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Bodipy-Phenylethynyl Anthracene Dyad: Spin-Orbit Charge Transfer Intersystem Crossing and Triplet Excited-State Equilibrium

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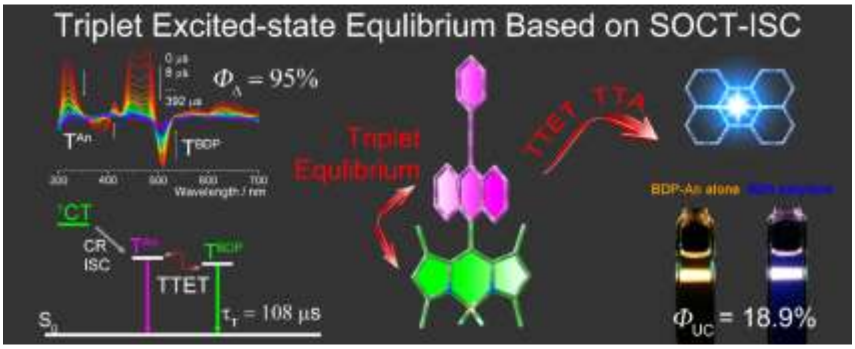
Graphical Abstract:



Highlights

- Novel orthogonal Bodipy-phenylethynyl anthracene dyad was prepared.
- Triple excited-state equilibrium in a photosensitizer showing SOCT-ISC.
- Efficient intersystem crossing was observed (Φ_Δ = 95%) without heavy atom effect.
- Efficient triplet-triplet annihilation upconversion was observed (Φ_{UC} = 18.9%).

Abstract

Spin-orbit charge transfer-induced intersystem crossing (SOCT-ISC) is a promising method to design heavy atom-free triplet photosensitizers (PSs). Herein, a new organic triplet PS, **BDP-An** (Bodipy-phenylethynyl anthracene dyad) has been synthesized and studied. In polar solvents, charge transfer (CT) emission band was observed, and the singlet oxygen quantum yield (Φ_{Δ}) is up to 95%. From femtosecond transient absorption (fs TA) spectra, SOCT-ISC mechanism was verified, the charge separation (CS) time takes1.6 ps, the lifetime of charge recombination (CR) is 3.8 ns, moreover the triplet state of phenylethynyl anthracene was also observed. In nanosecond transient absorption (ns TA) spectra, long-lived triplet states (τ_T = 108 μs) were observed, which are delocalized on both parts of the dyad, i.e. there is a triplet excited-state equilibrium. This is the first report on the triplet excited-state equilibrium observed in an electron donor/acceptor dyad showing SOCT-ISC. With **BDP-An** as the triplet donor and perylene as the triplet acceptor, triplet-triplet annihilation upconversion (TTA UC) was approved, the upconversion quantum yield was up to 18.9%, and the lifetime of TTA-based delayed fluorescence was determined as 70.8 μs.

Keywords: Anthracene; Bodipy, Intersystem crossing, triplet state equilibrium, TTA upconversion

1 Introduction

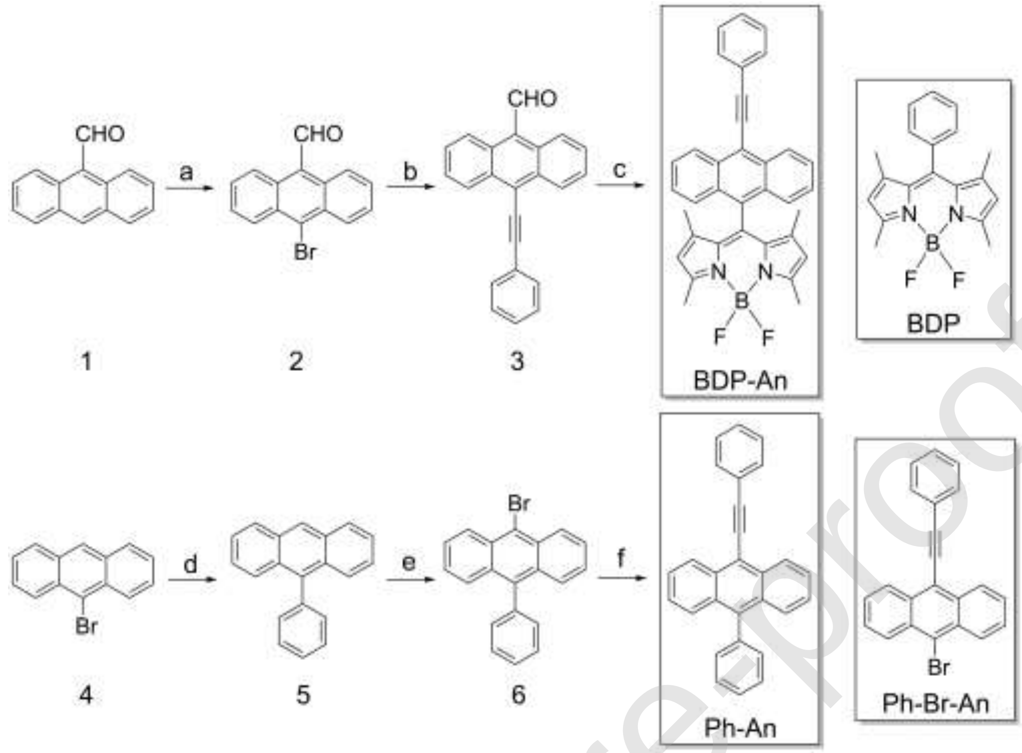
Triplet photosensitizers (PSs) have attracted more and more attention because of wide applications including photodynamic therapy (PDT) [1–4], photo-catalytic reaction [5–9], photovoltaics [10–13], photocatalytic water splitting [14–16] and triplet-triplet annihilation upconversion (TTA UC) [17–19]. Actually the transition from singlet excited state to triplet state is spin-forbidden, thus the method to enhance the intersystem crossing (ISC) has been an important research topic for triplet PSs. A few common methods are available to achieve efficient ISC. The heavy atom effect is a typical one, which can be achieved by introducing heavy atoms, such as Pt, Ru, Ir, I and Br, to organic chromophores [2,20–26]. However, the heavy atom effect is not always effective, especially for large chromophores [25]. Moreover, the triplet excited states of most heavy atom substituted PSs are short-lived due to the heavy atom effect [27,28], which limits their application. Furthermore, dark toxicity of heavy atoms is also a drawback in areas, such as PDT [1,29,30]. Another method to enhance ISC is establishing an π-π* ↔ n-π* transition [31–34]. Nevertheless, triplet PSs in this category are often limited in applications due to the weak absorption in visible spectral range.

Recently spin-orbit charge transfer-induced intersystem crossing (SOCT-ISC) has been employed to develop new triplet PSs. The electron donor/acceptor dyads have been reported to exhibit ISC [35–37]. Given the electron donor and acceptor adopt orthogonal geometry, through photoinduced electron transfer (PeT), charge-transfer (CT) states are formed, then charge recombination (CR) leads to molecular orbital angular momentum changes, which compensates the spin angular momentum change of ISC, therefore ISC is enhanced, namely the mechanism of SOCT-ISC [35,38]. Based on SOCT-ISC, new triplet PSs can be designed by covalently linking different electron donor (or acceptor) with a chromophore. More significantly, the photophysical properties can be readily changed by using different electron donor/acceptor and chromophores.

A series of heavy atom-free Bodipy-anthracene dyads showing high ISC efficiency have been reported in recent years [39–42]. Triplet states distributed on Bodipy subunit were observed through nanosecond transient absorption (ns TA) spectra, and the dyads were applied to TTA UC and PDT. Meanwhile, according to the previous report by our group [43], the extension of π–conjugation framework by C≡C bond at 9,10-position can inhibit ISC and lower the triplet energy levels of anthracene efficiently.

Herein, we modified anthracene moiety of Bodipy-anthracene dyad with the phenylethynyl group (**BDP-An**, Scheme 1), in order to adjust the energy levels and the triplet state quantum yield. Photophysical properties of **BDP-An** were studied with steady-state and time-resolved transient spectroscopies, electrochemistry as well as theoretical calculations. To verify SOCT-ISC mechanism and obtain the quantitative analysis of the photophysical processes, ns TA

Scheme 1. Synthesis of the compounds



(a) Br_2, CH_2Cl_2, stirred at RT for 8 h under N_2, yield: 53%. (b) Phenylacetylene, $PdCl_2(PPh_3)_2$, CuI, Na_2CO_3, THF, Et_3N, refluxed at 70 °C for 4 h under N_2, yield: 92%. (c) 2,4-Dimethylpyrrole, TFA, DCM, stirred at RT overnight under N_2; then DDQ, *N*,*N*-diisopropylethylamine, $BF_3{\cdot}Et_2O$, respectively, yield: 18%. (d) Phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, toluene, ethanol, refluxed for 24 h under N_2, yield: 86%. (e) NBS, CH_2Cl_2, 60 °C for 1 h under N_2, yield: 92%. (f) Phenylacetylene, $Pd(PPh_3)_4$, CuI, THF, diisopropylamine, refluxed for 18 h under N_2, yield: 65%.

spectra of **BDP-An** were studied, which showed a triplet excited-state equilibrium. To our best knowledge, this is the first report on the triplet excited-state equilibrium in an electron donor/acceptor dyad showing SOCT-ISC mechanism. With **BDP-An** as the triplet donor and perylene as the triplet acceptor, the first TTA UC with a triplet excited-state equilibrium PS based on SOCT-ISC was carried out, the upconversion quantum yield was up to 18.9%, and the lifetime of TTA-based delayed fluorescence was determined as 70.8 μs, which may be useful for applications such as time-resolved luminescence imaging studies [44,45].

2 Experimental section

2.1 General methods

All chemicals were analytically pure and used as received from suppliers. NMR spectra were recorded by Bruker spectrometers (400 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR) with $CDCl_3$ as solvent and TMS as standard at 0.00 ppm. UV−Vis absorption spectra were recorded with Agilent 8453 spectrophotometer (Agilent Ltd., USA). Emission spectra were recorded with RF-5301PC spetrofluorophotometer (Shimadzu Ltd., Japan). Fluorescence quantum yields of the compounds were measured with C13534-11 UV−NIR Absolute Photoluminescence quantum yield spectrometer (Hamamatsu Ltd., Japan). Luminescence lifetimes were measured with OB920 fluorescence lifetime instrument (Edinburgh Instrument Ltd., U.K.).

2.2 Synthesis of BDP-An

Compound **3** (200 mg, 0.65 mmol), which was synthesized according to the literature method [46,47], and 2,4-dimethylpyrrole (124 mg, 1.3 mmol) was dissolved in anhydrous dichloromethane (DCM, 150 mL) under nitrogen atmosphere. Then one drop of trifluoroacetic acid (TFA) was added, and the solution was stirred at room temperature overnight. Next dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 148 mg, 0.65 mmol) was added to the solution and the stirring at room temperature was continued for 30 minutes. At 0 °C, *N*,*N*-diisopropylethylamine (DIEA, 4 mL) was added to the solution with syringe and the mixture was stirred for 30 minutes at room temperature. After that 4 mL of boron trifluoride etherate ($BF_3{\cdot}OEt_2$) was added at 0 °C, and the solution was kept stirring for 2 hours. The reaction mixture was washed with water, the organic layer was dried over $NaSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified with column chromatography (silica gel, DCM/hexane = 1:1 as eluent, v/v) to give an orange solid **BDP-An** (61.6 mg, 18%) [48]. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.66–7.59 (m, 2H), 7.53–7.44 (m, 5H), 5.91 (s, 2H), 2.63 (s, 6H), 0.71 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.03, 142.93, 138.44, 132.36, 132.17, 131.70, 129.49, 129.43, 128.87, 128.64, 127.27, 126.98, 125.65, 123.24, 121.30, 119.35, 102.05, 85.95, 29.70, 14.74, 13.53. ESI-TOF-MS ($[C_{35}H_{27}BF_2N_2 + H]^+$): calcd *m/z* 525.2314, found *m/z* 525.2314.

2.3 Synthesis of Ph-An

Ph-An was synthesized according to the literature methods [49,50]. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.62–7.55 (m, 6H), 7.47–7.38 (m, 6H).

2.4 Singlet oxygen sensitization

The singlet oxygen quantum yield (Φ_Δ) of the compounds were measured with diphenylisobenzofuran (DPBF) as singlet oxygen scavenger. By following the change of absorbance (λ_{max} = 414 nm) of DPBF upon photo-irradiation of the mixture, the $^1O_2$ production

(1)

was monitored. The following equation, eqn(1) was used to calculate the singlet oxygen quantum yield.

$$\Phi_{\text{sam}} = \Phi_{\text{std}}\left(\frac{1-10^{-A_{\text{std}}}}{1-10^{-A_{\text{sam}}}}\right)\left(\frac{m_{\text{sam}}}{m_{\text{std}}}\right)\left(\frac{\eta_{\text{sam}}}{\eta_{\text{std}}}\right)^2$$

In the equation, “std” and “sam” stand for standard and sample, respectively. η, A, Φ and m stand for refractive index of the solvents, absorbance at excitation wavelength, singlet oxygen quantum yield and slope of the absorbance of DPBF changing with time. For measurement of Φ_Δ, 2,6-diiodobodipy (Φ_Δ = 87% in DCM, λ_{ex} = 510 nm) and $[\text{Ru(bpy)}_3]^{2+}$ (Φ_Δ = 57% in DCM, λ_{ex} = 440 nm) were used as standards. Optically matched solutions of samples and standards were used for measument.

2.5 Cyclic voltammetry

The electrochemical curves were recorded by a three-electrodes electrolytic cell on the CHI610D electrochemical workstation (CH Instruments, Inc., USA). The voltammograms were recorded at a rate of 100 mV/s in N_2 saturated dichloromethane, with ferrocene (Fc) as the internal reference and tetrabutylammonium hexafluorophosphate ($Bu_4N[PF_6]$, 0.1 M) as the supporting electrolyte. Glassy carbon electrode was used as the working electrode, and platinum electrode as the counter electrode.

2.6 Nanosecond transient absorption spectroscopy

The ns TA spectra of the compounds were recorded in N_2 saturated solvents on a LP980 laser flash photolysis spectrometer (Edinburgh Instruments Ltd. U.K.). The samples were excited with a nanosecond pulsed laser the wavelength is tunable in the range of 200–2200 nm, the typical laser power is 5 mJ per pulse (Opolette$^{TM.}$ 355II+UV nanosecond pulsed laser, OPOTEK, USA). The signals were digitized on a Tektronix TDS 3012B oscilloscope, and L900 software was used for processing the data. A collinear configuration of the pump and the probe beams was used in the measurement to enhance the signal-to-noise ratio.

2.7 Femtosecond transient absorption spectroscopy

The femtosecond transient absorption (fs TA) spectra were measured by a homemade pump−probe setup in combination with a mode-locked Ti-sapphire amplified laser system (Spitfire Ace, Spectra-Physics). Briefly, the system was amplified with wavelength 800 nm of duration 35 fs, repletion rate 1 kHz, and average power 4 W. The output beam was then split into two parts; 90% of the beam after frequency conversion in optical parametric oscillator (Topas, Light Conversion) into UV−VIS−IR in the range of 240−2400 nm was used as pump beam. The remaining 10% output beam was used to generate a white light continuum (WLC) in a 3 mm thickness rotated CaF_2 plate and serves as a probe beam. The probe beam passed through a variable delay line (up to 6 ns), and its absorbance change in the presence and in the absence of the pump beam is measured. The magic angle between pump and probe beam was set at 54.7° in order to avoid rotational depolarization effects. The entire setup was controlled by a PC with the help of LabView software (National Instruments). All measurements were performed at room temperature under aerated conditions. Global target analyses were carried out with the software Glotaran [51].

3 Results and discussion

3.1 Design and synthesis of the compounds

According to the previous reports on Bodipy-anthracene dyads [39,42], the compounds with anthracene attached at the *meso*-position of Bodipy showed higher ISC efficiency and triplet quantum yields. Therefore, we attach the phenylethynyl group to anthracene moiety and synthesized the target molecule **BDP-An** (Scheme 1) [46–48]. In order to study the photophysical properties of **BDP-An**, three compounds **BDP**, **Ph-An** [43, 49, 50] and **Ph-Br-An** were synthesized as reference. The corresponding reactions were with good yields and the molecular structures of the compounds were fully characterized (See ESI†, Fig. S1–S5).

3.2 UV−Vis absorption and fluorescence spectroscopy

The UV−Vis absorption spectra of the compounds are presented in Fig. 1a. Compared with reference compounds, the absorption profiles of **BDP-An** are the sum of the spectra of phenylethynyl anthracene moiety (structured absorption bands in the range of 350–440 nm)

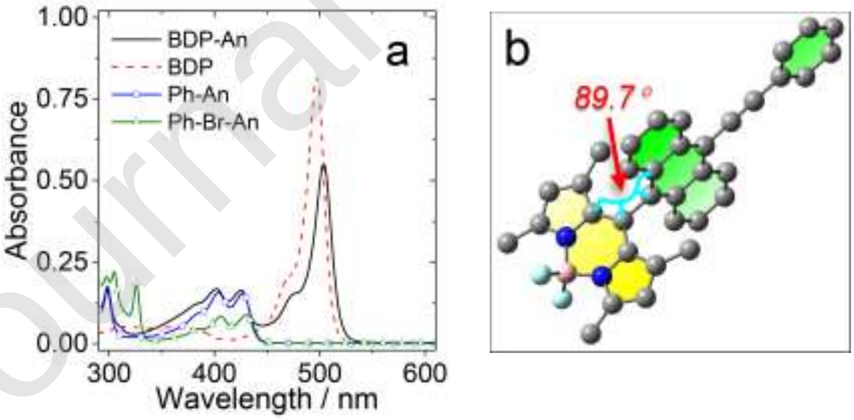


Fig. 1 (a) UV−Vis absorption spectra of **BDP-An**, **BDP**, **Ph-An** and **Ph-Br-An**, $c = 1.0 \times 10^{-5}$ M in acetonitrile, 20 °C. (b) Optimized ground state geometry and dihedral angle of **BDP-An** calculated with DFT at B3LYP/6-31G(d) level with Gaussian 09W.

and Bodipy moiety (sharp peak at 510 nm), and no absorption of charge-transfer (CT) state can be observed, which indicates negligible interaction of two chromophores in the ground state [37,52,53]. The density functional theory (DFT) calculation optimized geometry indicates an orthogonal conformation with a dihedral angle of 89.7° (Fig. 1b) between two subunits [54], thus π–conjugation between the Bodipy moiety and phenylethynyl anthracene moiety was inhibited in **BDP-An** [55].

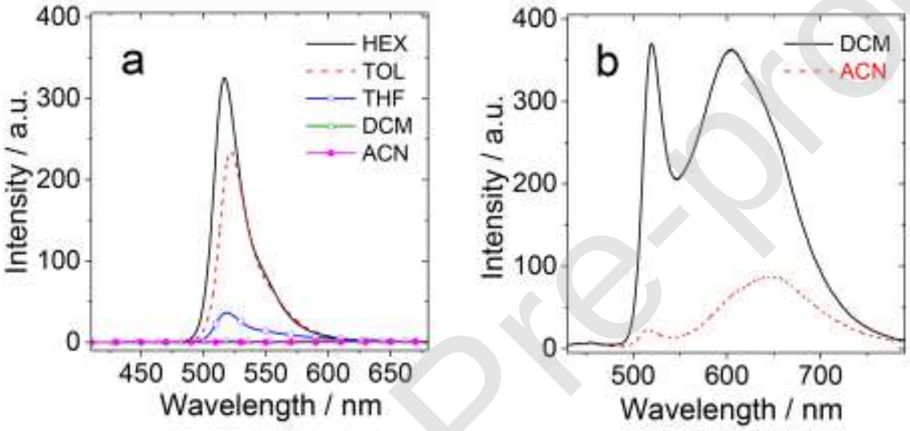


Fig. 2 (a) The emission spectra for **BDP-An** in different solvents, λ_{ex} = 400 nm, A_{400} = 0.140, 20 °C. (b) The emission spectra for **BDP-An** in polar solvents with high sensitivity of the spectrophotometer, λ_{ex} = 400 nm, $A_{400\ nm}$ = 0.100, 20 °C.

The fluorescence emission spectra of the compounds in different solvents were studied (Fig. 2). The emission band at 520 nm of **BDP-An** is attributed to the localized excited state (^{1}LE state) emission band of the Bodipy chromophore (Fig. 2a) compared with that of **BDP** (See ESI†, Fig. S7). By selective excitation of the phenylethynyl anthracene moiety, there was no corresponding luminescence band (See ESI†, Fig. S8) observed, which indicates high-efficiency Förster resonance energy transfer (FRET, See ESI†, Fig. S10) or charge separation (CS). The emission spectra of **BDP-An** were studied in different solvents. The fluorescence intensity of **BDP-An** decreased as the solvent polarity increased, and the fluorescence was almost completely quenched in polar solvents such as dichloromethane and acetonitrile, which indicates the photo-induced CS [56,57]. By comparison, the fluorescence intensity of reference compounds did not change obviously as the solvent polarity varied (See ESI†, Fig. S9).

By means of increasing the sensitivity of the spectrophotometer, the fluorescence emission of **BDP-An** in polar solvents was studied (Fig. 2b). In addition to the ^{1}LE state emission band at 520 nm, a broad band ranging from 540 nm to 800 nm was observed, which is assigned to CT emission band ($^1CT \rightarrow S_0$) [40,58]. Therefore, in polar solvents, the interaction between two subunits becomes more significant upon excitation.

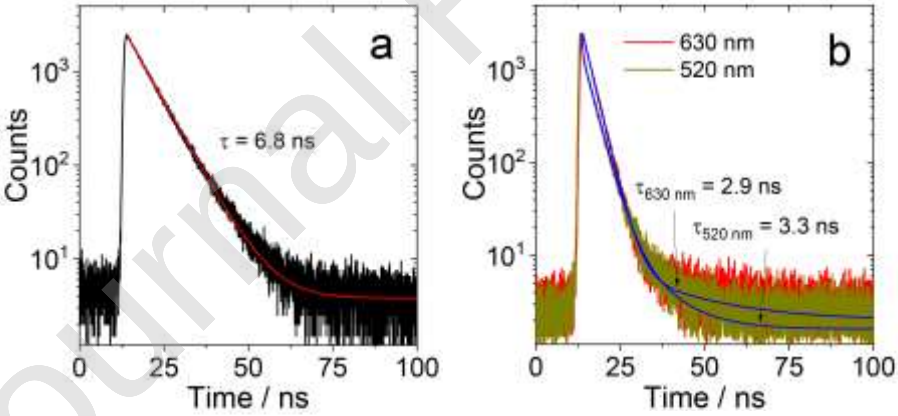


Fig. 3 Fluorescence lifetime decay curves of **BDP-An** in (a) hexane at 525 nm and (b) acetonitrile at 525 nm and 630 nm, λ_{ex} = 405 nm, c = 1.0 × 10^{-5} M, 20 °C.

Table 1. Photophysical properties of the compounds

	Solvent	λ_{abs} [a]	ε [b]	λ_{em}	Φ_F [c]	τ_F / ns [d]	τ_T / μs [e]	Φ_Δ [f]
BDP-An	HEX	401 / 505	1.7 [h] / 6.8 [i]	516	0.99	6.8	104 [k]	– [m]
	DCM	404 / 507	1.7 [h] / 6.2 [i]	520 / 604	0.05	5.3 / 5.3	78 [k] / 77 [l]	0.87
	ACN	402 / 504	1.7 [h] / 5.5 [i]	525 / 650	0.02	3.3 / 2.9	35 [k] / 108 [l]	0.95
BDP	HEX	501	8.9	510	0.57	3.1	– [n]	– [n]
	DCM	501	8.4	511	0.63	3.6	– [n]	– [n]
	ACN	497	8.2	507	0.55	3.5	– [n]	– [n]
Ph-An	HEX	402	1.6	437	0.77	3.9	– [o]	– [o]
	DCM	406	1.6	444	0.82	4.6	– [o]	– [o]
	ACN	404	1.6	440	0.76	4.6	– [o]	– [o]
Ph-Br-An	HEX	405	0.8	436	0.50	2.4	29	0.17
	DCM	409	0.8	442	0.73	3.6	35	0.19
	ACN	406	0.8	439	0.59	3.0	28	0.23

[a] Maximal UV–Vis absorption wavelength of each band in different solvents ($c = 1.0 \times 10^{-5}$ M). [b] Molar absorption coefficient, ε: 10^4 M^{-1} cm^{-1}). [c] Fluorescence quantum yields. [d] Luminescence lifetimes. [e] Triplet excited state lifetimes. Measured by nanosecond transient absorption spectroscopy in deaerated solutions. [f] Singlet oxygen quantum yields, with 2,6-diiodoBodipy as the standard ($\Phi_\Delta = 0.87$ in acetonitrile). [g] TTA upconversion quantum yields, with 2,6-diiodoBodipy as the luminescence quantum yield standard (Φ_F = 0.027 in acetonitrile). Upconversion quantum yields of **BDP-An** were measured at excitation laser power density of 50 mW cm^{-2}. [h] Absorption band of the phenylethynyl anthracene moiety. [i] Absorption band of the bodipy moiety. [k] Monitored by the band at 480 nm. [l] Monitored at 510 nm. [m] Not observed. [n] Not applicable. [o] Not determined.

The fluorescence lifetimes of the compounds were studied. In different solvents, there was no significant change of the fluorescence lifetimes of the reference compounds (Table 1). Nevertheless, the lifetime of ^{1}LE state of **BDP-An** was shortened from 6.8 ns in hexane to 3.3 ns in acetonitrile (Fig. 3). The fluorescence lifetime of ^{1}LE state is affected by two possible photophysical processes: FRET (Förster resonance energy transfer) and CS. In polar solvents, CS occurs so that the fluorescence is quenched, and the lifetime is shortened. The photophysical parameters of the compounds are summarized in Table 1.

3.3 Electrochemical studies: cyclic voltammetry and the Gibbs free energy changes of the photoinduced charge separation (ΔG_{CS})

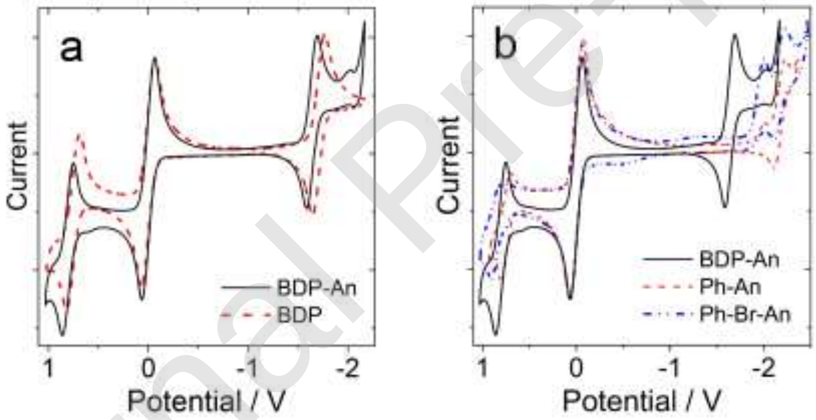


Fig. 4 (a) Cyclic voltammograms of **BDP-An** and **BDP**; (b) Cyclic voltammograms of **BDP-An**, **Ph-An** and **Ph-Br-An**. Ferrocene (Fc) was used as internal reference ($E_{1/2}$ = + 0.64 V, Fc^+/Fc). In deaerated CH_2Cl_2 solutions containing 1.0 mM PSs with the ferrocene, 0.10 M Bu_4NPF_6 as the supporting electrolyte, $Ag/AgNO_3$ as the reference electrode. Scan rates: 100 mV/s, 20 °C.

The electrochemical properties of the compounds were measured with cyclic voltammetry (Fig. 4) [59–61]. All compounds showed both oxidation and reduction waves, and corresponding data was listed in Table 2. For **BDP**, a reversible oxidation wave at +0.75 V was observed, as well as a reversible reduction wave at −1.71 V. For **Ph-An**, the oxidation and reduction waves were at +0.75 V and −2.17 V, respectively. For **Ph-Br-An**, the oxidation wave was at +0.91 V, and two reduction waves were at −2.00 V and −2.22 V. As for **BDP-An**, the first reversible reduction wave at −1.63 V was related to the Bodipy moiety, thus the reversible oxidation wave at +0.75 V should be related to the anthracene moiety, indicating that Bodipy moiety acts as electron acceptor and the phenylethynyl anthracene moiety acts as electron donor. Therefore, the charge separated state (CSS) of **BDP-An** should be composed of Bodipy radical anion and phenylethynyl anthracene radical cation.

Table 2. Electrochemical Redox Potentials of the compounds [a]

Compound	Oxidation(V)	Reduction(V)
BDP-An	+0.81	−1.63; −2.05
BDP	+0.75	−1.71
Ph-An	+0.75	−2.17
Ph-Br-An	+0.91	−2.00; −2.22

[a] Cyclic voltammetry in nitrogen saturated CH_2Cl_2 containing a 0.10 M Bu_4NPF_6 supporting electrolyte, Pt electrode as the counter electrode, glassy carbon electrode as the working electrode, Ag/$AgNO_3$ couple as the reference electrode, c = 1.0 mM, 20 °C.

The Gibbs free energy changes for the charge transfer processes of **BDP-An** were calculated with the Weller equation eqn (2), eqn(3) and eqn(4) [59,62].

$$\Delta G_{\mathrm{S}} = -\frac{e^2}{4\pi\varepsilon_{\mathrm{S}}\varepsilon_0 R_{\mathrm{CC}}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_{\mathrm{D}}} + \frac{1}{R_{\mathrm{A}}}\right)\left(\frac{1}{\varepsilon_{\mathrm{REF}}} - \frac{1}{\varepsilon_{\mathrm{S}}}\right) \quad (2)$$

$$\Delta G_{\mathrm{CR}} = -(\Delta G_{\mathrm{CS}} + E_{00}) \quad (3)$$

$$\Delta G_{\mathrm{CS}}^{0} = e[E_{\mathrm{OX}} - E_{\mathrm{RED}}] - E_{00} + \Delta G_{\mathrm{S}} \quad (4)$$

In the equations, ΔG_{S} is the static Coulombic energy, e is the electronic charge, E_{OX} is the half-wave potential for one-electron oxidation of the electron-donor unit, E_{RED} is the half-wave potential for one-electron reduction of the electron-acceptor unit, E_{00} is the energy level approximated with normalized UV−Vis absorption and fluorescence emission spectra, and ε_{S} is the static dielectric constant of the solvent. R_{CC} is the centre-to-centre separation distance between the electron donor (Phenylethynyl anthracene) and acceptor (Bodipy), determined by DFT optimization of the geometry. R_{D} is the radius of the electron donor, R_{A} is the radius of the electron acceptor, $\varepsilon_{\mathrm{REF}}$ is the static dielectric constant of the solvent used for the electrochemical studies, and ε_0 is the permittivity of free space. The solvents used in the calculation of free energy of the electron transfer are hexane (ε_{S} = 1.88), toluene (ε_{S} = 2.38), tetrahydrofuran (ε_{S} = 7.58), dichloromethane (ε_{S} = 8.93) and acetonitrile (ε_{S} = 37.5).

According to the calculation results of **BDP-An** (Table 3), in nonpolar solvents, such as *n*-hexane and toluene, CS is thermodynamically forbidden. While as solvent polarity increased, CS becomes thermodynamic allowed and the driving forces for CS become larger, as well as the energy level of charge separated state decreased, which is in agreement with the fluorescence emission studies (Fig. 2a).

Table 3. The Driving Forces of Charge Separation (ΔG_{CS}), Static Coulombic Energy (ΔG_S), and the Charge-separated States Energy Level (E_{CS})

	BDP-An				
	HEX [a]	TOL	THF	DCM	ACN
ΔG_{CS} [eV] [b]	0.11	0.05	−0.18	−0.19	−0.28
ΔG_S [eV]	0.10	0.02	−0.20	−0.21	−0.28
E_{CS} [eV]	2.54	2.46	2.24	2.22	2.16

[a] HEX, TOL, THF, DCM and ACN stand for n-hexane, toluene, tetrahydrofuran, dichloromethane and acetonitrile, respectively. [b] Singlet excited state, E_{00} is approximated with the crossing point of UV−Vis absorption and fluorescence emission after normalization at the singlet excited state.

Moreover, although the ground state redox potentials of Bodipy and phenylethynyl anthracene moieties are similar, the femtosecond transient absorption spectra (see later section) show that the excited Bodipy unit is the electron acceptor and the phenylethynyl anthracene unit is the electron donor.

3.4 Femtosecond transient absorption spectra

To reveal the photophysical processes and excited state dynamics of **BDP-An** after excitation, femtosecond transient absorption spectra of the compounds were measured (Fig. 5). According to the above results, possible photophysical processes of **BDP-An** in polar solvents are presented with the following equations (5), (6) and (7) [42]. Briefly, upon fs pulsed laser

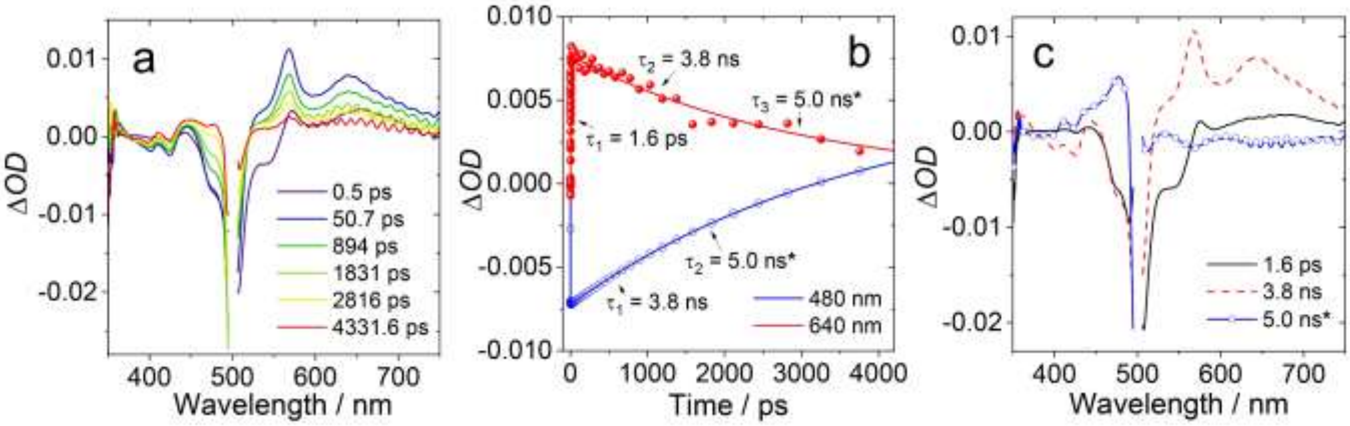


Fig. 5 (a) Femtosecond transient absorption spectra of **BDP-An** upon fs pulsed laser excitation. (b) Decay traces of **BDP-An**. (c) Evolution-associated difference spectrum (EADS) obtained by global analysis of the transient data. λ_{ex} = 500 nm in acetonitrile, 20 °C. * The time window of the fs TA measurements is 5.0 ns.

excitation, singlet excited state of Bodipy is generated, followed by PET, which results in formation of CSS, which is composed of Bodipy radical anion and anthracene radical cation. CSS undergoes CR and the triplet state of Bodipy (T_1[BDP-An*]) or phenylethynyl anthracene (T_1[BDP*-An]) is produced.

$$S_0(\mathrm{BDP} - \mathrm{An}) + h\upsilon \rightarrow S_1(\mathrm{BDP}^* - \mathrm{An}) \quad (5)$$

$$S_1(\mathrm{BDP}^* - \mathrm{An}) \rightarrow \mathrm{CT}(\mathrm{BDP}^{-\bullet}{-}\mathrm{An}^{+\bullet}) \quad (6)$$

$$\mathrm{CT}(\mathrm{BDP}^{-\bullet}{-}\mathrm{An}^{+\bullet}) \rightarrow T_1(\mathrm{BDP}^* - \mathrm{An}) \text{ or } T_1(\mathrm{BDP} - \mathrm{An}^*) \quad (7)$$

Fig. 5a shows the femtosecond transient absorption spectra of **BDP-An** in acetonitrile. Upon photoexcitation, the ground state bleaching (GSB) bands at 504 nm (Refer to Fig. 1a) were observed. At 570 nm, excited state absorption (ESA) band is due to Bodipy radical anion: it develops within 50 ps, indicating CS process [42, 63, 64]. Meanwhile, another ESA band centred at 640 nm developed, which is attributed to the phenylethynyl anthracene radical cation. The above processes correspond to the eqn(4) and eqn(5).

Subsequently, both ESA bands decayed within 3.8 ns, and a broad triplet ESA band centred at 490 nm ($T_1 \rightarrow T_n$ transition) developed. This ESA band didn't decay within the time scale of the measurements (5 ns), indicating SOCT-ISC process. All processes were further convinced by global analysis with the software GLOTARAN [51], the CS time constant is 1.6 ps, and the ISC time constant is 3.8 ns (Fig. 5c). Note the final species is with infinite lifetime for the fs TA measurements, and the spectrum is in good agreement with the nanosecond transient absorption studies (see next section). We also performed fs TA study with selective excitation into the anthryl unit, fast FRET was observed, the time is shorter than the IRF (Supporting Information, Figure S12).

3.5 Nanosecond transient absorption spectra

To further confirm the production of the triplet states of the dyad upon photoexcitation, ns TA spectra were measured. The ns TA spectra of **BDP-An** and **Ph-Br-An** in acetonitrile are presented in Fig. 6. For compound **Ph-Br-An** (Fig. 6c), two positive bands centred at 315 and 490 nm were observed, which are assigned to the $T_1 \rightarrow T_n$ excited state absorption of the phenylethynyl anthracene moiety. Note that the ground state bleaching band in the range of 350 nm–450 nm overlaps with the excited state absorption [65–67]. The transient signal at 490 nm decays within 28 μs, while the lifetime was greatly decreased to 247 ns (See ESI†, Fig. S19) in aerated solution which indicates that the positive peaks can be assigned to the triplet state absorption band (T_1[Ph-Br-An*]). In different solvents there was no great change of the singlet oxygen quantum yield of **Ph-Br-An** (Table 1), as well as the signal intensities of transient absorption (Δ*OD*, See ESI†, Fig. S17, S18), thus the solvent polarity does not have a significant effect on the triplet state quantum yield of **Ph-Br-An**.

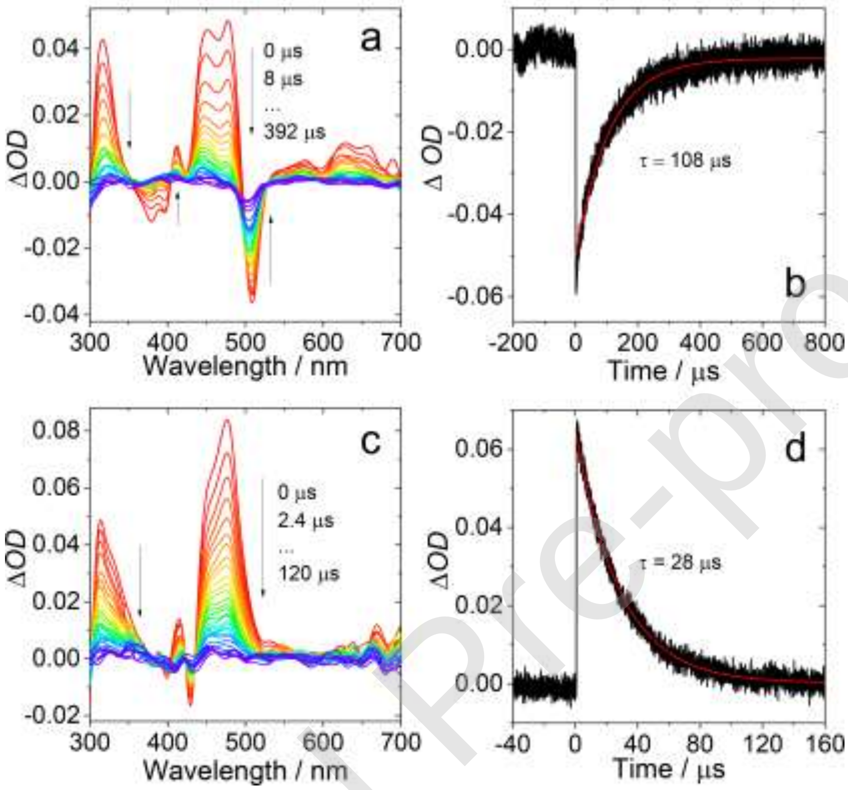


Fig. 6 (a) Nanosecond transient absorption spectra of **BDP-An** upon ns pulsed laser excitation and (b) decay trace at 510 nm in deaerated acetonitrile, λ_{ex} = 425 nm, c = 1.0 × 10^{-5} M, 20 °C. (c) Nanosecond transient absorption spectra of **Ph-Br-An** upon ns pulsed laser excitation (c = 5.0 × 10^{-5} M) and (d) decay trace at 490 nm in deaerated acetonitrile (c = 2.0 × 10^{-5} M), λ_{ex} = 425 nm, 20 °C.

For compound **BDP-An** (Fig. 6a), the transient absorption signals differ strongly in various solvents. In nonpolar solvents such as hexane (See ESI†, Fig. S13), the signal intensity is very weak. As the solvent polarity increased, the signal intensity was greatly enhanced, which is in agreement with the singlet oxygen quantum yields (Table 1) and SOCT-ISC mechanism. In polar solvents such as acetonitrile, upon nanosecond pulsed laser excitation, ground state bleaching bands at 400 and 510 nm were observed, corresponding to the phenylethynyl anthracene and Bodipy subunits, respectively (Fig. 6a). Meanwhile, two positive peaks centred at 315 and 490 nm can be attributed to the signal of the triplet state of phenylethynyl anthracene (T_1[BDP-An*]), similar to that of **Ph-Br-An**. Interestingly, a ground state bleaching band centred at 510 nm was observed, which is related to the Bodipy moiety. Thus the triplet state of Bodipy moiety is also populated, supported by the weak and broad bands in the range of 540–700 nm [39, 42, 68].

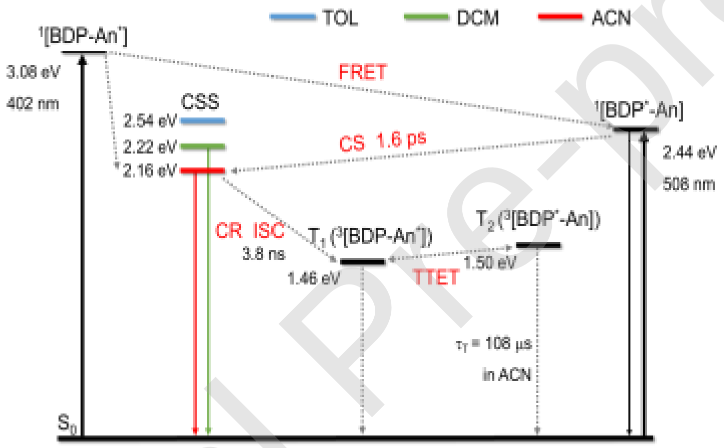
This result indicates triplet excited-state equilibrium of **BDP-An**. To the best of our knowledge, this is the first report on observation of the triplet excited-state equilibrium based on SOCT-ISC mechanism. Considering the fs TA result didn’t show significant triplet-triplet energy transfer (TTET), thus we propose that the time constant of TTET is between the time scale of ns TA and fs TA measurements, i.e. 10–100 ns. For the previous reported Bodipy-anthracene dyads [39, 42], the compounds with anthryl unit attached at the meso-position of Bodipy showed efficient ISC and high triplet quantum yields. However, no triplet excited-state equilibrium was observed for the previous Bodipy-anthracene dyads. The reason was that the triplet energy level of anthryl subunit (1.84 eV) is much higher than the triplet energy level of

Bodipy subunits (1.46 eV). In our case, however, the anthryl unit is π-conjugated the phenylethynyl moiety, the triplet energy level of anthracene subunit deceased to 1.50 eV, which makes the triplet excited-state equilibrium possible because the Bodipy unit is with similar triplet state energy level (1.46 eV). We noted the triplet state energy level for the 2,6-diethyl substituted Bodipy was reported as 1.61 eV, based on the phosphorescence in a Ru(II) complexes [69], however, the Bodipy unit in BDP-An is with different structure, therefore we estimated the triplet state energy level of the current Bodipy unit with TDDFT computations. It should be noted that the triplet state lifetime of **Ph-Br-An** may be reduced by the heavy atom of bromine whereas the triplet state of the dyad may be shortened by TTA self-quenching effect [41,43,70].

The decay trace at 410 nm and 480 nm (these are the excited state absorption bands of the phenylethynyl Anthracene triplet state) in ns transient absorption spectroscopy both showed mono-exponential decay (see Supporting Information, Figure S13), no growth phase was observed, which indicated that the triplet state of the phenylethynyl anthracene unit is not populated by intermolecular triplet state energy transfer, instead, it is due to the intramolecular triplet state energy transfer [71].

Based on the above results and time-dependent density functional theory (TD-DFT) calculations, the photophysical processes of **BDP-An** were illustrated with the simplified Jablonski diagram (Scheme 2). Upon excitation of the phenylethynyl anthracene moiety, the singlet excited state of Bodipy moiety is produced through effective FRET, followed with the ^{1}LE state emission of Bodipy chromophore in nonpolar solvents, or CS (τ = 1.6 ps) in polar solvents. CSS is composed of Bodipy radical anion and phenylethynyl anthracene radical cation, which formation is supported by the observation of CT emission band in the fluorescence spectra, as well as the radical ions in fs TA spectra. The triplet states localized on the phenylethynyl anthracene moieties (^{3}[BDP-An*]) are generated through ISC enhanced by CR (τ = 3.8 ns), then TTET occurs between two subunits, followed by the triplet states localized on the Bodipy moieties (^{3}[BDP*-An]) generated, i.e. the triplet excited-state equilibrium.

Scheme 2 Simplified Jablonski Diagram Illustrating the Photophysical Process of BDP-An ^{a}



^{a} The energy levels of the triplet states of **BDP-An** are obtained by time-dependent density functional theory calculations. The energy levels of the CSS are obtained from the electrochemical studies. The energy levels of the other excited states are derived from the above spectral data in acetonitrile. The lifetimes of the excited states are obtained with fs TA spectra data.

3.6 TTA upconversion and delayed fluorescence

With **BDP-An** as triplet donor and Perylene as triplet acceptor, TTA upconversion experiment was carried out excited by a 510 nm continuous wave (*cw*) laser in dichloromethane (Fig. 7) and acetonitrile (See ESI†, Fig. S20).

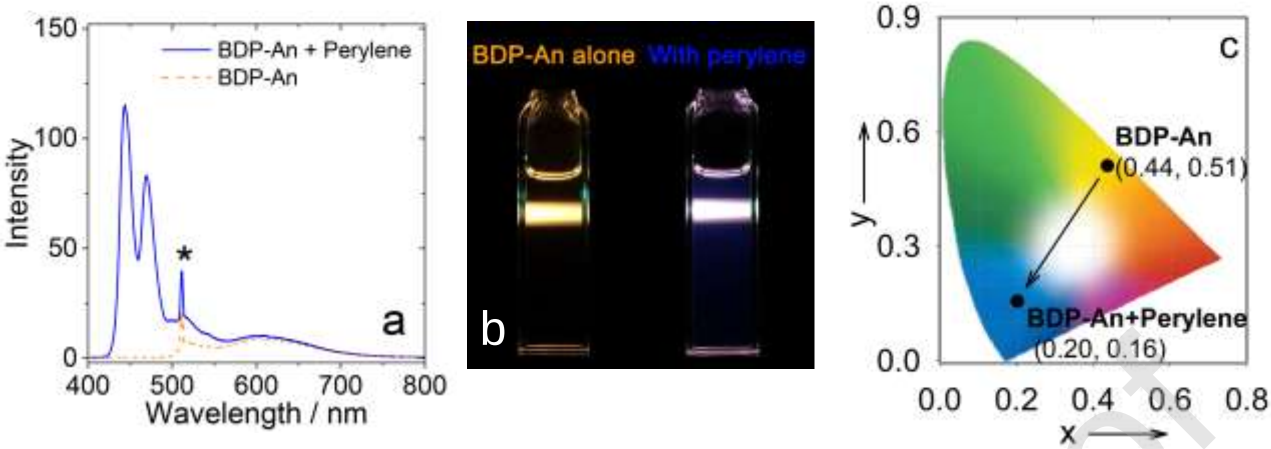


Fig. 7 (a) Upconversion with **BDP-An** as triplet donor and perylene as triplet acceptor, excited with 510 nm cw-laser (50 mW·cm^{-2}), [**BDP-An**] = 1.0 × 10^{-5} M, [perylene] = 1.7 × 10^{-5} M, in dearated dichloromethane, 20 °C. (b) Photographs of the emission of **BDP-An** alone and upconversion with perylene as triplet acceptor. (c) CIE diagram.

BDP-An alone gives a yellow emission which is the mixed emission of ^{1}LE and CT states. Upon addition of perylene, a new strong emission band in the range of 430–490 nm was observed, with the significant vibrational progression of perylene (Fig. 7a). The color change of luminescence in solution was obvious to the naked eyes, and the upconverted blue emission of perylene was observed, thus the upconversion of the mixture was confirmed (Fig. 7b). The CIE coordinates of the emission of **BDP-An** and the upconversion are presented in Fig. 7c. The upconversion quantum yield was determined as 18.9% in dichloromethane and 10.5% in acetonitrile. This was the first TTA upconversion achieved with a triplet excited-state equilibrium PS based on SOCT-ISC.

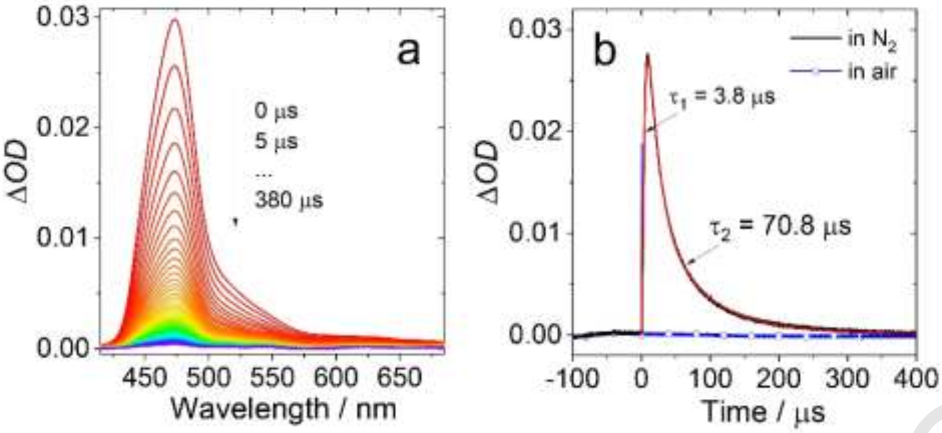


Fig. 8 (a) Delayed fluorescence spectrum of the mixture of **BDP-An** with Perylene, (b) decay trace of the fluorescence at 465 nm. [**BDP-An**] = 1.0×10^{-5} M, [Perylene] = 7.0×10^{-5} M in acetonitrile, λ_{ex} = 510 nm. The spike in the delayed fluorescence traces is the scattered laser, 20 °C.

The kinetics of the delayed fluorescence of TTA upconversion was studied with ns TA spectrometer in the emission mode (Fig. 8). The decay trace was fitted with double exponential decay model, which was composed of a rise phase with a lifetime constant of 3.8 μs and a decay component with the lifetime of 70.8 μs. The rise is due to the formation of the singlet excited state of perylene by TTET and TTA. The decay components indicate that the delayed fluorescence lifetime was 70.8 μs, which is due to the consumption of the triplet perylene by TTA. Such long-lived delayed fluorescence is crucial for applications such as time-resolved luminescence imaging studies [41,44,45,72].

4 Conclusion

In summary, we prepared an electron donor/acceptor dyad with phenylethynylanthracene and Bodipy (**BDP-An)**, with the aim to adjust the triplet state energy levels and the triplet quantum yield. **BDP-An** and the reference compounds were synthesized and characterized. In the ground state, the coupling between two chromophores of **BDP-An** is weak according to the absorption spectra and optimized ground state conformation. In nonpolar solvents, the fluorescence quantum yield (Φ_F) of ^{1}LE state emission of the Bodipy moiety was up to 99%. However, in polar solvents, the fluorescence was significantly quenched and the CT band was observed. Furthermore, the singlet oxygen quantum yield (Φ_Δ) was up to 95%, which indicates that CS becomes thermodynamically allowed. The electrochemical studies were in agreement with the above results, and revealed that CSS is composed of Bodipy radical anion and phenylethynyl anthracene radical cation. In femtosecond transient absorption spectra, upon fs pulsed laser excitation, CSS was generated, with that CR occurred and the triplet excited state of phenylethynyl anthracene was observed. Time constants of CS and CR were determined as 1.6 ps and 3.8 ns, respectively. In nanosecond transient absorption spectra, long-lived triplet states of Bodipy (τ_T = 108 μs) and phenylethynyl anthracene (τ_T = 35 μs) were observed simultaneously, which is the first report on triplet excited-state equilibrium of triplet PSs based on SOCT-ISC. With perylene as the triplet acceptor, **BDP-An** was applied to TTA UC, the quantum yield was up to 18.9% in dichloromethane, and the lifetime of delayed fluorescence was 70.8 μs, which is also the first report on TTA UC achieved with a triplet excited-state energy equilibrium PS based on SOCT-ISC. These results are important for in-depth understanding CR in organic molecules, designing new triplet PSs as well as adjusting the triplet properties of PSs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

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