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Supporting information

"Altering Singlet Fission Pathways in Perylene-Dimers; Perylene-Diimide versus Perylene-Monoimide"

Ilias Papadopoulos,^a David Gutiérrez-Moreno,^b Yifan Bo,^{a,c} Rubén Casillas,^{a,c} Phillip M. Greißel,^a Timothy Clark,^c Fernando Fernández-Lázaro,^{*b} and Dirk M. Guldi^{*a}

^{a.} Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstraße 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@fau.de

^{b.} Área de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, Avda. de la Universidad s/n, 03203 Elche, Spain. E-mail: fdofdez@umh.es

^{c.} Computer-Chemistry-Center, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen, Germany.

Table of Contents

General Experimental Methods	S2-S3
Synthesis	S4-S5
NMR and MALDI-TOF Spectra	S6–S10
Electrochemistry / Spectro-electrochemistry	S11-S14
Photophysical Characterization	S15–S54
Theory	S55–S62
Supporting References	\$63-\$64

General Experimental Methods

Materials

All the chemicals and materials were purchased and used as received unless otherwise noted. Perylene-diimide reference (**PDI-Ref**) was synthesized as previously described.¹ Column chromatography was performed with SiO₂ (40–63 μ m), and TLC plates coated with SiO₂ 60F254 were visualized by UV light. Toluene, Tetrahydrofuran, and 2-Methyltetrahydrofuran of HPLC quality (>99.9%) was used as purchased from ROTH. Benzonitrile of HPLC quality (>99.9%) was used as purchased from MERCK.

Chromatography / Electrochemistry / Spectroscopy

¹H and ¹³C NMR spectra were recorded on a Bruker Avance at 300 MHz (¹H NMR) and 75 MHz (¹³C NMR). NMR spectra were referenced to the residual solvent signal (¹H: CDCl₃, 7.24 ppm; ¹³C: CDCl₃, 77.0 ppm) and recorded at ambient probe temperature. CDCl₃ (99.8%, Deutero GmbH) was stored over 4 Å molecular sieves. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Microflex LRF20 instrument using dithranol as a matrix. IR spectra were measured with a Nicolet Impact 400D spectrophotometer.

Steady-state absorption measurements were obtained on a PerkinElmer Lambda2 UV/Vis two-beam spectrophotometer with a slit width of 2 nm and a scan rate of 240 nm•min. Emission spectra were recorded by using a Horiba Jobin Yvon FluoroMax-3 spectrometer with a slit width of 2 nm for excitation and emission and an integration time of 0.5 s in a wavelength range of 500-1000 nm. Fluorescence quantum yields (FQYs) were determined from corrected emission spectra following the standard methods using Rhodamine B (EtOH; FQY = 0.7 in EtOH)² as standard for **PDI-Ref** and Rhodamine 6G (EtOH; FQY = 0.95 in EtOH)³ as standard for **PMI-P-PMI**, **PDI-P-PDI**, and **PDI-N-PDI**. All electrochemical measurements were performed with a Methrom µAutlobab FraIII. A single-compartment, three electrode cell configuration was used for the differential pulse voltammetry (DPV) measurements, using a glassy carbon electrode (3 mm diameter) as a working electrode, a platinum wire as a counter electrode and a silver wire as a reference electrode. Ferrocene/ferrocenium redox couple (Fc/Fc⁺) was used as an internal standard for all measurements. Spectroelectrochemistry measurements were performed in a home-made three-necked spectro-electrochemical cell. The three electrode setup consisted of a platinum counter-electrode, a silver wire quasi-reference electrode, and a platinum grid as working electrode. All measurements were performed at room temperature in argon saturated toluene/acetonitrile (4/1; v/v) with a 0.1 M TBAPF₆ supporting electrolyte solution. To control the applied potentials a Metrohm PGStat 101 with a 2 min hold time was used. A Cary 5000 double beam spectrometer from Varian was used for the measurement of the UV/vis region. To record the spectra, the WinUV software was used.

Femto- / nanosecond transient absorption studies: The excitation was performed with an amplified CPA-2110 titanium:sapphire laser (1 kHz; 150 fs pulse width; 200 nJ laser energy) from Clark-MXR Inc. EOS SYSTEM from Ultrafast Systems, working with 1 kHz pump laser at 387, 460, 480, and 633 nm wavelength. Probing was performed with a 2 kHz continuous white light fiber laser. Data evaluation of the fs- and nsTA data has been conducted by means of multiwavelength and target analysis using the GloTarAn⁴ package. Target analysis was performed on the TA data sets using the proposed kinetic models. The analytic solution to the coupled differential equations that describe the kinetic model is convoluted with a Gaussian instrument response function. After the least-squares fitting has converged, the raw data matrix is deconvoluted using the specific solution to the kinetic model and parameters from the fit to obtain the species-associated spectra and their populations as a function of time. Cryostat supported measurements between 297 and 80 K were conducted using an Optistat DN2 cryostat from Oxford Instruments in 2-methyltetrahydrofuran (MeTHF, SIGMA-ALDRICH, anhydrous, \geq 99%).

Determination of the Triplet Quantum Yield

The triplet quantum yield (TQY) was determined by normalizing the ground state bleaching using GloTarAn target analysis and scaling the ratio of singlet and triplet excited state absorptions, as described in the literature.^{5–9} In short, this approach is based on the assumptions that: (1) the singlet excited state is delocalized over the entire molecule, thus bleaching both chromophores; (2) a single triplet excited state likewise bleaches the entire ground state singlet transition; (3) no overlying/additional features are located in the ground state bleaching area, which allows one to normalize the triplet excited state spectra relative to the singlet excited state ones; and (4) two triplet excited states of the dimer lead to a bleaching twice that of a single one. By combining these criteria and the kinetic model in a GloTarAn target analysis, one is able to determine the TQY, for which all transitions prior to the formation of the correlated triplet pair contribute to the overall yield. In light of these criteria, the overlap of transients with the GSB hampered the precise determination of accurate TQYs.

<u>Synthesis</u>

The perylenemonoanhydridediester,¹⁰ PMADE, or the perylenemonoanhydridemonoimide,¹¹ PMAMI, (0.67 mmol) was added to a 50 mL round bottom flask containing the arylenediamine (0.32 mmol), DMAP (0.67 mmol) and imidazole (3.5 g). The reaction was heated at 130 °C for 5 h under argon atmosphere. The mixture was cooled to 90 °C and centrifuged with deionized water. After drying the solid in vacuum at 75 °C, purification was carried out by silica-gel column chromatography.

PMI-P-PMI

From PMADE and *m*-phenylenediamine. Eluent: Chloroform:Acetone (10:1).

Yield: 51%.

¹H NMR (CDCl₃) δ 0.91 (t, *J* = 6.8 Hz, 12H), 1.37 (m, 16H), 1.47 (m, 8H), 1.83 (m, 8H), 4.35 (t, *J* = 6.9 Hz, 8H), 7.56 (m, 3H), 7.79 (t, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 4H), 8.23 (br, 8H) and 8.49 ppm (d, *J* = 7.8 Hz, 4H)

¹³C NMR (CDCl₃) δ 168.36, 163.28, 135.73, 135.15, 131.85, 131.55, 130.32, 129.23, 129.00, 128.77, 125.60, 122.63, 121.99, 66.02, 31.70, 29.85, 28.75, 25.85, 22.74 and 14.19 ppm
MALDI-TOF m/z [M⁻] calc. for C₇₈H₇₂N₂O₁₂: 1228.5091, experimental: 1228.5067
IR (KBr): 3072, 2954, 2927, 2856, 1706, 1669, 1593, 1510, 1499, 1458, 1415, 1357, 1296, 1265, 1199, 1169, 1117, 1067, 850, 808 and 748 cm⁻¹

UV-vis (CHCl₃) λ_{max} /nm (log ϵ): 478 (4.7) and 510 (4.8)

PDI-P-PDI

From PMAMI and *m*-phenylenediamine. Eluent: Chloroform:Acetone (20:1).

Yield: 51%.

¹H NMR (CDCl₃) δ 0.82 (m, 12H), 1.25 (br, 32H), 1.87 (m, 4H), 2.23 (m, 4H), 5.18 (m, 2H), 7.45 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.7 Hz, 1H) and 8.71 ppm (m, 16H)

¹³C NMR (CDCl₃) δ 163.17, 135.60, 134.78, 134.07, 131.73, 131.05, 129.96, 129.60, 129.34, 126.34, 126.19, 124.07, 123.20, 55.03, 32.50, 32.07, 31.94, 29.85, 29.51, 29.39, 27.17, 22.84, 22.75 and 14.21 ppm

MALDI-TOF m/z [M⁺] calc. for C₈₀H₇₄N₄O₈: 1218.5501, experimental: 1218.5606

IR (KBr): 3085, 2925, 2855, 1698, 1658, 1594, 1578, 1511, 1488, 1432, 1404, 1341, 1251, 1175, 1115, 965, 854, 811 and 746 cm⁻¹

UV-vis (CHCl₃) λ_{max} /nm (log ϵ): 459 (4.4), 492 (4.8) and 530 (5.1)

PDI-N-PDI

From PMAMI and 2,7-diaminonaphthalene. Eluent: Chloroform:Acetone (20:1). Yield: 61% ¹H NMR (CDCl₃) δ 0.83 (t, *J* = 6.7 Hz, 12H), 1.26 (br, 32H), 1.90 (m, 4H), 2.25 (m, 4H), 5.17 (m, 2H), 7.55 (dd, *J* = 8.8, 1.9 Hz, 2H), 7.88 (s, 2H), 8.15 (d, *J* = 8.7 Hz, 2H) and 8.63 ppm (m, 16H)

¹³C NMR (CDCl₃) δ 163.35, 134.60, 133.82, 133.10, 132.82, 131.48, 129.43, 129.31, 128.16, 127.32, 126.12, 125.95, 123.12, 55.07, 32.51, 31.96, 29.85, 29.42, 27.25, 22.77 and 14.21 ppm

MALDI-TOF m/z [M⁺] calc. for C₈₄H₇₆N₄O₈: 1268.5658, experimental: 1268.5864

IR (KBr): 3060, 2924, 2854, 1699, 1657, 1594, 1578, 1509, 1458, 1433, 1404, 1339, 1251, 1174, 1121, 968, 811 and 745 cm⁻¹

UV-vis (CHCl₃) λ_{max}/nm (log ϵ): 460 (4.6), 492 (5.1) and 529 (5.3)

NMR and MALDI-TOF Spectra



Fig. S1. ¹H NMR spectrum (top, 300 MHz, CDCl₃, rt) and ¹³C NMR spectrum (bottom, 75 MHz, CDCl₃, rt) of **PMI-P-PMI**.



Fig. S2. ¹H NMR spectrum (top, 300 MHz, CDCl₃, rt) and ¹³C NMR spectrum (bottom, 75 MHz, CDCl₃, rt) of **PDI-P-PDI**.



Fig. S3. ¹H NMR spectrum (top, 300 MHz, CDCl₃, rt) and ¹³C NMR spectrum (bottom, 75 MHz, CDCl₃, rt) of **PDI-N-PDI**.



Fig. S4. HR-Mass spectrum of PMI-P-PMI.



Fig. S5. HR-Mass spectrum of PDI-P-PDI.



Fig. S6. HR-Mass spectrum of PDI-N-PDI.

Electrochemistry / Spectro-electrochemistry



Fig. S7. Chemical structure of the perylene-diimide reference PDI-Ref.



Fig. S8. Differential pulse voltammetry assays of **PMI-P-PMI** (a), **PDI-Ref** (b), **PDI-P-PDI** (c), and **PDI-N-PDI** (d) in toluene/acetonitrile (4/1 v/v) with TBAPF₆ as supporting electrolyte at 0.1 M, using a glassy carbon working electrode (WE), a platinum wire counter-electrode (CE), and an Ag-wire as pseudo reference electrode (RE). The voltammograms are corrected against a Fc/Fc⁺ redox couple as internal standard. Scan directions are indicated by the colored arrows.



Fig. S9. Spectro-electrochemical assays of **PMI-P-PMI** showcasing the spectral features of the one-electron reduced (a) and one-electron oxidized (b) species in toluene/acetonitrile (4/1 v/v) in the visible and near-infrared (NIR) region with the indicated applied voltages.



Fig. S10. Spectro-electrochemical assays of **PDI-P-PDI** showcasing the spectral features of the one-electron reduced (a) and one-electron oxidized (b) species in toluene/acetonitrile (4/1 v/v) in the visible and near-infrared (NIR) region with the indicated applied voltages.



Fig. S11. Spectro-electrochemical assays of **PDI-N-PDI** showcasing the spectral features of the one-electron reduced (a) and one-electron oxidized (b) species in toluene/acetonitrile (4/1 v/v) in the visible and near-infrared (NIR) region with the indicated applied voltages.



Fig. S12. Absorption (a) and fluorescence (b) spectra of **PMI-P-PMI** in Tol (black), THF (red), and BN (blue), respectively.



Fig. S13. Absorption (a) and fluorescence (b) spectra of **PDI-Ref** in Tol (black), THF (red), and BN (blue), respectively.



Fig. S14. Absorption (a) and fluorescence (b) spectra of PDI-P-PDI in Tol (black), THF (red), and BN (blue), respectively.

Table S1. Fluorescence quantum yields (FQYs) in Tol, THF, and BN.

Solvent	PMI-P-PMI	PDI-Ref	PDI-P-PDI	PDI-N-PDI
Tol	80 %	100 %	95 %	89 %
THF	61 %	96 %	73 %	38 %
BN	66 %	85 %	86 %	69 %



Fig. S15. Absorption (solid lines) and fluorescence (dotted lines) spectra of **PMI-P-PMI** in MeTHF at 1.0×10^{-5} M at 297 K (black) and 140 K (red).



Fig. S16. Time-correlated single photon counting (TCSPC) spectra of a) **PMI-P-PMI** and c) **PMI-N-PMI** in MeTHF, measured between 297 and 80 K and of b) **PMI-P-PMI** and d) **PMI-N-PMI** Tol (black) and BN (red), respectively.

Temperature /K	τ / ns		
(MeTHF)	PMI-P-PMI	PMI-N-PMI	
297	4.19	4.16	
250	4.11	4.25	
200	3.94	4.03	
160	3.71	3.90	
140	3.50	3.70	
100	3.69	3.96	
80	3.68	3.95	
Tol	4.52	4.38	
BN	4.15	3.91	

Table S2. TCSPC lifetimes (τ) of **PMI-P-PMI** and **PMI-N-PMI** in MeTHF, measured between 297 and 80 K, in Tol, and BN.



Fig. S17. Time-correlated single photon counting (TCSPC) profiles of **PDI-Ref** in Tol (black), THF (red), and BN (blue).



Fig. S18. Time-correlated single photon counting (TCSPC) profiles of **PDI-P-PDI** in Tol (black), THF (red), and BN (blue).



Fig. S19. a) Time-correlated single photon counting (TCSPC) profiles in Tol (black), THF (red), and BN (blue) and b) normalized time-resolved emission spectra (TRES) in BN at various time delays of **PDI-N-PDI**.

Table S3. TCSPC lifetimes (τ) and relative amplitudes (Rel.A.) of **PDI-Ref**, **PDI-P-PDI**, and **PDI-N-PDI** in Tol, THF, and BN.

Solvent	PDI-Ref	PDI-P-PDI		PDI-N-PDI	
Solvent	τ ₁ / ns	τ ₁ / ns	τ ₂ / ns	τ ₁ / ns	τ ₂ / ns
	Rel.A. / %				
Tol	5.05 100	3.54 100	-	3.57 100	-
THF	5.35	3.10	10.33	1.38	3.71
	100	95.25	4.75	69.01	30.99
BN	4.93	3.14	26.43	2.45	26.04
	100	98.33	1.67	84.77	15.23



Fig. S20. Chemical structures of a) anthracene and b) *N*-methylfulleropyrrolidine (*N*-MFP) used as a triplet-triplet energy transfer (TTET) donors for the triplet-triplet sensitization experiments for **PMI-P-PMI**, **PDI-P-PDI** and **PDI-N-PDI**, respectively.



Fig. S21. a) NsTA spectra of the sensitized triplet excited state for **PMI-P-PMI** with anthracene as a sensitizer in toluene with a 387 nm excitation at room temperature at various time delays; b) respective triplet excited state spectrum at a 10 μ s time delay; c) respective time profiles of the anthracene triplet excited state (428 nm – black dots) and **PMI-P-PMI** triplet excited state (548 nm – red dots).



Fig. S22. a) NsTA spectra of the sensitized triplet excited state for **PDI-P-PDI** with *N*-methylfulleropyrrolidine (*N*-MFP) as a sensitizer in toluene with a 387 nm excitation at room temperature at various time delays; b) respective triplet excited state spectrum at a 10 μ s time delay; c) respective time profiles of the *N*-MFP triplet excited state (700 nm – black dots) and **PDI-P-PDI** triplet excited state (505 nm – red dots).



Fig. S23. a) NsTA spectra of the sensitized triplet excited state for **PDI-N-PDI** with *N*-methylfulleropyrrolidine (*N*-MFP) as a sensitizer in toluene with a 387 nm excitation at room temperature at various time delays; b) respective triplet excited state spectrum at a 10 μ s time delay; c) respective time profiles of the *N*-MFP triplet excited state (700 nm – black dots) and **PDI-N-PDI** triplet excited state (505 nm – red dots).



Fig. S24. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-Ref** in Tol with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 561, 710, and 920 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁) (black) and solvent relaxed singlet excited state (S₁)_{sol} (red) of **PDI-Ref** in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S25. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-Ref in Tol with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 560, 705, and 910 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁)_{sol} (red) of PDI-Ref in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S26. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-Ref in THF with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 555, 705, and 913 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁) (black) and solvent relaxed singlet excited state (S₁)_{sol} (red) of PDI-Ref in THF as obtained by target analysis. (d) Respective population kinetics.



Fig. S27. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-Ref in THF with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 565, 715, and 903 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁)_{sol} (red) of PDI-Ref in THF as obtained by target analysis. (d) Respective population kinetics.



Fig. S28. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-Ref** in BN with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 565, 710, and 921 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁) (black) and solvent relaxed singlet excited state (S₁)_{sol} (red) of **PDI-Ref** in BN as obtained by target analysis. (d) Respective population kinetics.



Fig. S29. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-Ref in BN with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 565, 715, and 903 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁)_{sol} (red) of PDI-Ref in BN as obtained by target analysis. (d) Respective population kinetics.

Solvent	τ(S ₁) / ps	$\tau(S_1)_{Sol} / ns$
Tol	7.00	4.83
THF	13.81	5.26
BN	2.40	4.54

Table S4. FsTA and nsTA lifetimes (τ) of **PDI-Ref** in Tol, THF, and BN.



Fig. S30. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-N-PDI in Tol with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 507, 532, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black) and solvent relaxed singlet excited state (S₁S₀)_{sol} (red) of PDI-N-PDI in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S31. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-N-PDI in Tol with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 507, 532, and 595 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁S₀)_{sol} (red) of PDI-N-PDI in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S32. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-N-PDI** in THF with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 507, 532, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), solvent relaxed singlet excited state (S₁S₀)_{sol} (red), and charge separated state (S₁S₀)_{CS} (blue) of **PDI-N-PDI** in THF as obtained by target analysis. (d) Respective population kinetics.



Fig. S33. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-N-PDI** in BN with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 510, 535, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), solvent relaxed singlet excited state (S₁S₀)_{sol} (red), and charge separated state (S₁S₀)_{CS} (blue) of **PDI-N-PDI** in BN as obtained by target analysis. (d) Respective population kinetics.



Fig. S34. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-N-PDI** in BN with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 510, 535, and 595 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁S₀)_{Sol} (red), charge separated state (S₁S₀)_{CS} (blue), and intersystem crossing induced triplet excited state ³(S₀T₁) (orange) of **PDI-N-PDI** in BN as obtained by target analysis. (d) Respective population kinetics.

Table S5. FsTA and nsTA lifetimes (τ) of **PDI-N-PDI** in Tol, THF, and BN.

Solvent	$\tau(S_1S_0)$ / ps	τ(S ₁ S ₀) _{Sol} / ns	$\tau(S_1S_0)_{CS}$ / ns	$\tau^1(T_1T_1)$ / ns	$\tau(T_1+T_1) / \mu s$	$\tau^3(S_0T_1)$ / μs
Tol	1.50	3.50	-	-	-	-
THF	0.40	1.40	7.62	35.25	81.72	-
BN	1.97	1.68	31.44	-	-	161.64



Fig. S35. (a) FsTA spectra ($\lambda_{ex} = 460 \text{ nm}$, 400 nJ) of **PMI-P-PMI** in Tol with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 501, 525, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), singlet excited state with charge transfer character (S₁S₀)_{CT} (red), and up-converted singlet excited state (S₁S₀)_{UC} (blue) of **PMI-P-PMI** in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S36. (a) FsTA spectra ($\lambda_{ex} = 460 \text{ nm}$, 400 nJ) of **PMI-P-PMI** in BN with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 501, 525, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), singlet excited state with charge transfer character (S₁S₀)_{CT} (red), and up-converted singlet excited state (S₁S₀)_{UC} (blue) of **PMI-P-PMI** in BN as obtained by target analysis. (d) Respective population kinetics.



Fig. S37. (a) FsTA spectra ($\lambda_{ex} = 460$ nm, 400 nJ) of **PMI-P-PMI** in MeTHF at 297 K with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 501, 525, and 595 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), singlet excited state with charge transfer character (S₁S₀)_{CT} (red), and up-converted singlet excited state (S₁S₀)_{UC} (blue) of **PMI-P-PMI** in MeTHF at 297 K as obtained by target analysis. (d) Respective population kinetics.



Fig. S38. (a) FsTA spectra ($\lambda_{ex} = 460$ nm, 400 nJ) of **PMI-P-PMI** in MeTHF at 140 K with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 501, 525, and 595 nm. (c) Deconvoluted and GSB normalized fsTA spectra of the singlet excited state (S₁S₀) (black), singlet excited state with charge transfer character (S₁S₀)_{CT} (red), and correlated triplet pair with charge transfer character ¹(T₁T₁)_{CT} (blue) of **PMI-P-PMI** in MeTHF at 140 K as obtained by target analysis. (d) Respective population kinetics.

Solvent	$\tau(S_1S_0) / ps$	$\tau(S_1S_0)_{CT}$ / ns	$\tau(S_1S_0)_{UC}$ / ns	$\tau^1(T_1T_1)_{CT}$ / ns
Tol	5.89	238.35	4.29	-
BN	5.31	158.08	3.97	-
MeTHF (297 K)	3.75	182.62	3.75	-
MeTHF (140 K)	2.54	530.69	-	6.67

Table S6. FsTA lifetimes (τ) of **PMI-P-PMI** in Tol and BN and in MeTHF at 297 and 140 K.



Fig. S39. Chemical structure of palladium(II) meso-tetraphenyl-tetrabenzoporphyrin (PdP) used as a triplet-triplet energy transfer (TTET) donor for the up-conversion experiments with **PMI-P-PMI**.



Fig. S40. Absorption (solid lines) and fluorescence (dash-dotted lines) spectra of **PMI-P-PMI** in a concentration range between 1.0×10^{-6} and 5.0×10^{-6} M and PdP (1.25×10^{-7} M) in THF; fluorescence spectra with 632 nm excitation.



Fig. S41. (a) Fluorescence spectra of **PMI-P-PMI** in THF with direct excitation (black line, $\lambda_{ex} = 460$ nm), indirect via excitation of PdP (red line, $\lambda_{ex} = 632$ nm), and without PdP (blue line, $\lambda_{ex} = 632$ nm). (b) Respective normalized fluorescence spectra of the directly excited (black line, $\lambda_{ex} = 460$ nm) and indirectly via excitation of PdP (red line, $\lambda_{ex} = 632$ nm) measurements.



Fig. S42. Target analysis of nsTA data of PdP (1.25×10^{-7} M) at 297 K in toluene. Upper part – species associated spectrum (SAS) (visible) of the deconvoluted triplet excited state (T₁) of PdP (black). Lower left – Population kinetic for the respective species. Lower right – differential absorption changes (raw data) obtained from room temperature pump–probe experiments (632 nm) with time delays between 500 ps and 350 µs.



Fig. S43. Target analysis of nsTA data of **PMI-P-PMI** (5.0×10^{-6} M) and PdP (1.25×10^{-7} M) at 297 K in toluene. Upper part – species associated spectrum (SAS) (visible) of the deconvoluted triplet excited state (T₁) of PdP (black). Lower left – Population kinetic for the respective species. Lower right – differential absorption changes (raw data) obtained from room temperature pump–probe experiments (632 nm) with time delays between 500 ps and 350 µs.



Fig. S44. Target analysis of nsTA data of **PMI-P-PMI** (1.0×10^{-5} M) and PdP (1.25×10^{-7} M) at 297 K in toluene. Upper part – species associated spectrum (SAS) (visible) of the deconvoluted triplet excited state (T₁) of PdP (black). Lower left – Population kinetic for the respective species. Lower right – differential absorption changes (raw data) obtained from room temperature pump–probe experiments (632 nm) with time delays between 500 ps and 350 µs.



Fig. S45. Target analysis of nsTA data of **PMI-P-PMI** (5.0×10^{-5} M) and PdP (1.25×10^{-7} M) at 297 K in toluene. Upper part – species associated spectra (SAS) (visible) of the deconvoluted triplet excited state (T₁) of PdP (black) and **PMI-P-PMI** (red). Lower left – Population kinetics for the respective species. Lower right – differential absorption changes (raw data) obtained from room temperature pump–probe experiments (632 nm) with time delays between 500 ps and 350 µs.



Fig. S46. Kinetic time profiles of **PMI-P-PMI** and PdP (1.25×10^{-7} M) in toluene at 440 nm at **PMI-P-PMI** concentrations of 0.0 M (black), 5.0 x 10^{-6} M (red), 1.0 x 10^{-5} M (blue), and 5.0 x 10^{-5} M (green), obtained from room temperature pump-probe experiments (632 nm) with time delays between 500 ps and 350 µs.

Table S7. Triplet excited state lifetimes of PdP (1.25×10^{-7} M) and **PMI-P-PMI** at the various **PMI-P-PMI** concentrations in Tol.

c(PMI-P-PMI) / M	$\tau(T_1) PdP / \mu s$	τ(T1) PMI-P-PMI / μs
0	69.34	-
5 x 10 ⁻⁶	47.03	-
1 x 10 ⁻⁵	36.24	-
5 x 10 ⁻⁵	11.10	43.04



Fig. S47. Plot of the pseudo-first-order rate constant of PdP (1.25×10^{-7} M) versus **PMI-P-PMI** concentrations in toluene at room temperature to calculate the rate constants for triplet-triplet sensitization with a value of 1.53×10^{9} M⁻¹s⁻¹.



Fig. S48. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-P-PDI** in Tol with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 535, 685, and 886 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black) and solvent relaxed singlet excited state (S₁S₀)_{sol} (red) of **PDI-P-PDI** in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S49. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-P-PDI in Tol with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 535, 685, and 858 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁S₀)_{sol} (red) of PDI-P-PDI in Tol as obtained by target analysis. (d) Respective population kinetics.



Fig. S50. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-P-PDI in THF with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 528, 705, and 910 nm. (c) Deconvoluted fsTA spectra of the singlet excited state (S₁S₀) (black), solvent relaxed singlet excited state (S₁S₀)_{sol} (red), and charge separated state (S₁S₀)_{CS} (blue) of PDI-P-PDI in THF as obtained by target analysis. (d) Respective population kinetics.



Fig. S51. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-P-PDI** in THF with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 504, 528, 595, and 704 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁S₀)_{Sol} (red), charge separated state (S₁S₀)_{CS} (blue), and intersystem crossing induced triplet excited state ³(S₀T₁) (orange) of **PDI-P-PDI** in THF as obtained by target analysis. (d) Respective population kinetics.



Fig. S52. (a) FsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of PDI-P-PDI in BN with time delays between 0 – 5.5 ns. (b) Respective time absorption profiles at 538, 728, and 941 nm. (c) Deconvoluted fsTA spectra of the solvent relaxed singlet excited state (S₁S₀) (black), solvent relaxed singlet excited state (S₁S₀)_{sol} (red), and charge separated state (S₁S₀)_{CS} (blue) of PDI-P-PDI in BN as obtained by target analysis. (d) Respective population kinetics.



Fig. S53. (a) NsTA spectra ($\lambda_{ex} = 480$ nm, 400 nJ) of **PDI-P-PDI** in BN with time delays between 0 – 350 µs. (b) Respective time absorption profiles at 510, 539, and 570, and 712 nm. (c) Deconvoluted nsTA spectra of the solvent relaxed singlet excited state (S₁S₀)_{Sol} (red), charge separated state (S₁S₀)_{CS} (blue), and intersystem crossing induced triplet excited state state ${}^{3}(S_{0}T_{1})$ (orange) of **PDI-P-PDI** in BN as obtained by target analysis. (d) Respective population kinetics.

Table S8. FsTA and nsTA lifetimes (τ) of **PDI-P-PDI** in Tol, THF, and BN.

Solvent	$\tau(S_1S_0)$ / ps	τ(S ₁ S ₀) _{Sol} / ns	$\tau(S_1S_0)_{CS}$ / ns	$\tau^3(S_0T_1)/\mu s$
Tol	1.82	3.49	-	-
THF	0.74	2.74	22.56	57.83
BN	3.13	2.56	41.64	39.29

Theory

For calculations, the end groups of PDI molecules and PMI molecules were replaced with isopropyl and methyl ester groups, respectively, to limit the conformational manifold in order to make the calculations more tractable. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed with Gaussian16.¹² The geometries of ground-(S₀) and excited states (S₁ and T₁) were optimized at the B3LYP-GD3BJ/TZVP level in gas phase.¹³ TD-DFT calculations were performed with the B3LYP, WB97XD, PBE0 and CAMB3LYP functionals and the results compared with the experimental data. Based on the results of DFT and TD-DFT calculations, the molecular electrostatic potentials and the hole-electron character were analyzed using the Multiwfn 3.6 software package.¹⁴



Fig. S54. Top view (left) and side view of optimized ground state geometries of PMI (blue) and PDI (red).



Fig. S55. Overlaid optimized ground state-geometries of phenylene-/naphthylene-linked dimers. a) PDI-N-PDI (black) and PDI-P-PDI (red); b) PMI-N-PMI (blue) and PMI-P-PMI (green).

Table S9. Optimized structures of the ground state, the distance between oxygen in the PDI/PMI moieties and hydrogens in the phenylene/naphthylene spacers, and angles between the PDI/PMI and phenylene/naphthylene planes of **PDI-N-PDI**, **PDI-P-PDI**, **PMI-N-PMI** and **PMI-P-PMI** at the B3LYP-GD3BJ/TZVP level.



Table S10. Ground-state dipole moment analysis in Debye, of the compounds investigated.Both the total magnitude and the Cartesian vector components together with theirvisualization are shown.

Excited Compound		Dipole moment			
state	Magnitude	Vector (<i>x</i> , <i>y</i> , <i>z</i>)	Visualization		
	PDI-N-PDI	0.3469	(0, -0.3469, 0)		
So	PDI-P-PDI	0.3664	(-0.0006, -0.3527, -0.0991)		
	PMI-N-PMI	0.0397	(0, 0.0397, 0)	A state of the sta	
	PMI-P-PMI	0.5323	(0, 0.5323, 0)	X X X X X X X X X X X X X X X X X X X	

 Table S11. ESP analysis results on 0.001 a.u. isodensity surfaces (negative regions are indicated in blue, and positive regions are indicated in red).

Compound	Side view	Top view	Scale bar
PDI-N-PDI			0.04 - 0.01 0.01
PDI-P-PDI		Contraction of the second seco	-0.04
PMI-N-PMI			
PMI-P-PMI			



Fig. S56. Percentage of the isodensity surface area in each ESP range of PDI-N-PDI, PDI-P-PDI, PDI, PMI-N-PMI and PMI-P-PMI.

Table S12. The distribution of HOMOs and LUMOs of **PDI-N-PDI**, **PDI-P-PDI**,**PMI-N-PMI** and **PMI-P-PMI** at the B3LYP-GD3BJ/TZVP level.

Compound	НОМО	LUMO
PDI-N-PDI		
PDI-P-PDI	A Strate A	A CONTRACT OF A
PMI-N-PMI	Transfer to Jack Street	
PMI-P-PMI	Transfer to State of the state	THE REAL PROPERTY AND A DECIMAL OF A DECIMAL



Fig. S57. Calculated absorption spectra with various functionals (absorption spectra at B3LYP, WB97XD, PBE0 and CAMB3LYP in red, blue, green and purple, respectively) with the TZVP basis set compared with experimental data (absorption in toluene in black, absorption in THF in grey, absorption in benzonitrile in light grey) of a) **PDI-N-PDI**, b) **PDI-P-PDI**, c) **PMI-N-PMI** and d) **PMI-P-PMI**.

Table S13. Calculated electronic absorption energies (ΔE_{cal}), oscillator strengths (f) and excitation assignments of $S_0 \rightarrow S_1$ of **PDI-N-PDI**, **PDI-P-PDI**, **PMI-N-PMI** and **PMI-P-PMI** at the TD-PBE0/TZVP level (H – 1, H, L, and L + 1 represent HOMO – 1, HOMO, LUMO, and LUMO + 1, respectively; the percentage contributions of orbital pairs to the wave functions of excited states are given in parentheses) and real-space representation of hole- and electron-distributions of $S_0 \rightarrow S_1$ of **PDI-N-PDI**, **PDI-P-PDI**, **PMI-N-PMI** and **PMI-P-PMI** at TD-PBE0/TZVP level (isovalue = 0.001 a.u., green and blue regions denote the hole and electron distribution, respectively).

Compound	ΔE_{cal} (eV)	f	Excitation assignment	Occupied orbitial	Unoccupied orbitial	Electron-hole distribution
PDI-N- PDI	2.396	1.04	$\begin{array}{c} H \rightarrow L \\ 61.6\% \end{array}$	The second of the second		
			H-1 → L+1 29.8%	The second se		The second second
			$\begin{array}{c} \text{H-2} \rightarrow \text{L} \\ 8.1\% \end{array}$	*******		
PDI-P- PDI	2.402	1.29	$\begin{array}{c} H \rightarrow L + 1 \\ 49.8\% \end{array}$	A A A A A A A A A A A A A A A A A A A		
			H-1 → L 49.7%	AND	A A A A A A A A A A A A A A A A A A A	
PMI-N- PMI	2.483	1.19	$\begin{array}{c} H \rightarrow L \\ 56.6\% \end{array}$	T. C.	The second se	
			$\begin{array}{c} H-1 \rightarrow L+1 \\ 41.7\% \end{array}$	THE REAL PROPERTY OF THE PARTY	THE REAL PROPERTY AND A DECIMAL OF A DECIMAL	

PMI-P- PMI	2.484	1.19	$\begin{array}{c} H \rightarrow L+1 \\ 49.9\% \end{array}$	Free Contraction of the Contract	THE REAL PROPERTY.	
			H-1 → L 49.7%	Transfer Transfer	C. S.	



Fig. S58. Overlaid optimized geometries at the ground and excited state of a) **PDI-N-PDI**, b) **PDI-P-PDI**, c) **PMI-N-PMI** and d) **PMI-P-PMI** (S₀ in green, S₁ in orange, T₁ in purple).

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