Supplementary Information

Photoinduced Symmetry Breaking-Charge Separation in the Aggregated State of Perylene Diimide: Effect of Hydrophobicity

Guangliu Ran[1,†], *Johar Zeb*[1,†], *Yanyan Song*[1], *Pablo A. Denis*[2], *Usman Ghani*[3], *Wenkai Zhang* [1,*]

1. Department of Physics and Applied Optics Beijing Area Major Laboratory, Center for Advanced Quantum Studies, Beijing Normal University, Beijing 100875, China

2. Computational Nanotechnology, DETEMA, Facultad de Química, UDELAR, CC 1157, 11800 Montevideo, Uruguay

3. State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

AUTHOR INFORMATION

Corresponding Author

*E-mail: wkzhang@bnu.edu.cn

Author Contributions

†These authors contributed equally.

1. Materials and Methods

All the essential materials and organic solvents were bought from the certified commercial resources and used as received. UV-Vis spectra were collected on an Agilent Technologies Cary 60 spectrophotometer using a 1-cm fused silica cuvette at room temperature. Time resolved transient absorption (TA) spectra and kinetic decay were performed by HARPIA spectrometer equipped with nonlinear optical parametric amplifier (OPA) and pharos high-resolution femtosecond laser. Emission spectra and fluorescence lifetime were measured by transient fluorescence spectrometer FLS980.

1.1 Synthesis of Perylene diimide (PDI)

N, N'-Bis (1-ethylpropyl6-undecyl) perylene-3,4,9,10-bis(dicarboximide) (**PDI**) were synthesized according to the previous literature [1].

1.2. Global analysis

For the global data analysis, CarpetView software was used. Three different kinetic models were employed, which based on their associated ultrafast transient species as shown in the **Figure 6A** and **Figure S7**. The relaxation time constants, τ_0, τ_1, τ_2, τ_3 and τ_4 are completely based on the experimental data. After running each model by CarpetView, the desired SADS spectra and the corresponding concentrations were measured.

2. Tables

Table S1. Time decay constants determined for **PDI** in pure DMF and binary DMF/water solvents with volume percentage of water 30% by exponential decay function.

PDI						
PDI-DMF (Pump-495nm)			**PDI-DMF:Water (Pump-495nm)**			
Probe (nm)	τ_1 (ps)	τ_2 (ns)	Probe (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
532	421 ± 70	2.1 ± 0.3	557	1.0 ± 0.1	11.8 ± 1.3	96 ± 7
695	218 ± 9	5.5 ± 0.6	619	2.0 ± 0.1	27.8 ± 1.2	404 ± 25
			789	4.5 ± 0.3	46.4 ± 3.4	521 ± 48

3. Absorption and emission spectra

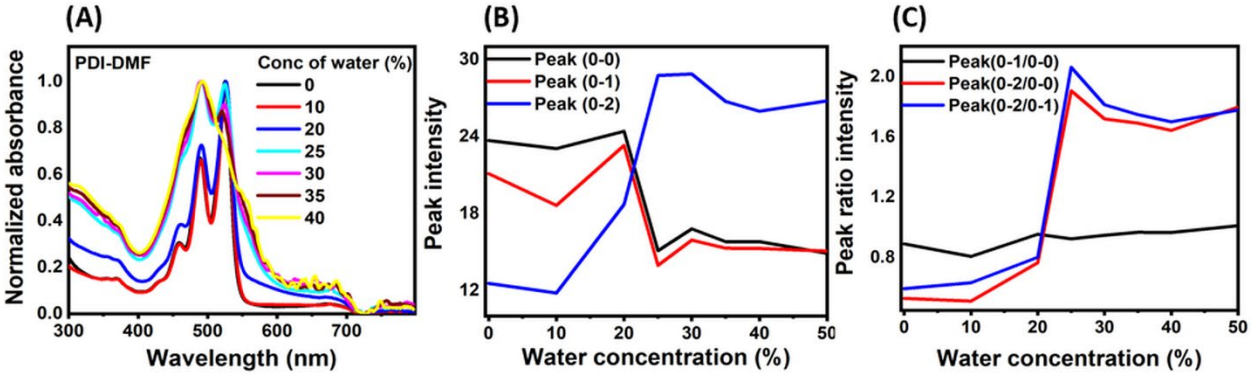

Figure S1: (A) Normalized absorption spectra of **PDI** in binary DMF/water solvents with volume percentage of water from 10 to 40%. An abrupt changed has shown as the water content reached to 25% with (B) Peak intensity and (C) Peak ratio intensity. This abrupt changed assigned the aggregated state of **PDI**.

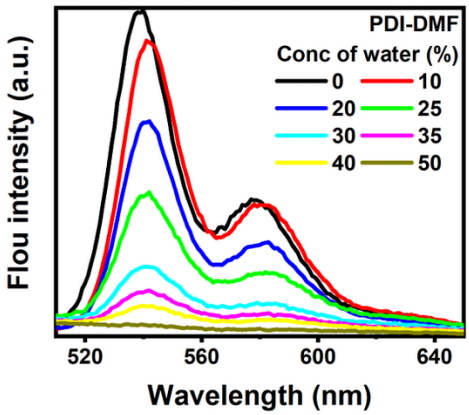

Figure S2: Fluorescence spectra of **PDI** in pure DMF and binary DMF/water solvents with volume percentage of water from 0 to 50%.

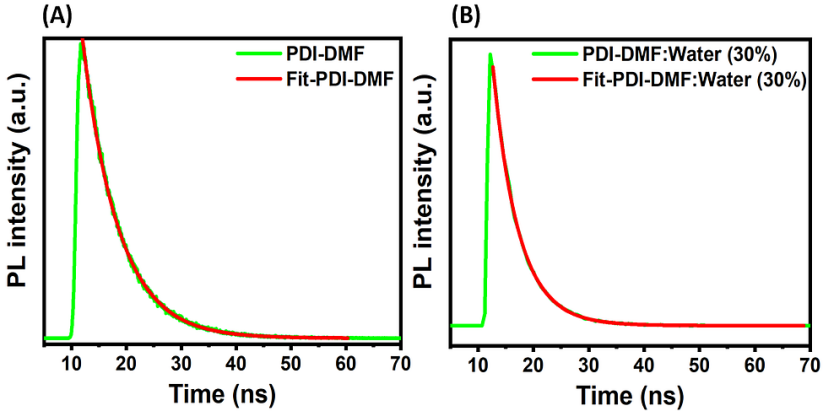

Figure S3: Fluorescence decay kinetics of **PDI** in (A) DMF and (B) binary DMF/water solvents with volume percentage of water at 30%.

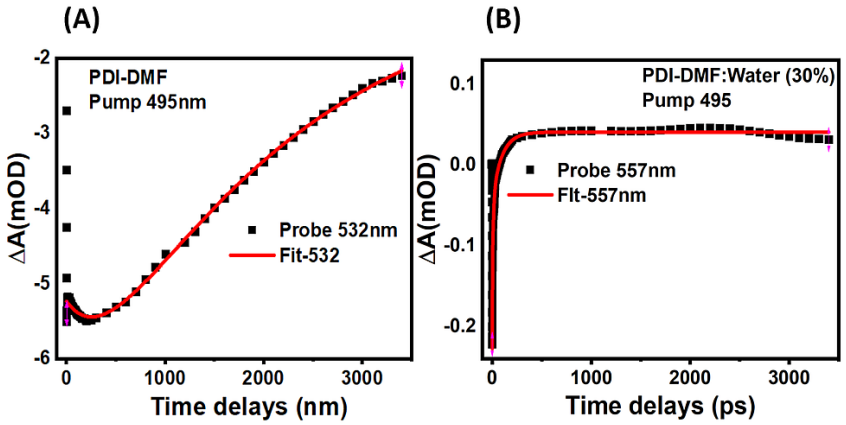

Figure S4: Relaxation dynamics of ground state bleaching (GSB) spectra for **PDI** in (A) DMF, probe at 532 nm, and (B) binary DMF/water solvents with volume percentage of water at 30%, probe at 557 nm.

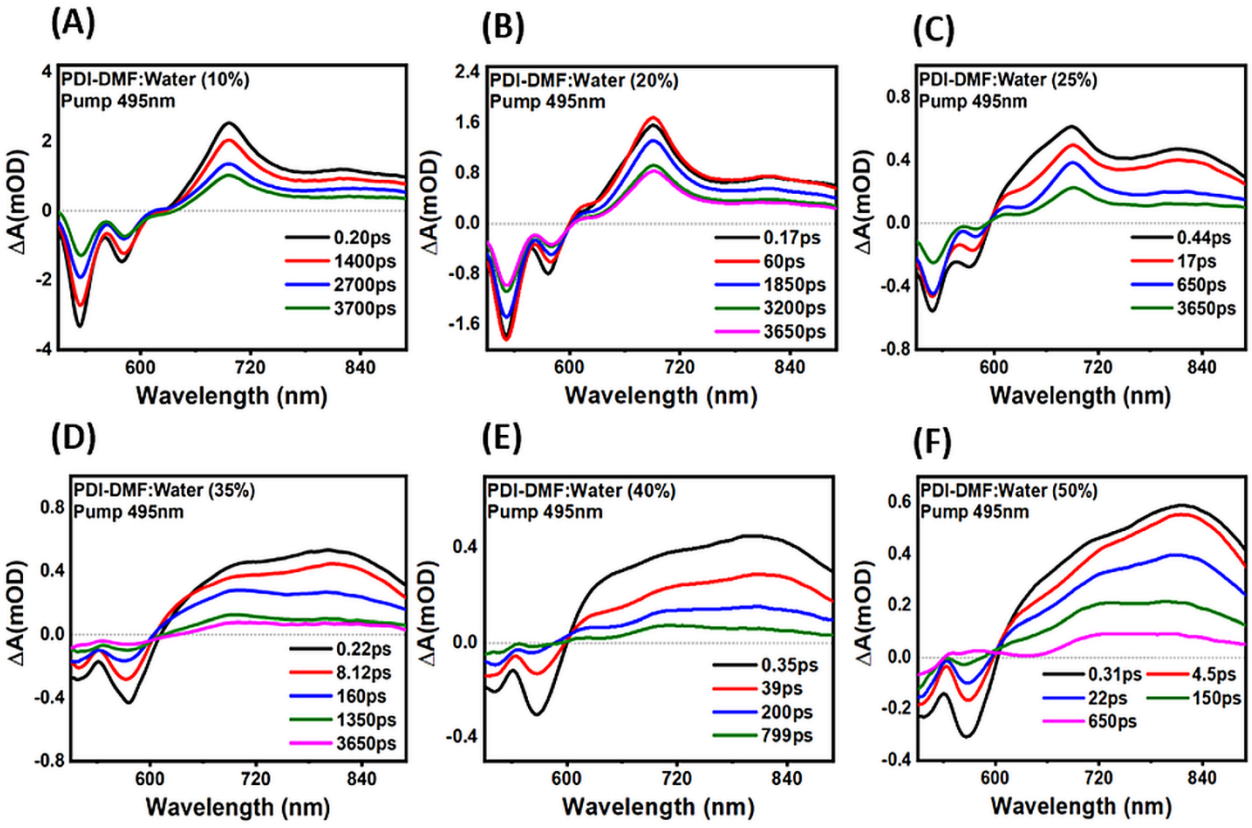

Figure S5: TA spectra of **PDI** in binary DMF/water solvents with volume percentage of water at (A) 10%, (B) 20%, (C) 25%, (D) 35%, (E) 40%, and (F) 50%, upon photoexcitation at 495 nm.

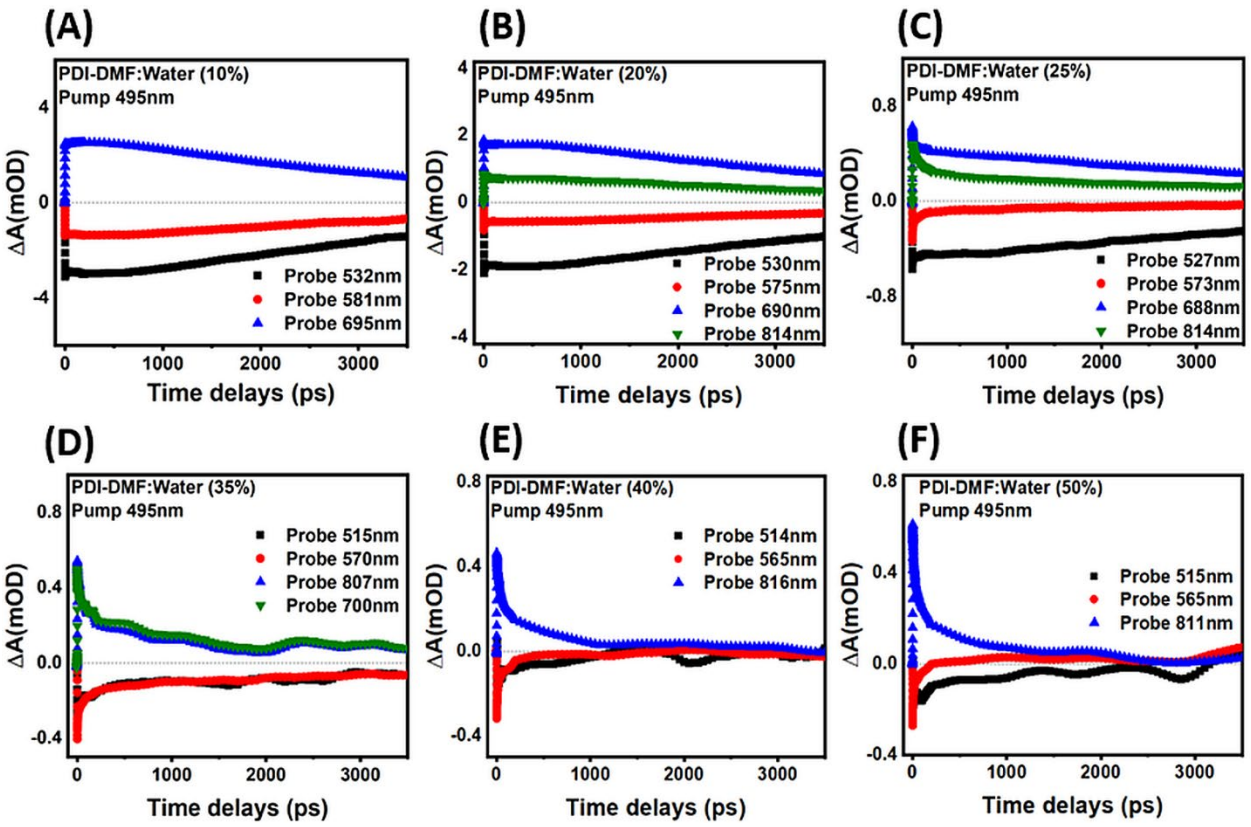

Figure S6: TA traces of **PDI** in binary DMF/water solvents with volume percentage of water at (A) 10%, (B) 20%, (C) 25%, (D) 35%, (E) 40%, and (F) 50%, upon photoexcitation at 495 nm with different probe pulses.

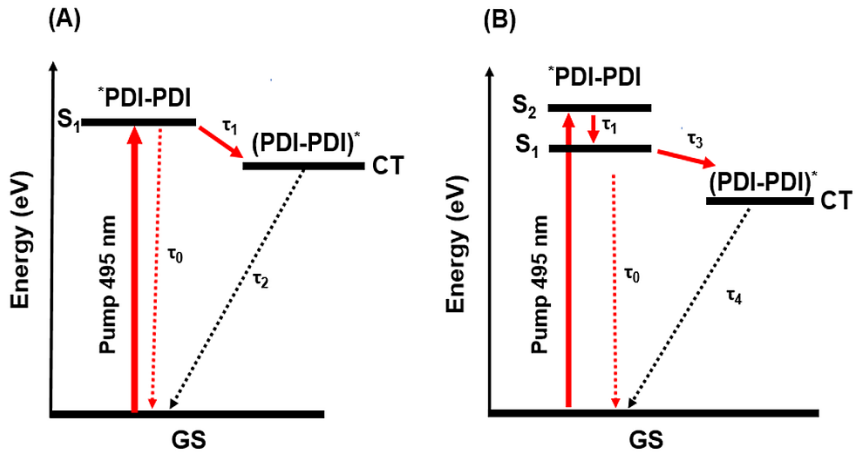

Figure S7: Kinetic model for **PDI** in DMF and binary DMF/water solvents with volume percentage of water at (A) 0, 10 and 20%, (B) Kinetic model for **PDI** in binary DMF/water solvents with volume percentage of water at 40 and 50%.

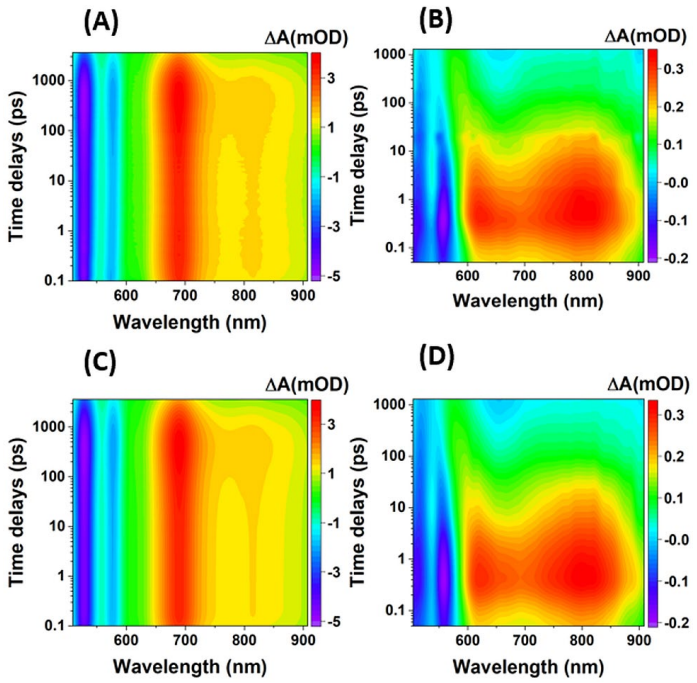

Figure S8: Color coded 2D and global analysis fit spectra of **PDI** in DMF with two different volume percentage of water, (A, B) Experimental pump-probe spectra, (C, D) Fit using kinetic model spectra. *Note: The left side (A, C) represents 0% and the right-side (B, D) represents 30%* volume percentage of water.

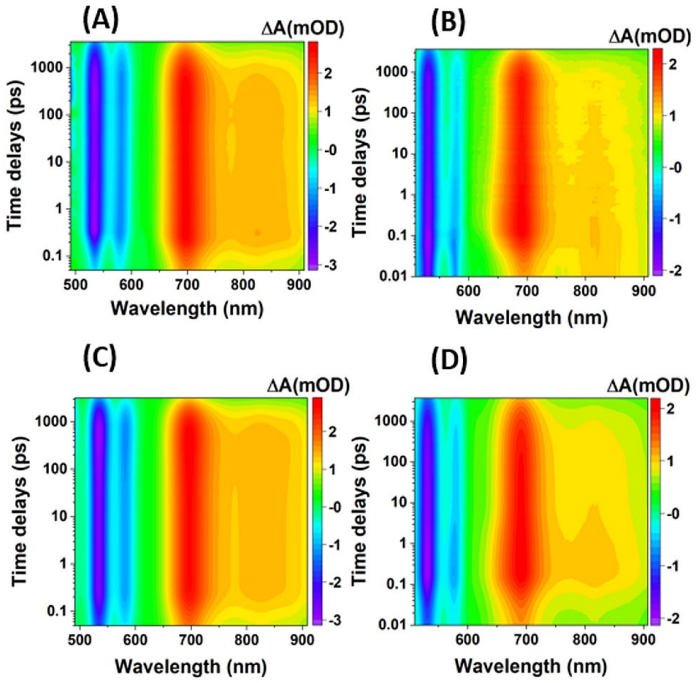

Figure S9: Color coded 2D and global analysis fit spectra of **PDI** in DMF with two different volume percentage of water, (A, B) Experimental pump-probe spectra, (C, D) Fit using kinetic model spectra. *Note: Note: The left side (A, C) represents 10% and the right-side (B, D) represents 20%* volume percentage of water.

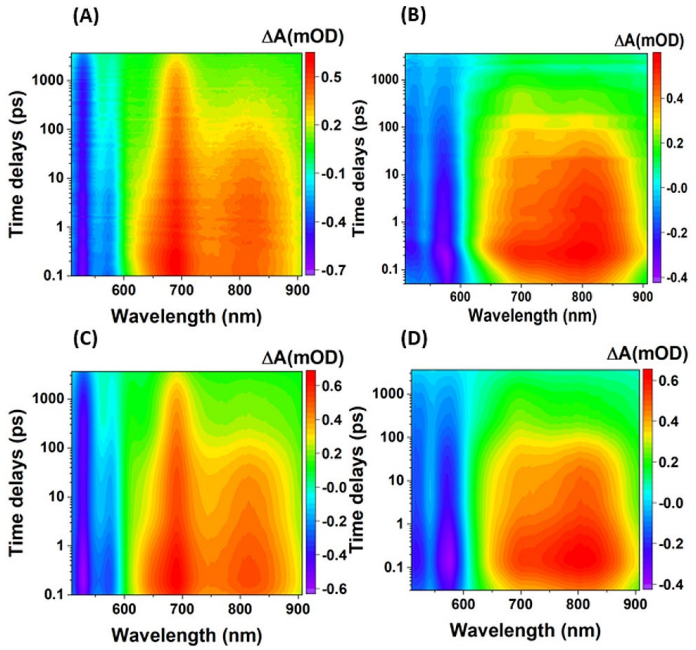

Figure S10: Color coded 2D and global analysis fit spectra of **PDI** in DMF with two different volume percentage of water, (A, B) Experimental pump-probe spectra, (C, D) Fit using kinetic model spectra. *Note: Note: The left side (A, C) represents 25% and the right-side (B, D) represents 35%* volume percentage of water.

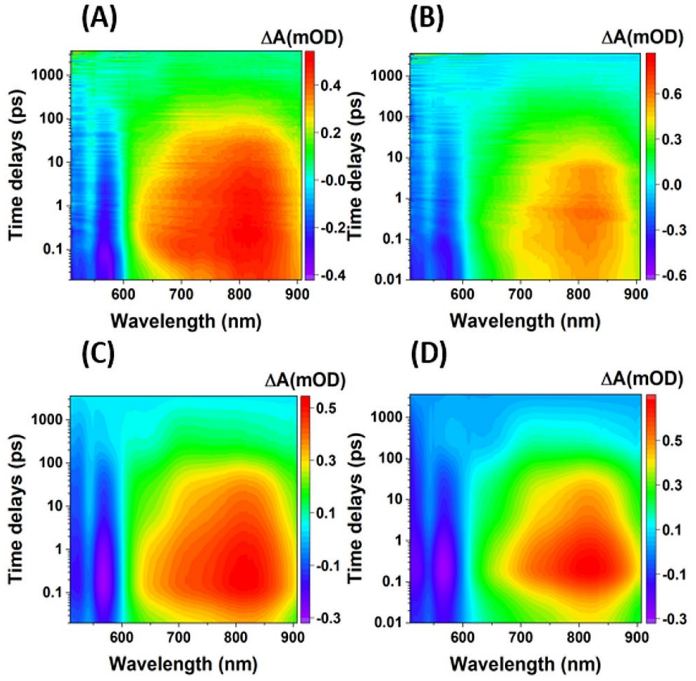

Figure S11: Color coded 2D and global analysis fit spectra of **PDI** in DMF with two different volume percentage of water, (A, B) Experimental pump-probe spectra, (C, D) Fit using kinetic model spectra. *Note: The left side (A, C) represents 40% and the right-side (B, D) represents 50%* volume percentage of water.

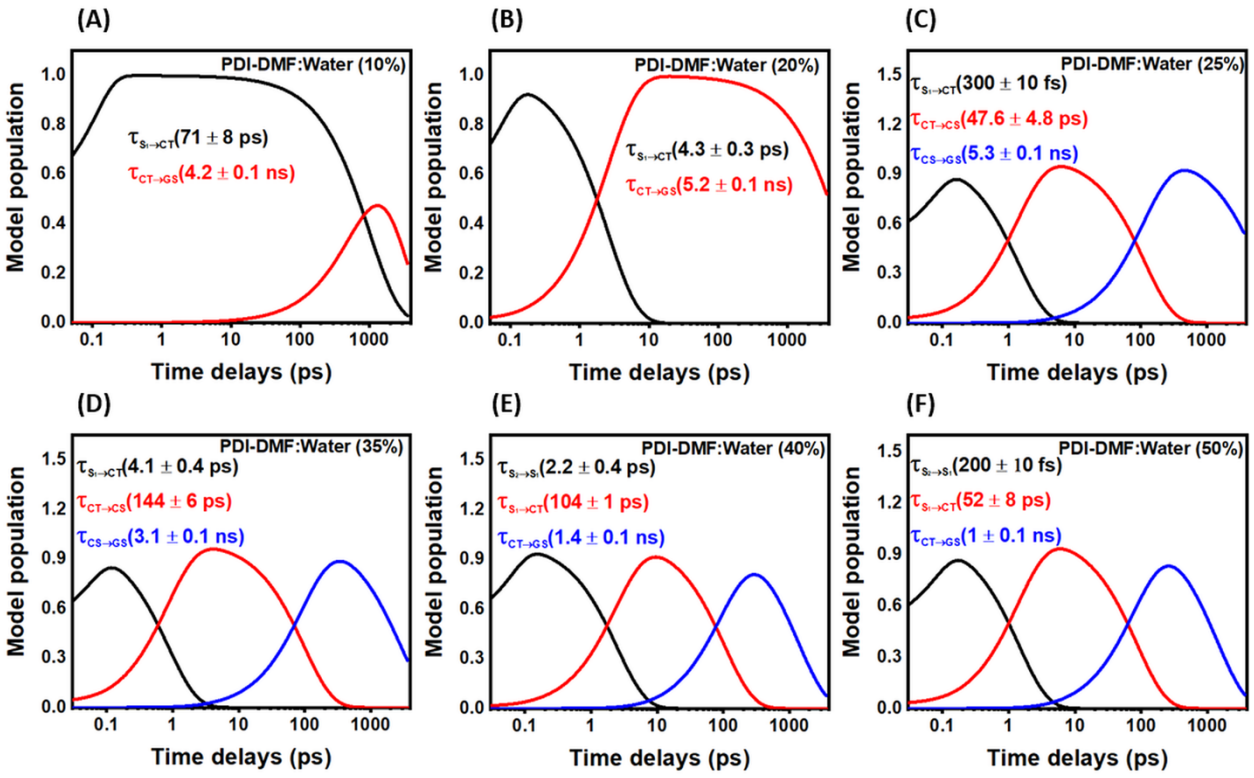

Figure S12: The excited state concentrations obtained from the best fit for **PDI** molecule in binary DMF/water solvents with volume percentage of water at (A) 10%, (B) 20%, (C) 25%, (D) 35%, (E) 40%, and (F) 50%.

References

1. Wang, H.; Chen, L.; Zhao, Z.; Xiao, Y. Aryl-Bisalkynyl Bridged Perylene Diimides Dimers: Efficient Synthesis, Properties and Improved Electron Mobilities. *Dyes Pigm.* **2017**, *144*, 184-189.