**Electronic Supporting Information for:**

# Observation of the Triplet Energy Transfer in Orthogonal Photoexcited Iodinated-BODIPY Dimers

*Andrey A. Sukhanov,[a]† Huaiman Cao,[b]† Xue Zhang,[b] Jianzhang Zhao,\*[b,c] and Yuri E. Kandrashkin\*[a]†*

[a] Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, 420029, Kazan, Russia. \*E mail: yuk@kfti.knc.ru (Y.E.K.)
[b] State Key Laboratory of Fine Chemicals, Frontiers Science Center for Smart Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China.
\*Email: zhaojzh@dlut.edu.cn (J.Z.)
[c] State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources, College of Chemistry, Xinjiang University, Urumqi 830017, P. R. China.

† These authors contributed equally to this work.

# Contents

# 1. Experimental Section

**1.1 General Information.** All the chemicals used in synthesis are analytically pure and were used as received. Solvents in reaction were dried prior to use. $^1$H and $^{13}$C NMR spectra were recorded on the Bruker Avance spectrometers (400 MHz). $^1$H and $^{13}$C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. The mass spectra were measured by HRMS (MALDI-TOF). UV-vis absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu Ltd., Japan). **BDP**, **DB**, **BDP-I** and **DB-I₂** were synthesized according to the literature methods.

**1.2. Singlet Oxygen Quantum Yield ($\Phi_\Delta$).** In order to monitor the singlet oxygen ($^1$O$_2$) production, 1,3-diphenylisobenzofuran (DPBF) was used as the $^1$O$_2$ scavenger. Eq. 1 was used to calculate the singlet oxygen quantum yield ($\Phi_\Delta$):

$$\Phi_{\text{sam}} = \Phi_{\text{std}} \left( \frac{1 - 10^{-A_{\text{std}}}}{1 - 10^{-A_{\text{sam}}}} \right) \left( \frac{m_{\text{sam}}}{m_{\text{std}}} \right) \left( \frac{\eta_{\text{sam}}}{\eta_{\text{std}}} \right)^2 \tag{S1}$$

where "sam" and "std" represent the sample and the standard, $\Phi$, $A$, $m$ and $\eta$ represent $\Phi_\Delta$, the plot of the absorbance at excitation wavelength, the slope of the absorbance of DPBF at 414 nm changing against irradiation time, and the refractive index of the solvent used for measurements, respectively. $\Phi_\Delta$ of compounds were measured in different solvents with **diiodo-BDP** as the standard ($\Phi_\Delta$ = 87% in DCM). [1]

**1.3. Nanosecond Transient Absorption Spectroscopy.** The nanosecond transient absorption (ns-TA) spectra were measured on a LP980 laser flash photolysis spectrometer (Edinburgh Instruments, Ltd., U.K.). The samples were excited with a nanosecond pulsed laser (OPOLette 355II) with tunable wavelength in the range 210−2400 nm (OPOTEK, U.S.A.). The signals were digitized with a Tektronix TDS 3012B oscilloscope. The data (kinetic decay traces and the transient difference absorption spectra) were analyzed with the L900 software. The intrinsic triplet-state lifetime was obtained by fitting the decaying traces at two different concentrations with the kinetic model, in which the triplet–triplet annihilation (TTA) self-quenching effect was taken into account.[2, 3] All samples were purged with N$_2$ for about ca. 15 min before measurements.

**1.4. Time-Resolved Electron Paramagnetic Resonance (TREPR) Spectroscopy.** Samples were dissolved in frozen solution toluene/(2-methyltetrahydrofuran, 2MeTHF)

(3/1, v/v) with a concentration of $1.0 \times 10^{-5}$ M. The measurements of time-resolved continuous-wave (CW) EPR were performed on an X-band EPR Elexsys E-580 spectrometer (Bruker). For the compound **DB-I$_2$**, TREPR spectra at 25 K, 40 K, 60 K, 65 K, 75 K, 80 K and 100 K were measured, and TREPR spectra of **BDP-I** at 80 K was measured. Optical excitation was carried out with an optical parametric oscillator (OPO) system (LP603 SolarLS) pumped by an Nd:YAG laser (LQ629 SolarLS) with a pulse energy of 1 mJ. The spectra were simulated using the EasySpin package based on Matlab.[4]

## 2. Synthesis of the Compounds

**2.1.** The synthesis of compounds **BDP**,[5] **BDP-I**,[6] **DB**[7, 8] and **DB-I$_2$**[8] have been reported.

**Scheme S1. Synthesis of the Dyads**[a]
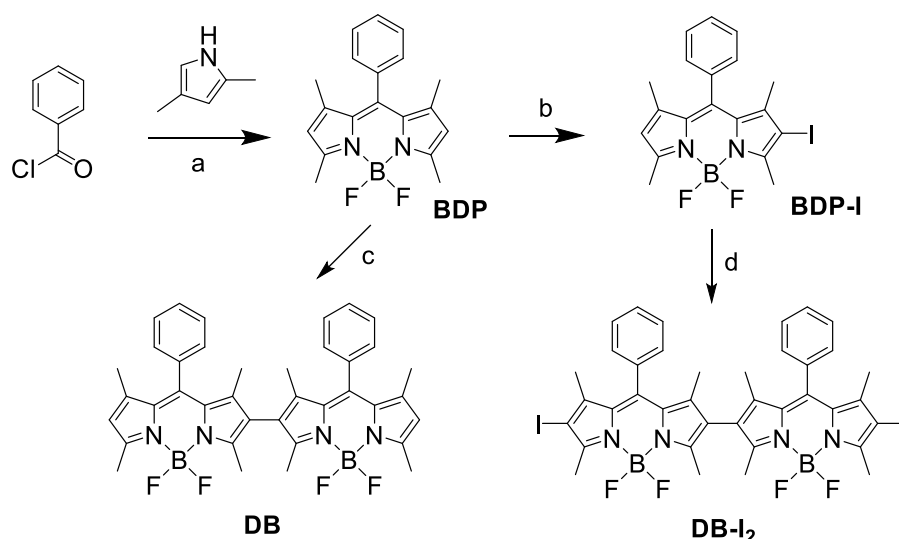


[a]Key: (a) 2,4-Dimethylpyrrole, TFA, overnight, DDQ, 2 h, Et$_3$N and BF$_3$·Et$_2$O, 2 h, CH$_2$Cl$_2$, yield: 30%. (b) N–Iodosuccinimide (NIS) (1.0 eq), 0 °C, 6.5 h, yield: 77%. (c) FeCl$_3$, CH$_2$Cl$_2$, 0°C, 20 min, yield: 20%; or phenyliodine(III) bis(trifluoroacetate) (PIFA), BF$_3$·Et$_2$O, −78°C to rt, 30 min, yield: 18%; (d) similar with (c), yield: 25%.

**2.2. Synthesis of DB.** (1) Under a N$_2$ atmosphere, **BDP** (129.6 mg, 0.4 mmol) was dissolved in dry dichloromethane (DCM, 20 mL). Anhydrous FeCl$_3$ (288 mg, 1.4 mmol) was added at room temperature. After stirring for 20 min, methanol (10 mL) was added to quench the reaction, and then the mixture was stirred for additional 30 min. The organic phase was washed with H$_2$O (2 × 20 mL) and then dried over anhydrous Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the crude residue was purified by column chromatography (silica gel. DCM/ petroleum ether = 1:3, v/v) to give a deep red solid. Yield: 25.3 mg, 20%. (2) **BDP** (129.6 mg, 0.4 mmol) was dissolved in dry dichloromethane (DCM, 10 mL). Phenyliodine(III) bis(trifluoroacetate) (PIFA) (46.5 mg,

0.108 mmol) and $BF_3 \cdot Et_2O$ (0.030 mL) were quickly added at −78°C. After the reaction was stirred for ca. 30 min, the reaction was warmed to room temperature. Water was added and then the aqueous phase was extracted with DCM. The organic phase was then dried over anhydrous $Na_2SO_4$ and evaporated to remove solvent. The crude residue was purified by column chromatography (silica gel. DCM/ petroleum ether = 1:3, v/v) to give a deep red solid. Yield: 23.4 mg, 18%. $^1H$ NMR (CDCl$_3$, 400 MHz) $\delta$ = 7.52–7.45 (m, 6 H), $\delta$ = 7.33 (d, $J$ = 6.9 Hz, 2 H), $\delta$ = 7.26 (d, $J$ = 8.5 Hz, 2 H), $\delta$ = 5.99 (s, 2 H), $\delta$ = 2.56 (s, 6 H), $\delta$ = 2.35 (s, 6 H), $\delta$ = 2.56 (s, 6 H), $\delta$ = 1.37 (s, 6 H), $\delta$ = 1.12 (s, 6 H) ppm. HRMS (MALDI-TOF): calcd for $C_{38}H_{36}B_2F_4N_4$, $m/z$, 646.3062; found $m/z$, 646.3073.

**2.3. Synthesis of Compound DB-I$_2$. DB-I$_2$** was obtained as a red-violet solid by following a procedure similar with that of **DB**. Yield: 38.1 mg, 25%. $^1H$ NMR (CDCl$_3$, 400 MHz) $\delta$ = 7.54–7.46 (m, 6 H), $\delta$ = 7.31 (d, $J$ = 6.0 Hz, 2 H), $\delta$ = 7.24 (d, $J$ = 6.8 Hz, 2 H), $\delta$ = 2.64 (s, 6 H), $\delta$ = 2.36 (s, 6 H), $\delta$ = 2.56 (s, 6 H), $\delta$ = 1.38 (s, 6 H), $\delta$ = 1.12 (s, 6 H) ppm. HRMS (MALDI-TOF): calcd for $C_{38}H_{34}B_2F_4I_2N_4$, $m/z$, 898.0995; found $m/z$, 898.0990.

# 3. Molecular Structure Characterization Data
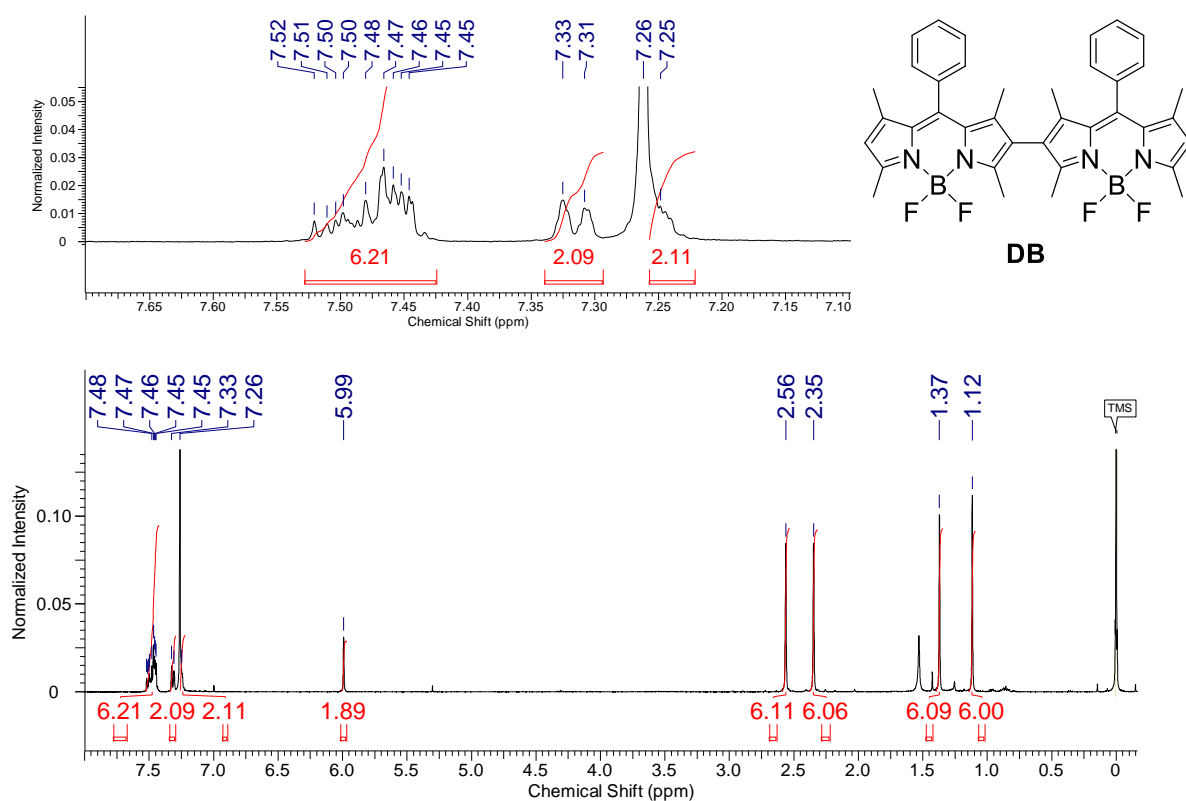


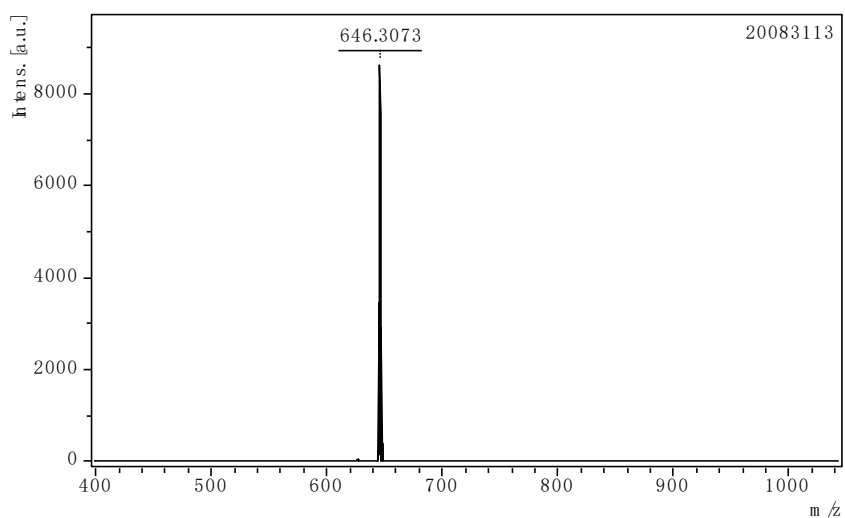**Figure S1.** $^1H$ NMR spectrum of **DB** (400 MHz, CDCl$_3$).

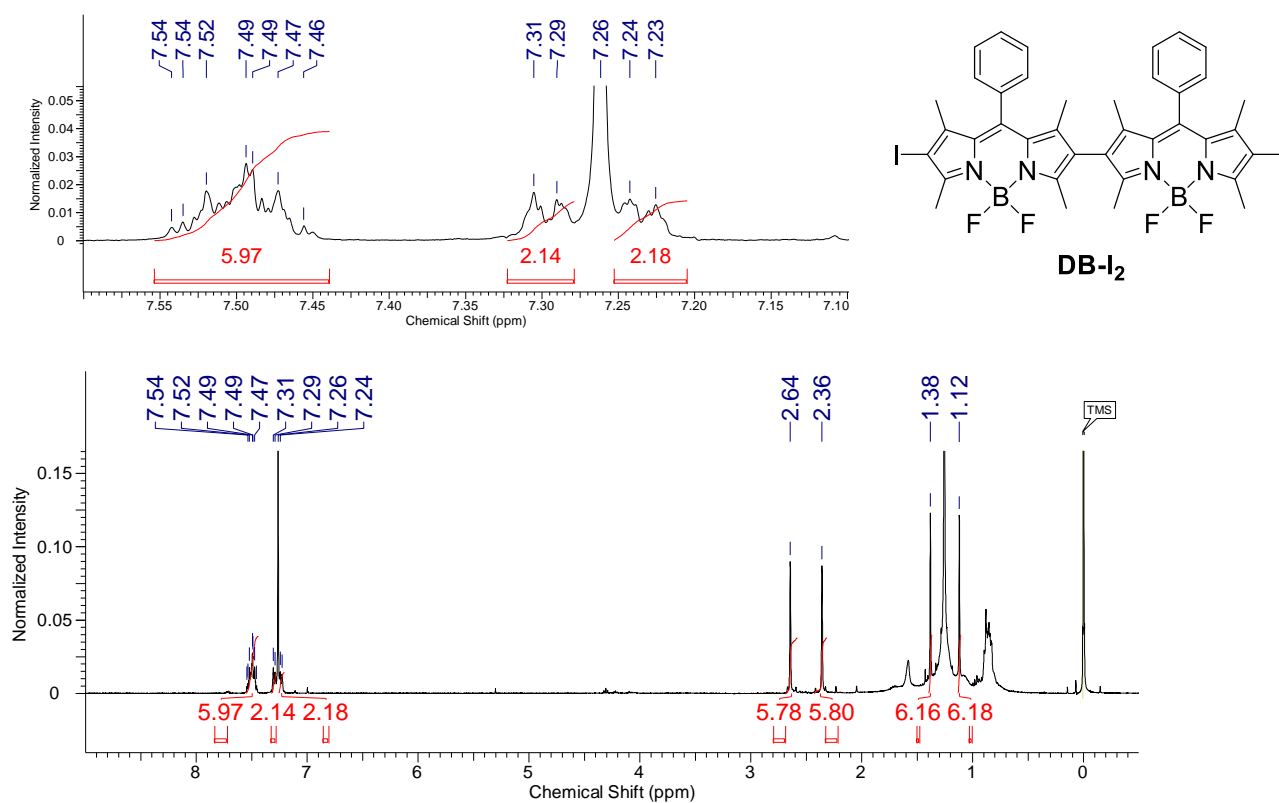**Figure S2.** MALDI-TOF high resolution mass spectrum of **DB**.



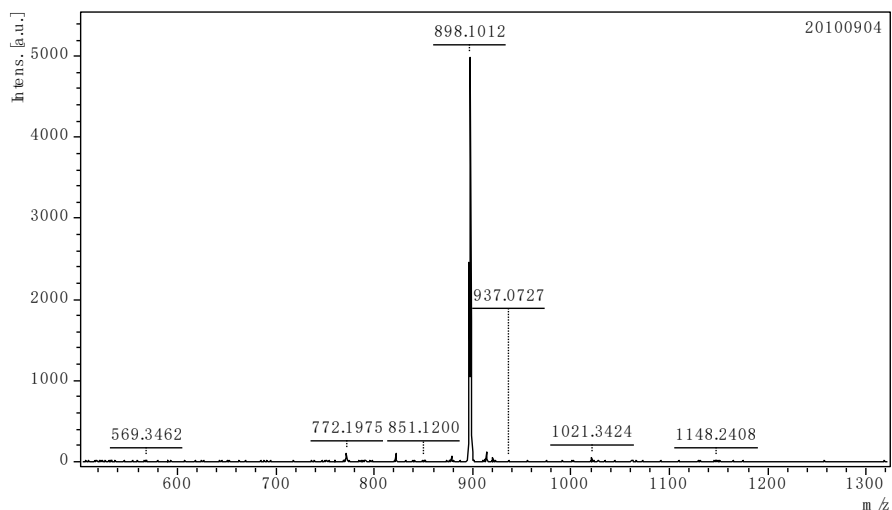**Figure S3.** $^{1}$H NMR spectrum of **DB-I$_2$** (400 MHz, CDCl$_3$).

**Figure S4.** MALDI-TOF high resolution mass spectrum of **DB-I$_2$**.

## 4. Steady State UV–Vis Absorption and Fluorescence Emission Spectra
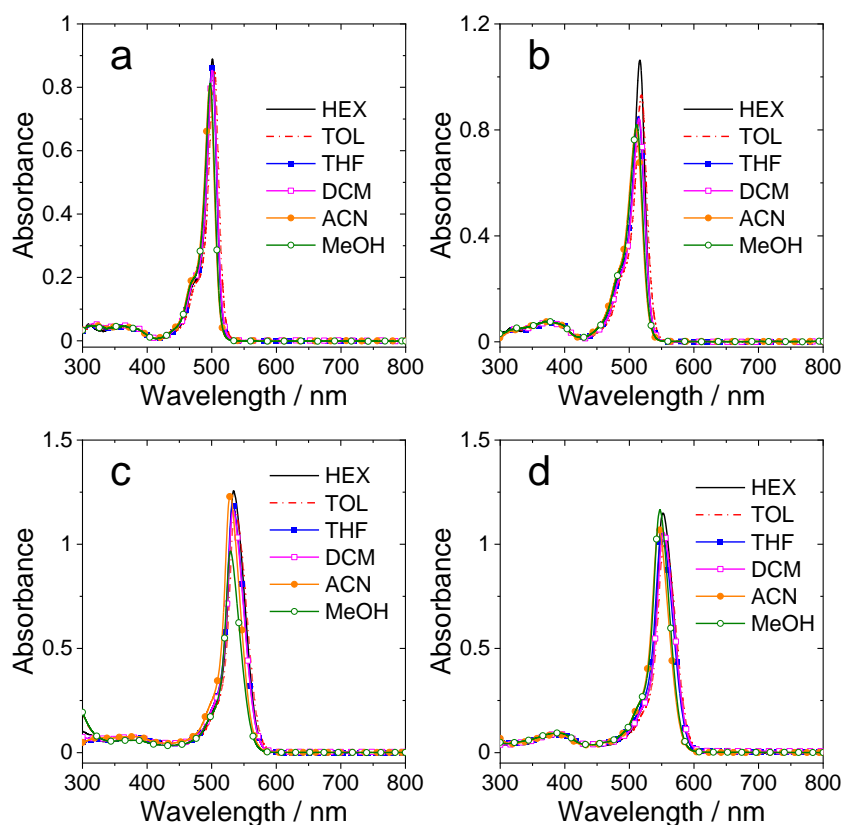


**Figure S5.** UV–vis absorption spectra of (a) **BDP**; (b) **BDP-I**; (c) **DB** and (d) **DB-I$_2$** in different solvents. $c$ = 1.0 × 10$^{-5}$ M; 20 °C.
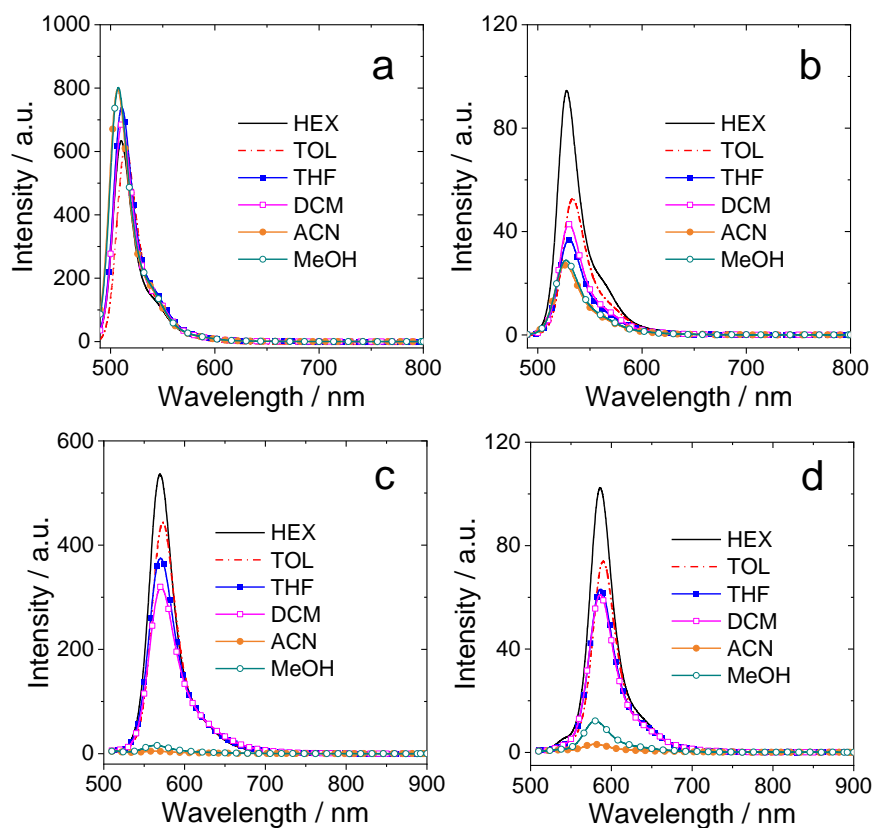
**Figure S6.** Fluorescence emission spectra of (a) **BDP**, (b) **BDP-I** (c) **DB** and (d) **DB-I₂** in different solvents; Optically matched solvents were used (the solutions of the sample and the standard should give same absorbance at the excitation wavelength), $A$ = 0.100, $\lambda_{ex}$ = 480 nm for **BDP** and **BDP-I**, $\lambda_{ex}$ = 500 nm for **DB** and **DB-I₂**, 20 °C.
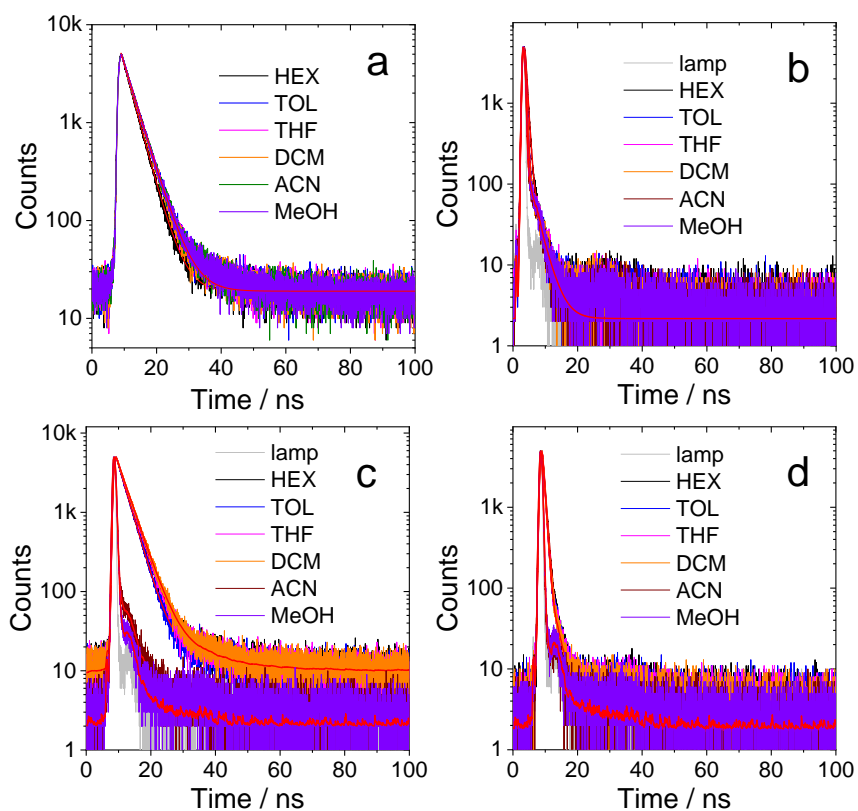
**Figure S7.** Fluorescence decay traces of (a) **BDP**, (b) **BDP-I**, (c) **DB** and (d) **DB-I$_2$**. Excited with picoseconds pulsed laser (510 nm). In different solvents, $c$ = 1.0 × 10$^{-5}$ M, 20 °C.
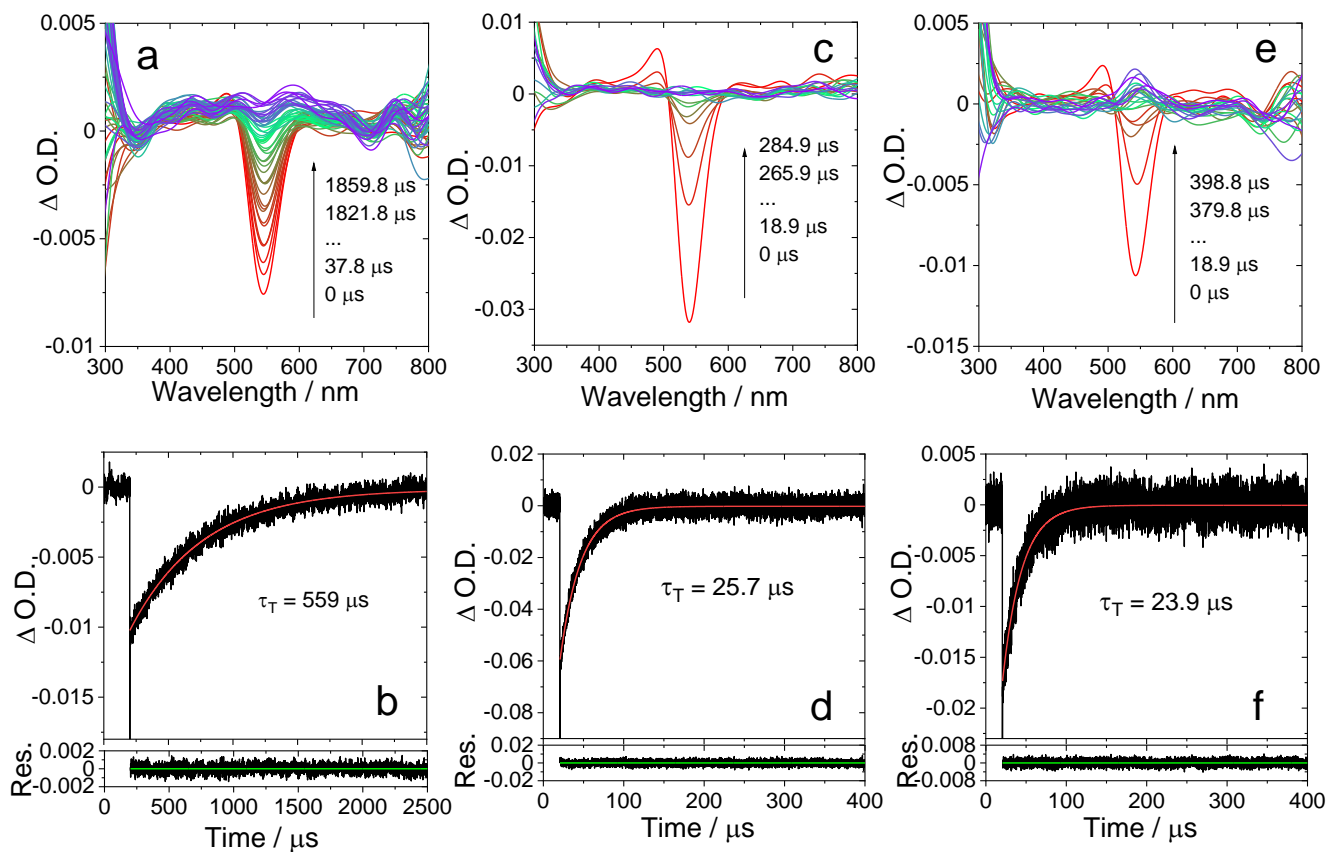
# 5. Nanosecond Transient Absorption Spectroscopy



**Figure S8.** Nanosecond transient absorption (Ns-TA) spectra (a) and decay trace (b) of **DB** in deaerated toluene. $c$ (**DB**) = 5.0 × 10⁻⁶ M. Ns-TA spectra (c) and decay trace (d) of **DB** in deaerated dichloromethane. Ns-TA spectra (e) and decay trace (f) of **DB** in deaerated toluene. $c$ (**DB**) = 1.0 × 10⁻⁵ M, $\lambda_{ex}$ = 520 nm, $\lambda_{em}$ = 530 nm.
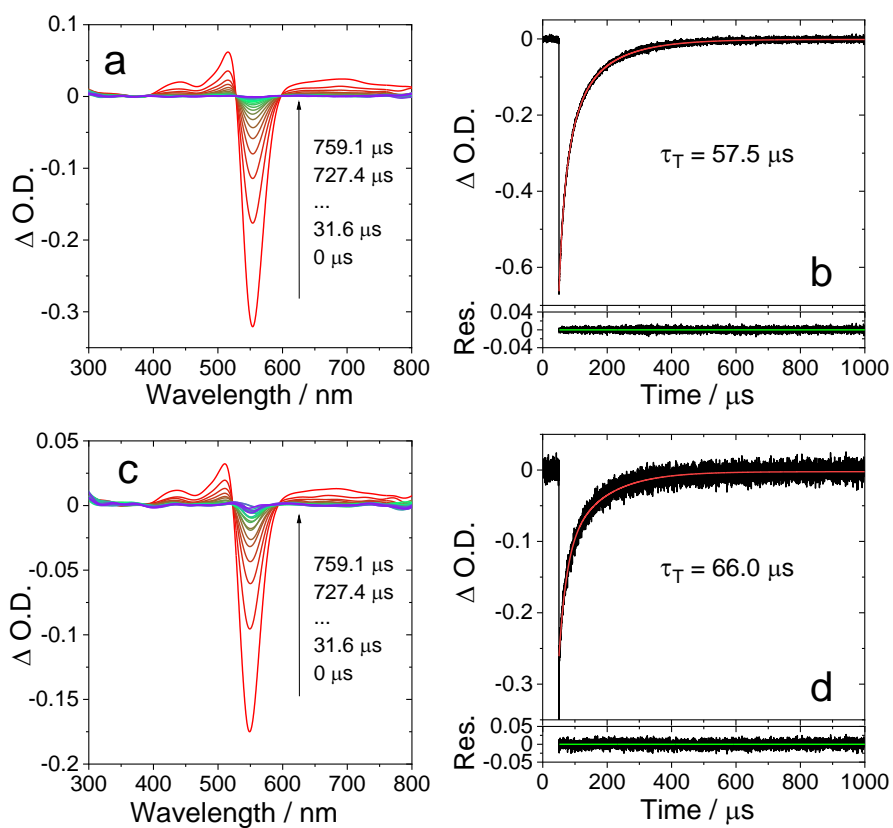
**Figure S9.** Ns-TA spectra (a) and decay trace (b) of **DB-I₂** in deaerated dichloromethane. Ns-TA spectra (c) and decay trace (d) of **DB-I₂** in deaerated acetonitrile. $c$ (**DB-I₂**) = $1.0 \times 10^{-5}$ M, $\lambda_{ex}$ = 540 nm, $\lambda_{em}$ = 555 nm.

## 6. Intrinsic Triplet State Lifetime Fitting

If the triplet state lifetime of compound is long and the triplet state quantum yield is high, the effect of triplet–triplet annihilation cannot be neglected, which will contribute additional lifetime quenching factor to the decay of the transient absorption. In this case, the triplet state lifetime will be reduced significantly and shorter than the intrinsic lifetime. The corresponding differential equation for the triplet concentration

$$\frac{dc_T}{dt} = -k_1 c_T - k_2 c_T{}^2 \tag{S2}$$

has the solution

$$c_T(t) = \frac{c_0 k_1}{\exp(k_1 t) \cdot (c_0 k_2 + k_1) - c_0 k_2} \tag{S3}$$

where $c_0$ is the initial triplet concentration. This leads to the following equation for the triplet state lifetime

$$A(t) = \frac{A_0 \tau_2 / \tau_1}{\exp(t / \tau_1) \cdot (1 + \tau_2 / \tau_1) - 1} \tag{S4}$$

where $A_0$ is the initial transient absorption intensity, $\tau_1 = 1/k_1$ is the intrinsic, unimolecular lifetime of the triplet state, and $\tau_2 = 1/c_0 k_2$. The triplet state lifetime of **BDP-I** and **DB-I$_2$** were fitted by Eq. S4.
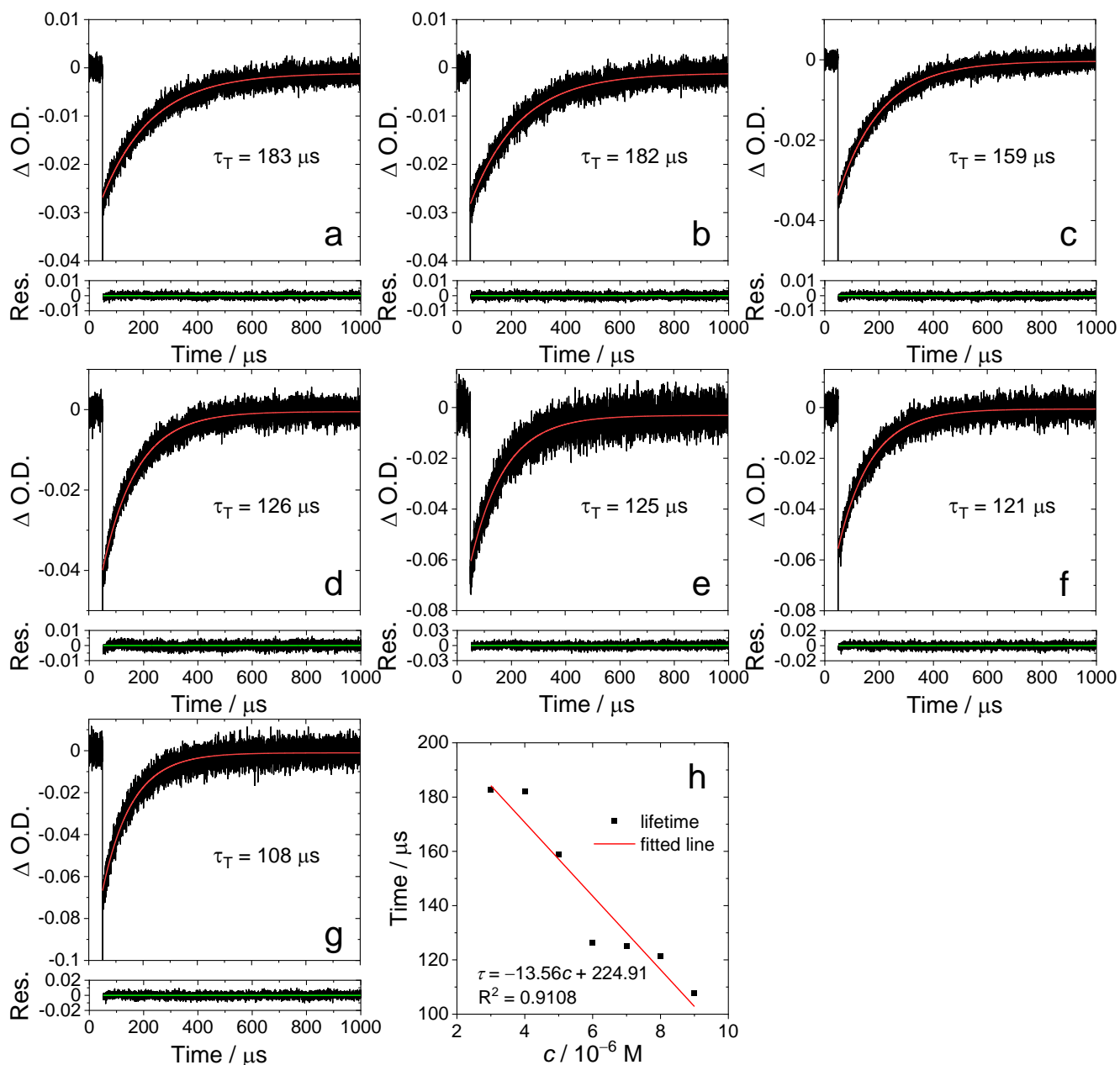
**Figure S10.** The decay traces of **BDP-I** in deaerated toluene, measured with nanosecond transient absorption spectroscopy. The concentrations of **BDP-I** are (a) $3.0 \times 10^{-6}$ M, (b) $4.0 \times 10^{-6}$ M, (c) $5.0 \times 10^{-6}$ M, (d) $6.0 \times 10^{-6}$ M, (e) $7.0 \times 10^{-6}$ M, (f) $8.0 \times 10^{-6}$ M, (g) $9.0 \times 10^{-6}$ M. $\lambda_{ex}$ = 535 nm, $\lambda_{em}$ = 515 nm, 20 °C. (h) Dependence of the triplet state lifetimes on the concentrations of **BDP-I** in deaerated toluene.

## 7. Time-Resolved Electron Paramagnetic Resonance (TREPR) Spectral Data

**Table S1.** Temperature dependence of the ZFS parameters and the rate constant of the triplet excited state of **DB-I$_2$**

| $T$ (K) | $D$ (MHz) | $E$ (MHz) | $k$ ($\mu s^{-1}$) |
|---------|-----------|-----------|---------------------|
| 25 | | 550±10 | 314 |
| 40 | | 545±10 | 347 |
| 60 | | 540±14 | 377 |
| 65 | −2650 | 510±14 | 518 |
| 75 | | 480±20 | 622 |
| 80 | | 460±28 | 680 |
| 100 | | 430±28 | 754 |

## 8. References

1. C. Zhang, J. Zhao, S. Wu, Z. Wang, W. Wu, J. Ma, S. Guo and L. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 10566–10578.

2. Z. Lou, Y. Hou, K. Chen, J. Zhao, S. Ji, F. Zhong, Y. Dede and B. Dick, *J. Phys. Chem. C*, 2018, **122**, 185–193.

3. Z. Wang, M. Ivanov, Y. Gao, L. Bussotti, P. Foggi, H. Zhang, N. Russo, B. Dick, J. Zhao and M. Di Donato, *Chem. –Eur. J.*, 2020, **26**, 1091–1102.

4. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.

5. W. Wu, J. Zhao, H. Guo, J. Sun, S. Ji and Z. Wang, *Chem. –Eur. J.*, 2012, **18**, 1961–1968.

6. Z. Wang and J. Zhao, *Org. Lett.*, 2017, **19**, 4492–4495.

7. Z. Li, Y. Chen, X. Lv and W.-F. Fu, *New J. Chem.*, 2013, **37**, 3755–3761.

8. S. Rihn, M. Erdem, A. De Nicola, P. Retailleau and R. Ziessel, *Org. Lett.*, 2011, **13**, 1916–1919.