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Molecular Structure-Intersystem Crossing Relationship of Heavy Atom-Free BODIPY Triplet Photosensitizers

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ABSTRACT: A thiophene-fused BODIPY chromophore displays large triplet state quantum yield ($\Phi_T = 63.7 \%$). In contrast, with the two thienyl moieties are not fused into the BODIPY core, intersystem crossing (ISC) becomes inefficient and the Φ_T remains low ($\Phi_T = 6.1 \%$). First principle calculations including spin-orbit coupling (SOC) were performed to quantify the ISC. We find larger SOC and smaller singlet-triplet energy gaps for the thiophene-fused BODIPY derivative. Our results are useful for study the photochemistry of organic chromophores.

KEYWORDS: BODIPY; Intersystem Crossing; Spin-orbit coupling; Thiophene; Triplet State

Triplet photosensitizers are versatile compounds which have been widely used in photodynamic therapy (PDT),¹ as photocatalysts in photocatalytic hydrogen production (H_2) and photoredox organic reactions,² as well as in photoinduced charge separation,^{3a-3c} and triplettriplet annihilation upconversion.^{3d-3g} The triplet photosensitizers play the pivotal role by first harvesting light leading to the singlet excited states and then promoting the formation of triplet state *via* intersystem crossing (ISC). Finally, they may trigger intermolecular electron or energy transfer processes. In order to facilitate the ISC, the most well-known approach is to take advantage of the heavy atom effect, obtained with metallic coordination centers such as Ir(III), Pt(II), Ru(II), or alternatively with iodine atoms (I).⁴ The heavy atom-effect is proportional to Z^4 (Z is the atomic number). As a consequence, a larger heavy atom effect is expected for Pt or Ir than for S and Br.⁴ It is indeed well-known that most of the Ir(III), Pt(II) or Ru(II) transition metal complexes show efficient and ultrafast ISC.⁵ For example, $Ru(bpy)_3Cl_2$ (bpy = 2,2'biphenylpyriding) displays a quantum yield of triplet state formation of 100%. Previously, it was also shown that iodine substitution on the π -core of the boron dipyrromethane (BODIPY) chromophore is an effective approach to access efficient organic triplet photosensitizers.⁶

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Significant heavy atom effect obtained with non-metallic atoms other than iodine remains scarce, though designing efficient triplet photosensitizers with lighter atoms, such as sulfur, would be of tremendous interest. While some oligothiophene compounds are known to form triplet excited states upon photoexcitation, this effect was not thoroughly studied for small molecules which contain thiophene moieties.^{7a,7b} During the preparation of this manuscript, a thiophene fused BODIPY derivative was reported to show ISC capability, but the detailed mechanism was not studied.^{7c}

Scheme 1. Compounds Used in the Study



Recently a thiophene-fused BODIPY dye was reported to show very weak fluorescence.^{8a} Normally BODIPY compounds show strong fluorescence.^{8b-8d} We consequently envisioned that efficient ISC could be attained with this compound (**BDP-1**, Scheme 1). Herein we present the synthesis and spectroscopic characterization of this BODIPY derivative. The generation of triplet excited states was confirmed with nanosecond transient absorption spectroscopy and rationalized with *ab initio* calculations. We found that triplet formation with the heavy atom-free **BDP-1** is more efficient (triplet formation quantum yield, $\Phi_T = 63.7\%$) than with the BODIPY derivative presenting non-fused thiophene rings (**BDP-3**, $\Phi_T = 6.1\%$). Theoretical calculations show that for **BDP-1** a higher-lying triplet state, i.e. T₂, which is energetically aligned to the spectroscopic S₁ state is responsible for the enhanced ISC processes. In short, we demonstrate that the incorporation of sulfur atoms into the π -conjugation skeleton of BODIPY is an efficient approach to attain high quantum yield of triplet formation.



Figure 1. UV–Vis absorption of BDP-1, BDP-2 and BDP-3. $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.

The UV-vis absorption spectra of the compounds were studied (Figure 1). **BDP-1** shows strong absorption at 571 nm. In comparison **BDP-3** shows a blue-shifted absorption band peaking at 529 nm. **BDP-1** undergoes a very slight blue shift in polar solvents compared with non-polar solvents (Supporting Information, Figure S7). This result indicates that the ground state presents a larger dipole moment than the first singlet excited states. Similar results were observed for both **BDP-2** and **BDP-3** (see Figure S7 in the Supporting Information).

Fluorescence spectra were also recorded (Figure 2). **BDP-1** shows weak fluorescence ($\Phi_F = 4.0 \%$). **BDP-3** shows red-shifted emission at 608 nm and a larger Stokes shift. **BDP-2** fluoresces at 516 nm. These experimental evidences are in agreement with an extended π -conjugation in **BDP-1** as compared with **BDP-3**.



Figure 2. The normalized emission spectra of BDP-1 (black, $\lambda_{ex} = 530$ nm, $A_{530} = 0.20$), BDP-2 (red, $\lambda_{ex} = 470$ nm, $A_{470} = 0.26$) and BDP-3 (blue, $\lambda_{ex} = 498$ nm, $A_{498} = 0.23$), in toluene. 20 °C.



Figure 3. (a) Nanosecond transient absorption of **BDP-1** after pulsed laser excitation ($\lambda_{ex} = 560$ nm), (b) Decay trace of **BDP-1** at 569 nm in deaerated toluene, $c = 1.0 \times 10^{-5}$ M, 20 °C.

To investigate the triplet state generation in **BDP-1**, nanosecond transient absorption spectra were recorded (Figure 3). Upon pulsed laser excitation, a bleaching band at 566 nm was observed. Excited state absorption (ESA) at 491 nm was also observed. The lifetime of the transient was determined to be 170.5 μ s. The transient was significantly quenched in aerated solution, hence it is related to the formation of a triplet excited state (Supporting Information,

 Figure S18). The triplet state quantum yield (Φ_T) of **BDP-1** amounts to 63.7% (see Table 1, determined with the singlet state depletion method). No significant triplet state formation was observed in **BDP-2** (Φ_T is negligible). A similar nanosecond transient absorption spectrum was observed for **BDP-3** (see SI, Figure S17). However, a lower triplet excited state quantum yield was observed for **BDP-3** ($\Phi_T = 6.1\%$) than for **BDP-1**. The photophysical properties of the compounds are summarized in Table 1.

In order to rationalize the different ISC of **BDP-1** – **BDP-3**, the relative energy level of the singlet and triplet states, as well as the spin-orbit coupling (SOC) of the compounds were studied. The ISC rate between the n-singlet (S_n) and m-triplet (T_m) excited states (k_{ISC}) obeys the empirical Fermi Golden rule equation (Eq. 1),

$$k_{\rm ISC} = \frac{2\pi}{\hbar} \left\langle S_{\rm n} \left| \hat{H}_{\rm SO} \right| T_{\rm m} \right\rangle^2 \times [\rm FCWD]$$
(Eq. 1)

where the bracket term stands for their associated SOCs and FCWD accounts for the Franck-Condon weighted density of states. From a computational viewpoint, the calculation of ISC rates first requires the assignment of the main photodeactivation channels, followed by accurate calculations of (i) relative energy levels of the involved excited states, (ii) SOC matrix elements, (iii) vibrational frequencies and (iv) Huang-Rhys factors. Computing all parameters on Eq.(1) becomes rapidly prohibitive for large molecules.⁹ Instead, semi-quantitative and qualitative strategies are often used to rationalize the efficiency of ISC processes.¹⁰ Based on the computation of k_{ISC} values relying on accurate *ab initio* electronic structure data it is concluded that two main factors, i.e. substantial electronic and/or vibronic SOC and small T_m-S_n energy gaps, govern the efficiency of the ISC processes.⁹ Herein, we report theoretical estimates of SOCs and relative T_m-S_n energy gaps to rationalize the efficient ISC in **BDP-1** as compared with those occurring in both **BDP-2** and **BDP-3**. Modeling the electronically excited state properties of BODIPY dyes is still a significant challenge for quantum chemical methods due to the well documented *cyanine challenge*, which roots on the need of capturing large differential electron correlation effects in these compounds.¹¹ Recent time-dependent density functional theory (TD-DFT) studies of the excited states of BODIPY dyes concluded that, among the available pool of exchange-correlation functionals, M06-2X outperforms the rest of functionals.¹² However, TD-DFT still systematically overshoots the transition energies of BODIPY dyes by ca. 0.4 eV. Therefore correcting the TD-DFT values with transition energies obtained at the scaled-opposite-spin configuration interaction singles with double corrections, i.e. SOS-CIS(D) was advocated as a much more accurate approach.¹³

 Table 1. Photophysical Parameters of the Compounds

	$\lambda_{ m abs}{}^{ m a}$	ε^{b}	$\lambda_{\rm em}$ (eV) ^c	$\Phi_{\mathrm{F}}\left(\% ight)^{d}$	$\tau_{\rm F}({\rm ns})^e$	$\tau_{\mathrm{T}}(\mu s)^{f}$	$\Phi_{ riangle}(\%)^g$	$\Phi_{\mathrm{T}}(\%)^{h}$
BDP-1	571 nm (2.17 eV)	8.35	582 nm (2.13 eV)	4.0 ^{<i>i</i>}	1.35	170.5	58.1	63.7
BDP-2	500 nm (2.48 eV)	9.71	516 nm (2.41 eV)	99.0 ⁱ	5.30	-	-	-
BDP-3	529 nm (2.35 eV)	5.65	608 nm (2.04 eV)	11.2	4.59	389.9	4.93	6.1

^{*a*} In toluene (1.0×10^{-5} M). ^{*b*} Molar extinction coefficient at the absorption maxima. $\varepsilon \cdot 10^4$ M⁻¹ cm⁻¹. ^{*c*} In toluene. ^{*d*} Fluorescence quantum yields. DiiodoBodipy ($\Phi_F = 0.027$ in CH₃CN) was used as standard. ^{*e*} Luminescence lifetime, $\lambda_{ex} = 405$ nm, at RT, in toluene. ^{*f*} Triplet state lifetime, determined with nanosecond time-resolved transient absorption spectroscopy, **BDP-1** $\lambda_{ex} = 560$ nm, **BDP-3** $\lambda_{ex} = 532$ nm, 1.0×10^{-5} M in deaerated toluene. ^{*g*} Quantum yield of singlet oxygen ($^{1}O_2$), with DiiodoBodipy as standard ($\Phi_{\Delta} = 0.83$ in CH₂Cl₂), 1.0×10^{-5} M in CH₂Cl₂. ^{*h*} Triplet quantum yields upon direct photoexcitation (462 nm). Ru(bpy)₃Cl₂ ($\Phi_T = 1.0$ in H₂O) was used as standard. ^{*i*} Literature value. ^{6b, 8a}

Table 2 lists the TD-M06-2X and SOS-CIS(D) vertical excitation energies for the lowest singlet and triplet excited states of **BDP-1**, **BDP-2** and **BDP-3** at their optimized ground state geometries (see computational details in the Supporting Information). As expected, the SOS-CIS(D) excitation energies of the spectroscopic state (S_1) are in a better agreement with the

position of measured UV-Vis absorption bands (see Table 2). Regarding their intensities, BDP-1 shows a larger oscillator strength than **BDP-3**, in accordance to the experimental evidences. TD-06-2X systematically overestimates and underestimates by ca. +0.4 and -0.25 eV the excitation energies of the singlet and triplet excited states, respectively, as compared to SOS-CIS(D). In view of these evidences, we discuss only the SOS-CIS(D) values in the following. To evaluate the main $S_n \rightarrow T_n$ ISC channels, only the excited states which are below the experimental λ_{exc} of photoexcitation are considered ($\lambda_{exc} = 462 \text{ nm} / 2.68 \text{ eV}$, see Table 1). Upon photoexcitation, there are two possible $S_n \rightarrow T_n$ ISC channels for the spectroscopic state (S₁) of **BDP-1**, i.e. $S_1 \rightarrow T_2$ and $S_1 \rightarrow T_1$. Due to the smaller energetic gap between T_2 and S_1 (i.e. 0.24 eV, see Table 2), we propose $S_1 \rightarrow T_2$ to be the most important triplet deactivation funnel for **BDP-1**. In contrast, for **BDP-2** and **BDP-3** only the $S_1 \rightarrow T_1$ ISC channel is energetically accessible. Table 2 also collects the SOCs obtained with quadratic response (QR)-TD-DFT/6-31G* calculations between the involved T_m and S_1 excited states (see computational details in the Supporting Information). As expected for organic compounds, the SOCs amount only to a few cm⁻¹. As seen in Table S3, the effect of increasing the basis set on the SOCs calculations is almost negligible, so that the results are almost converged at the (QR)-TD-DFT/6-31G* level of theory. It should be recalled that SOCs values between 0.2 and 5.0 cm^{-1} are considered large enough to induce ISC on a nanosecond time scale.¹⁴

The SOCs for **BDP-1** are one order of magnitude larger than in the two other dyes, since the sulfur atom contributes to the involved lowest excited states of **BDP-1** (see the assignment of the excited states in Table 2 and the involved orbitals in Figure 4). In **BDP-3** the sulfur atom located at the peripheral ligand does not contribute to the BODIPY-like excited states (see Table 2 and Figure 4). Therefore, since **BDP-1** possesses the largest SOCs and the smallest singlet-triplet



Figure 4. Involved Kohn-Sham orbitals (M06-2X/6-311+G(2d,p) in the lowest excited states of **BDP-1** and **BDP-3**.

Table 2. Lowest Vertical Singlet and Triplet Electronic Transition Energies (in eV) and Oscillator Strengths (in parenthesis) of BDP-1, BDP-2 and BDP-3 at TD-M06-2X and SOS-CIS(D) Levels of Theory. Vertical Singlet-Triplet Splitting (in eV) and SOCs (in cm⁻¹) between the Involved T_m and S₁ States

	States / Assignment ^{<i>a</i>}	TD-M06-2X	SOS- CIS(D)	$\Delta E_{\text{SOS-CIS(D)}}$ (S ₁ -T _x)	$ \begin{cases} \langle S_1 \hat{H}_{SO} T_m \rangle^b \\ (x-; y-; z-components) \end{cases} $
BDP-1	S ₁ (H \rightarrow L, c = 0.67; H-1 \rightarrow L, c = -0.20)	2.72 (0.913)	2.32	_	_
	$T_1 (H \rightarrow L, c = 0.72)$	1.24	1.50	0.82	(0.0; 0.0; -3.2)
	$T_2 (H-1 \rightarrow L, c = 0.68)$	2.35	2.56	-0.24	(-1.2; -1.3; 0.0)
BDP-2	$S_1 (H \rightarrow L, c = 0.70)$	2.99 (0.539)	2.51	_	_
	$T_1 (H \rightarrow L, c = 0.71)$	1.60	1.83	0.68	(-0.3; 0.0; 0.0)
BDP-3	$S_1(H \rightarrow L, c = 0.70)$	2.76 (0.772)	2.29	_	_
	$T_1 (H \rightarrow L, c = 0.69)$	1.50	1.73	0.56	(-0.4; -0.2; 0.2)

^{*a*} Only the excited states which are below the experimental λ_{exc} of photoexcitation are considered ($\lambda_{exc} = 462 \text{ nm} / 2.68 \text{ eV}$). ^{*b*} Values obtained at the QR-TD-DFT/6-31G* level of theory at the T₁ optimized geometry.

energy gap among all the BODIPY dyes, it will easily undergo photodeactivation through ISC. Indeed, as discussed above, **BDP-1** yields the largest quantum yields of singlet oxygen (Φ_{Δ}) and triplet generation (Φ_{T} . see Table 1). Comparison of **BDP-3** with **BDP-2** is more qualitative, though the slightly increased SOCs and the lowest singlet-triplet energy gaps in **BDP-3** compared with **BDP-2**, point to slightly increase ISC channel for the latter, in accordance with the experimental observations.

In summary, we find that a heavy atom-free thiophene-fused BODIPY (**BDP-1**) shows efficient ISC, with triplet state quantum yield (Φ_T) of 63.7%. In comparison, two reference BODIPY derivatives which either contain no sulfur atom (**BDP-2**) or thiophene groups not participating directly in the π -conjugation pathway of the BODIPY core (**BDP-3**), do not show any significant ISC (Φ_T is negligible for **BDP-2**, and Φ_T is only 6.1% for **BDP-3**). Theoretical calculations demonstrate that the increased ISC mechanisms for **BDP-1** as compared with **BDP-**2 and **BDP-3** are due to i) the participation of the sulfur atom on the lowest-lying excited states, which leads to moderate SOCs and ii) a small singlet-triplet energy gap in **BDP-1**. These insights are useful to design heavy atom-free triplet photosensitizers and to understand the fundamental photochemistry of the ISC mechanisms of organic chromophores.

EXPERIMENTAL SECTION

General Remarks. All the chemicals are analytically pure and were used as received. Solvents were dried and distilled prior to use. Fluorescence lifetimes were measured with OB920 luminescence lifetime spectrometer (Edinburgh, U.K.). Compound **BDP-1** was prepared following the reported method.^{8a} **BDP-2** and **BDP-3** were reported previously.¹⁵

Compound 2. Into a 100 mL flask (dry, under Ar) was placed CH₂Cl₂ (30 mL), and cooled using an ice bath before AlCl₃ (4.9 g, 36.8 mmol) was added. A dropping funnel was charged

with acetyl chloride (2.68mL, 39.2 mmol) in CH₂Cl₂ (30 mL), and this solution was added to the AlCl₃ suspension over a period of 10-min. After about 30 min of being stirred at 0 °C, most of the AlCl₃ had been dissolved. A second dropping funnel was charged with 3-bromothiophene (0.574 mL, 1.00 g, 6.13 mmol) in CH₂Cl₂ (30 mL), and this mixture was added to the reaction mixture over a 10-min period. The reaction was left to proceed at 0 °C for 30 min and then warmed slowly to room temperature (RT) for another hour. Then the reaction mixture was cooled to 0 °C once again, and water was added carefully. The reaction mixture was diluted with CH₂Cl₂ and water was added. The water layer was extracted twice with CH₂Cl₂, and washed with saturated NaHCO₃, brine and finally dried over anhydrous MgSO₄. Evaporation of the solvent and purification by column chromatography (hexane: CH₂Cl₂ = 1:1) gave compound **2** as a yellow liquid (2.4 g, 98%). ¹H NMR (CDCl₃, 400 MHz): δ 7.55 (d, *J* = 4.9 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 2.68 (s, 3H).

Compound 3. To the mixture containing **2** (204 mg, 1 mmol), CuI (19 mg, 0.1 mmol) and Cs₂CO₃ (651 mg, 2 mmol) in DMSO (1 mL), ethyl isocyanoacetate (124 mg, 1.1 mmol) was added dropwise at RT. After stirring at 50°C for 4 h, the reaction mixture was extracted with CH₂Cl₂. The organic layer was washed with brine twice, then the organic layer was dried over MgSO₄ and filtrated. The filtrate was condensed with evaporation, and the silica gel column chromatography with hexane as a mixture eluent (hexane: ethyl acetate = 9:1) gave compound **3** as a white solid (110 mg, 53%). ¹H NMR (CDCl₃, 400 MHz): δ 7.64 (d, *J* = 5.3 Hz, 2H), 7.38 (s, 1H), 7.12 (d, *J* = 5.3 Hz, 2H), 2.42 (s, 6H).

Compound 4. The mixture containing **3** (340 mg, 1.63 mmol) and aq NaOH solution (1.032 g, in 7.2 mL H₂O) in 13.5 mL of ethanol was refluxed for 1 h. After cooling to RT, HCl (10%) was added dropwise to acidify. The products were extracted with CH_2Cl_2 , and the organic layer was washed with brine, dried over MgSO₄ and filtrated. Evaporation of the filtrate yielded compound

4 as a dark purple solid (268 mg, 90%). ¹H NMR (400 MHz, DMSO-d₆): δ 8.94 (s, 1H), 7.31 (d, J = 5.3 Hz, 1H), 6.91 (d, J = 5.3 Hz, 1H), 4.40 (q, J = 21.3 Hz, 2H), 2.52 (s, 3H), 1.41 (t, J = 14.2 Hz, 3H).

Compound 5. The solution of **4** (150 mg, 0.83 mmol) dissolved in trifluoroacetic acid (2.7 mL) was stirred at 50 °C for 20 min, and then triethyl orthoformate (512 mg, 3.46 mmol) was added. After stirring at 50 °C for 30 min, excess amounts of diethyl ether and satd NaHCO₃ aq were poured into the reaction solution. The organic layer was washed with brine and water, dried over MgSO₄, filtrated and condensed by evaporation afforded 5 as a brown solid (110 mg, 80.4%). ¹H NMR (400 MHz, CDCl₃): δ 12.43 (s, 1H), 11.51 (s, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 6.94 (d, *J* = 5.3 Hz, 1H), 2.41 (s, 3H).

Compound BDP-1. To the solution of **5** (200 mg, 1.2 mmol) in CH₂Cl₂, POCl₃ (227 mg, 1.5 mmol) was added dropwise at 0 °C. After stirring at room temperature for 3 days in the dark, triethylamine (0.84 mL, 6 mmol) was added dropwise at 0 °C. After stirring at 0 °C for 15 min, BF₃·Et₂O (1.1 mL, 8.9 mmol) was added dropwise, and then the mixture was stirred at room temperature for 2 days. The reaction was quenched by adding 10 mL of water, and the products were extracted with CH₂Cl₂. The organic layer was washed with water twice and brine, dried over MgSO₄, filtrated, and condensed by evaporation. The residue was passed through the silica gel column with the mixture eluent (hexane: CH₂Cl₂ = 5:1) afforded **BDP-1** as a dark purple solid (10 mg, 5%). ¹H NMR (CDCl₃, 500 MHz): δ 7.64 (d, *J* = 5.3 Hz, 2H), 7.38 (s, 1H), 7.12 (d, *J* = 5.3 Hz, 2H), 2.42 (s, 6H). TOF HRMS EI⁺: calcd ([C₁₅H₁₁BF₂N₂S₂]⁺) *m/z* = 332.0425, found *m/z* = 332.0417.

Theoretical Computations. The geometries of the singlet ground state (S_0) of **BDP-1**, **BDP-2** and **BDP-3** were optimized at the M06-2X/6-31G(d) level of theory. Gas phase TD-M06-2X and

SOS-CIS(D) vertical singlet and triplet excitation energies were obtained at this geometry using the 6-311+G(2d,p) and the 6-31+G(d) basis set, respectively. The geometries of the lowest singlet (S₁) and triplet (T₁) excited states were also optimized at the TD-M06-2X/6-31G(d) level of theory. SOCs were computed using the quadratic-response TD-DFT approach,¹⁶ i.e. QR-TD-DFT, as implemented in the Dalton program¹⁷ at their T1 optimized geometries. The SOC operator makes use of a semi-empirical effective single-electron approximation.¹⁸ For the latter calculations the B3LYP functional in combination to the 6-31G(d) basis set was used. SOS-CIS(D) and TD-DFT calculations were carried out with the Q-Chem¹⁹ and Gaussian09²⁰ program packages, respectively.

Triplet State Quantum Yield (Φ_{T} **).** The triplet quantum yields were determined with the singlet state depletion method.²¹ The Φ_{T} values were obtained by comparing the ΔA_{S} of the optically matched sample solution at 452 nm in a 1 cm cuvette to that of the reference using the equation [Eq. (2)]:

$$\Phi_T = \Phi_T^{Ru} \frac{\varepsilon_S^{Ru}}{\varepsilon_S} \frac{\Delta A_S}{\Delta A_S^{Ru}}$$
(Eq. 2)

where the superscript represents the reference, ΔA_S is the absorbance change of the triplet transient difference absorption spectrum at the minimum of the bleaching band, and ε_S is the ground-state molar absorption coefficient at the UV–vis absorption band maximum.

ASSOCIATED CONTENT

Supporting information

Molecular structure characterization, additional spectra, atom coordinates, absolute energies of the optimized geometries and more computation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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