Supporting information

Solvent effects on triplet-triplet annihilation upconversion kinetics of perylene with Bodipy-phenyl-C_{60} photosensitizer

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Contents

1. Gibbs free-energy calculations

Using the redox potentials and the optimized molecular geometries, the thermodynamic driving forces for charge-recombination (ΔG_{CR}) and charge-separation (ΔG_{CS}), as well as charge-separated state energy (E_{CSS}), of Bodipy-phenyl-C_{60} dyad were calculated with the Weller equations (S1)–(S3).

$$\Delta G_{CR} = -\left[E_{OX}\left(BDP^{+}/BDP\right) - E_{RED}\left(C_{60}/C_{60}^{-}\right)\right] - \Delta G_s \quad \text{(S1)}$$

$$\Delta G_{CS} = -\Delta G_{CR} - \Delta E_{00} \quad \text{(S2)}$$

$$E_{CSS} = \left[E_{OX}\left(BDP^{+}/BDP\right) - E_{RED}\left(C_{60}/C_{60}^{-}\right)\right] + \Delta G_s \quad \text{(S3)}$$

where $E_{OX}(BDP^{+}/BDP)$ was the half-wave potential for one electron oxidation of the electron donor Bodipy unit, $E_{RED}(C_{60}^{-}/C_{60})$ was the half-wave potential for one-electron reduction of the electron acceptor C_{60} unit, ΔE_{00} was the crossing point of the absorption and fluorescence spectra, *e.g.* 2.36 eV for Bodipy-phenyl-C_{60}, and ΔG_s was the static Coulombic energy which could be calculated with the dielectric continuum model as the equation (S4).

$$\Delta G_s = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_{CC}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_D} + \frac{1}{R_A}\right)\left(\frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_s}\right) \quad \text{(S4)}$$

where e was the electronic charge, ε_0, ε_S and ε_{REF} represented the vacuum permittivity, the dielectric constants of solvent and reference, respectively. In present experiments, the solvents were dichloromethane (ε_s = 9.1) and toluene (ε_{REF} = 2.24). R_{CC} was the center-to-center distance between the electron donor and the electron acceptor, which was 13.1 Å in the Bodipy-phenyl-C_{60} dyad suggested by DFT optimized geometry. R_D and R_A represented the radius of electron donor and electron acceptor, and they were estimated to be 6.1 Å and 3.6 Å in the dyad by using the maximum extension radius of the molecular electron cloud in space.

Table S1 Electrochemical redox potentials of C_{60}, B-1 and B-2[a]

	E(ox) / V	E(red) / V
C_{60}	-	-0.67, -1.07, -1.52
Bodipy	1.12	-1.32
C_{60}-Bodipy	1.14	-0.79, -1.18, -1.32, -1.71

[a] Cyclic voltammetry in Ar saturated DCM containing a 0.1 M Bu_4NPF_6 as supporting electrolyte. Working electrode was glassy carbon electrode, the counter electrode was Pt electrode, and the reference electrode was $Ag/AgNO_3$ electrode. Scan rates: 0.05 V/s, 20℃. Ferrocene (Fc) was used as internal reference ($E_{1/2}$ = +0.38 V) vs saturated calomel electrode (SCE).

Table S2 Dielectric constant (ε), static Coulombic energy ($^{\Delta G_S}$), thermodynamic driving forces for the charge-separation ($^{\Delta G_{CS}}$) and charge-separated state energy (E_{CCS})

Solvent	ε	$\Delta G_s/J$	$\Delta G_{CS}/eV$	E_{CCS}/eV
1,4-dioxane	2.21	$+9.46\times10^{-20}$	+0.18	2.52
Toluene	2.24	$+9.26\times10^{-20}$	+0.17	2.51
Chlorobenzene	5.65	$+3.01\times10^{-21}$	-0.39	1.95
Dichlorobenzene	6.83	-7.16×10^{-21}	-0.45	1.93
THF	7.58	-1.20×10^{-20}	-0.49	1.89

2. Femtosecond time-resolved transient absorption spectra.

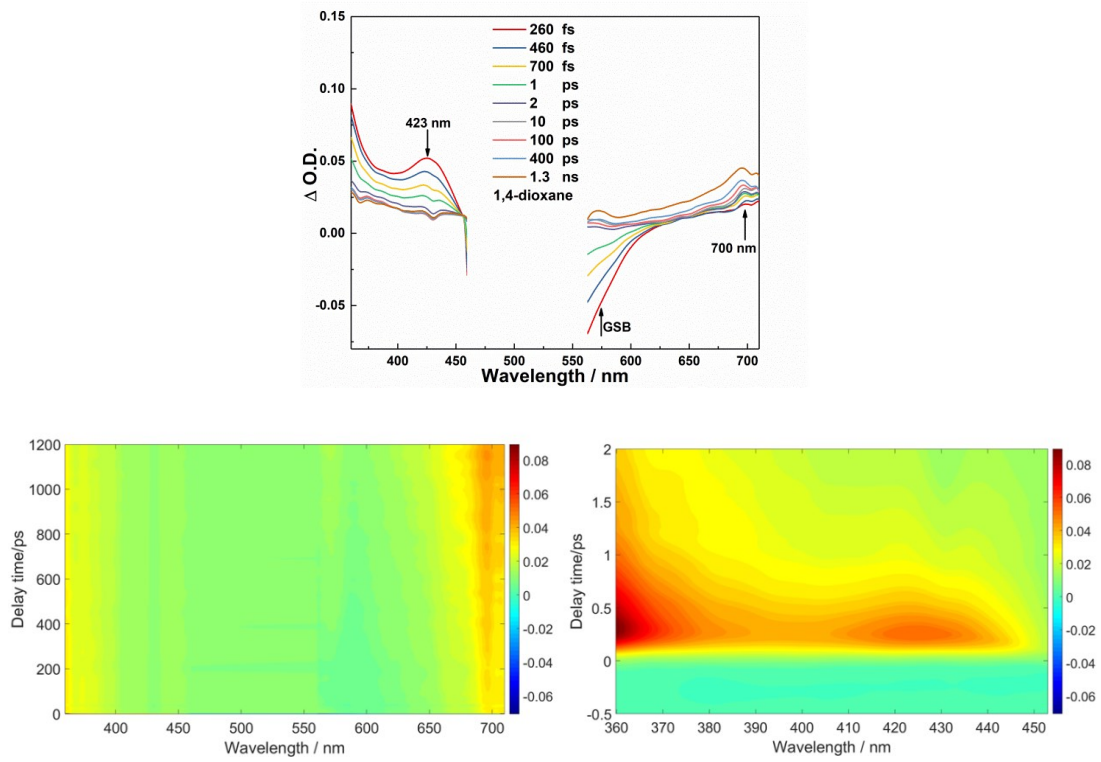

Figure S1. Femtosecond transient absorption spectra of B-2 in 1,4-dioxane, excited at 532 nm, 25ºC.

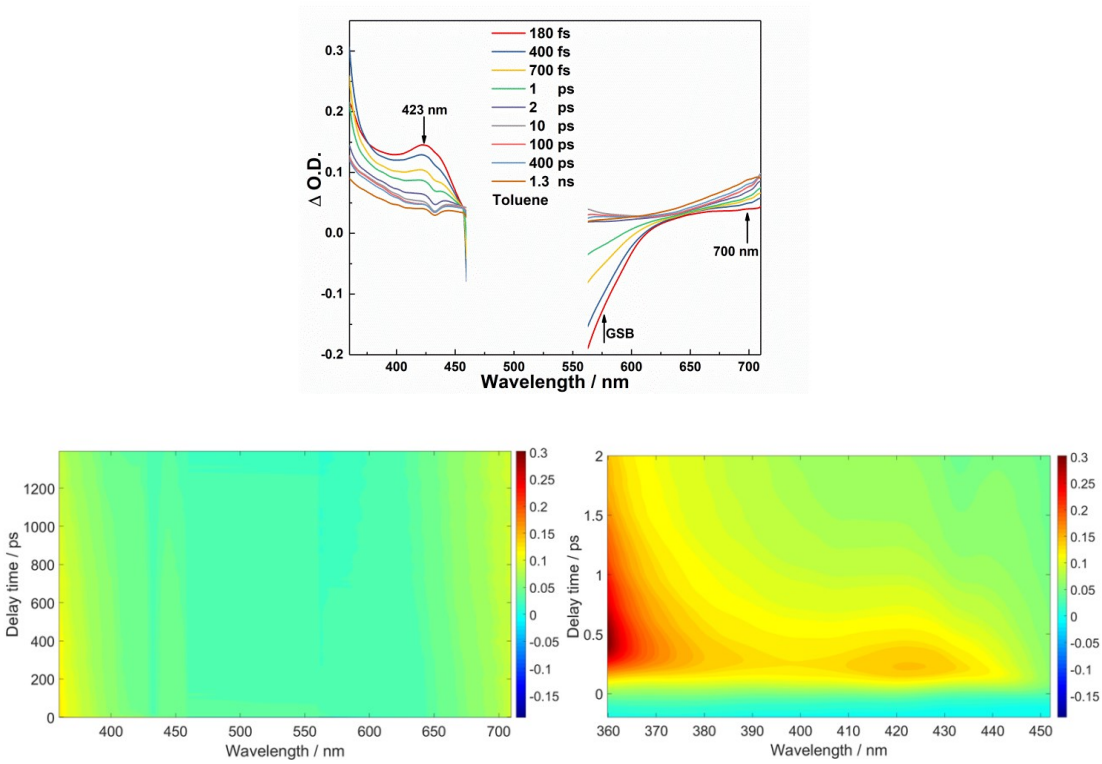

Figure S2. Femtosecond transient absorption spectra of B-2 in toluene, excited at 532 nm, 25ºC.

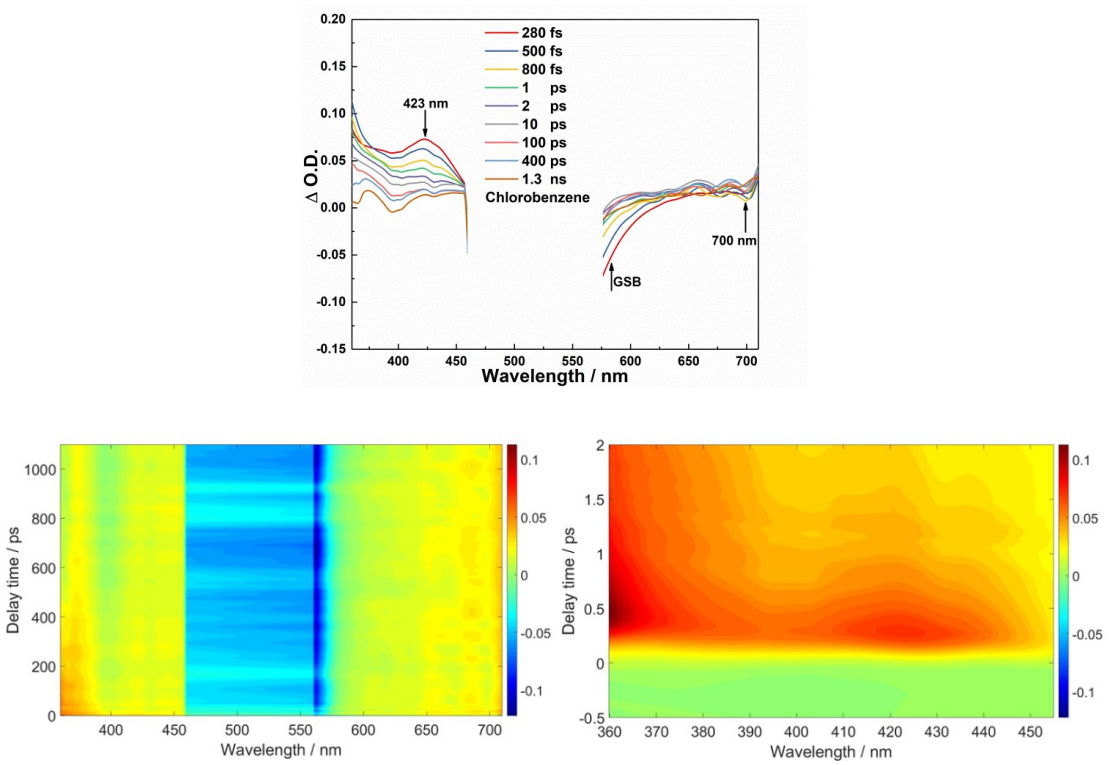

Figure S3. Femtosecond transient absorption spectra of B-2 in chlorobenzene, excited at 532 nm, 25ºC.

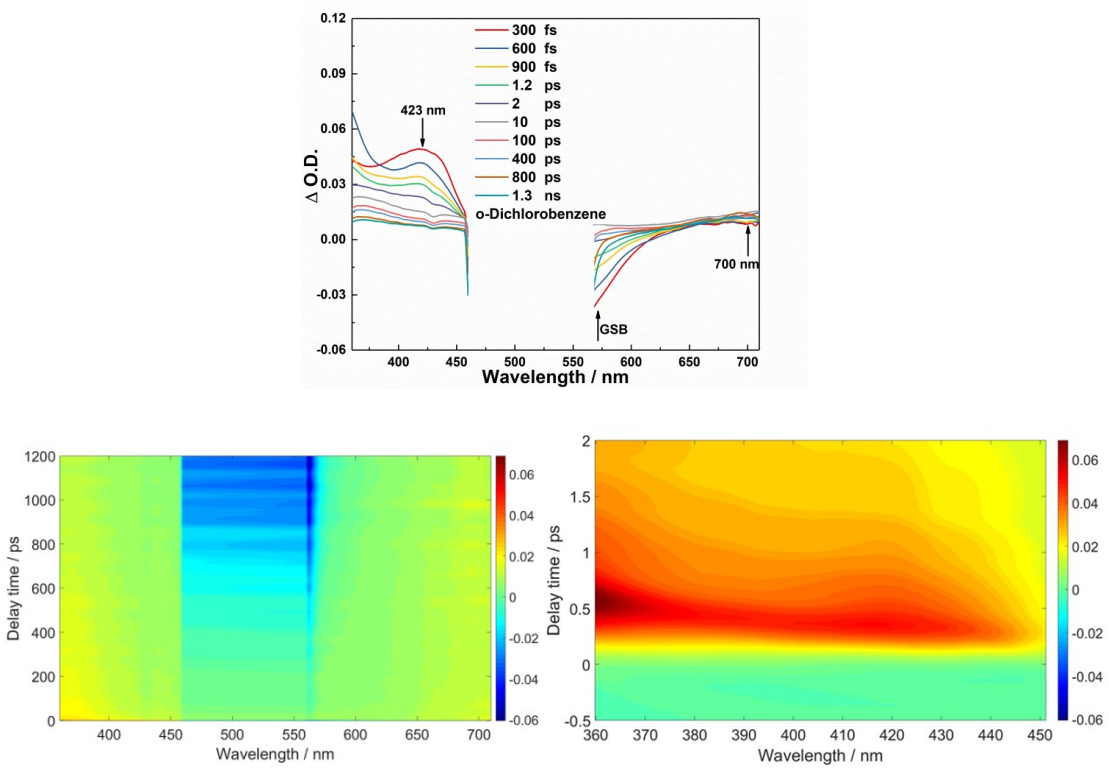

Figure S4. Femtosecond transient absorption spectra of B-2 in dichlorobenzene, excited at 532 nm, 25ºC.

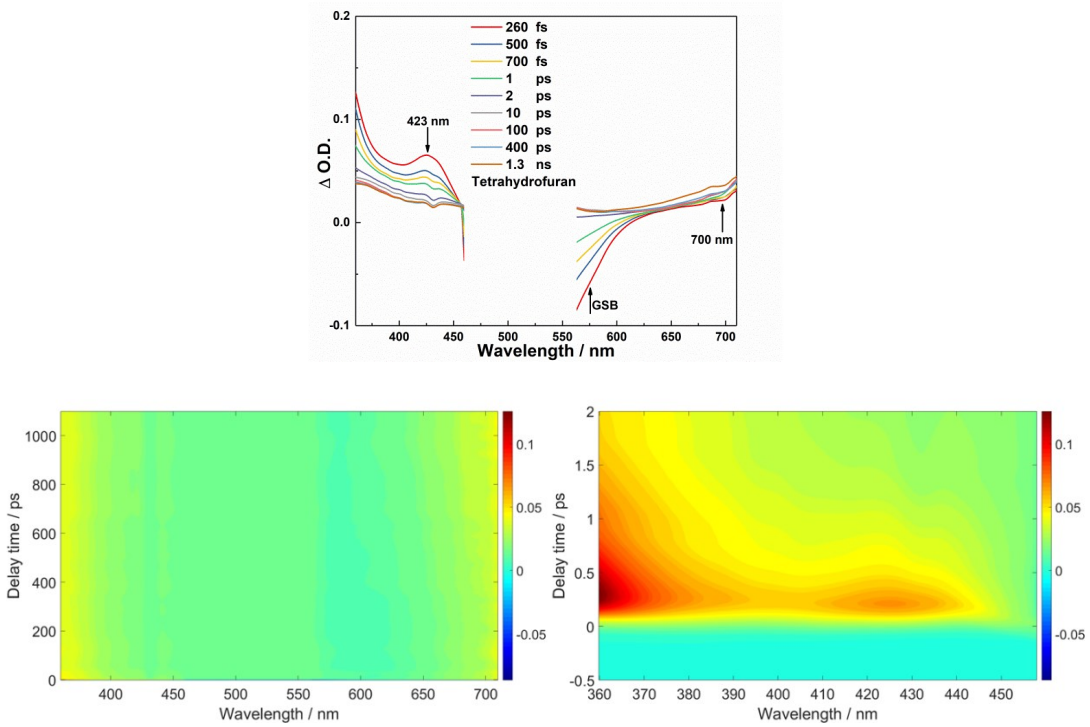

Figure S5. Femtosecond transient absorption spectra of B-2 in THF, excited at 532 nm, 25ºC.

3. Nanosecond time-resolved transient absorption spectra

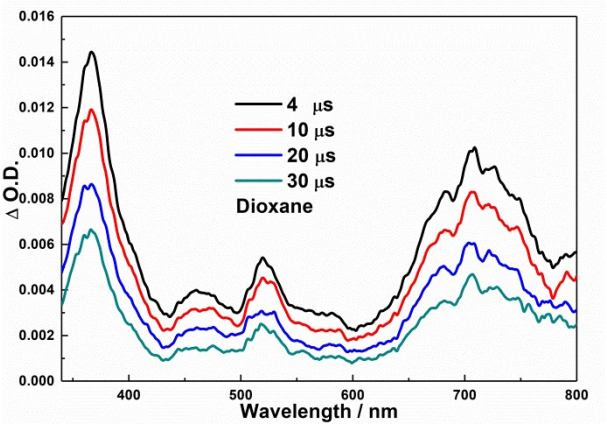

Figure S6. Nanosecond time-resolved transient absorption spectra of B-2 in deaerated 1,4-dioxane.

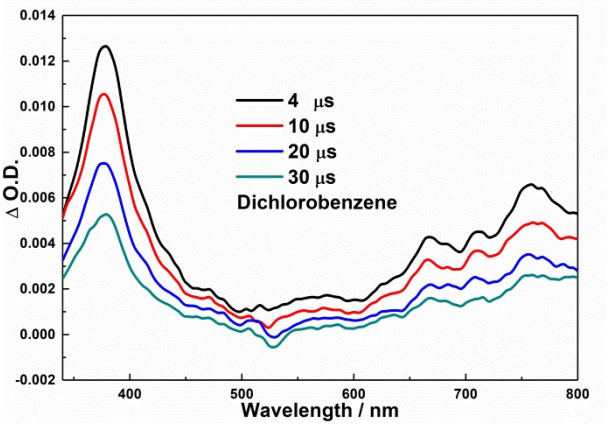

Figure S7. Nanosecond time-resolved transient absorption spectra of B-2 in deaerated dichlorobenzene.

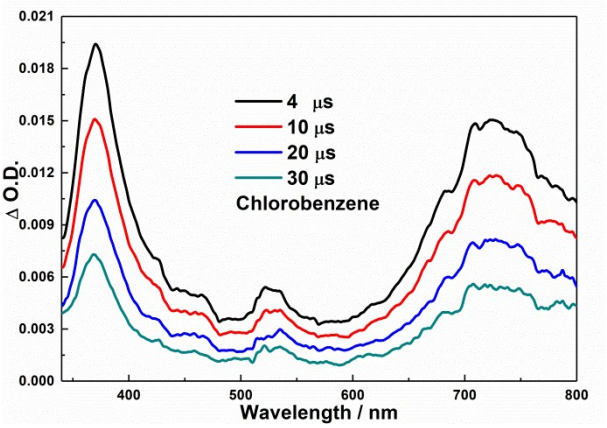

Figure S8. Nanosecond time-resolved transient absorption spectra of B-2 in deaerated chlorobenzene.

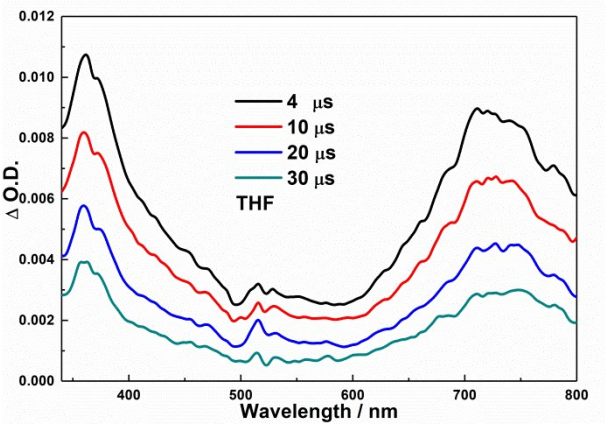

Figure S9. Nanosecond time-resolved transient absorption spectra of B-2 in deaerated THF.

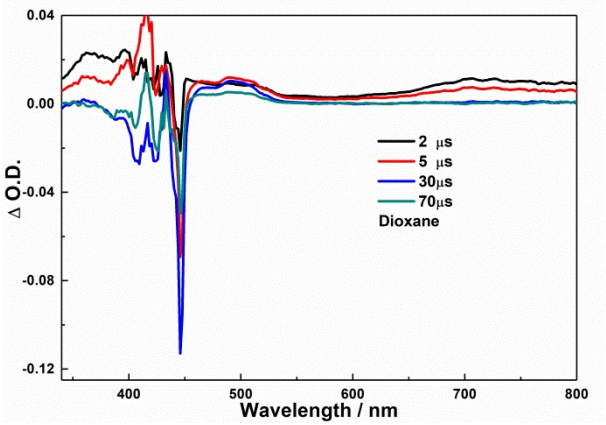

Figure S10. Nanosecond time-resolved transient absorption spectra of B-2 and perylene in deaerated 1,4-dioxane.

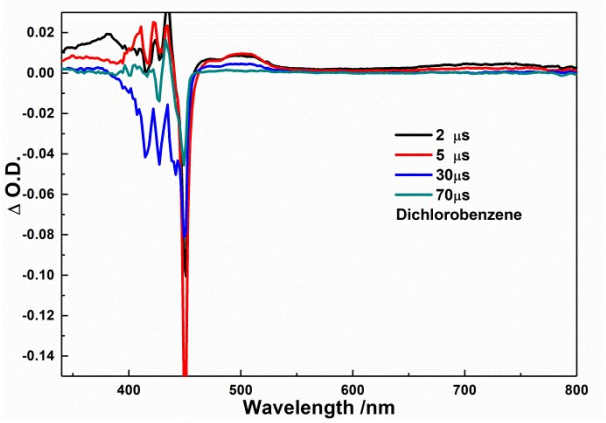

Figure S11. Nanosecond time-resolved transient absorption spectra of B-2 and perylene in deaerated dichlorobenzene.

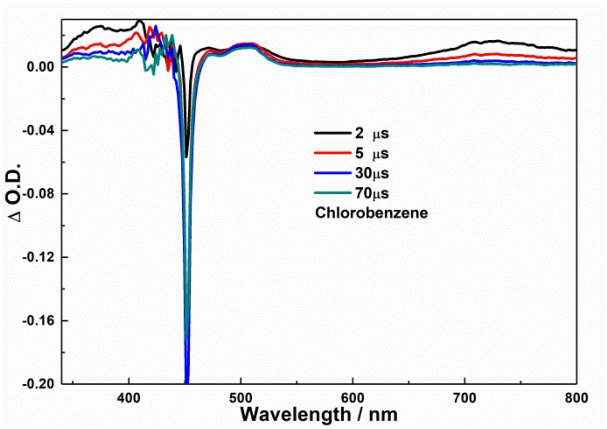

Figure S12. Nanosecond time-resolved transient absorption spectra of B-2 and perylene in deaerated chlorobenzene.

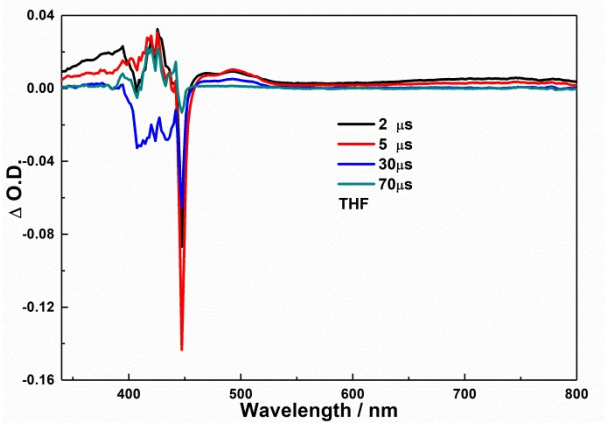

Figure S13. Nanosecond time-resolved transient absorption spectra of B-2 and perylene in deaerated THF.

4. Decay curves of B-2 with different concentration of perylene

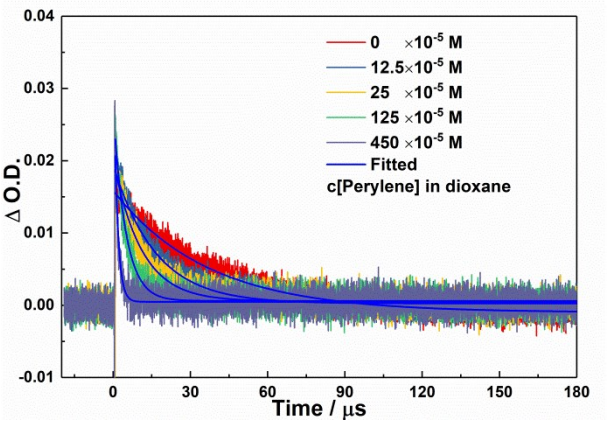

Figure S14. Decay curves of B-2 with different concentration of perylene in dioxane.

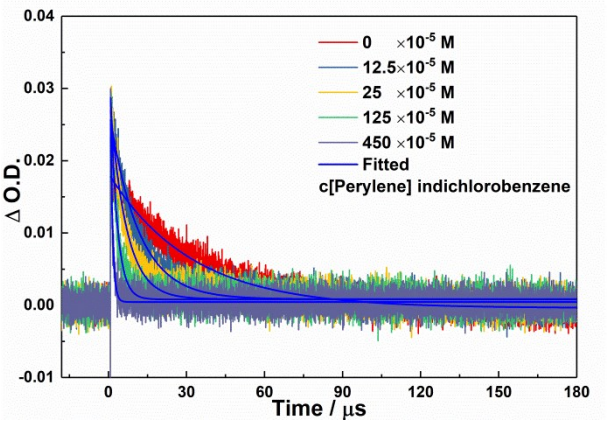

Figure S15. Decay curves of B-2 with different concentration of perylene in dichlorobenzene.

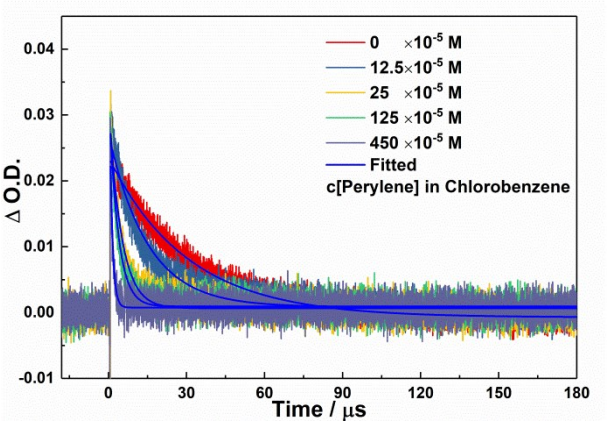

Figure S16. Decay curves of B-2 with different concentration of perylene in chlorobenzene.

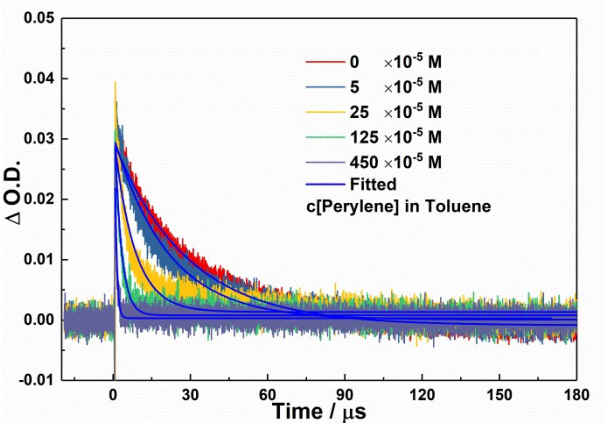

Figure S17. Decay curves of B-2 with different concentration of perylene in toluene.

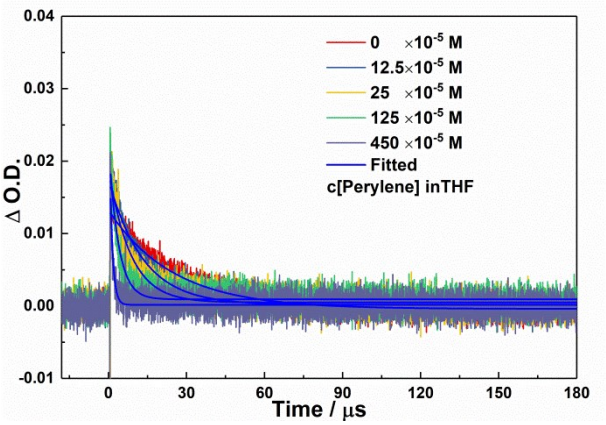

Figure S18. Decay curves of B-2 with different concentration of perylene in THF.

Table S3. Lifetime of triplet B-2 with different concentration of perylene.

Toluene		**Chlorobenzene**		**Dichlorobenzene**		**Dioxane**		**THF**	
c[Pery][a]	$\tau/\mu s$	c[Pery][a]	$\tau/\mu s$	c[Pery][a]	$\tau/\mu s$	c[Pery][a]	$\tau/\mu s$	c[Pery][a]	$\tau/\mu s$
0 (Air)	0.34	0 (Air)	0.34	0 (Air)	0.47	0 (Air)	0.44	0 (Air)	0.37
0 (Ar)	29.5	0 (Ar)	30.4	0 (Ar)	31.8	0 (Ar)	36.7	0 (Ar)	24.9
0.5	21.1	1.25	15.0	1.25	16.6	1.25	16.5	1.25	13.2
2.5	8.0	2.5	9.2	2.5	11.2	2.5	11.0	2.5	8.5
5.0	3.5	5.0	4.9	5.0	6.3	5.0	6.2	5.0	5.0
12.5	1.3	12.5	1.7	12.5	2.6	12.5	2.4	12.5	1.9
25	0.65	25	0.86	25	1.4	25	1.2	25	0.92
45	0.35	45	0.47	45	0.82	45	0.70	45	0.52

[a] The unit of perylene concentration, $\times 10^{-4}$ M.

5. UV-Vis and fluorescence emission spectra of perylene and B-2

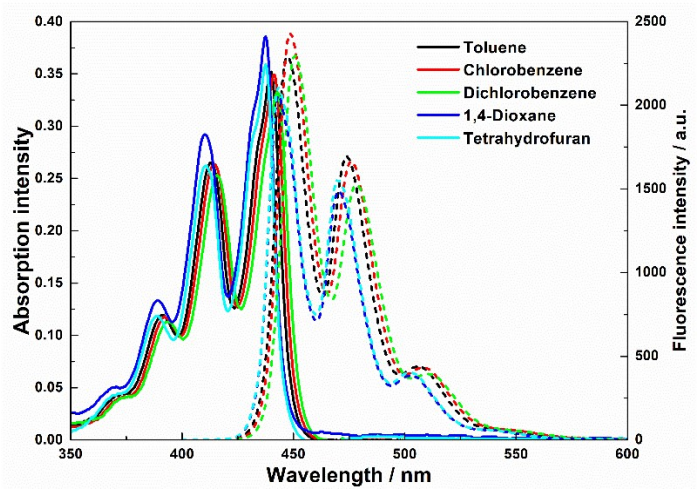

Figure S19. UV-Vis absorption and fluorescence emission spectra of perylene in different solvents.

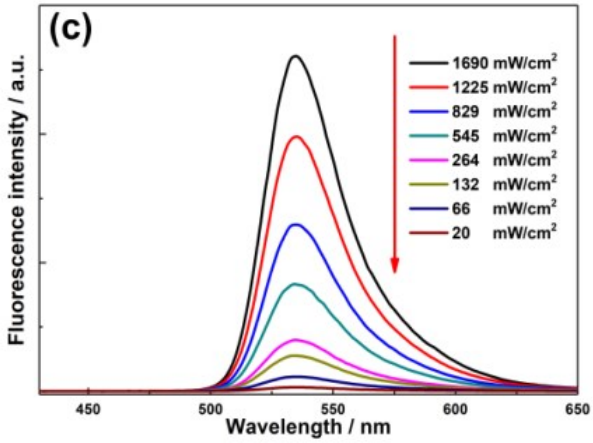

Figure S20. Dependence of normal fluorescence intensity of B-1 in toluene on the excitation power density at 532 nm.

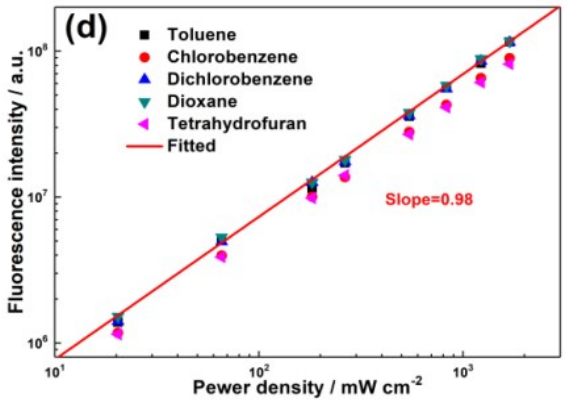

Figure S21. A logarithmic plot of fluorescence intensity of B-1 with excitation power density at 532 nm.

6. The fitted parameters of TTA upconversion.

Table S4. The fitted parameters, β and the first-order rate constants k_T, of TTA upconversion.

Solvent	Viscosity	Polarity	β	k_T (10^6 s^{-1})
THF	0.55	4.2	0.878	0.00441
Toluene	0.59	2.4	0.931	0.00240
Chlorobenzene	0.8	2.7	0.890	0.00321
Dichlorobenzene	1.33	2.7	0.865	0.00232
1,4-Dioxane	1.54	4.8	0.925	0.00137

7. The reported heavy-atom-free photosensitizers in TTA upconversion.

Table S5. The reported heavy-atom-free photosensitizers and annihilators, as well as their TTA upconversion performances.

Sensitizer	Acceptor	solvent	λ_{ex} (nm)[a]	λ_{em} (nm)[b]	Φ_{UC} (%)[b]	Ref.
C_{60}-C-2	perylene	toluene	589	450	7.0	4
4CzTPN-Ph	DPA	solid	532	435	0.3	5
4CzIPN	QP	benzene	445	355	3.9	6
4CzPN–DBP	DBP	toluene	450	390	3.7	7
compound-1	DPA	toluene	445	435	11.3	8
BB-1	perylene	CH_2Cl_2	532	450	3.7	9
BDP-TEMPO-2	perylene	toluene	520	450	6.7	10
4CzPN-DBP	DBP	toluene	450	390	1.7	11
BTZ-DMAC	DPA	toluene	532	435	1.9	12
BDP-AN-1	perylene	CH_2Cl_2	510	450	15.8	13
BDP-2	perylene	toluene	510	450	3.2	14
(NDI)-C_{60}-1	1CBPEA	toluene	589	500	0.5	15
TTM-1Cz	DPA	toluene	635	435	0.3	16
QDM	perylene	THF	532	450	0.2	17
Bodipy-C_{60}	Perylene	toluene	532	450	8.0	18
Bodipy-C_{70}	perylene	toluene	532	450	10.3	19
DCF-MPYM	DPA	THF	635	428	11.2	20

[a] Excitation wavelength; [b] Maximum of UC emission wavelength.

[b] The maximum upconversion quantum yield of 100%.

Table S6. Dynamic rates of the transient absorption band of B-2 at 700 nm in different solvents.

Solvent	ε (25°C) [a]	$1/\tau_1$ (s^{-1})	$1/\tau_2$ (s^{-1})
1,4-Dioxane	2.21	1.61×10^{12}	1.00×10^{8}
Toluene	2.24	1.54×10^{12}	1.43×10^{8}
Chlorobenzene	5.65	1.18×10^{12}	8.13×10^{8}
Dichlorobenzene	6.83	1.47×10^{12}	7.03×10^{8}
THF	7.58	1.75×10^{12}	4.08×10^{8}

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