Supporting Information for:

The Rhodamine–Perylene Compact Electron Donor–Acceptor Dyad: Spin-Orbit Charge-Transfer Intersystem Crossing and the Energy Balance of the Triplet Excited States

Muhammad Imran,† Dongyi Liu, † Kaiyue Ye, Xue Zhang and Jianzhang Zhao*

State Key Laboratory of Fine Chemicals, Frontiers Science Center for Smart Materials Oriented Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, E–208 West Campus, 2 Ling Gong Rd., Dalian 116024, P. R. China.

E–mail: zhaojzh@dlut.edu.cn

† These authors contributed equally to this work.

Contents

1. General Information

All the chemicals used in synthesis are analytically pure and were used as received. Solvents in reactions were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on the Bruker Avance spectrometers (400 MHz). ^{1}H and ^{13}C NMR 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 (ESI).

2. Molecular Structure Characterization Data

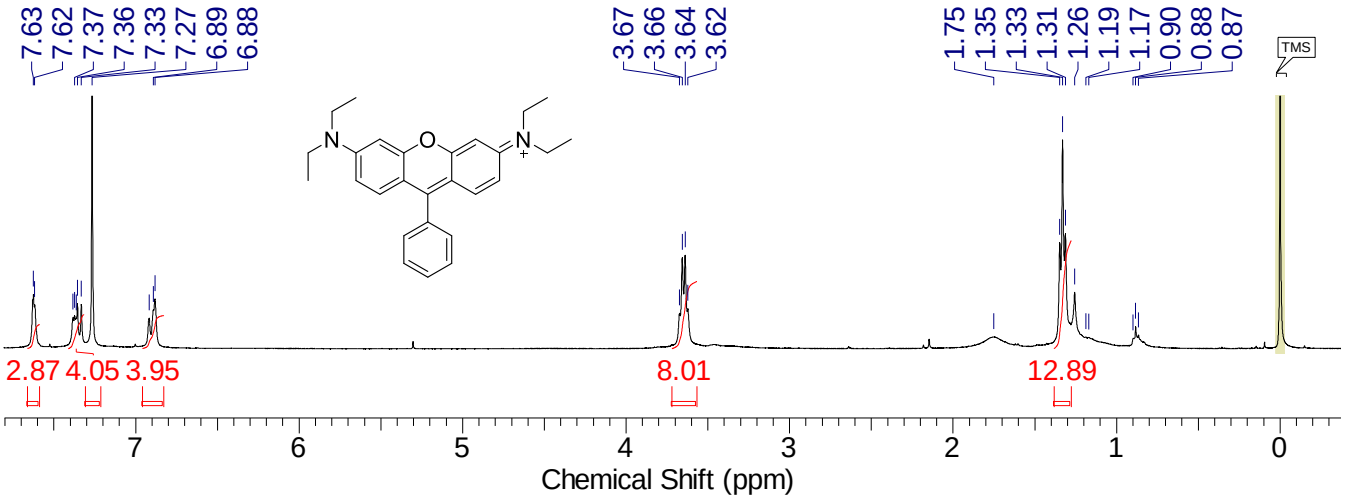

Figure S1. ^{1}H NMR spectrum of RB-Ph ($CDCl_3$, 400 MHz).

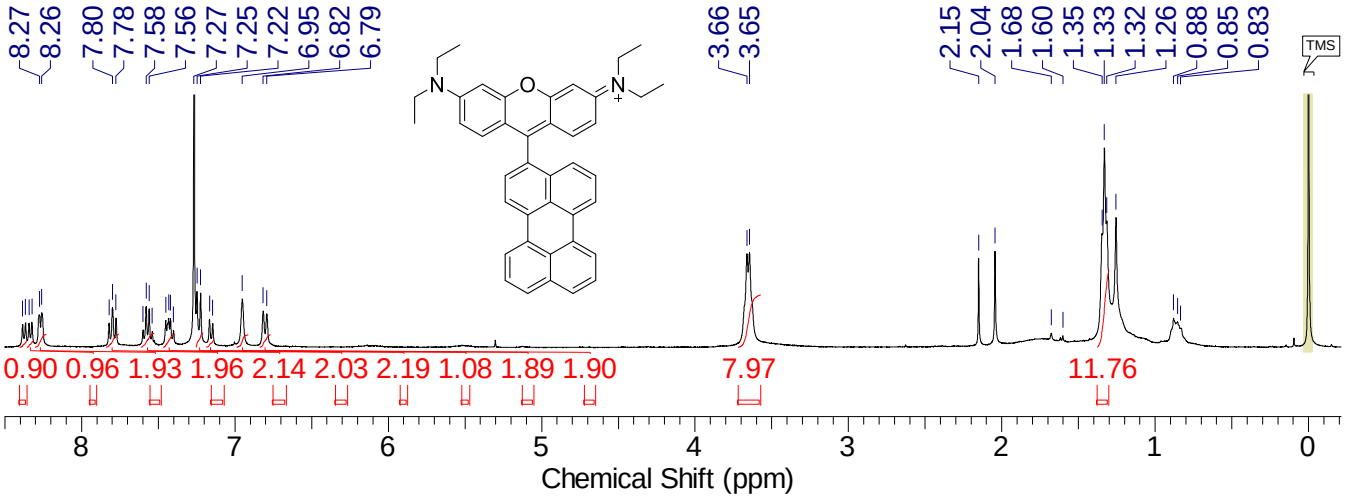

Figure S2. ^{1}H NMR spectrum of RB-Pery ($CDCl_3$, 400 MHz).

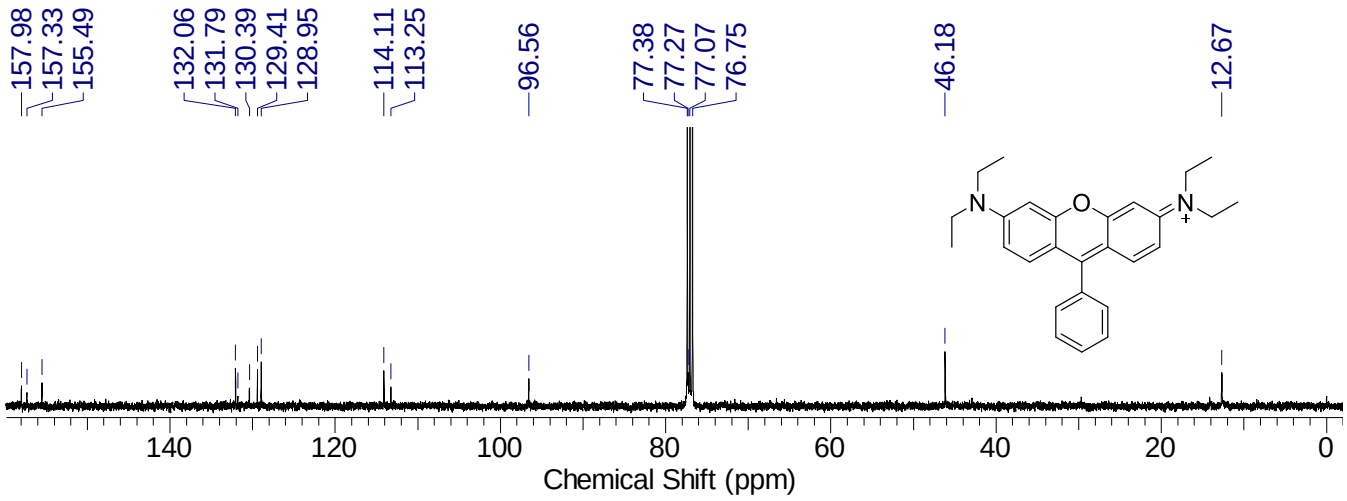

Figure S3. ^{13}C NMR spectrum of RB-Ph ($CDCl_3$, 126 MHz).

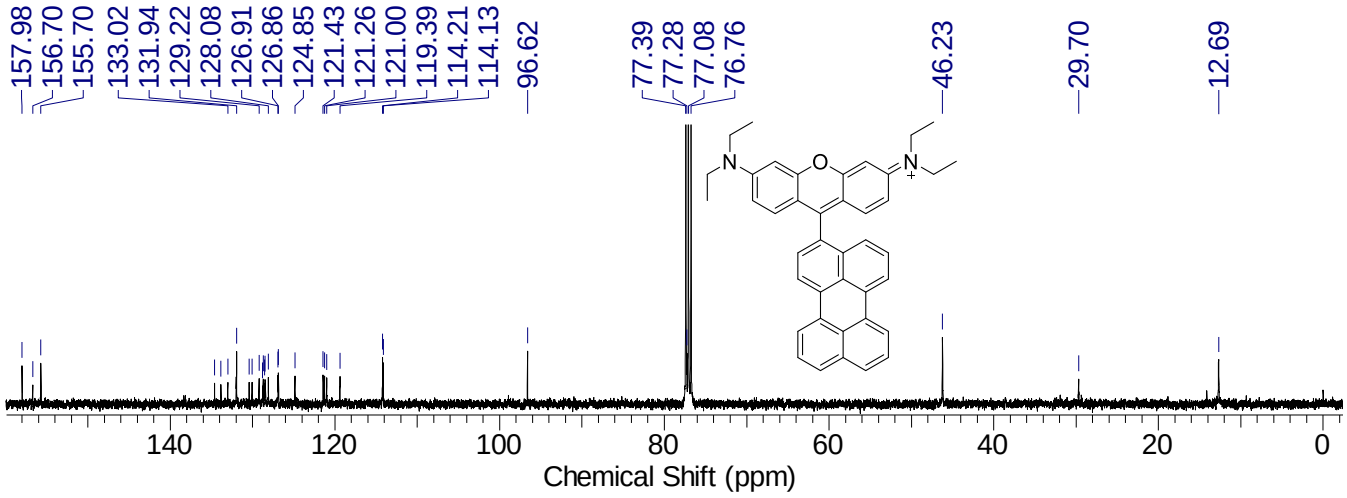

Figure S4. ^{13}C NMR spectrum of RB-Pery ($CDCl_3$, 126 MHz).

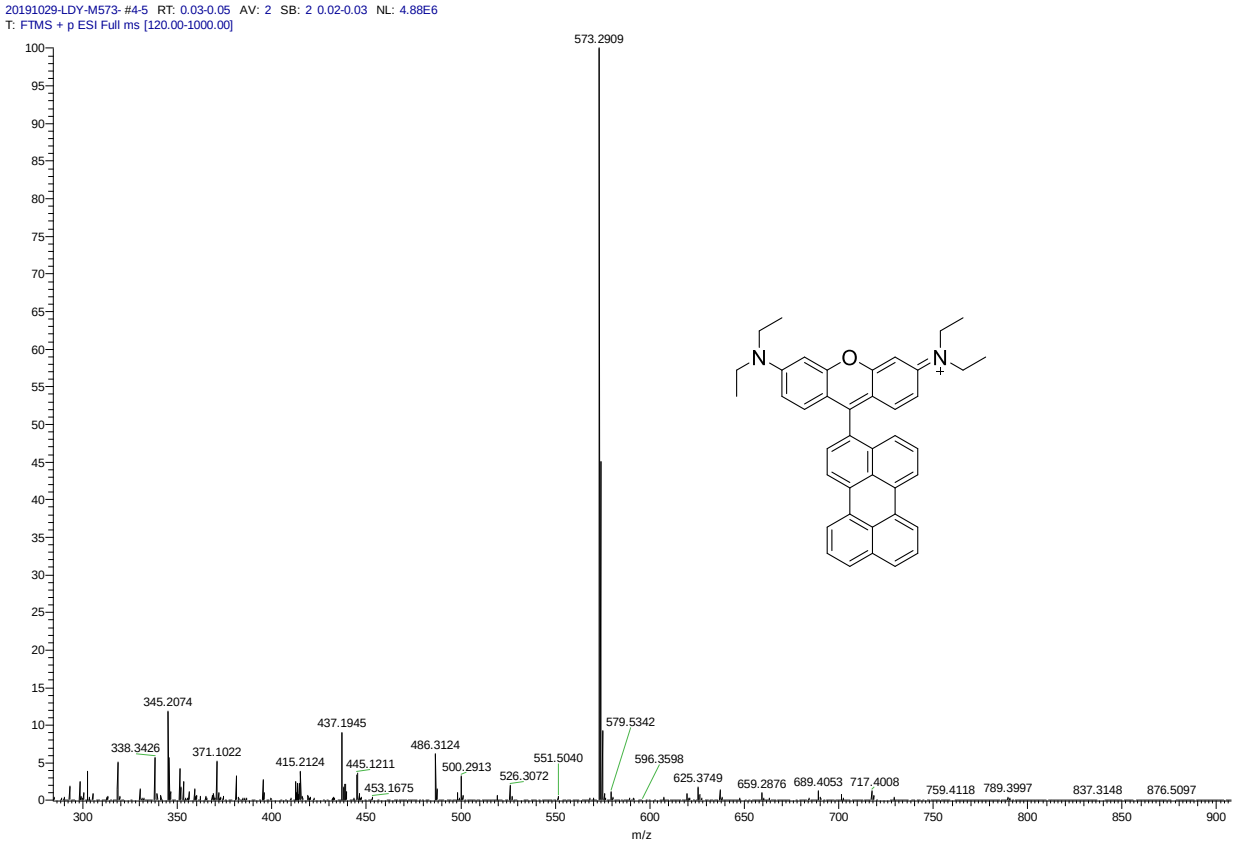

Figure S5. ESI-HRMS of RB-Pery.

3. UV–vis Absorption and Fluorescence Emission Spectra

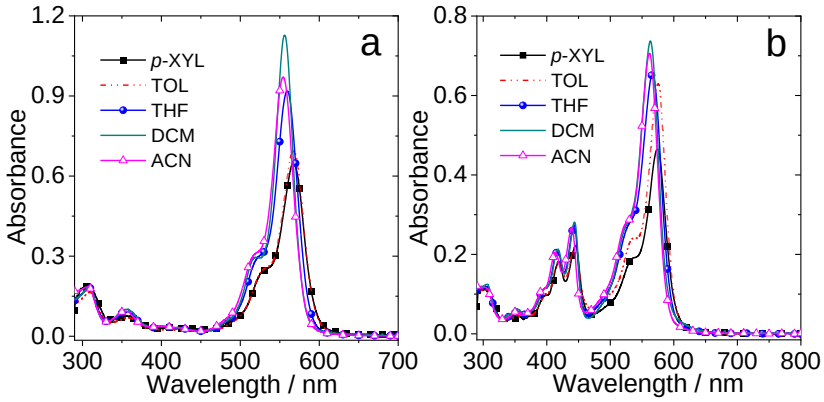

Figure S6. UV-vis absorption spectra of compound (a) RB-Ph and (b) RB-Pery in different solvents. $c = 1.0 \times 10^{-5}$ M.

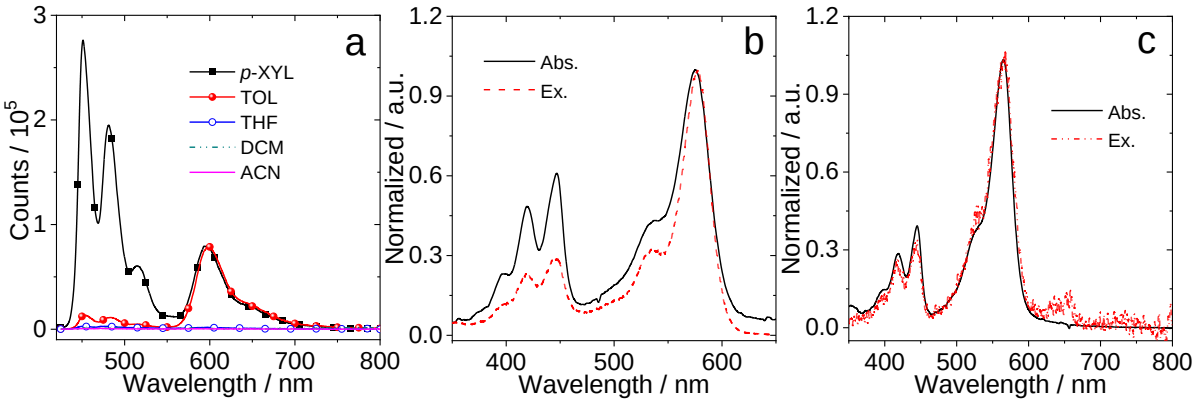

Figure S7. (a) Fluorescence emission spectra (optically-matched solutions were used, A = 0.10) of RB-Pery in different polarity solvents, λ_{ex} = 415 nm. Normalized UV-vis absorption and fluorescence excitation spectra of RB-Pery (b) in *p*-XYL monitored at 650nm and (c) in DCM monitored at 800 nm. $c \approx 1.0 \times 10^{-5}$ M. 25 °C.

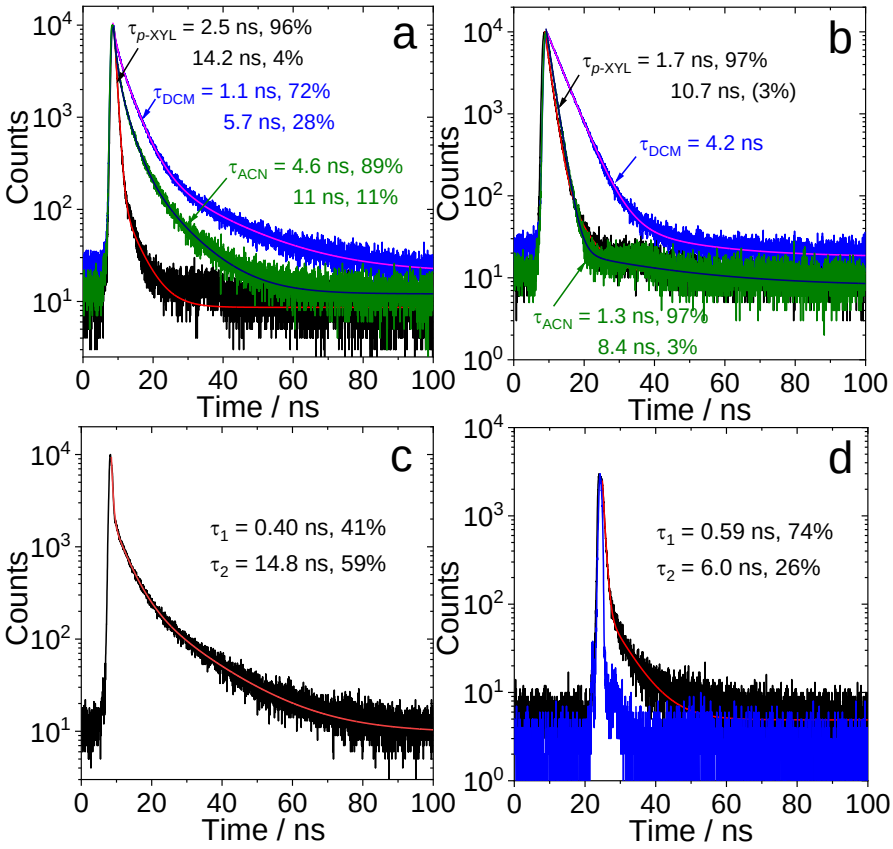

Figure S8. Fluorescence decay traces of the compounds in different solvents (a) RB-Pery monitored at 585 nm and (b) RB-Ph monitored at 585 nm. Fluorescence decay trace of the RB-Pery in DCM (c) monitored at 630 nm and (d) monitored at 690 nm. Excited with a 405 nm picosecond pulsed laser. $c \approx 1.0 \times 10^{-5}$ M. 25 °C.

Table S1. Absolute Photo-luminescence Quantum Yield of the Compounds in different solvents[a]

Compounds	*p*-XYL	TOL	THF	DCM	ACN
Pery	75.5%	77.7%	75.0%	82.2%	77.0%
RB-Ph	12.9%	14.2%	28.8%	71.9%	21.0%
RB-Pery	7.0% [b]	2.4% [b]	_[d]	_[d]	_[d]
	6.1% [c]	6.0% [c]			

[a] Error bar: ± 0.1, Pery and RB-Ph (λ_{ex} = 415 nm), RB-Pery (λ_{ex} = 506 nm), A = 0.10, 25 °C. [b] Excitation at perylene moiety. [c] Excitation at rhodamine moiety. [d] Not observed.

Table S2. Luminescence Lifetime of the Compounds in different solvents [a]

Compounds	*p*-XYL (ns)	TOL (ns)	THF (ns)	DCM (ns)	ACN(ns)
Pery	4.0 ± 0.3	3.9 ± 0.3	4.2 ± 0.3	4.5 ± 0.3	4.3 ± 0.4
RB-Ph	1.7 (97%)	1.3 (97%)	2.6 ± 0.3	4.2 ± 0.3	1.6 ± 0.3
	10.7 (3%) ± 0.2	8.5 (3%) ± 0.2			
RB-Pery	2.5 (96%)	3.3 (96%)	3.8 (37%)	1.1 (72%)	4.6 (89%)
	14.2 (4%)± 0.2	16.7 (4%)± 0.2	10.4 (63%)± 0.3	5.7 (28%)± 0.2	11.0 (11%)± 0.2

[a] c = 1.0 × 10^{-5} M, λ_{ex} = 405 nm, 25 °C. The values in the table are in %.

4. Singlet Oxygen Quantum Yields

Table S3. Singlet Oxygen Quantum Yields of Compounds in Different Solvents [a]

Compounds	*p*-XYL (33.5)	TOL (33.9)	THF (37.4)	DCM (41.1)	ACN (46.0)
Pery	4.8 ± 0.5	3.0 ± 0.5	8.2 ± 1	4.0 ± 0.5	16.2 ± 1
RB-Ph	– [b]	– [b]	– [b]	– [b]	– [b]
RB-Pery	8.0 ± 1	2.7 ± 0.5	– [b]	– [b]	– [b]

[a] Rose Bengal was used as standard (Φ_Δ = 76% in MeOH) for RB-Ph and RB-Pery, $Ru(bpy)_3(PF_3)_2$ was used as standard (Φ_Δ = 57% in DCM) for Pery, the values are in %. The values in parenthesis are the E_T (30) values of the solvents, in kcal mol^{-1}. [b] Not observed.

5. Electrochemical Study

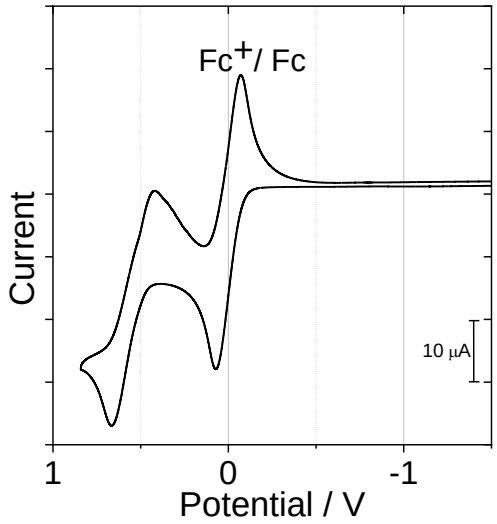

Figure S9. Cyclic voltammogram of perylene. Conditions: in deaerated DCM containing 0.10 M Bu_4NPF_6 as supporting electrode, $Ag/AgNO_3$ as reference electrode, redox potentials are *versus* Fc/Fc^+. Scan rates: 50 mV/s. $c = 1.0 \times 10^{-3}$ M. 25 °C.

6. Nanosecond Transient Absorption Spectroscopy

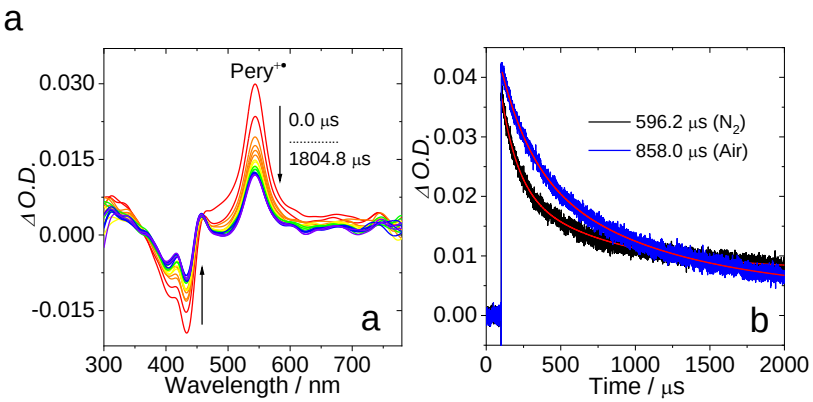

Figure S10. (a) Transient absorption spectra of Pery in deaerated DCM and (b) decay traces at 540 nm in DCM, c = 2.0 × 10^{-5} M, λ_{ex} = 432 nm. 25 °C.

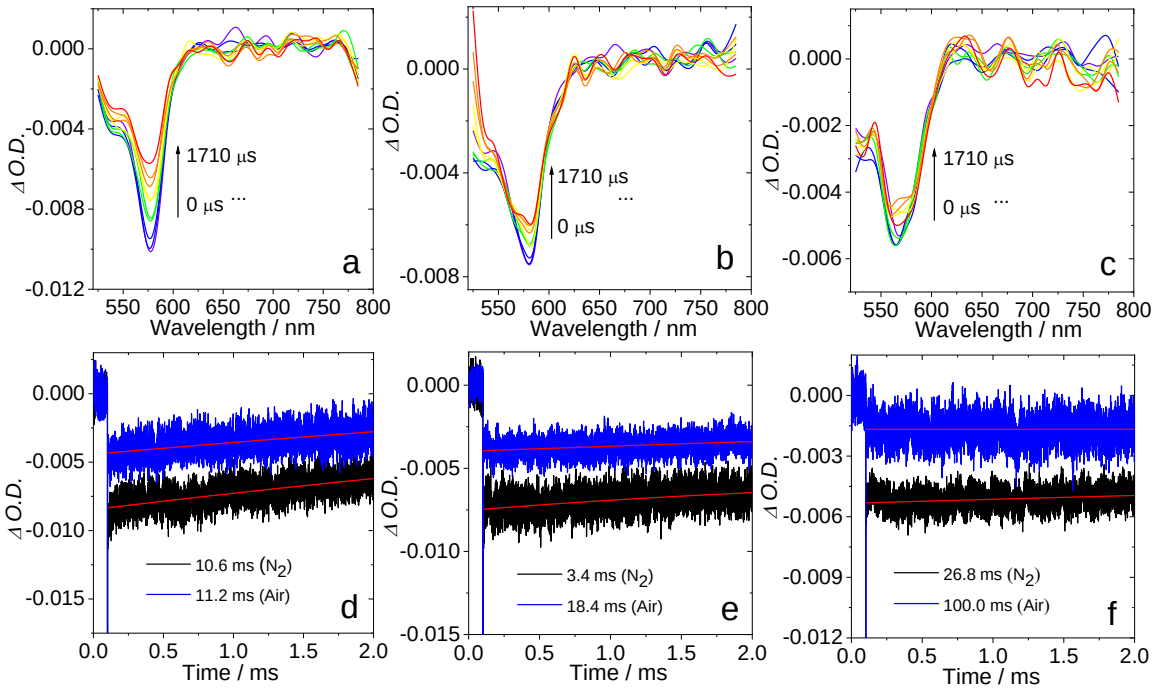

Figure S11. Transient absorption spectra of RB-Pery, (a) in deaerated *p*-XYL, c = 1.0 × 10^{-5} M; (b) in deaerated TOL, c = 1.0 × 10^{-5} M; (c) in deaerated THF, c = 2.0 × 10^{-5} M; (d-f) respective decay traces at 575 nm under aerated and deaerated conditions. λ_{ex} = 570 nm. 25 °C.

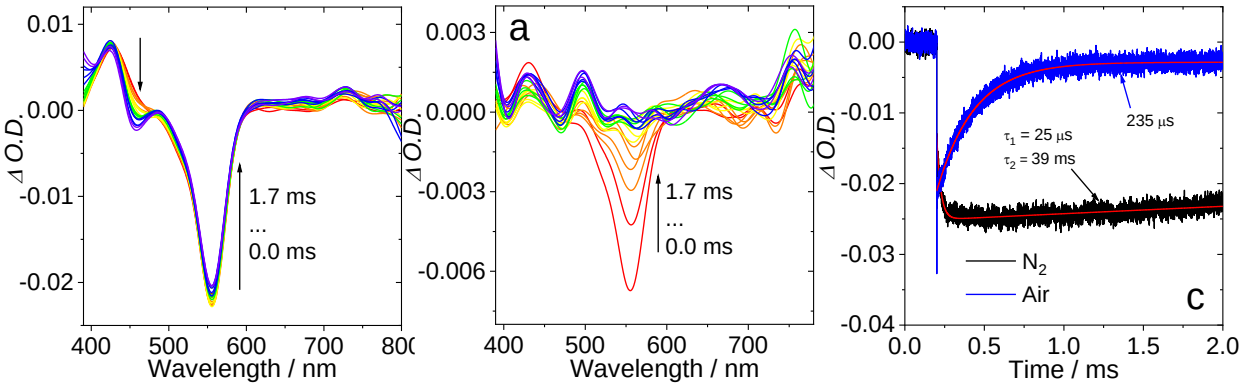

Figure S12. Transient absorption spectra of RB-Ph (c = 1.0 × 10^{-4} M) upon adding TEA (c = 4.0 × 10^{-3} M) (a) in deaerated DCM, (b) in aerated DCM and (c) decay traces at 560 nm in both cases. λ_{ex} = 550 nm. 25 °C.

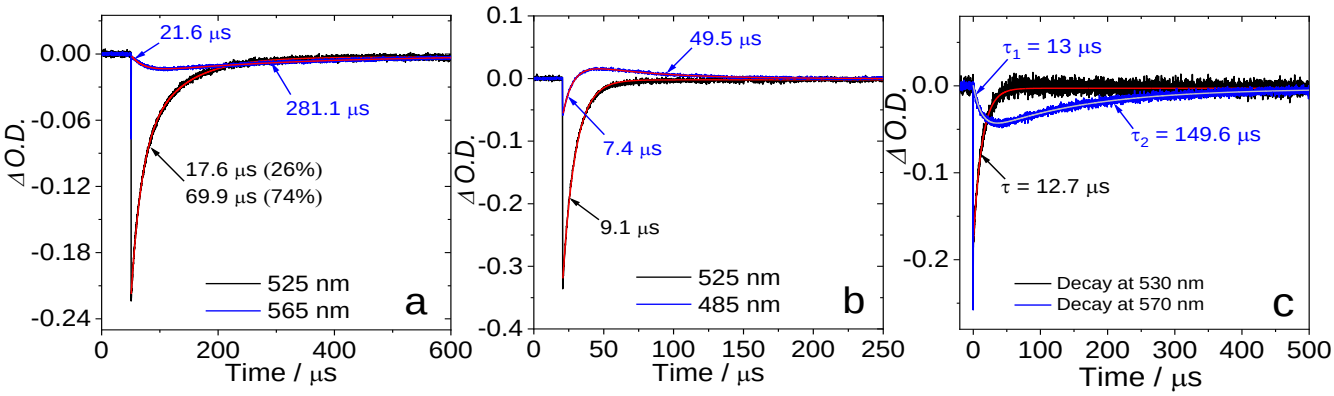

Figure S13. Intermolecular triplet-triplet energy transfer (TTET): from diiodo-BDP to RB-Ph, Pery and RB-Pery measured by ns-TA spectroscopy; (a) selected kinetic traces of the mixture of the ns-TA spectra of diiodo-BDP and RB-Ph. (b) selected kinetic traces of the mixture of the ns-TA spectra of diiodo-BDP and Pery. (c) selected kinetic traces of the mixture of the ns-TA spectra of diiodo-BDP and RB-Pery. The concentration of diiodo-BDP was fixed c[diiodo-BDP] = 5.0 × 10^{-6} M and 1:1 molar ratios were used in every case. The ns-TA spectra are given in the main text. In deaerated ACN, λ_{ex} = 520 nm. 25 °C.

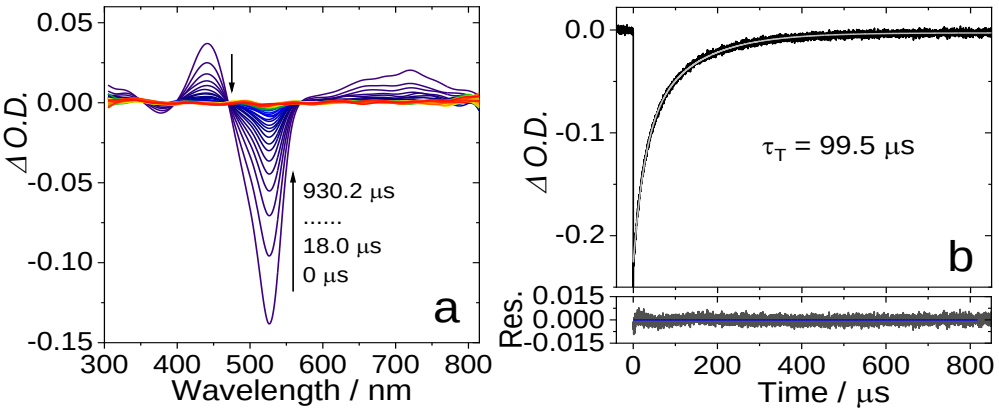

Figure S14. (a) Nanosecond transient absorption spectra of diiodo-BDP and (b) decay trace at 530 nm; c = 5.0 × 10^{-6} M in deaerated ACN. λ_{ex} = 520 nm. 25 °C.

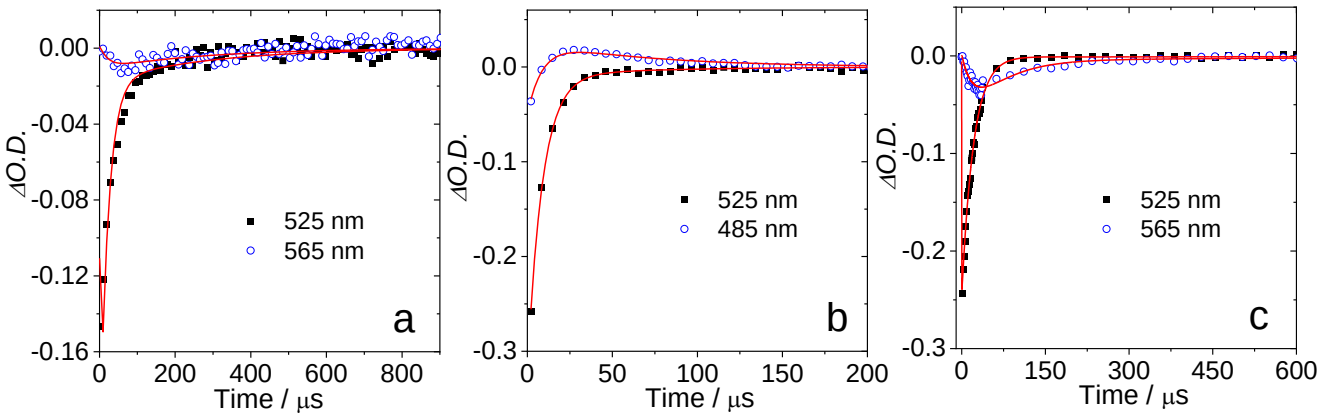

Figure S15. Selected kinetic decay traces obtained after global fitting analysis (a) from ns-TA data of diiodo-BDP/RB-Ph mixture (b) from ns-TA data of diiodo-BDP/Pery mixture and (c) from ns-TA data of diiodo-BDP/RB-Pery. The respective raw data and SADS spectra are given in the main text Figure 6 and 7.