Long-Lived Triplet Excited State Accessed with Spin–Orbit Charge Transfer Intersystem Crossing in Red Light-Absorbing Phenoxazine-Styryl BODIPY Electron Donor/Acceptor Dyads

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Orthogonal phenoxazine-styryl BODIPY compact electron donor/acceptor dyads were prepared as heavy atom-free triplet photosensitizers (PSs) with strong red light absorption (ε = 1.33 × 10^5 M^-1 cm^-1 at 630 nm), whereas the previously reported triplet photosensitizers based on the spin-orbit charge transfer intersystem crossing (SOCT-ISC) mechanism show absorption in a shorter wavelength range (<500 nm). More importantly, a long-lived triplet state (τ_T = 333 μs) was observed for the new dyads. In comparison, the triplet state lifetime of the same chromophore accessed with the conventional heavy atom effect (HAE) is much shorter (τ_T = 1.8 μs). Long triplet state lifetime is beneficial to enhance electron or energy transfer, the primary photophysical processes in the application of triplet PSs. Our approach is based on SOCT-ISC, without invoking of the HAE, which may shorten the triplet state lifetime. We used bisstyrylBodipy both as the electron acceptor and the visible light-harvesting chromophore, which shows red-light absorption. Femtosecond transient absorption spectra indicated the charge separation (109 ps) and SOCT-ISC (charge recombination, CR; 2.3 ns) for BDP-1. ISC efficiency of BDP-1 was determined as Φ_r = 25% (in toluene). The dyad BDP-3 was used as triplet PS for triplet-triplet annihilation upconversion (upconversion quantum yield Φ_UC = 1.5%; anti-Stokes shift is 5900 cm^-1).

1. Introduction

Triplet photosensitizers (PSs) are compounds showing intersystem crossing (ISC) to populate triplet excited state upon photoexcitation. Much attention has been paid to the design of new triplet PSs and for their applications in photo-redox catalytic organic reactions,[1] photodynamic therapy (PDT),[2] H_2 production by photocatalytic water splitting,[3] triplet-triplet annihilation upconversion (TTA-UC),[4] and photovoltaics.[5] The triplet state production is via ISC, a spin forbidden non-radiative electronic transition. A traditional strategy of enhancing ISC is to introduce transition metal atoms such as Ru, Ir, Pt or other heavy atoms, such as I or Br.[6] However, drawbacks of this heavy atom effect (HAE) are the high cost of the synthesis, and the toxicity of the compounds. Moreover, the triplet state lifetime of these PSs is shortened since the HAE enhance not only the ISC of S_1→T_n but also the T_1→S_0 ISC process.[7]

Charge recombination (CR)-induced ISC was known for electron donor/acceptor dyads with a long and rigid linker between donor and acceptor.[8] A large distance, thus a weak electronic coupling and a small electron exchange energy (U), is indispensable for the radical pair ISC (RP ISC) mechanism in these conventional electron donor/acceptor dyads. This type of ISC is based on the hyperfine interaction enhanced 1CT→3CT process (CT: charge transfer), followed by 3CT→1LE locally excited triplet state (1LE) internal conversion (given the purpose is to access the 1LE, not the long-lived CT state). However, these conventional electron donor/acceptor dyads are difficult to prepare, and generally the molecular structures are not optimized for triplet PS preparation, and the visible light-harvesting ability is poor. When the linker between the electron donor and acceptor was reduced in length, for instance by a direct link between donor and acceptor in compact dyads, the electronic coupling and the electron exchange energy increase, and RP ISC is inhibited.[9]

Recently, efficient ISC was observed for the CR in some compact electron donor/acceptor dyads via the so-called spin orbit charge transfer intersystem crossing (SOCT-ISC).[10] The ISC process requires conservation of the total angular momentum,
i.e. the sum of orbital angular momentum and spin angular momentum.\textsuperscript{110} Given the electron donor and acceptor moieties in a dyad adopt orthogonal orientation, the change of molecular orbital angular momentum of the CR will offset the change of electron spin angular momentum of ISC.\textsuperscript{110b} Therefore, conservation of angular momentum is satisfied in the ISC of an orthogonal electron donor-acceptor dyad. Hence the SOCT-ISC is efficient in orthogonal electron donor/acceptor dyad. It should be pointed out some electron donor/acceptor dyads undergo twisted intramolecular charge transfer (TICT) may also show the charge recombination induced ISC.

Advantages of these novel compact electron donor/acceptor dyads are their simple molecular structure and long triplet state lifetimes. These features are important for applications of triplet PSs in photocatalysis and PDT. Several chromophores have been used for preparation of electron donor/acceptor compact dyads showing SOCT-ISC, such as acridinium,\textsuperscript{110a} anthracene,\textsuperscript{110b} perylene,\textsuperscript{112} BODIPY,\textsuperscript{110c,118} and perylenemonomide/perylenediimide,\textsuperscript{114} etc. However, triplet PSs based on SOCT-ISC showing red light absorption were rarely reported.\textsuperscript{115} In some cases, long-lived \( ^1 \)CT state was observed for the compact dyad.\textsuperscript{116} On the other hand, although BODIPY-derived triplet PSs showing red light absorption have been reported, for instance the 2,6-diiodostyrylBodipy,\textsuperscript{117} and the 2,6-diodoaazaBodipy,\textsuperscript{118} the triplet state lifetimes of these red light-absorbing triplet PSs are short (~1.8 \( \mu \)s), which is a clear disadvantage for the applications in PDT,\textsuperscript{116} TTA-UC,\textsuperscript{117,119} or photocatalysis, etc.\textsuperscript{120} In these applications, the intermolecular electron transfer or triplet energy transfer efficiency increases with longer triplet state lifetime of the PSs.

Inspired by the previous results, herein we selected styryl BODIPY as the electron acceptor and red-light-absorbing chromophore, and phenoxazine (PXZ) as the electron donor, in order to design compact, orthogonal electron donor/acceptor dyads as novel heavy atom-free triplet PSs showing red light-absorption and long-lived triplet states (Scheme 1). PXZ has been used in thermally activated delayed fluorescence materials (TADF),\textsuperscript{21} and photovoltaics.\textsuperscript{114} Compared with the previously used phenothiazine (PTZ, oxidation potential \( E_{ox} = +0.21 \) V vs. Fc/Fc\(^{-}\)), PXZ has a more planar \( \pi \)-conjugated structure and different redox properties (oxidation potential \( E_{ox} = +0.36 \) V vs. Fc/Fc\(^{-}\)).\textsuperscript{121} It may provide different solvent polarity-dependency for the SOCT-ISC. To obtain more PSs with red light-absorption, large \( \pi \)-conjugated carbazole moiety is attached at the 2,6-positions of BODIPY (BDP-3, Scheme 1), which may change the triplet state lifetime or triplet state energy, and finally the ISC efficiency.

The photophysical properties of the dyads were studied by steady-state and time-resolved transient spectroscopies. The CS and CR were studied with femtosecond transient absorption spectra, and the triplet state spectra and lifetimes were studied with nanosecond transient spectroscopies. The CS and CR were studied with femtosecond transient absorption spectra, and the triplet state spectra and lifetimes were studied with nanosecond transient absorption spectra. The new heavy atom-free triplet PSs were used for TTA-UC, and larger anti-Stokes shift was achieved (0.68 eV) than the recently reported

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**Scheme 1.** Synthesis of the Compounds. a) \( n \)-C\(_5\)H\(_9\)Br, DMF, KOH, \( N_2 \), stirred at RT for 2 h, yield: 60\%; b) POCl\(_3\), DMF, \( N_2 \), 90 °C, 2 h, yield: 65\%; c) 2,4-dimethylpyrrole, TFA, DDQ, TEA, BF\(_3\)Et\(_2\)O, DCM, RT, \( N_2 \), yield: 6\%; d) aryl aldehyde, \( p \)-toluenesulfonic acid, piperidine, 15 min, yield: 42\% for \( R = H \) and 13\% for \( R = CN \); e) NIS, DCM, RT for 2 h, yield: 89\%; f) KI, KIO\(_3\), acetic acid, 85 °C, 10 min, 39\%; g) \( n \)-C\(_5\)H\(_9\)Br, DMSO, NaH, \( N_2 \), stirred at RT for 2 h, yield: 90\%; h) PdCl\(_2\)(PPh\(_3\))\(_2\), PPh\(_3\), Cul, TEA, TMSA, \( N_2 \), 80 °C, 6 h; then stirred at RT over night, yield: 70\%; i) PdCl\(_2\)(PPh\(_3\))\(_2\), PPh\(_3\), Cul, TEA and THF, \( N_2 \), 85 °C, 2 h, yield: 60\%.
2. Results and Discussion

2.1. Molecular Structure Designing Rationales

Phenoxazine (PXZ) is used as electron donor. Styryl BODIPY is selected as electron acceptor and red-light-absorbing chromophore. The cyano groups attached to the styryl BODIPY moiety in BDP-2 will enhance the electron withdrawing ability, which may produce a more efficient charge transfer. The PXZ moiety was attached at the 8-position (meso-position) of styryl BODIPY. Therefore, the steric hindrance imposed by 1,7-methyl groups on the styryl BODIPY will restrict the rotation of PXZ, thus the dyads will adopt a perpendicular orientation between donor and acceptor. Styryl BODIPY shows strong red light-harvesting ability. The π-conjugated structure of BDP-3 may lead to different triplet state properties, such as triplet state lifetime and triplet state energy. All molecular structures were fully characterized (refer to Experimental section and Supporting Information).

A single crystal of BDP-1 was obtained by slow diffusion between n-hexane and DCM. The molecular structure determined by single crystal X-ray diffraction of BDP-1 is presented in Figure 1. The dihedral angle between the electron donor (PXZ) and the acceptor (styryl BODIPY) is 71.4°, which is slightly different from the result of DFT calculation (89.7°), refer to later section. It also shows less orthogonality compared with the reported PTZ-styryl BODIPY dyad (−81.9°).[15] The possible reason is that the better planarity of PXZ compared to PTZ weakens the conformational restriction between the PXZ and styryl BODIPY moieties. The deviation from coplanar geometry of the styryl moieties is 10.9° and 28.4° due to the π-π stacking in the single crystal, because the DFT optimization of the ground state geometry indicated planar geometry. The structure of the styryl BODIPY moiety of BDP-1 is more twisted than the reported PTZ-styryl BODIPY molecule (10.9° and 28.4° vs 4.7° and 1.2°).[15]

![Figure 1. Single-crystal structure of BDP-1 with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.](image1.png)

2.2. UV-Vis Absorption and Fluorescence Emission Spectra

The UV-Vis absorption spectra of the compounds were studied (Figure 2). The dyad BDP-1 shows similar absorption compared with the reference Styryl-BDP in the region of 550–700 nm, which indicates negligible electronic coupling between the electron donor (PXZ) and the electron acceptor (styryl BODIPY) at the electronic ground state. A similar result was observed for BDP-2, the absorption is similar as that of Styryl-BDP-CN. However, the absorption band of BDP-2 is slightly red-shifted compared to BDP-1. The UV-Vis absorption of BDP-3 and BDP-4 were also studied (Figure 2b). For BDP-3, a broad absorption band centered at 600 nm was observed, which shows the same absorption profile as the reference compound BDP-4. We conclude that the electronic coupling between donor and acceptor is also weak at the ground state of BDP-3. These features are similar to those observed for the BDP-PXZ dyads.[22]

Fluorescence spectra in different solvents were studied (Figure 3). For BDP-1 (Figure 3a), structured emission bands centred at 630 nm and 685 nm were observed, which is similar to the unsubstituted compound Styryl-BDP (refer to the Supporting Information, Figure S11b). The fluorescence quantum yield (ΦF) was determined as 73% in n-hexane (Table 1), which is similar to Styryl-BDP (ΦF = 77%, Table 1). The results indicate that CT is inefficient in a non-polar solvent. However, the fluorescence is significantly quenched in more polar solvents. For instance, the ΦF in toluene is almost half of that in n-hexane and it further decreased to 0.2% in acetonitrile (ACN) (Table 1). We attributed the fluorescence quenching to the electron transfer and formation of CT state, and the CT state is a dark state. Similar results were obtained for the dyad BDP-2 (Figure 3b), but quenching of the fluorescence is more significant in polar solvents. For instance, the fluorescence quantum yield is 35.4% in n-hexane but it decreases to 0.5% in toluene (Table 1). In toluene, a broad and red-shifted emission band centred at 768 nm was observed, along with the LE emission band at 651 nm (Figure 4a). However, the emission at longer

![Figure 2. UV-Vis absorption spectra of compounds a) BDP-1, BDP-2, Styryl-BDP and Styryl-BDP-CN; b) BDP-3 and BDP-4. c = 1.0 × 10−5 M in toluene. 20°C.](image2.png)
all the sample solution show the same absorbance at the excitation wavelength ($\lambda_{ex}=570$ nm), 20 °C.

Table 1. The photophysical properties of compounds.

| Solvent | $\lambda_{max}$ [nm] | $\lambda_{em}$ [nm] | $\tau_f$ [ns] | $\Phi_F$ [a] | $\Phi_A$ [b] | $\tau_A$ [ns] | $\Phi_I$ [c] |
|---------|----------------------|-------------------|--------------|-------------|-------------|--------------|-------------|
| BDP-1  | HEX                  | 620 (1.40)        | 5.4                      | 0.732       | _RI         | _RI         | _RI         |
|        | TOL                  | 630 (1.33)        | 4.9                      | 0.393       | _RI         | _RI         | _RI         |
|        | ACN                  | 619 (1.23)        | 2.9                      | 0.002       | _RI         | _RI         | _RI         |
| BDP-2  | HEX                  | 629 (0.57)        | 4.3                      | 0.354       | _RI         | _RI         | _RI         |
|        | TOL                  | 639 (0.54)        | 2.6/2.3                  | 0.005/0.018 | _RI         | _RI         | _RI         |
|        | ACN                  | 628 (0.53)        | 1.5                      | 0.003       | _RI         | _RI         | _RI         |
| BDP-3  | HEX                  | 597 (0.67)        | 3.0                      | 0.484       | 0.04        | 394.4       | 0.04        |
|        | TOL                  | 600 (0.60)        | 2.4                      | 0.299       | 0.12        | 392.7       | 0.13        |
|        | ACN                  | 590 (0.60)        | 1.4                      | 0.003       | _RI         | _RI         | _RI         |
| BDP-4  | HEX                  | 596 (0.66)        | 2.9                      | 0.462       | 0.03        | 278.8       | 0.05        |
|        | TOL                  | 597 (0.57)        | 1.9                      | 0.360       | 0.04        | 244.0       | 0.04        |
|        | ACN                  | 587 (0.60)        | 0.07                     | 0.022       | _RI         | _RI         | _RI         |
| Styryl-BDP | HEX               | 619 (1.15)      | 5.2                      | 0.768       | _RI         | _RI         | _RI         |
|         | TOL                  | 628 (1.06)        | 4.7                      | 0.768       | _RI         | _RI         | _RI         |
|         | ACN                  | 617 (1.04)        | 0.05                     | 0.065       | _RI         | _RI         | _RI         |
| Styryl-BDP-CN | HEX               | 627 (0.78)     | _ RI                    | _ RI        | _ RI        | _ RI        | _ RI        |
|         | TOL                  | 636 (0.97)        | 4.2                      | 0.652       | _ RI        | _ RI        | _ RI        |
|         | ACN                  | 627 (0.96)        | 4.4                      | 0.612       | _ RI        | _ RI        | _ RI        |

[a] $E_c(30)$ values are HEX (31.0), TOL (33.9) and ACN (45.6), in kcal mol$^{-1}$. [b] $c = 1.0 \times 10^{-4}$ M, in nm. [c] Molar absorption coefficient. $\varepsilon = 10^3$ M$^{-1}$ cm$^{-1}$. [d] Fluorescence wavelength, in nm. [e] Fluorescence lifetime, $\dot{\lambda}_{em}=635$ nm, in ns, $\varepsilon = 1.0 \times 10^{-5}$ M. [f] Absolute fluorescence quantum yield. [g] Singlet oxygen quantum yield, methylene blue (MB) as standard ($\Phi_{S}=0.57$ in DCM). [h] Triplet state lifetime, in ns. [i] Triplet quantum yield, methylene blue (MB) as standard ($\Phi_{T}=0.50$ in methanol). [j] The transition of CT to CT (CT-CN). [k] Intrinsic triplet state lifetimes. Obtained by fitting of the experimental curves based on the kinetic model with triplet-triplet annihilation self-quenching effect considered. [l] Not observed.

Figure 3. Fluorescence emission spectra of the compounds in different solvents. a) BDP-1; b) BDP-2, and c) BDP-3. Optically matched solutions were used, i.e. all the sample solution show the same absorbance at the excitation wavelength ($\lambda_{ex}=570$ nm, 20 °C.

Figure 4. Comparison of the fluorescence emission spectra of the compounds in toluene: a) BDP-1, BDP-2, Styryl-BDP and Styryl-BDP-CN; b) BDP-3 and BDP-4. Optically matched solutions were used ($A=0.195$), $\lambda_{em}=570$ nm, 20 °C.

wavelength was quenched in polar solvent (Supporting Information, Figure S10b). Considering the relative fluorescence emission intensity and the quantum yields, the CT state of BDP-2 is in principle also a dark state.

In toluene, the fluorescence is quenched both for BDP-1 and BDP-2 compared with the reference compounds Styryl-BDP and Styryl-BDP-CN. Furthermore, it is further quenched for BDP-2 compared with BDP-1 in toluene (Figure 3a). We attribute the significant quenching of the fluorescence of BDP-2 as compared to BDP-1 to the electron-withdrawing --CN groups, and the more significant CT in BDP-2. For BDP-3, the emission was quenched obviously in polar solvents, indicating an efficient CT. Compared with the reference compound BDP-4, the emission was slightly quenched in non-polar solvents such as n-hexane and toluene (Figure 4b and Table 1). However, the emission was quenched further in polar solvents, for instance,
Φ$_{r}$ is 0.001 and 0.105 in DCM for BDP-3 and BDP-4, respectively (Supporting Information, Table S2).

The fluorescence decay traces were studied using the time-correlated single-photon counting (TCSPC) detection method (Figure 5 and Supporting Information, Figure S12). The fluorescence lifetimes of BDP-1 show solvent polarity dependency (Figure 4a). In non-polar solvents (n-hexane and toluene), the decay trace is mono-exponential. However, it shows a biexponential decay in polar solvents, such as ACN. The average lifetimes decrease from 5.4 ns (in n-hexane), to 2.9 ns (a short component of 0.06 ns with a population ratio of 30% and a longer component of 4.2 ns, in 70%) in ACN, meanwhile the fluorescence quantum yield decreased by 366-fold (Figure 3a and Table 1). Similar results are observed for BDP-2 (Figure 5b and Table 1). The decay kinetics of BDP-2 shows a sharper decrease along with increasing solvent polarity (Figure 5b). The lifetimes are also shorter than BDP-1 in the same solvent (Table 1). For instance, the lifetime of BDP-2 shows a biexponential decay with a short component of 0.12 ns (60%) and a longer component of 3.5 ns (40%). The fluorescence lifetime of BDP-1 and BDP-2 are 4.9 ns and 2.6 ns in toluene, respectively, which indicates that the CS of BDP-2 is more efficient than that of BDP-1. We propose the bi-exponential decay is attributed to the existence of an equilibrium between the emissive state with a dark state (CT state), or electron transfer probability for the molecules at the LE state, and the probability is less than unity.$^{[6b]}$ For BDP-3, a similar conclusion can be obtained (Supporting Information, Figure S12a). The fluorescence in n-hexane is mono-exponential with a lifetime of 3.0 ns. However, in ACN it turned to a bi-exponential decay with an average lifetime of 1.4 ns (with a short component of 0.10 ns (70%) and a longer component of 4.4 ns (30%)), indicating the fluorescence quenched further in polar solvents.

2.3. Electrochemical Studies

The electrochemical properties of the dyads were studied by cyclic voltammetry (Figure 6, Table 2, Supporting Information, Figure S22 and Table S4). For BDP-1, the reversible oxidation wave at +0.32 V (vs Fc/Fc$^+$) is attributed to the PXZ moiety, another quasi-reversible oxidation wave at +0.55 V is attributed to the styryl BODIPY moiety, as is the quasi-reversible reduction wave at −1.44 V. Therefore, PXZ is more likely the electron transfer agent.

| Table 2. Redox potentials, driving forces of charge separation ($\Delta G_{\text{CS}}$), charge recombination ($\Delta G_{\text{CR}}$), and the energy of the CSS of the compounds ($E_{\text{CSS}}$) in different solvents.$^{[5e]}$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | $E_{\text{ox}}$ ($[V]$) | $E_{\text{red}}$ ($[V]$) | $\Delta G_{\text{CS}}$ ($[eV]$) | $\Delta G_{\text{CR}}$ ($[eV]$) | $E_{\text{CSS}}$ ($[eV]$) | $E_{\text{CSS}}$ ($[eV]$) | $E_{\text{CSS}}$ ($[eV]$) | $E_{\text{CSS}}$ ($[eV]$) |
| BDP-1$^{[4i]}$  | +0.55           | −1.44           | 0.09            | −0.03           | −0.36           | −0.44           | 2.05           | 1.93           | 1.60           | 1.51           |
|                 | +0.32           | −1.26           | −0.004          | −0.13           | −0.47           | −0.57           | 1.93           | 1.80           | 1.45           | 1.35           |
| BDP-2$^{[4i]}$  | +0.70           | −1.52           | −0.25           | −0.29           | −0.36           | −0.38           | 1.73           | 1.70           | 1.52           | 1.49           |
|                 | +0.33           | −0.83           | −0.25           | −0.29           | −0.36           | −0.38           | 1.73           | 1.70           | 1.52           | 1.49           |

[a] Cyclic voltammetry in N$_2$, saturated DCM containing 0.10 M Bu$_4$NPF$_6$, supporting electrolyte; Pt electrode was used as counter electrode; working electrode is glassy carbon electrode; Ag/AgCl couple as the reference electrode. $E_{\text{ox}}$ is the energy difference between the potential minima, approximated with the crossing point of UV-Vis absorption and fluorescence emission spectra after normalization. $[b]$ $E_{\text{ox}} = 1.96$ eV. $[c]$ $E_{\text{ox}} = 1.92$ eV. $[d]$ $E_{\text{ox}} = 1.98$ eV. $[e]$ The value was obtained by setting the oxidation potential of Fc$^+/\text{Fc}$ as 0. $[f]$ The redox potentials are approximated based on the redox potential measured in DCM.
donor and styryl BODIPY serves as electron acceptor. The reduction wave of BDP-2 was observed at $-1.26 \text{ V}$, indicating the stronger electron accepting ability of the styryl BODIPY moiety with cyano groups attached, as compared with styryl BODIPY. Similar results were obtained for BDP-3. Only one reversible oxidation wave at $+0.34 \text{ V}$ and one quasi-reversible reduction wave at $-1.52 \text{ V}$ were observed, indicating that PXZ serves as electron donor and the BODIPY moiety serves as electron acceptor. Compared with the previously reported BDP-PXZ dyads, the oxidation potential of PXZ is similar ($0.32 \text{ V}$ vs $0.36 \text{ V}$, vs Fc/Fc$^{-}$). PXZ dyads, the oxidation potential of PXZ is similar ($0.32 \text{ V}$ vs )

The Weller equations (Supporting Information, Equations S1–S4) were used to determine the energy of the charge separated state (CSS) and the driving forces of intramolecular charge separation ($\Delta G_{CS}$)[8c]. The results are summarized in Table 2 (For detailed information please refer to the Supporting Information).

The calculation of $\Delta G_{CS}$ indicates that charge separation is thermodynamically forbidden in $n$-hexane due to the positive $\Delta G_{CS}$ value ($+0.09 \text{ eV}$) for BDP-1, which agrees with the unquenched fluorescence of styryl BODIPY moiety in $n$-hexane ($\Phi_f = 73.2\%$ in Table 1). However, thermodynamically allowed charge separation is possible in other more polar solvents according to the negative $\Delta G_{CS}$ values of BDP-1, which also agrees with fluorescence quenching of the styryl BODIPY moiety (Table 1). For BDP-2 and BDP-3, the $\Delta G_{CS}$ values are all negative, indicating charge separation is thermodynamically allowed in both nonpolar and polar solvents. For the previously reported BDP-PXZ dyads, the $\Delta G_{CS}$ values are all more negative. For instance, the $\Delta G_{CS}$ values are $-0.40 \text{ eV}$ and $-0.74 \text{ eV}$ in toluene and ACN, respectively. For BDP-1, the $\Delta G_{CS}$ is $-0.44 \text{ eV}$ in ACN, indicating the CS driving force is weaker for BDP-1. It may reduce the CS and SOCT-ISC efficiency.

2.4. Femtosecond Transient Absorption Spectroscopy

Femtosecond transient absorption spectra (fs TA) were measured in order to reveal the excited state dynamics of the dyads. For BDP-1, the triplet state signal was observed in toluene (Figure 7), but no triplet state signal was observed in ACN. Hence we assume that the CS and CR are both much faster in ACN. In toluene, the intense ground state bleaching (GSB) band at 630 nm was immediately generated upon excitation (Figure 7a). An excited state absorption (ESA) band in the range of 420–550 nm increased in intensity in less than 1 ps. This ESA band is attributed to the $S_1$–$S_0$ transition, and the increasing process may be due to vibrational relaxation. The negative band at 700 nm is assigned to stimulated emission (SE) of the localized singlet state (`StyrylBDP$^*$`). However, no obvious absorption band of the PXZ radical cation (around 540 nm, Supporting Information, Figure S23b)[23] and the styryl BODIPY

Figure 7. Femtosecond transient absorption spectra of BDP-1. a) Transient absorption spectra in toluene. $\lambda_{ex} = 630 \text{ nm, } c = 1.0 \times 10^{-5} \text{ M}$, b) species-associated difference spectra (SADS), and c) decay traces at selected wavelengths. d) Transient absorption spectra of BDP-1 in ACN ($\lambda_{ex} = 625 \text{ nm, } c = 1 \times 10^{-5} \text{ M}$), e) species-associated difference spectra (SADS), and f) Decay traces at selected wavelengths. SADS were obtained by global fitting in sequential model. 20°C.
radical anion (around 670 nm, Supporting Information, Figure S23a) were observed.

One possible reason is that the CS efficiency is not very high ($\Phi_T = 0.39$ in toluene). Furthermore, the radical anion absorption of styryl-BDP in the range of 650–680 nm (Supporting Information, Figure S23a and S23b, obtained by spectroelectrochemistry), overlaps with ESA signals of the singlet state of Styryl-BDP (Figure 7a and Supporting Information, Figure S21). Moreover, the signal of the radical cation of PXZ also overlaps with the singlet state signal of styryl-BDP in the range of 530–550 nm (Figure 7a and Supporting Information, Figure S21). Thus, we can’t distinguish the characteristic 1styril-BDP* and the "CSS states unambiguously. The fs TA spectra of the reference compound Styryl-BDP were also recorded in toluene (Supporting Information, Figure S21). No fast decay of the GSB or the SE bands were observed, indicating that no CS exist in Styryl-BDP. Therefore, the CS is most likely responsible for the fast decay of BDP-1 in toluene.

Species-associated difference spectra (SADS) obtained by global fitting were used to analyse the photophysical processes (Figure 7b). The species with the shortest lifetime (0.12 ps) is assigned to the unrelaxed $S_1$ state. The species with a lifetime of 109 ps displays the characteristic styryl BODIPY ESA signals (Supporting Information, Figure S21) and is assigned the relaxed $S_1$ state, indicating that CS process takes 109 ps. Subsequently, the slow CR takes 2.3 ns, and a long-lived species with infinite lifetime (on the time scale of the fs-TA experiment) is obtained, which is attributed to the triplet state. The final species is assigned as the $T_1$ state on account of showing a weak ESA band in the range 650-750 nm ($T_1\rightarrow S_0$ absorption) and a GSB band at 630 nm, which is in agreement with ns TA data (Figure 8a). Therefore, we conclude that the triplet state is generated by the CR and the SOCT-ISC (CR) takes 2.3 ns.

In ACN, no triplet state signal was observed (Figure 7d). The ESA band located in the range of 440–570 nm is attributed to the $S_1\rightarrow S_0$ absorption. Due to the higher CS efficiency, absorption bands of the styryl-BDP radical anion and the PXZ radical cation were more obvious. The absorption bands centered at 670 nm and 545 nm were attributed to styryl-BDP* and PXZ*, respectively, which is in agreement with the results of spectroelectrochemical studies (refer to the Supporting Information, Figure S23a and S23b). Based on the SADS, we determined the time constants of the CS and CR as 0.79 ps and 3.5 ps, respectively (Figure 7e), which are faster than the CS (109 ps) and CR (2.2 ns) in toluene.

For BDP-2, the fluorescence was quenched significantly in toluene ($\Phi_F = 0.005$ vs. 0.393 of BDP-1). In toluene, a GSB band centered at 640 nm and a strong ESA band centered at 468 nm (Supporting Information, Figure S19a) were observed, which are assigned to the $S_1$ state. Subsequently, an absorption band at 670 nm intensified along with the decreasing ESA band at 469 nm, which is attributed to the formation of [StyrylBDP-CN]* (Supporting Information, Figure S23c). Finally, along with the decreasing of the absorption band centered at 670 nm, the ESA signal in the range of 650-750 nm becomes stronger, which is characteristic for the $T_1\rightarrow T_n$ absorption of BDP-2, corroborated by the ns TA spectra (Supporting Information, Figure S13a). Therefore, we conclude that ISC occurs via CR. Based on the results from SADS (Supporting Information, Figure S19b), we determine that CS takes place in 1.2 ps, which is much faster than in BDP-1 (109 ps in toluene). Following the CS, slow CR (SOCT-ISC) continuing for 1.6 ns leads to the generation of the triplet state of BDP-2. In the polar solvent ACN, results similar to those of BDP-1 were obtained (Supporting Information, Figure S19e). Faster CS (0.3 ps) and CR (1.6 ps) are observed. No triplet state formation was observed, which agrees with the lack of singlet oxygen photosensitizing of the dyad BDP-2 (Table 1).

Different results were obtained for BDP-3 (Supporting Information, Figure S19). Upon excitation, the GSB band was observed in the range of 550–750 nm. It is broader than the UV-Vis absorption, which is attributed to the overlap of the GSB and the SE band. According to spectroelectrochemical results (Supporting Information, Figure S24), we determine the absorption of the radical anion and the radical cation centered at 580 nm and 540 nm, respectively. Based on the SADS analysis and the fast decay of ESA at 480 nm, we determine that CS takes 3.2 ps in toluene. The lifetime of the $^1$CT state in toluene is ca. 4.0 ns. No triplet state formation was observed within the time resolution of our instrument setup.

2.5. Nanosecond Transient Absorption Spectroscopy: Triplet State Properties

Nanosecond transient absorption spectra were used to study the triplet state production of the dyads (Figure 8 and
triplet PSs, i.e. the triplet state lifetime becomes much longer as heavy atom-free compact electron donor/acceptor dyads as the reference compound state is also localized on the BODIPY moiety. The intrinsic triplet state energy in polar solvent will accelerate CR to the S0 state, because the CR occurs normally in the Marcus inverted region, i.e. the lower CT state energy in polar solvent will accelerate CR to the S0 state, thus inhibiting SOCT-ISC.\[6b\]

The apparent triplet state lifetimes (\(\tau_T\)) for BDP-1 and BDP-2, respectively, at a specific concentration. However, triplet-triplet annihilation (TTA) will quench the triplet state and shorten the triplet state lifetime, especially for the compounds showing strong absorption at the excitation wavelength, high ISC efficiency and long-lived triplet state. Therefore, the intrinsic triplet state lifetime was determined by fitting the decay traces at two different concentrations with a kinetic model including TTA self-quenching.\[25\] The intrinsic triplet state lifetime of BDP-1 obtained with this kinetic model is \(\tau_T = 333.2 \mu s\), which is much longer than the apparent triplet state lifetime \(\tau_T = 270.0 \mu s\), indicating TTA quenching. For BDP-2, the intrinsic triplet state lifetime \(\tau_T = 382.2 \mu s\) is also longer than the experimental values (242.7 \(\mu s\)). Notably the triplet state lifetime of BDP-1 is prolonged 185-fold \((\tau_T = 333.2 \mu s)\) as compared to the triplet state of the same parent chromophore, i.e. bisstyryl-BODIPY, but accessed by the HAE in 2,6-diiodostyryl BODIPY (1.8 \(\mu s\)).\[17\] These results demonstrated one of the advantage of using the compact electron donor/acceptor dyads as heavy atom-free triplet PSs, i.e. the triplet state lifetime becomes much longer than that accessed with the conventional HAE.\[15\] Long-lived triplet state lifetime are important for photocatalysis, PDT and TTA-UC.

The ISC efficiency depends on the solvent polarity (Table 1). For instance, the triplet state quantum yield (\(\Phi_T\)) for BDP-1 is 25% in toluene (Table 1). However, in other solvents, no triplet state formation was observed. Similar results were observed for BDP-2. Therefore, we conclude that the ISC mechanism is based on charge recombination for BDP-1 and BDP-2. Due to the short distance between electron donor/acceptor and strong electron coupling, SOCT-ISC is the most likely mechanism, instead of RP ISC. The poor SOCT-ISC in polar solvent may be due to the fast CR to the ground state \((S_0\) state), because the CR occurs normally in the Marcus inverted region, i.e. the lower CT state energy in polar solvent will accelerate CR to the \(S_0\) state, thus inhibiting SOCT-ISC.\[6b\]

For BDP-3, the characteristic GSB and ESA signals are similar as the reference compound BDP-4 (Figure 8c and Supporting Information, Figure S13c), which demonstrates that the triplet state is also localized on the BODIPY moiety. The intrinsic triplet state lifetime was determined as 392.7 \(\mu s\) in toluene (Table 1).

Theoretical computations were performed to study the ESA bands of \(T_1 \rightarrow T_n\) transitions (Supporting Information, Figure S18). For BDP-1, the ESA bands centered at 700 nm, 500 nm and 375 nm are attributed to the \(T_1 \rightarrow T_9\), \(T_1 \rightarrow T_{10}\) and \(T_1 \rightarrow T_{22}\) transitions, respectively (Supporting Information, Figure S18a). Similar results were obtained for BDP-2. The ESA band at 735 nm is attributed to the \(T_1 \rightarrow T_9\) transition and the bands at 500 nm and 395 nm were assigned to the \(T_1 \rightarrow T_{10}\) and \(T_1 \rightarrow T_{22}\) transitions, respectively (Supporting Information, Figure S18b). The results of the calculations for BDP-3 deviated from the experimental results (Supporting Information, Figure S18c).

Due to the different \(\pi\)-conjugated structure of BDP-3 compared with styryl BODIPY (Scheme 1), we assume the \(T_1\) state energy of BDP-3 is different from BDP-1 and BDP-2. We selected BODIPY (\(E_{T1} = 1.14 eV\))\[26\] and 9,10-diphenylanthracene (DPA) \((E_{T1} = 1.77 eV)\)[27] as triplet energy acceptors and BDP-3 as the energy donor. The triplet state lifetime of BDP-3 decreased from 402.0 \(\mu s\) to 339.1 \(\mu s\) in the presence of BODIPY (Supporting Information, Figure S16). Meanwhile, a new GSB band appeared at around 500 nm, which is assigned to the GSB band of BODIPY. The decay at 500 nm is composed of two components, the increasing component is attributed TTET between BDP-3 and BODIPY. These results demonstrate that the \(T_1\) state energy of BDP-3 is higher than 1.65 eV. On the contrary, no reduction of the triplet state lifetime of BDP-3 was observed when DPA was used as the energy acceptor (Supporting Information, Figure S17). Therefore, we conclude that the \(T_1\) state energy of BDP-3 is in the range of 1.65 ~ 1.77 eV.
2.6. DFT Computations

The ground-state geometries of the dyads were optimized (Figure 9). The relative orientations between electron donor (PXZ) and acceptor (BODIPY chromophore) are all nearly orthogonal for all the dyads, which should be beneficial for SOCT-ISC. For instance, the dihedral angle between PXZ and styryl BODIPY in BDP-1 is 89.7°, very close to orthogonal geometry. The π-conjugated structure of styryl BODIPY moiety of BDP-1 shows minor distortion (by 1.8° and −1.7° at the two arms, respectively) (Figure 9a). These distortions are smaller than those observed in the single crystal structure (10.9° and 28.4°), the discrepancy may be due to the packing effect in the single crystal. The previously reported SOCT-ISC dyad BDP-PXZ has a similar dihedral angle between PXZ and BODIPY as found for BDP-1 (85.6° vs 89.7°).[22]

For BDP-2, the relative orientations between the PXZ and the styryl BODIPY moieties are also orthogonal, and the distortions of the styryl moieties are 1.6° and −1.5° (Figure 9). However, for BDP-3, the BODIPY chromophore moiety has better planarity (Supporting Information, Figure S25). The potential energy surfaces (PES) of the dyads against the torsional angles between electron donor and acceptor were also constructed (Supporting Information, Figure S26). For the three dyads, the thermally accessible dihedral angles between the electron donor and acceptor are all in the range of 65° ~ 113°. The range is similar (ca. 70° ~ 110°) for the reported PTZ-Styryl BODIPY dyads.[15]

The frontier molecular orbitals of the dyads are presented in Figure 10. For BDP-1, the lowest unoccupied molecular orbital (LUMO) is confined to the styryl BODIPY moiety, and the highest occupied molecular orbital (HOMO) is localized on the PXZ moiety, indicating that electron transfer is possible. Slight delocalization was observed. For BDP-2, the HOMO and LUMO are exclusively localized on the PXZ and styryl BODIPY moieties, respectively. For BDP-3, a similar result was observed. The MOs demonstrate that the attachment of electron withdrawing groups may alter the HOMO and LUMO energies. Compared with BDP-1, the HOMO energy of BDP-2 decreases from −4.90 eV to −5.02 eV and the LUMO energy shows a similar change (from −2.69 eV to −3.09 eV). The lack of overlap of the MO leads to more significant fluorescence quenching in BDP-2.

The triplet state spin density surfaces were studied at the optimized triplet state geometries (Figure 11). The unpaired electrons are localized on the styryl BODIPY moiety for BDP-1 and BDP-2, which agrees with nanosecond transient absorption spectra (Figure 8). The spin density surfaces of the radical anion and the radical cation of BDP-1 were also studied (Figure 12). The spin density of the radical anion is entirely restricted to the styryl BODIPY moiety. On the contrary, the spin density surface of the radical cation is completely localized on the PXZ moiety.

These results further imply that PXZ serves as electron donor and styryl BODIPY as the electron acceptor. Similar results were obtained for BDP-2 and BDP-3 (Supporting Information, Figure S29).

2.7. Application of the Dyads in TTA Upconversion

Recently, the application of heavy atom free triplet PSs on triplet-triplet annihilation upconversion (TTA-UC) has attracted particular interest.[25] Traditional heavy atom-free triplet PSs with absorption in the red range show low triplet energies, such as methylene blue (1.44 eV)[36] and 2,6-diiodostyryl BODIPY (ca. 1.13 eV).[31] Due to the low triplet state energy of BDP-1 (1.14 ~ 1.20 eV) and BDP-2 (1.14 ~ 1.20 eV), the dyad BDP-3 was selected as the triplet PS of TTA-UC. The dyad BDP-3 has high triplet state energy (1.65 ~ 1.77 eV) and long intrinsic triplet state lifetime (392.7 μs in toluene), which is ideal for application for TTA-UC. TTA-UC was studied with BDP-3 as PS and perylene as annihilator (Figure 13). Upon 589 nm cw laser excitation, only fluorescence of BDP-3 was observed in absence of annihilator. A new emission peak appear in the region of 420–520 nm after addition of 4.0 eq. annihilator, which is attributed to the upconverted fluorescence of perylene (Figure 13a). The anti-Stokes shift of this TTA-UC system is 5905 cm−1, and the upconversion quantum yield (ΦUC) is 1.5% (in toluene). The anti-Stokes shift of BDP-3 is comparable to the previously reported SOCT-ISC PSs applied in TTA-UC (ca. 3276–5900 cm−1).[13a,22,32]

The power dependence of the upconversion emission intensity was measured (Supporting Information, Figure S31). The integrated upconversion emission intensity increased almost linearly rather than quadratically with the excitation laser power, indicating efficient TTET and TTA for the TTA-UC system.

Finally, the intermolecular TTET was studied by Stern-Volmer analysis of the quenching by monitoring the triplet state lifetime of BDP-3 (Supporting Information, Figure S32 and Table S5). The Stern-Volmer quenching constant (KSV = 1.74 × 104 M−1) and quenching efficiency (fQ = 40.0%), indicating that intermolecular TTET is efficient.

The photophysical processes of BDP-1 are summarized in Scheme 2. Upon excitation at 630 nm, the dyad is excited to the S1 state (LE state localized on styryl BODIPY moiety). The...
following CS leads to generation of a CS state, especially in polar solvents. $\Delta G_{\text{CS}}$ is positive and therefore CS is inhibited in $n$-hexane, resulting in unquenched fluorescence of the styryl BODIPY moiety (Table 1). In toluene, the fluorescence of the LE state is quenched by CS (rate constant 109 ps), subsequent CR leads to population of $T_1$ ($^1\text{LE}$ state). According to DFT calculations, SOCT-ISC to yield $T_3$ is also possible because the two states have similar energies. Ultrafast $T_3\rightarrow T_1$ internal conversion will nevertheless populate $T_1$. The CR (ISC) rate constant was determined as 2.3 ns by femtosecond transient
Similar photophysical processes are summarized for BDP-2 (Supporting Information, Figure S33). CS occurs within 3.4 ps. The triplet state is confined to the styryl BODIPY moiety. It is produced by SOCT-ISC, with time constant of 1.4 ns (in toluene), and triplet state quantum yield \( \Phi_T = 22\% \) (in toluene). For the dyad BDP-3, fast CS (3.2 ps) was observed, as well as a slow CR (4.0 ns). However, no triplet state signal was observed in femtosecond transient absorption spectra, due to the slow CR (SOCT-ISC) kinetics.

3. Conclusions

In summary, we prepared a series of phenoxazine-styryl BODIPY compact electron donor/acceptor dyads as novel heavy atom-free triplet photosensitizers (PSs), based on the newly developed spin-orbit charge transfer intersystem crossing (SOCT-ISC) strategy. The striking property of the new triplet PSs is the strong absorption of red light \( (\varepsilon = 1.33 \times 10^5 \text{ M}^{-1} \text{cm}^{-1} \text{ at 630 nm}) \), and the long triplet state lifetime \( (\tau_T = 333 \mu\text{s}) \), prolonged by a factor of 180 compared to the triplet state of the same styryl BODIPY chromophore but accessed by the conventional heavy atom effect \( (\tau_T = 1.8 \mu\text{s}) \). Femtosecond transient absorption spectra show that the charge separation and SOCT-ISC (charge recombination) take 109 ps and 2.3 ns, respectively. The triplet state energies of the dyads BDP-1 and BDP-2 are 1.14–1.20 eV and BDP-3 is 1.65–1.77 eV, determined by triplet energy transfer studies. The dyad BDP-3 was used as triplet PSs for triplet-triplet annihilation upconversion (upconversion quantum yield \( \Phi_{UC} = 1.5\% \) in toluene; anti-Stokes shift is 5905 cm\(^{-1}\)). Our results are useful for the design of novel heavy atom-free triplet PSs showing red light-absorption and more importantly long-lived triplet states. These triplet PSs are useful for photo-redox catalytic organic reaction, photodynamic therapy, and triplet-triplet-annihilation photon upconversion.
Experimental Section

Materials and Equipment

All compounds used for synthesis are analytically pure. Solvents for synthesis were freshly dried before using. 1H and 13C NMR spectra were recorded on Bruker 400/500 MHz spectrometers. HRMS (high resolution mass spectra) were recorded with MALDI-TOF-MS and ESI-MS spectrometers. Fluorescence spectra were recorded on a F55 spectrophotofluorimeter (Edinburgh Instrument Ltd, UK). UV-Vis spectra were recorded on a 8453 A UV-Vis spectrophotometer (Agilent Ltd, USA). The time-resolved emission spectra were recorded on a O8920 luminescence lifetime spectrometer (Edinburgh Instrument Ltd, UK).

Synthesis of BDP-1

Compound 3 (50 mg, 0.1 mmol), benzaldehyde (42.4 mg, 0.4 mmol), p-toluenesulfonic acid (PTSA) (15 mg, 0.08 mmol) and piperidine (0.5 mL) were dissolved in dry toluene (5 mL) and heated to 140 °C for 3 h. The organic layer was collected and dried over anhydrous Na2SO4. The crude product was dissolved in DCM and washed with water after cooling to room temperature. The organic layer was collected and dried over anhydrous Na2SO4. The crude product was purified by column chromatography (silica gel, PE/DCM = 2/1, v/v) to obtain BDP-1 as dark violet solid (24 mg, yield: 60%). M.p. > 250 °C. 1H NMR (400 MHz, DMSO-d6): δ = 8.38 (s, 2H), 8.23 (d, 2H, J = 8.0 Hz), 7.66–7.58 (m, 6H), 7.51–7.48 (m, 2H), 7.25–7.22 (m, 2H), 6.92 (s, 3H), 6.79–6.71 (m, 4H), 4.42 (t, 4H, J = 8.0 Hz), 3.65 (t, 2H, J = 6.0 Hz), 2.69 (s, 6H), 1.86 (s, 6H), 1.76 (t, 4H, J = 6.0 Hz), 1.62 (t, 2H, J = 6.0 Hz), 1.50–1.44 (m, 2H), 1.33–1.27 (m, 4H), 0.99 (t, 3H, J = 6.0 Hz), 0.88 (t, 6H, J = 8.0 Hz). MALDI-TOF-HRMS: m/z [M]+ Calcd for C63H48BF3N4O+: m/z = 795.4859, found: m/z = 795.4841.

Synthesis of BDP-3

Under N2 atmosphere, compound 4 (30 mg, 0.04 mmol) and 7 (80 mg, 0.32 mmol) was dissolved in mixed solvent TEA/THF (10 mL, 1:1, v/v). Then PdCl2(PPh3)2 (7 mg), PPh3 (5 mg) and Cul (3.8 mg) were added and the reaction was heated to 60 °C for 3 h. The product was washed with water after cooling to room temperature. The organic layer was collected and dried over anhydrous Na2SO4. The crude product was purified by column chromatography (silica gel, PE/DCM = 2/1, v/v) to obtain BDP-3 as dark violet solid (24 mg, yield: 60%). M.p. > 250 °C. 1H NMR (400 MHz, DMSO-d6): δ = 8.38 (s, 2H), 8.23 (d, 2H, J = 8.0 Hz), 7.66–7.58 (m, 6H), 7.51–7.48 (m, 2H), 7.25–7.22 (m, 2H), 6.92 (s, 3H), 6.79–6.71 (m, 4H), 4.42 (t, 4H, J = 8.0 Hz), 3.65 (t, 2H, J = 6.0 Hz), 2.69 (s, 6H), 1.86 (s, 6H), 1.76 (t, 4H, J = 6.0 Hz), 1.62 (t, 2H, J = 6.0 Hz), 1.50–1.44 (m, 2H), 1.33–1.27 (m, 4H), 0.99 (t, 3H, J = 6.0 Hz), 0.88 (t, 6H, J = 8.0 Hz). MALDI-TOF-HRMS: m/z [M]+ Calcd for C63H48BF3N4O+: m/z = 795.4859, found: m/z = 795.4841.

Femtosecond Transient Absorption Spectra

The femtosecond transient absorption spectra were performed on a Ti:sapphire laser amplifier-optical parametric amplifier system with 52 fs pulse duration and 1 kHz repetition rate (Spectra-Physics, Spitfire Pro XP, TOPAS) and a commercial setup of an ultrafast transient absorption spectrometer (Spectra Physics, Helios). The excitation wavelength was determined by steady UV-Vis absorption spectra. Perpendicular angle between the probe and the pump beam polarization direction was used. The Surface Xplorer and Glotaran software were used for processing the experimental data after chip correction.

NanoSecond Transient Absorption Spectra

Nano-second transient absorption spectra were recorded on a LP980 laser flash photolysis spectrometer (Edinburgh Instruments, Ltd UK). All the sample solutions are deaerated with N2 for ca. 15 min before measuring. The samples were excited with a nano-second pulsed laser (OpoletteTM, the wavelength is tunable in the range of 210–2400 nm. OPOTEK, USA). The typical laser power is 5 mJ per pulse. The signal was digitized on a Tektronix TDS 3012B oscilloscope. The data were analyzed with the L900 software. The intrinsic triplet state lifetime was obtained by fitting of the decay traces of the compounds at different concentrations with a kinetic model that takes into account of the triplet-triplet-annihilation quenching effect.[2,21]

Single Crystal X-Ray Crystallography

X-ray diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å) at 200 K using the SMART and SAINT programs. The structure was solved by direct method of SHELXTL-97 and refined by full-matrix least-squares using the SHELXL-2014 program on a PC. H atoms were generated geometrically. Detailed crystallographic data and structure refinement parameters are available in the Supporting Information, Table S1. The crystallographic data for the structure can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk with CCDC number: 1990853.
Triple State Quantum Yield ($\Phi$)

The triplet state quantum yields were determined by the ground state bleaching method based on the data measured by nanosecond transient absorption spectra using the following equation:

$$\Phi_{\text{sam}} = \Phi_{\text{std}} \left( \frac{\varepsilon_{\text{sam}}}{\varepsilon_{\text{std}}} \right) \left( \frac{\Delta A_{\text{sam}}}{\Delta A_{\text{std}}} \right)$$

In the equation, “sam” and “std” represent sample and standard, respectively. $\Phi$ is the triplet state quantum yield, $\varepsilon$ is the molar absorption coefficient determined by UV-Vis absorption spectra, $\Delta A$ is the optical intensity of the GS band determined by nanosecond transient absorption spectra. Optically matched solutions were used (the absorbance of sample and standard solutions is the same at the excitation wavelength) for the measurement of determination of $\Delta A$. Methylene blue (MB) as standard ($\Phi_{\text{std}}=0.50$ in methanol).

DFT Calculation

All DFT calculations were performed using the Gaussian 09 program package.[13] The ground state geometries, spin density calculations of triplet state and radical anion/cation were optimized by using density functional theory (DFT) at the B3LYP/6-31G(d) level. The spin density calculations of triplet state were performed by setting the charge as 0 and spin as triplet. The spin density calculations of radical anion and cation were performed by setting the charge as $-1$ and $+1$, respectively and spin was set as doublet automatically. The frontier molecular orbitals and the energy levels of the compounds calculated by TD-DFT at the B3LYP/6-31G(d) level.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: BODIPY · charge transfer · intersystem crossing · photosensitizers · triplet state

[1] a) Y. Wu, W. Zhu, Chem. Soc. Rev. 2013, 42, 2039–2058; b) A. Maldotti, A. Molinari, R. Amadelli, Chem. Rev. 2002, 102, 3811–3836; c) N. Zhang, S. R. Samanta, B. M. Rosen, V. Percec, Chem. Rev., 2014, 114, 5848–5958.
[2] a) J. P. Celli, B. Q. Spring, I. Rizvi, C. L. Evans, K. S. Samkoe, S. Verma, B. W. Pogue, T. Hasam, Chem. Rev. 2010, 110, 2795–2838; b) S. G. Avwah, Y. You, RSC Adv. 2012, 2, 11169–11183; c) A. Kamakew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, Chem. Soc. Rev. 2013, 42, 77–88;
[3] a) Z. Wang, J. Zhao, Org. Lett. 2017, 19, 4492–4495; b) M. A. Filatov, S. Karudethadh, P. M. Polestshuk, H. Savoie, K. J. Flanagan, C. S. E. Sitte, M. Telfittchko, F. Laqui, R. B. Wolfe, M. O. Senge, J. Am. Chem. Soc. 2017, 139, 6282–6285; c) K. F.-Z. Yang, N. Feng, Chem. Asian J. 2017, 12, 2447–2456; e) M. A. Filatov, Org. Biomol. Chem, 2020, 18, 10–27; f) W. Hu, L. Miu, X.-F. Zhang, W. Yang, W. Han, L. Zhao, J. Phys. Chem. C 2019, 123, 15944–15955; g) X.-F. Zhang, N. Feng, Spectrochim. Acta Part A 2018, 189, 13–21; h) S. Das, W. G. Thornbury, A. N. Bartynski, M. E. Thompson, S. E. Bradford, J. Phys. Chem. Lett, 2018, 9, 3264–3270; i) Y. Hou, T. Biskup, S. Rein, Z. Wang, L. BuSsotti, N. Russo, P. Foggio, J. Zhao, M. Di Donato, G. Mazzone, S. Weber, J. Phys. Chem. C. 2018, 122, 27850–27865.
[4] a) M. W. Kwok, C. Ma, P. Matousek, A. W. Parker, D. Phillips, W. T. Toner, M. Towrie, P. Zuo, D. L. Phillips, Phys. Chem. Chem. Phys. 2003, 5, 3643–3652.
[5] a) M. Imran, A. A. Sukhanov, Z. Wang, A. Karatay, J. Zhao, Z. Mahmood, A. Elmali, V. K. Voronkova, M. Hayvali, Y. H. Xing, S. Weber, J. Phys. Chem. C. 2013, 123, 7010–7024.
[6] a) Z. Wang, J. Zhao, Angew. Chem. Int. Ed., 2013, 52, 200–204; b) Z. E. X. Dance, Q. Mi, J. Phys. Chem. A 2019, 123, 16243–16248; i) V.-N. Nguyen, Y. Yim, S. Park, J. Yoon, Angew. Chem. Int. Ed. 2010, 49, 20120–20124.
L. Huang, J. Zhao, S. Guo, C. Zhang, J. Ma, J. Org. Chem. 2013, 78, 5627–5637.

[18] a) Gorman, J. Killoran, C. O’Shea, T. Kenna, W. M. Gallagher, D. F. O’Shea, J. Am. Chem. Soc. 2004, 126, 10619–10631; b) N. Adarsh, R. R. Avirah, D. Ramaiah, Org. Lett. 2010, 12, 5720–5723; c) S. Guo, L. Ma, J. Zhao, B. Küçüköz, A. Karatay, M. Hayvali, H. G. Yaglioglu, A. Elmali, Chem. Sci. 2014, 5, 489–500.

[19] J. Zhao, S. Ji, H. Guo, RSC Adv. 2011, 1, 937–950.

[20] a) Z. Shi, J. Li, Q. Han, X. Shi, C. Si, G. Niu, P. Ma, M. Li, Inorg. Chem. 2019, 58, 12529–12533; b) S. Ghosh, C. K. Jana, Org. Biomol. Chem. 2019, 17, 10153–10157.

[21] a) H. Tanaka, K. Shizu, H. Miyazaki, C. Adachi, Chem. Commun. 2012, 48, 11392–11394; b) Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka, C. Adachi, Nat. Photonics 2014, 8, 326–332.

[22] Y. Dong, A. A. Sukhanov, J. Zhao, A. Elmali, X. Li, B. Dick, A. Karatay, V. K. Voronkova, J. Phys. Chem. C 2019, 123, 22793–22811.

[23] T. Akasaka, A. Nakata, M. Rudolf, W.-W. Wang, M. Yamada, M. Suzuki, Y. Maeda, R. Aoyama, T. Tsuchiya, S. Nagase, D. M. Guldi, Org. Lett. 2012, 14, 2594–2597.

[24] a) Z. Lou, Y. Hou, K. Chen, J. Zhao, S. Ji, F. Zhong, Y. Dede, B. Dick, J. Phys. Chem. C 2018, 122, 185–193; b) Z. Wang, A. A. Sukhanov, A. Toffoletti, F. Sadiq, J. Zhao, A. Barbon, V. K. Voronkova, B. Dick J Phys Chem C 2019, 123, 265–274.

[25] W. Wu, X. Cui, J. Zhao, Chem. Commun. 2013, 49, 9009–9011; b) J. Peng, X. Guo, X. Jiang, D. Zhao, Y. Ma, Chem. Sci. 2016, 7, 1233–1237.

[26] A. Gorman, J. Killoran, C. O’Shea, T. Kenna, W. M. Gallagher, D. F. O’Shea, J. Am. Chem. Soc. 2004, 126, 10619–10631; b) N. Adarsh, R. R. Avirah, D. Ramaiah, Org. Lett. 2010, 12, 5720–5723; c) S. Guo, L. Ma, J. Zhao, B. Küçüköz, A. Karatay, M. Hayvali, H. G. Yaglioglu, A. Elmali, Chem. Sci. 2014, 5, 489–500.

[27] a) A. Gorman, J. Killoran, C. O’Shea, T. Kenna, W. M. Gallagher, D. F. O’Shea, J. Am. Chem. Soc. 2004, 126, 10619–10631; b) N. Adarsh, R. R. Avirah, D. Ramaiah, Org. Lett. 2010, 12, 5720–5723; c) S. Guo, L. Ma, J. Zhao, B. Küçüköz, A. Karatay, M. Hayvali, H. G. Yaglioglu, A. Elmali, Chem. Sci. 2014, 5, 489–500.

[28] a) W. Wu, X. Cui, J. Zhao, Chem. Commun. 2013, 49, 9009–9011; b) J. Peng, X. Guo, X. Jiang, D. Zhao, Y. Ma, Chem. Sci. 2016, 7, 1233–1237.

[29] D. R. Sears, R. A. Hollins, A. U. Khan, R. W. Chambers, P. Radlick, J. Am. Chem. Soc. 1967, 89, 5455–5456.

[30] Z. Ma, X. Yuan, B. Küçüköz, S. Li, C. Zhang, P. Majumdar, A. Karatay, X. Li, H. G. Yaglioglu, A. Elmali, J. Zhao, M. Hayvali, J. Mater. Chem. C 2014, 2, 3900–3913.

[31] Z. Wang, J. Zhao, M. Di Donato, G. Mazzone, Chem. Commun. 2019, 55, 1510–1513.

[32] Gaussian 09, Revision 09 W, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Peters, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnensberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Kendall, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc. Wallingford CT, 2009.