	0.04	0.03	
	dichloromethane	506/366	9.7/1.5	518	0.14	5.5	82	0.82	0.80	10.1
	acetonitrile	502/366	8.7/1.5	510/634	0.01/0.01	$5.0^{i}/3.0^{j}$	78	0.86	0.96	3.9
BDP-AN-3	toluene	516/367	8.0/1.0	556	0.39	4.2	127	0.20	0.31	5.9
	dichloromethane	513/367	7.8/1.0	584	0.10	3.0	118	0.24	0.20	5.6
	acetonitrile	510/367	7.5/1.0	524/627	0.01/0.02	$2.6^{i}/1.3^{j}$	137	0.11	0.16	
BDP-AN-4	toluene	520/364	8.7/1.2	568	0.42	4.1	102	0.11	0.17	2.5
	dichloromethane	517/364	8.9/1.2	575	0.20	3.3	116	0.13	0.21	2.1
	acetonitrile	513/364	8.4/1.2	587	0.04	$1.8^{i}/1.3^{j}$	125	0.05	0.06	
BDP ^k	toluene	503	8.8	515	0.90 ^k	3.4	1	1	1	1

^{*a*}In toluene $(1.0 \times 10^{-5} \text{ M})$. ^{*b*}Molar absorption coefficient $(10^4 \text{ M}^{-1} \text{ cm}^{-1})$. ^{*c*}Fluorescence quantum yield, **BDP** as standard $(\Phi_L = 0.9 \text{ in toluene})$. ^{*d*}Luminescence lifetimes. ^{*e*}Triplet-state lifetimes. Measured by ns TA in deaerated solutions. ^{*J*}Singlet oxygen quantum yield (Φ_{Δ}) , diiodobodipy as a standard $(\Phi_{\Delta} = 0.87 \text{ in DCM})$. ^{*g*}Triplet state quantum yield, measured with ns TA, with IBDP as the standard $(\Phi_T = 0.88 \text{ in toluene})$. ^{*h*}TTA UC quantum yield, with IBDP as the standard $(\Phi_F = 0.027 \text{ in acetonitrile})$. Upconversion quantum yield of **BDP-AN-1/BDP-AN-2** and **BDP-AN-3/BDP-AN-4** were measured at 50 mW cm⁻² and 100 mW cm⁻², respectively. ^{*i*}At short wavelength. ^{*j*}At long wavelength. ^{*k*}Literature values. ^{*i*}Not applicable.

Scheme 1. Simplified Jablonski Diagram Illustrating the Photophysical Process in BDP-AN-1



Most of the triplet PSs for TTA UC are based on the heavy atom effect to enhance the ISC.³ Use of heavy-atom-free triplet PSs with a SOCT–ISC mechanism in TTA upconversion has never been reported. However, Bodipy–anthracene dyads, especially **BDP-AN-1** and **BDP-AN-2**, show a strong absorption of visible light ($\varepsilon = 8.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and an efficient ISC ($\Phi_T = 90\%$) and long-lived triplet state (85 μ s), and TTA UC was carried out with these new PSs (Figure 4, for



Figure 4. (a) Upconversions with **BDP-AN-1** as triplet PS and perylene as triplet acceptor. Excited with 510 nm cw-laser (50 mW cm⁻²). c[perylene] = 3.0×10^{-5} M, in deaerated dichloromethane, 20 °C. Inset: Photographs of **BDP-AN-1** alone and the upconversion. (b) CIE diagram.

BDP-AN-1). Perylene was used as the triplet acceptor, and a 510 nm continuous wave (cw) laser was used for excitation. **BDP-AN-1** alone gave a yellowish emission due to the residue fluorescence of the Bodipy unit. Upon addition of perylene, the blue emission of perylene was observed, which is the upconverted fluorescence of perylene. The upconversion quantum yield with **BDP-AN-1** as the triplet PS was determined as 15.8%, which is competitive with the conventional heavy atom PSs (**IBDP**, 15.1% measured under the same conditions, Figure S22). This study presents a new opportunity to tune the TTA UC with external stimuli,¹⁶ such as by monitoring the in vivo redox stress.¹²

In conclusion, we prepared a series of Bodipy-anthracene dyads with the two components assuming orthogonal geometry to enhance the spin-orbital charge-transfer intersystem crossing. As such, heavy-atom-free efficient triplet photosensitizers were obtained. The PSs show strong absorption of visible light, efficient triplet-state formation (quantum yield, 90%), and long triplet-state lifetimes (85 μ s). Moreover, we found that the dipole moment orientation of the anthracene moiety (electron donor) exerts a significant effect on ISC efficiency; thus, the previously suggested orthogonal geometry of the chromophore is not exclusively sufficient to achieve efficient SOCT-ISC. The SOCT-ISC triplet PSs are employed in triplet-triplet annihilation upconversion for the first time, and the upconversion quantum yield is up to 15.8%. Our finding may be useful for future molecular structural design of new efficient triplet PSs, photocatalysis, external stimulateresponsive PDT, TTA upconversion and for fundamental photochemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b02047.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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