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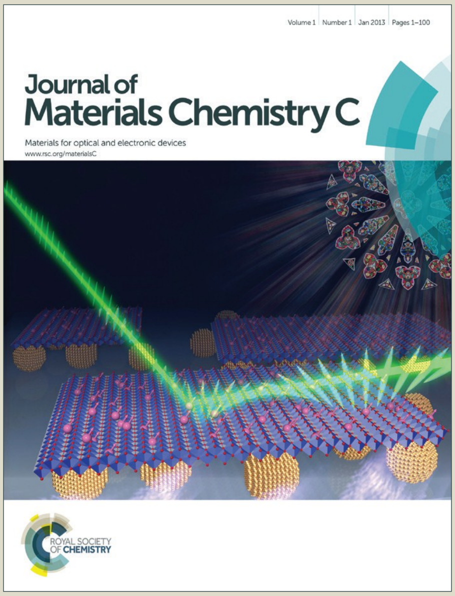

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PAPER

Triplet excited state of diiodoBOPHY derivatives: preparation, study of the photophysical properties and application in triplet-triplet annihilation upconversion

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Pyrrole-BF_2-based chromophore bis(difluoroboron) 1,2-bis((pyrrol-2-yl)methylene) hydrazine (BOPHY) was used for the first time for preparation of new triplet photosensitizers. The UV-vis absorption spectra shows that the absorption bands of the photosensitizers cover 400–700 nm range. Nanosecond time-resolved transient absorption spectra show that the triplet excited state of the compounds were populated upon photoexcitation and compound diiodoBOPHY (**C-2**) is with a long triplet excited state lifetime of 177.2 μs. The triplet state energy level of **C-2** was demonstrated to be higher than the traditional Bodipy chromophores. DFT/TDDFT calculations were carried out for rationalization of the photophysical properties of the compounds. **C-2** was used in triplet-triplet annihilation upconversion, with 9,10-diphenylanthracene (DPA) as the triplet energy acceptor. The TTA upconversion quantum yield is 2.8%. With the styryl substituents on the BOPHY core, the sensitizers demonstrated lower triplet state energy level and shorter triplet state lifetime. With these triplet photosensitizers, photooxidation of 1,3-diphenylisobenzofuran (DPBF) by singlet oxygen ($^1O_2$) photosensitizing was also carried out.

Introduction

The study of triplet excited state properties is crucial for development of novel functional molecular materials which have been widely used in photocatalysis,[1–8] photodynamic therapy,[9–15] molecular switches[16–18] and the triplet-triplet annihilation (TTA) upconversion.[19–22] Typical organic triplet photosensitizers usually contain a spin converter such as C_{60},[23–27] or heavy atoms such as bromine or iodine atoms.[28–30] However, all these organic triplet photosensitizers are base on traditional organic fluorescent chromophores such as boron-dipyrromethene (Bodipy), naphthalenediimide (NDI), perylenebisimide (PBI) and rhodamine, etc.

Pyrrole-BF_2 chromophore bis-(difluoroboron) 1,2-bis((pyrrol-2-yl)methylene) hydrazine (**BOPHY**) have been designed and synthesized base on hydrazine-Schiff base linked bispyrrole, reported by Ziegler and Jiao.[31,32] The BOPHY chromophore has two BF_2 units in six-membered chelate rings appended with pyrrole units on the periphery. Derivatization through Knoevenagel reaction was reported.[31,32] The ultrafast dynamics of this new **BOPHY** chromophore was studied by Ziegler and co-workers.[33] Moreover, base on the single vinyl derivatives of BOPHY, turn-on pH sensor was developed.[34] However, no triplet state properties of this kind of new Bodipy-like chromophores were reported because the intersystem crossing (ISC) process in these BOPHY derivatives are unefficient.[28–30,35] Iodine chloride (ICl) was used to synthesize heavy element contain BOPHY or styryl-BOPHY derivatives by Ziessel and co-workers, however, no triplet state properties and application were reported.[36]

We have been investigating the triplet state photosensitizers which can be used in TTA upconversion, photocatalytic organic reactions or photooxidation by singlet oxygen ($^1O_2$) photosensitizing, etc.[21,35,37] Our strategy is to design the photosensitizers which show strong absorption ability and/or broadband absorption in visible spectral region, long triplet excited state lifetime, and good photostability, etc. Several representative organic triplet photosensitizers have been reported, such as metal free compounds iodo-Bodipy or iodo-aza Bodipy,[30,38–41] C_{60}-Bodipy,[25–27] and C_{60}-PBI conjugates.[42] We also studied transition metal complexes as triplet photosensitizers which show strong absorption of visible light, such as Pt(II), Ru(II), Re(I) complexes.[43–47] However, all of these triplet state photosensitizers are based on traditional chromophores. New chromophores need to be used to design triplet state photosensitizers.

In order to address this challenge, herein we used the pyrrole-BF_2 chromophore bis-(difluoroboron) 1,2-bis((pyrrol-2-yl)methylene) hydrazine (**BOPHY**) for preparation of new triplet photosensitizer, and iodine was used to enhance the intersystem crossing (ISC).[10,29] In order to tune the UV–vis absorption wavelength of the triplet state photosensitizers, we used different styryl moieties as substituent to modify the chromophore. The styryl moieties are coplanar with π-

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conjugation framework of BOPHY and intramolecular charge transfer (ICT) can be used to tune the photophysical properties of the sensitizers.[34,48] With the increase of π-conjugation system, the UV–vis absorption band of the compounds were extended to 400–700 nm. The photophysical properties of these compounds are studied through steady-state UV–vis absorption and emission spectra, nanosecond time-resolved transient absorption spectra and DFT/TDDFT calculation. Triplet state quantum yield and singlet oxygen ($^1O_2$) quantum yields were determined and compared with traditional diiodoBodipy or styryl-diiodoBodipy sensitizers. In the kinetics of the intermolecular triplet state energy transfer study, the triplet state energy of compound **C-2** was determined to be higher than traditional Bodipy (compound **3**). We also used these new triplet photosensitizers in TTA upconversion study and upconversion emission was observed with compound **C-2** as photosensitizers. The upconversion quantum yield for **C-2** was determined as 2.8%.

Experimental section

General Methods

The compounds **C-1** and **C-2** were prepared following the reported methods.[31,36] The compounds **C-3** – **C-6** were synthesized by the following methods.[36] A solution of **C-2** (1 eq), aldehyde (5 eq) and *p*-TsOH (400 mg) in toluene (50 ml) and piperidine (1 ml) was refluxed at 140 °C . The mixture was diluted with dichloromethane and washed with water. The aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography.

Synthesis of Compound C-3

Synthesized according to the General Methods. Yield: 35.6 mg (24.7%). Mp > 250 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.57 (s, 1H), 8.43 (s, 1H), 7.97 (d, 1H, *J* = 16.0 Hz), 7.44 (d, 2H, *J* = 8.8 Hz), 7.13 (d, 1H, *J* = 16.4 Hz), 6.80 (d, 2H, *J* = 8.8 Hz), 4.15–4.12 (m, 3H), 2.36 (s, 3H), 2.34 (s, 3H). MALDI–HRMS (TOF): calcd ($[C_{23}H_{23}B_2N_5F_4I_2]^+$) *m/z* = 721.0165, found *m/z* = 721.0150.

Synthesis of Compound C-4

Synthesized according to the General Methods. Yield: 20.9 mg (14.5%). Mp > 250 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.54 (s, 1H), 7.93 (d, 1H, *J* = 16.4 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.22 (d, 1H, *J* = 16.8 Hz), 7.06 (d, 12H, *J* = 8.8 Hz), 3.82 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H). MALDI–HRMS (TOF): calcd ($[C_{22}H_{20}N_4B_2F_4OI_2]^+$) *m/z* = 707.9849, found *m/z* = 707.9841.

Synthesis of Compound C-5

Synthesized according to the General Methods. Yield: 20.8 mg (15.0%). Mp > 250 °C. 1H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1 H), 8.57 (s, 1 H), 8.51 (s, 1 H), 7.91 (d, 1 H, *J* = 16.8 Hz), 7.45 (d, 2 H, *J* = 8.8 Hz), 7.16 (d, 1 H, *J* = 16.4 Hz), 6.87 (d, 2 H, *J* = 8.4 Hz), 2.37 (s, 3H), 2.34 (s, 3H). MALDI–HRMS (TOF): calcd for ($[C_{21}H_{18}N_4B_2F_4OI_2]^+$) *m/z* = 693.9692, found *m/z* = 693.9718.

Synthesis of Compound C-6

Synthesized according to the General Methods. Yield: 52.1 mg (31.6%). Mp > 250 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 8.60 (s, 1 H), 8.53 (s, 1 H), 8.38 (s, 1 H), 8.26 (d, 1 H, *J* = 7.6 Hz), 8.19 (d, 1 H, *J* = 16.8 Hz), 7.76–7.70 (m, 2H), 7.66 (d, 1H, J = 8.4 Hz), 7.50 (t, 1H, *J* = 15.2 Hz), 7.39 (d, 1H, *J* = 16.8 Hz), 7.25 (t, 1H, *J* = 14.8 Hz), 4.44 (t, 2H, *J* = 14.0 Hz), 2.40 (s, 3 H), 2.35 (s, 3 H), 1.81–1.74 (m, 2H), 1.32–1.28 (m, 2H), 0.89 (t, 3H, *J* = 14.8 Hz). MALDI–HRMS (TOF): calcd for ($[C_{31}H_{29}N_5B_2F_4I_2]^+$) *m/z* = 823.0635, found *m/z* = 823.0616.

Nanosecond Transient Absorption Spectra

The nanosecond time-resolved transient absorption spectra were measured on LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK) and recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values of triplet state photosensitizers were obtained by monitoring the decay trace of the transients with the LP900 software. All samples in flash photolysis experiments were deaerated with N_2 for ca. 15 min before measurement, and the gas flow was maintained during the measurement.

Triplet State Quantum Yield

Triplet state quantum yield was measured based on singlet depletion method, using a nanosecond time-resolved transient difference absorption spectra were measured on LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK). Triplet state quantum yield were measured with Rose bengal (RB, Φ_T = 0.9 in methanol) and Methylene blue (MB, Φ_T = 0.57 in CH_2Cl_2) as standard. Optically matched solutions of standard and the photosensitizers were used. The sample solution was degassed for at least 15 min with N_2 or Ar, and the gas flow is kept during the measurement. Triplet state quantum yields (Φ_T) were calculated according to the following equation:

$$\Phi_{\mathrm{T}}^{\ \mathrm{bod}} = \Phi_{\mathrm{T}}^{\ \mathrm{ref}} \times \frac{\varepsilon^{\mathrm{ref}}}{\varepsilon_{\mathrm{bod}}} \times \frac{\Delta A_{\mathrm{s}}^{\ \mathrm{bod}}}{\Delta A_{\mathrm{s}}^{\ \mathrm{ref}}}$$

Singlet Oxygen Quantum Yield (Φ_Δ)

Singlet oxygen quantum yield (Φ_Δ) of the photosensitizers were calculated according to the following equation and take Rode Bengal (RB) as standard (Φ_Δ = 0.8 in CH_3OH). The absorbance of the $^1O_2$ scavenger 1,3-diphenylisobenzofuran (DPBF) was adjusted around 1.0 in air saturated toluene. Then, the photosensitizer was added to the cuvette, and the photosensitizer's absorbance was adjusted around 0.2–0.3 at the excitation wavelength. The solution in the cuvette was irradiated with monochromatic light for 10 s. Absorbance was measured after each irradiation. The slope of plots of absorbance of DPBF at 414 nm vs irradiation time for each photosensitizer was calculated.

$$\Phi_{(\mathrm{bod})} = \Phi_{(\mathrm{ref})} \times \frac{k_{(\mathrm{bod})}}{k_{(\mathrm{ref})}} \times \frac{F_{(\mathrm{ref})}}{F_{(\mathrm{bod})}} \qquad \text{(eq. 1)}$$

In the equation 1, 'bod' and 'ref' designate the photosensitizers and 'RB', respectively, *k* is the slope of the curves of absorbance of DPBF (414 nm) vs the irradiation time, *F* is the absorption correction factor which is given by $F = 1–10^{–OD}$ (OD is the optical density, i.e. absorbance of the solution at the irradiation wavelength).

TTA Upconversion

For the upconversion experiments, the mixed solution of the photosensitizer and the acceptor was degassed for at least 15 min with N_2, the gas flow is kept during the measurement. The upconverted fluorescence was recorded with spectrofluorometer and the upconversion quantum yield (Φ_{uc}) were determined with the fluorescence of compound **4** as the standard (Φ_F = 2.7% in CH_3CN). The upconversion quantum yields were calculated with the following equation (Eq. 2), where Φ_{uc}, A, I, η represent the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the solvents.

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right)\left(\frac{I_{sam}}{I_{std}}\right)\left(\frac{\eta_{sam}}{\eta_{std}}\right) \qquad \text{(Eq. 2)}$$

DFT Calculations.

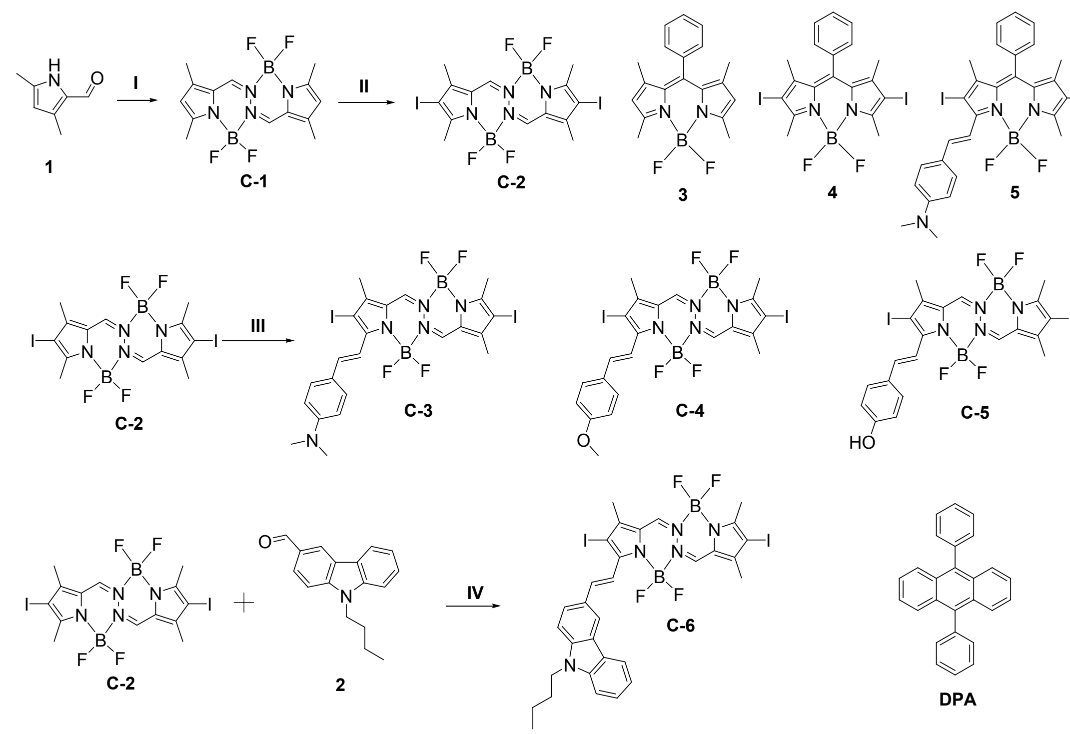
The geometries and the spin density surfaces of the photosensitizers were optimized using density functional theory (DFT) with B3LYP functional and 6–31G (d) basis set. No imaginary frequencies were observed for all the optimized structures. The excitation energy and the energy gaps between S_0 state and the triplet excited states of the compounds were approximated with the ground–state geometry. All these calculations were performed with Gaussian 09W.

Results and discussion

Molecular Designing Rationales

BODIPY is particularly attractive because of it's intense absorption, high fluorescence quantum yields and excellent photostability.[49–54] Our strategy of designing organic triplet state photosensitizers is to use heavy element such as iodine to reduce fluorescence quantum yields and to enhance ISC of the chromophore.[10,29] Furthermore, several modifiable positions on BODIPY structure makes it possible to design rationally and fine-tune the energy levels of the S_1 and T_1 excited state of the sensitizers.[49–54]

Recently a BODIPY analogue, BOPHY, was reporeted.[31,32] But this new chromophore was not studied for formation of triplet excited states. First, we designed compound **C-2** as the photosensitizer (Scheme 1). The iodine atom is attached to the core of **BOPHY** to ensure efficient ISC.[30] Dimethylaminostyryl has been selected to modify compound **C-3** through Knoevenagel condensation reaction.[36] For the previous report, dimethylaminostyryl was used to modify Bodipy, iodo-Bodipy, BOPHY or iodo-BOPHY derivatives, and the aromatic alkenes moiety take a coplanar geometry with π-conjugation of BOPHY, both S_1 and T_1 state energy levels could be tuned.[30,48] In order to modulate the S_1 and T_1 state energy levels, **C-4**, **C-5** and **C-6** were synthesized to compare with



Scheme 1. Preparation of the BOPHY Triplet Photosensitizer. Key: (I) Hydrazine hydrate 80%, EtOH, AcOH, dry CH_2Cl_2, DIPEA and BF3•Et_2O, yield 3.7%. (II) Dry $CHCl_3$, ICl and CH_3OH, 30 °C, yield 85.0%. (III) Aromatic aldehyde, dry toluene, *p*-TsOH and piperidine, 140 °C, yield: 14.5%–31.6%. (IV) Dry toluene, *p*-TsOH and piperidine, 140 °C, yield: 31.6%. 9,10-diphenylanthracene (**DPA)** was used as acceptor of triplet-triplet annihilation upconversion.

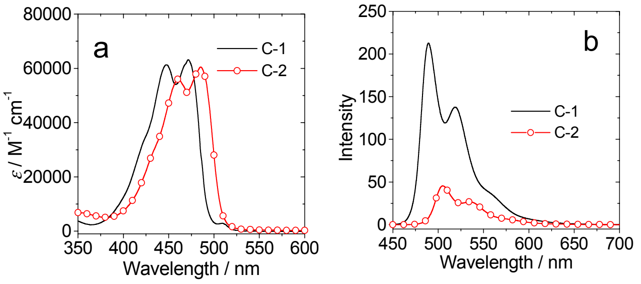


Fig. 1 (a) UV–vis absorption spectra of **C–1** and **C–2**. c = 1.0 × 10^{-5} M. (b) Fluorescence emission spectra of **C–1** and **C–2** (λ_{ex} = 430 nm. Optically matched solution was used). In toluene. 20 °C.

compound **C-3**. These iodinated styrylBOPHY derivatives were prepared by Knoevenagel condensation reaction with satisfying yields.

UV–vis Absorption and Fluorescence Emission Spectroscopies

The steady state UV–vis absorption spectra of the compounds **C-1** and **C-2** were studied (Fig. 1a). **C-1** gives two absorption peaks at 447 nm and 472 nm, the molar extinction coefficient of these two peaks are 61400 M^{-1} cm^{-1} and 63200 M^{-1} cm^{-1}, respectively. Compared with **C-1**, the absorption band of **C-2** have a red shift about 13 nm. The molar extinction coefficient of compound **C-2** is slightly smaller than compound **C-1** (56100 M^{-1} cm^{-1} and 60600 M^{-1} cm^{-1}, respectively. Table 1). The fluorescence emission spectra of **C-1** and **C-2** were studied (Fig. 1b). Compound **C-1** gives two strong emission peaks at 489 nm and 518 nm. The fluorescence quantum yield of **C-1** was reported as 92.0% in CH_2Cl_2.[31] The S_1 state energy level is approximated as 2.54 eV with the emission maxima, which is higher than the traditional BODIPY dyes (2.40 eV). For compound **C-2**, much weaker emission peak than **C-1** was observed and the fluorescence quantum yield of **C-2** was 17%.[36] The S_1 state energy level was approximated as 2.46 eV with the emission of **C-2**. This is higher than the traditional diiodoBODIPY dyes which has been approximated as 2.23 eV.

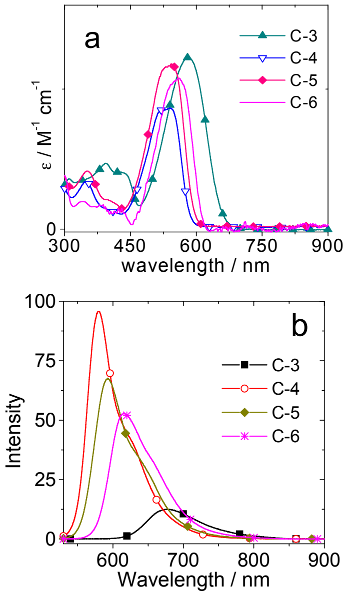


Fig. 2 (a) UV–vis absorption spectra of **C-3**, **C-4**, **C-5** and **C-6**. c = 1.0 × 10^{-5} M. (b) Fluorescence emission spectra of **C-3**, **C-4**, **C-5** and **C-6** (λ_{ex} = 520 nm. Optically matched solution was used). In toluene, 20 °C.

The UV–vis absorption spectra of the **C-3** – **C-6** were studied (Fig. 2a). For **C-3**-**C-6**, the UV–vis absorption band cover a wide range form 430 nm to 700 nm. **C-4** and **C-5** have similar absorption band at 450–600 nm due to their similar molecular structures. With the efficient ICT of dimethylamino, much longer absorption wavelength for **C-3** was observed and the red shifts is 41 nm.

The fluorescence emission spectra of **C-3**-**C-6** were studied (Fig. 2). Due to the efficient ICT, **C-3** shows weak fluorescence emission (Φ_F = 3.0%). With inefficient ICT effect, the fluorescence quantum yield of **C-4**, **C-5** and **C-6** are much higher (Φ_F = 18.8–34.0%). For **C-6**, the fluorescence quantum yield is 18.8%, which is between **C-3** (Φ_F = 3.0%) and **C-4** (Φ_F = 34.0%). More details were summarized in Table 1.

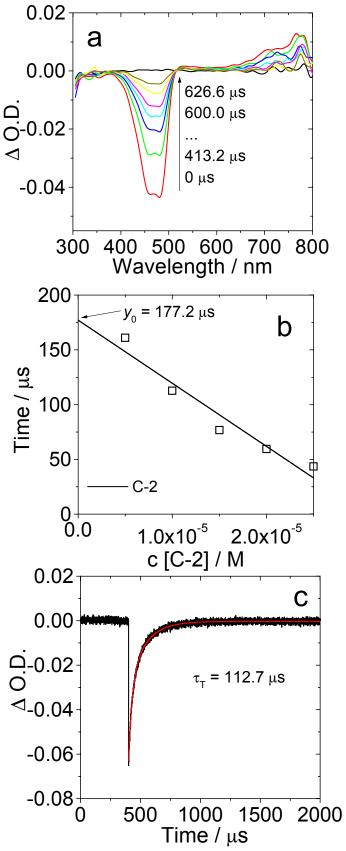


Fig. 3 (a) Nanosecond transient absorption spectra of **C-2**. (b) Plotting of the triplet state life time for **C-2** at different concentration. λ_{ex} = 483 nm. (c) The decay trace of **C-2** at 485 nm (λ_{ex} = 483 nm), c = 1.0 × 10^{-5} M). c = 1.0 × 10^{-5} M, in toluene. 20 °C.

Table 1. Photophysical Parameters of the Compounds. [a]

	λ_{abs}	ε [b]	λ_{em} [c]	Φ_F / % [d]	τ_F [e] /ns	τ_T [f] / µs	Φ_T / %
C-1	447/472	6.14/6.32	489/518	92.0 [i]	2.75	– [h]	– [h]
C-2	461/485	5.61/6.06	505/534	17.0 [i]	0.86	177.2	43.6 [g]
C-3	581	6.13	677	3.0	1.26	5.4	11.8 [g]
C-4	540	4.32	579	34.0	2.10	7.2	23.6 [g]
C-5	543	5,91	593	24.1	1.68	8.8	21.6 [g]
C-6	561	5.40	617	18.8	1.79	10.1	20.2 [g]

[a] In toluene. [b] Molar absorption coefficient, ε: 10^4 M^{-1} cm^{-1}, ($c = 1.0 \times 10^{-5}$ M). [c] Optically matched solution was used. [d] Fluorescence quantum yields. Compound **4** (Φ_F = 2.7% in CH_3CN) was used as standard. [e] Fluorescence lifetimes. [f] Triplet state lifetimes, measured by transient absorptions. For **C-2**, extrapolation method was used. [g] Triplet state quantum yield. Take the Rose Bengal as stand (Φ_T = 0.9 in methanol). [h] Not applicable. [i] Literature values.[31]

Nanosecond Transient Absorption Spectroscopy

In order to study the triplet excited state of the photosensitizers, the nanosecond time-resolved transient absorption spectra (TA) of the compounds were studied (Fig. 3).[55] For **C-2**, a significant bleaching band at 460 nm and 480 nm were observed upon pulsed laser excitation, which is due to the depletion of the ground state of **C-2** (Fig. 3a). In the region of 610–800 nm, a positive transient absorption band was observed, which is the absorption of excited state (ESA) of compound **C-2**.[30] The transient would be quenched by oxygen (O_2), therefore the transient is attributed to the triplet excited state. The triplet excited state lifetime of **C-2** was determined as 112.7 µs in toluene ($c = 1.0 \times 10^{-5}$ M) and it is slightly shorter than the traditional diiodoBodipy (133.0 µs).[63] As the concentration of the compound increased, the triplet state lifetime would become shorter due to the self–quenching (See ESI†, Fig. S13).[38] Extrapolation method was used to determine the triplet excited life time of compound **C-2** (Fig. 3b) as 177.2 µs. Interestingly, the triplet excited state of compound **C-2** was solvent polarity-sensitive. In polar solvent, such as DMF, the triplet excited state life time of compound **C-2** was decreased as compared with the result in less polar solvent at the same concentration (See ESI†, Fig. S14). Note, due to the weak signal, no satisfactory spectra can be determined for **C-4**. The absorption peak of **C-8** is at 561 nm.

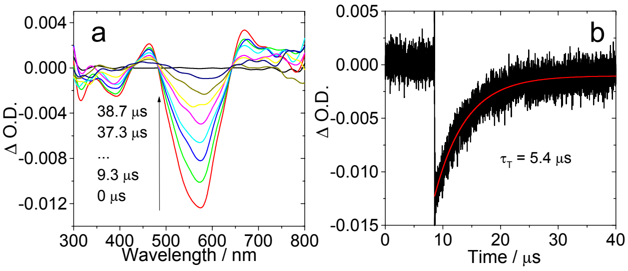


Fig. 4 (a) Nanosecond transient absorption spectra of **C-3** ($c = 2.0 \times 10^{-5}$ M). 20 °C. (b) The corresponding decay trace of **C-3** at 581 nm (λ_{ex} = 585 nm, $c = 1.0 \times 10^{-5}$ M). In toluene. 20 °C.

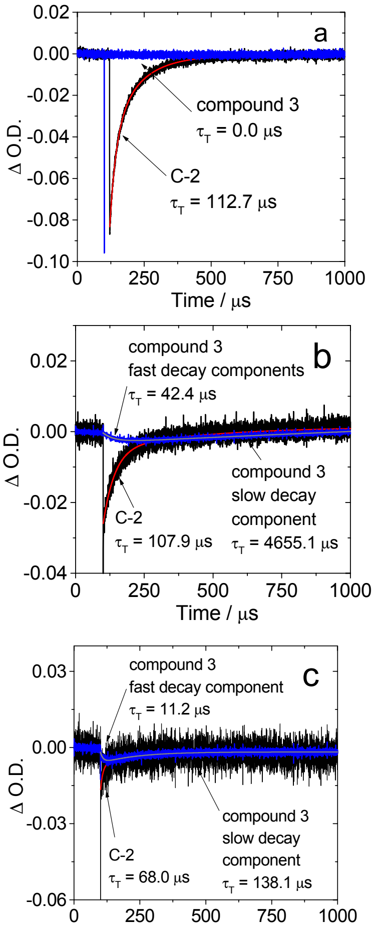


Fig. 5 Intermolecular triplet-triplet energy transfer (TTET) between compound **C-2** (energy donor) to **3** (energy acceptor). The decay traces were monitored at 485 nm (decay of triplet state of **C-2**) and 515 nm (accumulation and decay of the triplet state of **3**), respectively. The energy donor was selectively excited with OPO pulsed laser at 483 nm. (a) Respetive decay curves of **C-2** and **C-3** alone upon 483 nm excitation. c [**C-2**] = 1.0×10^{-5} M, c [**3**] = 1.0×10^{-5} M, . (b) c [**C-2**] = 1.0×10^{-5} M, c [**3**] = 3.3×10^{-6} M. (c) c [**C-2**] = 1.0×10^{-5} M, c [**3**] = 1.0×10^{-5} M. 20 °C. In toluene. Note in (a), **C-2** and **3** were not mixed together.

For **C-3**, significant bleaching band at 575 nm were observed upon pulsed laser excitation (Fig. 4a). In the region of 425–480 nm and 640–800 nm, positive transient absorption bands were observed, which are the absorption of triplet excited state of **C-3**.[30] The triplet excited state lifetime of **C-3** in toluene was determined as 5.4 µs ($c = 1.0 \times 10^{-5}$ M) (Fig. 4b). Similar studies were carried out for **C-4**-**C-6** (See ESI†, Fig. S15).

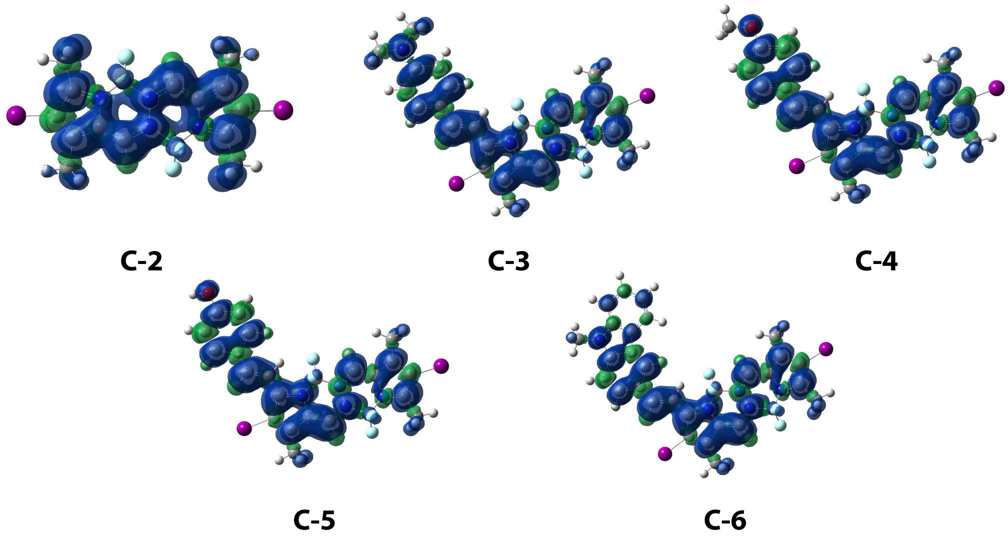


Fig. 6 Isosurfaces of spin density of **C-2** – **C-6** at the optimized triplet state geometries. Toluene was used as the solvent in the calculations. Calculation was performed at B3LYP/6-31G(d)/LANL2DZ level with Gaussian 09W.

The study of long-distance intermolecular energy transfer (EnT) or electron transfer (ET) has attracted much attention because it is crucial for photosynthesis,[56] photoredox catalytic organic reactions,[2,3,57] and photodynamic therapeutic reagents.[37,38] However, long-range triplet energy transfer with chromophores showing strong visible light-absorption as energy donor or acceptor was rarely studied. On the other hand, triplet energy acceptor is also important in study of photophysical properties such as determination of the triplet state energy levels of chromophores.[59] Usually carotene or anthracene were used as the triplet energy acceptors.[60–62] Only a few report on the study of new and robust triplet energy acceptors.

Herein, the kinetics of the intermolecular triplet state energy transfer was studied with monitoring the decay traces at specific wavelengths for compound **C-2** and **3** (Bodipy) (Fig. 5). Previously, we have reported this kind of study with compound **4** as triplet energy donor and di-styryl-Bodipy as energy acceptor.[63] Base on the earlier study and the DFT calculations in this paper (see later section), we used compound **C-2** as the energy donor and compound **3** as the energy acceptor (Fig. 5). Without addition of **3**, **C-2** shows a long triplet excited state lifetime as 112.7 μs. Due to the lack of any heavy atoms, no significant triplet-state formation was observed for compound **3** (Fig. 5a). When compound **C-2** and **3** were mixed together with a molar ratio of 1:0.33 and 1:1, the lifetime of **3** was determined as 42.4 μs and 11.2 μs. The lifetime of **3** (monitored at 515 nm) appears as 4655.1 μs and 138.1 μs, respectively (Fig. 5b and 5c). At the same time, the lifetime of the triplet state of compound **C-2** quenched from 112.7 μs to 68.0 μs, and the quenching efficiency was calculated as 39.7%. This intermolecular energy transfer effect is weaker due to the low triplet state quantum yield of compound **C-2** (43.6%. Fig. 1).[63] As the intermolecular energy transfer (ET) process was observed, we can confirm that the triplet state energy level (T_1) of compound **C-2** is higher than the traditional BODIPY dyes.[63–65] This experiment result is supported by the DFT computations.

DFT Calculations on the Photophysical Properties of the Triplet Photosensitizers

DFT calculations were carried out for rationalization of the photophysical properties of the compounds. First, in order to study the triplet excited states of the compounds, the spin density surfaces of compounds **C-2** – **C-6** were studied by DFT calculations (Fig. 6).[66–70] The triplet state spin density surfaces of the compounds are localized on the whole chromophore part, indicating delocalized distribution of the spin unpaired electrons.

The lowest triplet excited state optimized geometry of **BOPHY** moiety in the molecular structure isn't in the same plane. For compound **C-2**, the face angle of the two symmetry planes has been approximated as 13°, due to the influence of steric hindrance, the face-face angle in compound **C-3**-**C-6** has been approximated as 14–18°. This result is different from traditional diiodoBodipy derivatives that the two pyrrole units are in the same plane.[38] On the other hand, the face angle between aromatic alkenes moiety and the connect bispyrrole chelate plane has been approximated as 1–3°, which is similar to the traditional styryl-diiodoBodipy.[16]

On the basis of the optimized ground-state geometry, the UV–vis absorption and the virtual $S_0 \rightarrow T_n$ excitations of the compound **C-2** and **C-3** were calculated with TDDFT method to study the photophysical processes (Fig. S20, S21 and Table 2). For **C-2**, the calculated UV–vis absorption band ($S_0 \rightarrow S_1$) is located at 423 nm and HOMO→LUMO is the major component of the transition. For T_1 state, the HOMO→LUMO is the major component of the transition and the energy level of T_1 state was calculated as 2.00 eV (618 nm).

Table 2. Selected parameters for the UV–vis absorption and triplet state energy of the compounds. Electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low–lying excited states of **C-2** and **C-3**. calculated by TDDFT//B3LYP/6–31G(d), based on the optimized ground state geometries (acetonitrile was used as solvent in the calculation)

	Electronic transition [a]	TDDFT/B3LYP/6-31G(d)			
		Excitation energy	*f* [b]	Composition [c]	CI [d]
C-2	$S_0 \rightarrow S_1$	2.93 eV (423 nm)	1.0600	H → L	0.7056
	$S_0 \rightarrow T_1$	2.00 eV (618 nm)	0.0000	H→ L	0.6809
	$S_0 \rightarrow T_2$	2.60 eV (477 nm)	0.0000	H–3 → L	0.3382
				H–1 → L	0.4826
				H → L+1	0.3871
	$S_0 \rightarrow T_3$	2.96 eV (419 nm)	0.0000	H–3 → L	0.3900
				H–1 → L	0.4656
C-3	$S_0 \rightarrow S_1$	2.09 eV (594 nm)	1.0976	H →L	0.7052
	$S_0 \rightarrow S_2$	2.93 eV (423 nm)	0.5586	H–1 → L	0.6334
	$S_0 \rightarrow S_3$	3.16 eV (391 nm)	0.3307	H →L+1	0.6224
	$S_0 \rightarrow T_1$	1.44 eV (860 nm)	0.0000	H → L	0.6544
	$S_0 \rightarrow T_2$	2.24 eV (682 nm)	0.0000	H–1 → L	0.5410
				H → L+1	0.3078
	$S_0 \rightarrow T_3$	2.53 eV (489 nm)	0.0000	H–1 → L	0.3526
				H → L+1	0.4769

[a] Only selected excited states were considered. Numbers in parentheses are the excitation energy in wavelength. [b] Oscillator strength. [c] H stands for HOMO and stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wave function for each excitations. CI coefficients are in absolute values.

For **C-3**, the energy-minimized geometry at ground state indicated the styryl moiety is coplanar with π-conjugation with the chromophore part. The calculated UV–vis absorption bands ($S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$) are located at 594 nm, 423 nm and 391 nm, respectively. The HOMO→LUMO, HOMO–1→LUMO and HOMO→LUMO+1 are the respective major components of the transitions. This calculation result is in agreement with the UV–vis absorption data, for which the absorption peaks were observed at 581 nm, 425 nm and 393 nm, respectively. For T_1 state, HOMO→LUMO is the major component of the transition and the energy level of T_1 state was calculated as 1.44 eV (860 nm). Similar DFT/TDDFT calculation results as **C-3** were obtained for **C-4** – **C-6** (Fig. S22–S24 and Table S1-S2). For **C-6**, the calculated UV–vis absorption band ($S_0 \rightarrow S_1$) is located at 562 nm. This result is in agreement with the UV–vis absorption data, for which the absorption peak was observed at 561 nm. The HOMO→LUMO is the major component of the transition.

We noted the T_1 state energy level of **C-2** is higher than compounds **3** and **4**. We compared the HOMO and energy levels of **C-2** and those of the normal Bodipy. The HOMO and LUMO energy level of **C-2** were found as –5.98 eV and –2.65 eV, respectively. Thus the HOMO/LUMO energy gap is 3.33 eV. For the normal BODIPY (i.e. diiodoBODIPY), the HOMO and LUMO energy levels were found as –5.64 eV and –2.75 eV, respectively. Thus the HOMO/LUMO energy gap is 2.89 eV. These data indicate that the T_1 energy level of **C-2** is higher than the reference compound (diiodoBODIPY), due to the increased HOMO/LUMO energy gap. Similar results were found for compound **4** (for which the HOMO/LUMO energy levels are –5.34 eV and –2.34 eV, respectively, and the energy gap is 3.0 eV).

Photooxidation of DPBF by Singlet Oxygen ($^1O_2$) photosensitizing

In order to study the photosensitizing ability of these new triplet state photosensitizers, the compounds were used as singlet oxygen ($^1O_2$) photosensitizer for photooxidation, with 1,3-diphenylisobenzofuran (**DPBF**) as the ($^1O_2$) scavenger. The singlet oxygen quantum yield (Φ_Δ) is useful to evaluate the triplet excited state properties of the photosensitizers.[26,27]

For compound **C-2**, the Φ_Δ was calculate as 0.58, which was with **4** (Φ_Δ = 0.87 in CH_2Cl_2) as standard (Fig. 7a and table 3). This result is lower than compound **4** that, which has been reported as 0.87 in CH_2Cl_2.[38] The fluorescence quantum yield of compound **C-2** is 17.0%,[36] which is much higher than that of compound **4** (Φ_F =2.7 in CH_3CN and Φ_F = 3.6 in toluene).[30] With these reasons, triplet state quantum yield of compound **C-2** was calculated as 43.6% in toluene, which was take Rose Bengal (Φ_Δ = 90% in CH_3OH) as standard.

For compound **C-4**, **C-5** and **C-6**, the $\Phi_\triangle$ were calculated as 0.43, 0.41 and 0.49, respectively (Fig. 7b and table 3). This is much higher than compound **C-3** that, which were calculate as 0.35. Recent years, our group has report several singlet oxygen ($^1O_2$) quantum yields of acid-activatable singlet oxygen photosensitizers.[71] For example, compound **5** shows a week singlet oxygen ($^1O_2$) quantum yield before acid added (Table 3). Compared with compound **5**, **C-2** – **C-6**, show higher singlet oxygen ($^1O_2$) quantum yields.

Table 3. Singlet oxygen quantum yields (Φ_Δ) for the photooxidations of DPBF using different triplet photosensitizers.

	Φ_Δ		Φ_Δ
C-2	0.58[a]	C-6	0.49 [b]
C-3	0.35 [b]	**4**	0.87 [c]
C-4	0.43[b]	**5**	0.06 [c]
C-5	0.41 [b]		

[a] With **4** as standard (Φ_Δ = 0.87 in CH_2Cl_2).[b] With Rose Bengal (RB) as standard (Φ_Δ = 0.80 in CH_3OH). [c] Literature values.[38] Note the absorbance of the photosensitizers at excited wavelength are between 0.2–0.3.

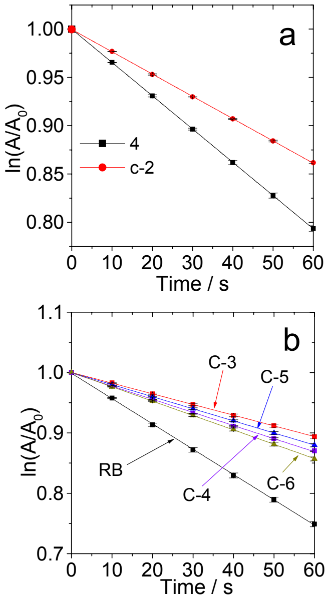


Fig. 7 Singlet oxygen photosensitizing with different photosensitizers by plotting of the ln(A/A_0) of 1,3-diphenylisobenzofuran (DPBF) at 414 nm vs. photoirradiation time. In toluene, 20 °C. (a) Excited at 500 nm. (b) Excited at 550 nm. Optically matched solutions were used. The absorbance of the photosensitizers at excited wavelength are between 0.2–0.3. For **4**, the solvent is CH_2Cl_2. For RB, the solvent is CH_3OH. The error bars are added on the data points.

Application of the Triplet Photosensitizers in Triplet-Triplet Annihilation Upconversion

In recent years, triplet-triplet annihilation (TTA) upconversion has attracted much attention.[20,21,28] Traditional triplet photosensitizers are transition metal compounds such as Pt (II)/Pd (II) porphyrin complexes. Our group have developed a series of transition metal complexes with strong absorption in visible region and long-lived triplet excited states as photosensitizers for TTA upconversion, which are different from the conventional transition metal complexes.[21,70] We also prepared iodo-/bromo-chromophores or organic chromophore-C_{60} dyads for TTA upconversion.[26,30,37]

The TTA upconversion with compound **C-2** as triplet photosensitizer was studied (Fig. 8a). For **C-2**, a strong fluorescence emission of the photosensitizers at 502 nm was observed. In the presence of triplet acceptor **DPA**, the upconverted emission in the range of 390–475 nm was observed. Upon photoexcitation of the triplet photosensitizer or acceptor alone, no upconversion emission was observed. Thus the TTA upconversion in Fig. 8a was verified. The upconversion quantum yield for **C-2** was determined as 2.8%.

Table 4. Triplet Excited State Lifetimes (τ_T), Stern-Volmer Quenching Constant (Ksv), and Bimolecular Quenching Constants (kq) of the BOPHYs[a]

	τ_T (μs)	K_{sv} (10^5 M^{-1})	k_q (10^9 M^{-1} s^{-1})	Φ_{UC} /% [b]	η / (10^3 M^{-1} cm^{-1}) [c]
C-2	161.0	5.9	3.7	2.8	0.9

[a] Photosensitizer concentration at 5.0 × 10^{-6} M for **C-2**. In deaerated toluene, 20 °C. [b] Excited with 473 nm laser. [c] Overall upconversion capability, $\eta = \varepsilon \times \Phi_{UC}$, where ε is the molar extinction coefficient of the triplet photosensitizer at the excitation wavelength and Φ_{UC} is the upconversion quantum yield. With **DPA** as the triplet acceptor. c [**C-2**] = 5.0 × 10^{-6} M.

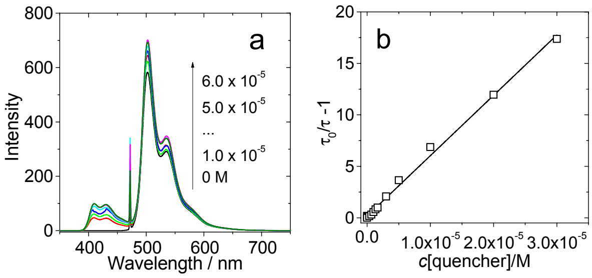


Fig. 8 TTA upconversion data. (a) **C-2** as photosensitizer and DPA as acceptor (increasing concentration was used). Excited by blue laser (λ_{ex} = 473 nm, 5 mW). c[**C-2**] = 5.0 × 10^{-6} M in toluene. 20 °C. (b) Stern-Volmer plots for quenching of the triplet lifetime of photosensitizers with triplet energy acceptor **C-2**. **DPA** as the triplet acceptor. c [**C-2**] = 5.0 × 10^{-6} M. In toluene. 20 °C.

In order to study the origin of the TTA upconversion, the quenching of the triplet-state lifetime of the photosensitizer by the triplet energy acceptor DPA was studied (Fig. 8b). Quenching constant of 5.9 ×10^5 M^{-1} was observed for **C-2** and the bimolecular quenching constant was calculated as 3.7×10^9 M^{-1} s^{-1} with the triplet state lifetime as 161.0 μs (c [**C-2**] = 5.0 × 10^{-6} M, See Table 4 and ESI †, Fig. S16).

Conclusions

In conclusion, a new class of triplet state photosensitizers based on bis-(difluoroboron) 1,2-bis((pyrrol-2-yl)methylene) hydrazine (**BOPHY**) were prepared. This class of new triplet state photosensitizers shows UV–vis absorption in the range of 400–700 nm. The photophysical properties of these photosensitizers were studied with the steady-state UV–vis absorption spectra, fluorescence spectroscopy, nanosecond time-resolved transient absorption spectra and DFT/TDDFT computations. Due to the effect of heavy atom of iodine and efficient ICT of different styryl moiety, the fluorescence emission of diiodoBOPHY and styryl-diiodoBOPHY are much weaker than the unsubstituted **BOPHY** chromophore. Population of the long–lived triplet state was observed for diiodoBOPHY, and the triplet excited state lifetime was determined as 177.2 μs. DFT calculations were used to rationalize the photophysical properties. The photosensitizers were used for TTA upconversion study and significant upconversion was observed for diiodoBOPHY. With the study of intermolecular triplet-triplet energy transfer (TTET), we confirm that the triplet state energy level (T$_1$) of diiodoBOPHY is higher than the traditional BODIPY dyes. The singlet oxygen ($^1O_2$) quantum yield of diiodoBOPHY was determined as 0.58, which is only slightly lower than the traditional triplet state photosensitizer diiodoBodipy. These results are useful for development of new organic triplet photosensitizers.

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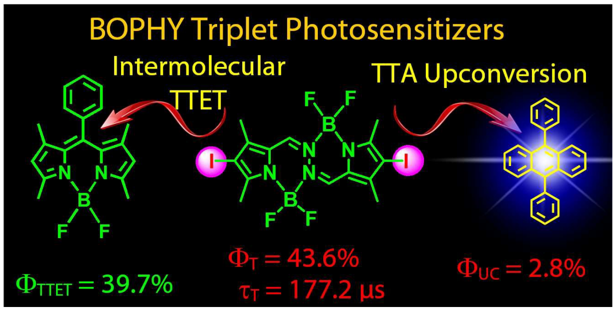
Graphical Abstract:

Triplet excited state of diiodoBOPHY derivatives: preparation, study of the photophysical properties and application in triplet-triplet annihilation upconversion

Caishun Zhang and Jianzhang Zhao*



Pyrrole-BF_2-based chromophore (BOPHY) was used for preparation of triplet photosensitizers and the photophysical properties were studied with transient absorption spectroscopy.