Supporting Information for

Self-Assembly of Supramolecular Light-Harvesting Arrays From Covalent Multi-Chromophore Perylene-3,4:9,10-bis(dicarboximide) Building Blocks

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Proton nuclear magnetic resonance spectra were recorded on Mercury 400 NMR spectrometer using TMS as an internal standard. Laser desorption mass spectra were obtained with a PE Voyager DE-Pro MALDI-TOF mass spectrometer using dithranol as a matrix. Solvents and reagents were used as received except for MTHF, which was purified by passing it through a column of basic alumina immediately before use. Flash and thin-layer chromatography was performed using Sorbent Technologies (Atlanta, GA) silica gel. All solvents were spectrophotometric grade. Toluene was purified by passing it through series CuO and alumina columns (GlassContour).

Synthesis

1,4-dibromo-2,3,5,6-tetramethylbenzene (1)

1,2,4,5-tetramethylbenzene (5 g, 37.3 mmol) and iodine (0.197 g, 0.779 mmol) was added to 200 ml dichloromethane. A solution of Br_2 (4.5 ml, 87.8 mmol) in 20 ml dichloromethane was then added dropwise under a dry N_2 atmosphere to the reaction flask over 25 min while being careful to exclude all light. The reaction mixture was refluxed for 1 hour.

Excess Br_2 was quenched by the addition of 10 ml of 5 M aqueous sodium hydroxide. The organic fraction was then washed three times with distilled water and dried over $MgSO_4$. The solvent stripped on a rotary evaporator and the product recrystallized from dichloromethane to afford **1** (8.461 g, 78%). ^{1}H NMR ($CDCl_3$) δ: 2.484 (s, 12H).

***p*-(3,3,4,4-tetramethyl-2,5-dioxaborolyl)nitrobenzene (2)**

4-iodonitrobenzene (7g, 28.1 mmol), pinacolborane (6.22 ml, 42.2 mmol), triethylamine (12.0 ml, 84.3 mmol), and [1,1'-bis(diphenylphosphino)-ferrocene]dichloropalladium (II) (0.70g, 0.86 mmol), were added to 100 ml dioxane and heated to 90° C for 9 hours. The solvent was stripped on a rotary evaporator to give a black sticky residue. This was adsorbed onto silica gel and chromatographed using 1/1 (V/V) chloroform / hexane to afford **2** (4.42 g, 62%). ^{1}H NMR ($CDCl_3$) δ: 8.190 (d, J = 8.5 Hz, 2H), 7.957 (d, J = 8.5Hz, 2H), 1.361 (s, 12H).

1,2,4,5-tetramethyl-3,6-(p-nitrophenyl)-benzene (3)

(1) (2.31 g, 7.91 mmol) was added to 100 ml toluene. Sodium carbonate (2.53 g, 23.8 mmol) in 10 ml water was added to the reaction flask along with palladium (0) tetrakistriphenylphosphine (0.57 g, 0.493 mmol). **(2)** (4.11 g, 16.5 mmol) in 45 ml absolute ethanol was added and the reaction mixture was brought to reflux under dry N_2. The total reaction time was 4.25 hours. The aqueous fraction was separated from the organic fraction and then extracted three times with ethyl ether. All organic fractions were combined and the solvent removed on a rotary evaporator. The crude product was adsorbed onto silica gel and chromatographed using chloroform / hexanes (1:1) as the mobile phase to afford **(3)** (1.22 g, 41%). ^{1}H NMR ($CDCl_3$) δ: 8.348 (d, J = 8.5 Hz, 4H), 7.381 (d, J = 8.5 Hz, 4H), 1.941 (s, 12H).

1,2,4,5-tetracarboxylic acid-3,6-(p-nitrophenyl)-benzene (4)

(3) (0.998 g, 2.65 mmol), pyridine (38 ml), water (4.3 ml) were combined in a 100 ml r.b. flask and heated to 100° C. $KMnO_4$ (2.10 g, 13.3 mmol) was added over a 5 min. period. The reaction mixture was brought to reflux temperature and held for 5.5 hours after which the warm solution was separated from the MnO_2 by filtration, and the solvent distilled under reduced pressure. Water (50 ml) and NaOH (1.83 g, 45.6 mmol) were added to the residual solid, and heated to 100° C with stirring. $KMnO_4$ (2.15 g, 13.6 mmol) was added in small portions followed by heating to reflux for 3.25 hours. Absolute ethanol (6 ml) was carefully added to the hot reaction mixture to destroy excess $KMnO_4$. Solid MnO_2 was removed by filtering the solution while still warm. The filtrate was acidified (pH = 3) using aqueous HCl (37 %). After removing the solvent by evaporation, acetone was added to the residue, and the mixture stirred for 5 min. NaCl was removed from the mixture by filtration and excess solvent removed on a rotary evaporator to give **4** (1.11 g, 84%). M.S.: 496.1 (calcd. 496.04).

1,2:4,5-tetracarboxylic dianhydride-3,6-(p-nitrophenyl)-benzene (5)

Compound **4** (0.918 g, 1.85 mmol), glacial acetic acid (11.11 g, 185 mmol), and acetic anhydride (0.377 g, 3.69 mmol) were combined and refluxed for 3 hours under nitrogen with stirring. After cooling, the crystalline anhydride was filtered off, washed with acetic acid and dried to give **5** (0.315 g, 37%). M.S.: 460.13 (calcd. 460.02). ^{1}H NMR (CD_3COCD_3) δ: 8.461 (d, J = 8.5 Hz, 4H), 7.750 (d, J = 8.5 Hz, 4H),

1,7-dibromoperylene-3,4:9,10-tetracarboxydianhydride (6)

3,4:9,10-perylenetetracarboxylic dianhydride (28.52 g, 72.7 mmol) was added to 420 ml concentrated sulfuric acid and stirred at 55° C for 24 hrs. Iodine (0.685 g, 2.70 mmol) was added to the reaction mixture and stirred for an additional 5 hrs. at 55° C. Bromine (8.3 ml, 162 mmol) was added dropwise to the reaction flask over 1 hr. and stirred for 24 hrs. at 85° C.

Excess bromine was then displaced with N_2. Water (66 ml) was added dropwise to the cooled mixture and the precipitate filtered off. The crude product was washed with 220 ml 86 % H_2SO_4 followed by water (two times) to afford crude **6** (32.32 g, 81%). This product was used without further purification. M.S.: 549.0 (calcd. 550.11).

1,7-(3',5'-di-t-butylphenoxy)perylene-3,4:9,10-tetracarboxydianhydride (PDA) (7)

Compound **6** (4.01 g, 7.29 mmol), 3,5-di-*tert*-butylphenol (4.50 g, 23.9 mmol), and cesium carbonate (4.75 g, 13.5 mmol) were combined in 250 ml N,N-dimethylformamide and brought to reflux for 4 hours under nitrogen with stirring. The reaction mixture was then added to 80 ml cold acetic acid and cooled to -8° C overnight. The mixture was filtered, washed with cold methanol, and dried to yield **7** (5.22 g, 90%). M.S.: 799.9 (calcd. 800.3). ^{1}H NMR ($CDCl_3$) δ: 9.698 (d, J = 8.4, Hz, 2H), 8.681 (d, J = 8.4 Hz, 2H), 8.371 (s, 2H), 7.423 (t, J = 1.7, 2H), 7.034 (d, J = 1.7, 4H), 1.359 (s, 36H).

***N*-(2'-ethylhexyl)-1,7-(3',5'-di-t-butylphenoxy)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (PIA) (8)**

Compound **7** (1.65 g, 2.06 mmol) was added to 125 ml pyridine and heated to 50° C with stirring. 2-ethylhexylamine (0.139 g, 1.01 mmol) in 5 ml pyridine was added dropwise and the temperature raised to bring the reaction mixture to reflux. The total reaction time was 2 hrs. The reaction mixture was cooled, the solvent stripped on a rotary evaporator, and the crude product flash chromatographed using chloroform as the mobile phase to give **8** (0.406 g, 41%). The remaining material consists mostly of diimide and dianhydride that can be recycled. M.S.: 912.3 (calcd. 911.48). ^{1}H NMR ($CDCl_3$) δ: 9.707 (d, J = 2.6 Hz, 1H), 9.686 (d, J = 2.6 Hz, 1H), 8.641 (d, J= 5.035 Hz, 1H), 8.626 (d, J = 5.035 Hz, 1H), 8.364 (s, 1H), 8.332 (s, 1H), 7.387 (t, J

= 1.7 Hz,1H), 7.372 (t, J = 1.7 Hz ,1H), 7.027 (d, J = 1.7 Hz, 2H), 7.024 (d, J = 1.7 Hz 2H), 4.109 (m, 2H), 1.984 (m, 1H), 1.344 (m, 6H), 1.218 (s, 18H), 1.203 (s, 18 H), 0.914 (m, 8H).

***N,N*-(2'-ethylhexyl)-(4'-aminophenyl)-7-(3',5'-di-t-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (9)**

1,4-Phenylenediamine (0.200 g, 1.85mmol) and imidazole (1.72 g, 25.2 mmol) were added to 25 ml pyridine and heated to 120° C. Anhydride **8** (0.145 g, 0.181 mmol) in 3 ml pyridine was added dropwise over 20 minutes. The solution was refluxed for 8 hrs. The reaction mixture was then cooled to room temperature upon which 25 ml water, 30 ml chloroform and 10 drops of HCl were added. The aqueous fraction was separated, and then re-extracted three times with chloroform. All organic fractions were combined, washed with dilute $NaHCO_3$ solution, and then stripped of solvent. The crude product was purified by flash chromatography using chloroform as the mobile phase to yield **9** (0.132 g, 83%). M.S.: 1001.1 (calcd. 1001.53) ^{1}H NMR ($CDCl_3$) δ: 9.700 (d, J = 3.7 Hz, 1H), 9.687 (d, J = 3.7 Hz, 1H), 8.665 (d, J = 8.5 Hz, 1H), 8.632 (d, J = 8.5 Hz, 1H), 8.358 (s, 1H), 8.346 (s, 1H), 7.347 (m, 2H), 7.083 (d, J = 9.2 Hz), 7.039 (d, J = 1.8, 2H), 7.021 (d, J = 1.8Hz, 2H), 6.801 (d, J = 9.2 Hz, 2H), 4.096 (m, 2H), 1.902 (m, 1H), 1.340 (s, 18H), 1.329 (s, 18H), 1.252 (m, 6H), 0.915 (m, 4H), 0.858 (m, 4H).

3,6-(p-nitrophenyl)-benzene-1,2:4,5-bis(dicarboximide)-PDI$_2$ (10)

Compound **5** (0.025 g, 0.054 mmol), **9** (0.217 g, 0.216 mmol), and imidazole (0.300 g, 4.41 mmol) were added to 4 ml pyridine and refluxed under nitrogen with stirring for 24 hrs. The reaction mixture was then stripped of solvent, dissolved in 30 ml chloroform and washed with 50 ml water. The aqueous fraction was back extracted three times with chloroform. All organic fractions were combined and the solvent stripped on a rotary evaporator. The crude product was chromatographed using chloroform / acetone (90:10) as a mobile phase to afford **10**

(0.035 g, 27%). M.S.: 2426.8 (calcd. 2427.07) ^{1}H NMR ($CDCl_3$) δ: 9.637 (d, J = 7.9 Hz, 4H), 8.598 (dd, J = 7.9 Hz, 4H), 8.412 (d, J = 8.5 Hz, 4H), 8.269 (s, 2H), 8.242 (s, 2H), 7.753 (d, J = 8.5 Hz, 4H), 7.566 (d, J = 8.5 Hz, 4H), 7.449 (d, J = 8.5 Hz, 4H), 7.340 (s, 4H), 7.002 (br., 8H), 4.073 (m, 4H), 1.897 (m, 2H), 1.168 – 1.464 (m, 84H), 0.831 - 0.938 (m, 16H).

3,6-(p-aminophenyl)-benzene-1,2:4,5-bis(dicarboximide)-PDI$_2$ (11)

Compound **10** (0.030 g, 0.012 mmol), $SnCl_2(H_2O)_2$ (0.105 g, 0.465 mmol), were added to 5 ml tetrahydrofuran with 4 drops 37% HCl and stirred at room temperature for 5 hours. The reaction mixture was diluted with 50 ml DCM and washed once with 0.1 M sodium bicarbonate and two times with water. The organic solvent was removed on a rotary evaporator and the crude product filtered through a silica pad using DCM as the eluent to afford **11** (0.061 g, quant. yield). M.S.: 2366.1 (calcd. 2367.12) ^{1}H NMR ($CDCl_3$) δ: 9.662 (d, J = 7.9 Hz, 4H), 8.606 (m, 4H), 8.327 (s, 2H), 8.303 (s, 2H), 7.592 (d, J = 8.5 Hz, 4H), 7.342 (m, 10H), 7.016 (m, 10 H), 6.771 (d, J = 8.5 Hz, 4H), 3.91 - 4.12 (br. m, 8H), 1.905 (m, 2H), 1.4 – 1.1 (br. 84H), 0.9 – 0.8 (br. 16H).

PI-PDI$_4$ (12)

Compound **11** (0.020 g, 0.008 mmol) and anhydride **8** (0.040 g, 0.044 mmol), were added to 2 ml freshly distilled quinoline (KOH) with a catalytic amount of zinc acetate and heated to 180°C for 4.5 days adding an additional 0.035 g of **8** after 36 hrs. of reacting. The reaction mixture was cooled, poured into 45 ml cold methanol, the precipitated product recovered and chromatographed on silica gel using methylene chloride as the mobile phase to afford **12** (0.031 g, 88.4%). M.S.: 4151.1 (calcd. 4154.1).

1,7-(p-nitrophenyl)-3,4:9,10-perylene-tetracarboxydianhydride (13)

Dianhydride **6** (1.012 g, 1.84 mmol), p-(tri-n-butylstannyl)nitrobenzene (2.69 g, 6.53 mmol), and tetrakistriphenylphosphine-Pd(0) (60 mg, 0.055 mmol) were added to 50 ml of dry toluene. The mixture was sonicated for 5 min. then heated to reflux under N_2 for 36 hrs. The reaction mixture turned from bright red to deep purple. The solvent was stripped on a rotary evaporator and the residue filtered through a pad of silica gel to yield **13** (0.775 g, 66%). M.S.: 634.0 (calcd. 634.06).

***N,N*-(4-aminophenyl)-1,7-(p-nitrophenyl)-perylene-3,4:9,10-dicarboximide (14)**

Compound **13** (73 mg, 115 mmol), 1,4-phenylenediamine (0.129 g, 1.19 mmol), and imidazole (1.0 g, 15.6 mmol) were added to 60 ml of dry pyridine and brought to reflux under N_2 for 6 hrs, cooled, and washed with water (3) times to remove excess imidazole. The solvent was stripped on a rotary evaporator and the residue chromatographed on silica gel using 4/1 (V/V) $CHCl_3$/acetone as the eluent to yield **14** (0.051 g, 54%). M.S.: 813.4 (calcd. 814.18). ^{1}H NMR ($CDCl_3$) δ: 8.639 (s, 4H), 8.394 (dd, J = 8.5 Hz, 4H), 8.290 (d, J = 8.1 Hz, 1H), 8.258 (d, J = 8.1 Hz, 1H), 7.783 (dd, J = 8.5 Hz, 4H), 7.680 (s, 1H), 7.659 (s 1H), 7.076 (d, J = 8.7 Hz, 4H), 6.834 (d, J = 8.7 Hz, 4H), 3.87 (m, 4H).

***N,N*-(PDI)-1,7-(p-nitrophenyl)-perylene-3,4:9,10-dicarboximide (15)**

Compound **8** (0.104g, 0.114 mmol), **14** (0.030g, 0.047 mmol), and imidazole (200 mg, 3.1 mmol) were added to 5 ml pyridine and brought to reflux under N_2 for 24 hrs, cooled, diluted with chloroform and washed with water (3) times to remove imidazole. The solvent was stripped on a rotary evaporator and the solid chromatographed on silica gel using 9.5/0.5 (V/V) $CHCl_3$/ acetone as the eluent to yield **15** (0.079 g, 27%). M.S.: 2600.0 (calcd. 2601.11).

***N,N*-(PDI)-1,7-(p-aminophenyl)-perylene-3,4:9,10-dicarboximide (16)**

Compound **15** (0.063 g, 0.024 mmol), tin chloride-dihydrate (0.163 g, 0.72 mmol), and hydrochloric acid (37 %) (6 drops) were added to 8 ml tetrahydrofuran and stirred at room temperature under nitrogen for 9 hours. The reaction mixture was diluted with $CHCl_3$, washed with water (4) times and the solvent stripped on a rotary evaporator to afford **16** (0.061 g, quantit. conversion). M.S.: 2541.4 (calcd. 2541.16).

PDI_5 (17)

Compounds **16** (0.030 g, 0.012 mmol) and **8** (0.056 g, 0.061 mmol) were added to 2 ml of quinoline with a catalytic amount of zinc acetate and heated to 200°C for 24 hrs. The reaction mixture was poured into cold methanol, the precipitate recovered and chromatographed on silica gel using 9.5/0.5 (V/V) $CHCl_3$/ acetone as the eluent to yield **17** (0.015 g, 29%). M.S.: 4328 (calcd. 4328.10).

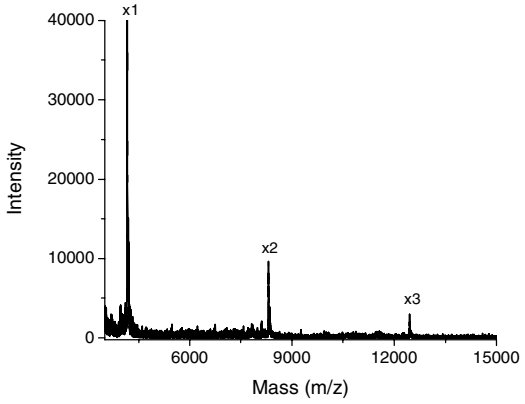


Figure S1A. MALDI/TOF mass spectrum of PI-PDI_4.

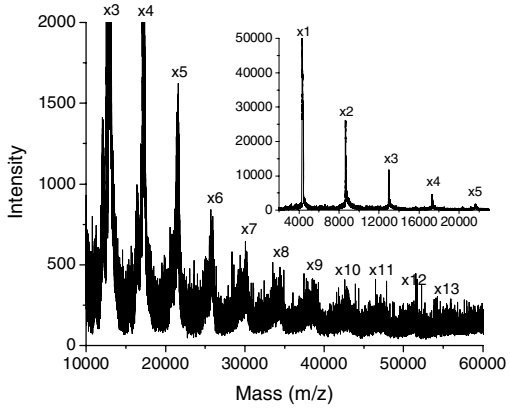


Figure S1B. MALDI/TOF mass spectrum of PDI_5.

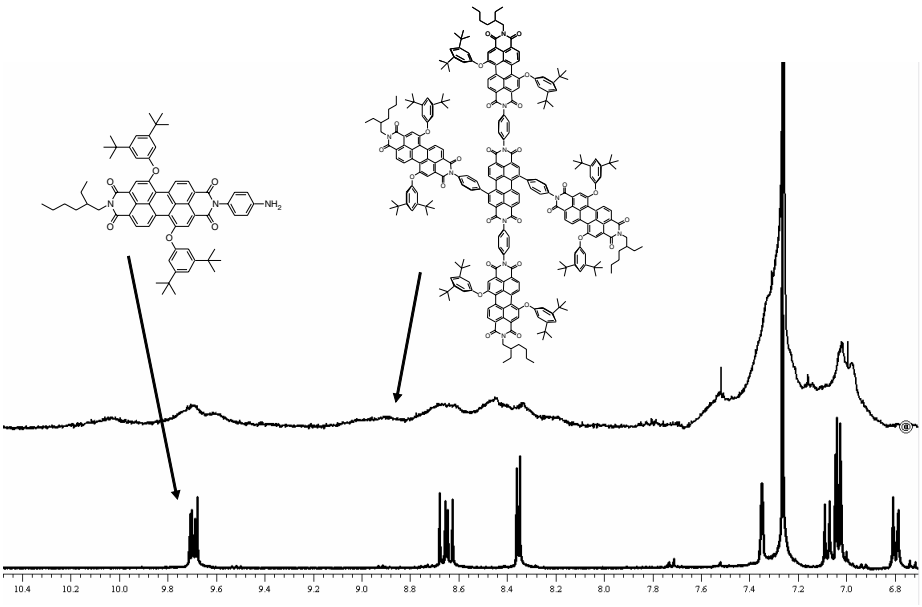


Figure S2. H-NMR spectra of the aromatic region of 10^{-3}M PDI_5 and a monomeric PDI reference molecule in $CDCl_3$.

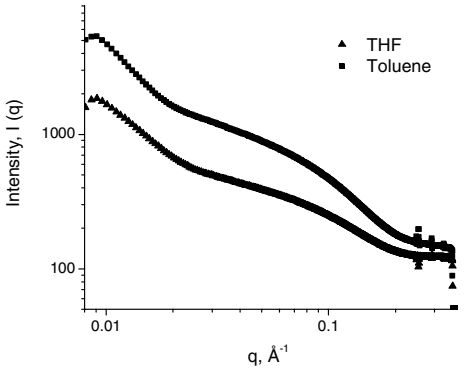
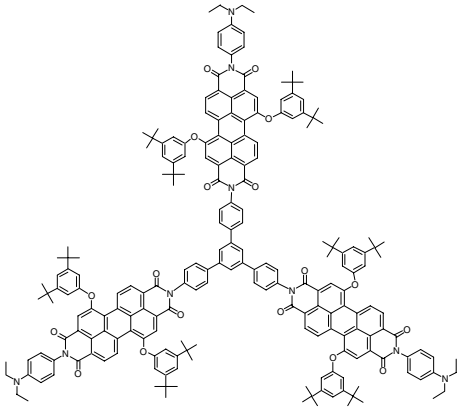


Figure S3. Experimental scattering data for PDI_5 (low *q* region).



tris(DEA-PDI)

Figure S4A. Structure of compound used as a standard for SAXS data.

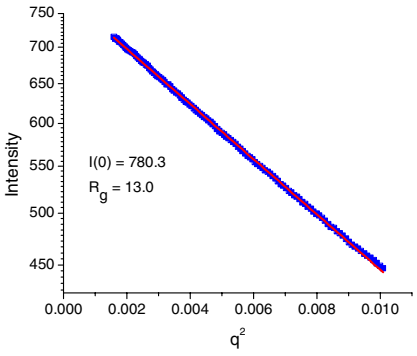


Figure S4B. Guinier fit (red line) of the SAXS for the tris(DEA-PDI) dimer in toluene. Dimeric nature of the compound in toluene was indicated by vapor pressure osmometry and NMR measurements.

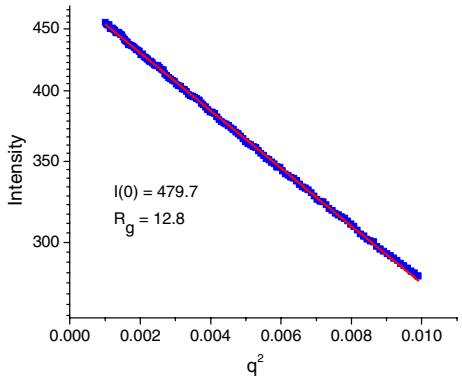


Figure S4C. Guinier fit (red line) of the SAXS data for the tris(DEA-PDI) dimer in THF.

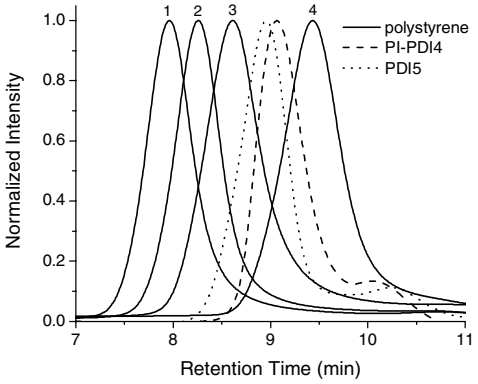


Figure S5. GPC traces for polystyrene references having molecular weights of (1) 29,300 (2) 18,700 (3) 13,700 (4) 3,700 and PI-PDI_4 and PDI_5.

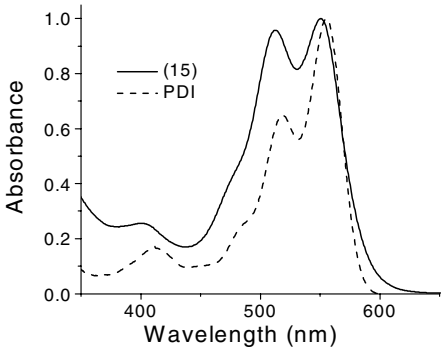


Figure S6. Normalized optical absorption spectra of (**15**) and PDI monomer.

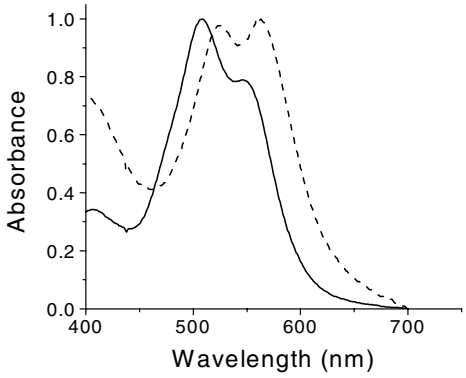


Figure S7. Optical absorption spectra of PDI_5 (——) and PI-PDI_4 (-----) spin coated on a methylsilylated quartz surface.

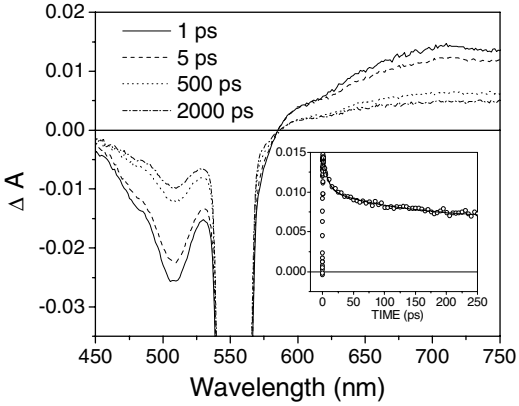


Figure S8. Transient absorption spectra of PDI_4-PI following excitation at 550 nm. Inset: Kinetics monitored at 715 nm.