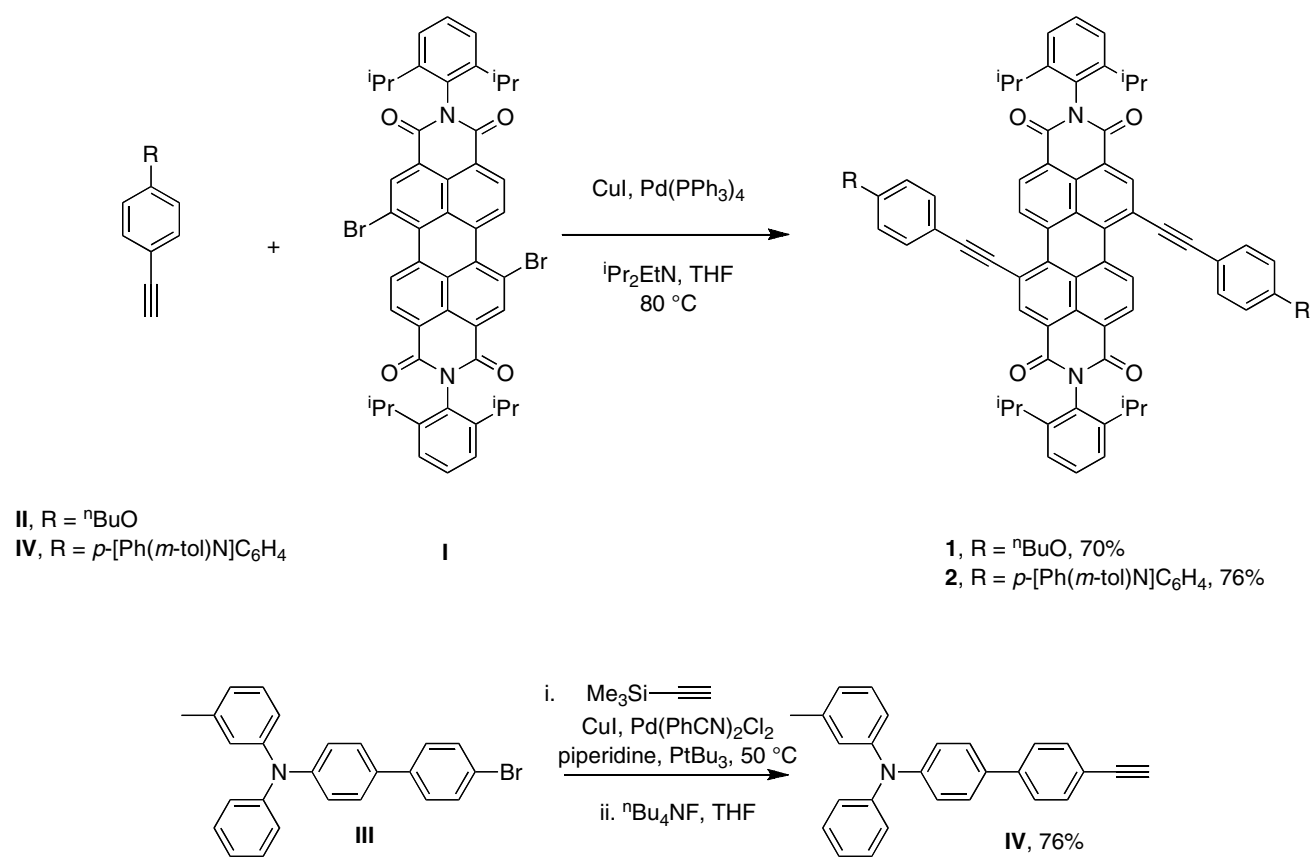


Inter versus intra-molecular photoinduced charge separation in solid films of donor/acceptor molecular dyads

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Supplementary Information

Experimental Details for Synthesis



Scheme S1. Synthesis of **1**, **2**, and the intermediate, **IV**.

Compounds **1** and **2** were synthesized as shown in Scheme S1.

1. CuI (0.008 g, 0.042 mmol) and Pd(PPh₃)₄ (0.02 g, 0.02 mmol) were added to a deoxygenated solution of **I**¹ (0.20 g, 0.23 mmol) in THF (10 mL) and ¹Pr₂EtN (20 mL). After the resultant solution was further deoxygenated for 10 minutes, **II** (0.11 g, 0.63 mmol) was added. The reaction was heated at 80 °C under argon for 15 h. After cooling to room temperature, the reaction mixture was poured into 2 M HCl (150 ml) solution and extracted with CH₂Cl₂. The organic phase was dried over MgSO₄ and was filtered. The solvents were removed under reduced pressure and the residue was purified by flash chromatography eluting with 1:1 CH₂Cl₂ / hexane to give **1** (0.17 g, 70%). ¹H NMR (300 MHz, CDCl₃) δ 10.26 (d, *J* = 8.4 Hz, 2H), 9.05 (s, 2H), 8.83 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 4H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 4H), 6.97 (d, *J* = 7.5 Hz, 4H), 4.05 (t, *J* = 6.5 Hz, 4H), 2.80 (septet, *J* = 6.6 Hz, 4H), 1.75 (m, 4H), 1.60-1.52 (m, 4H), 1.20 (d, *J* = 6.9 Hz, 24H), 0.90 (t, *J* = 7.2 Hz, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 163.9, 163.7, 160.9, 146.1, 138.6, 135.2, 134.3, 134.0, 131.3, 130.9, 130.2, 128.6, 127.9, 124.6, 123.4, 122.5, 121.4, 115.5, 114.2 (two peaks separated by ca. 3.7 Hz), 100.12, 90.3, 68.4, 31.6, 29.7, 24.5, 19.6, 14.3. HRMS (MALDI): calcd. for C₇₂H₆₆N₂O₆: 1054.4921; found: 1054.5165. Elemental analysis: calcd. for C₇₂H₆₆N₂O₆, C 81.95, H 6.30, N 2.65; found C 81.45, H 6.56, N 2.61.

IV. Pd(PhCN)₂Cl₂ (0.06 g, 0.15 mmol), CuI (0.06 g, 0.30 mmol) and piperidine (15 mL) were added to an ampoule containing **III**² (2.02 g, 4.86 mmol) and the mixture was deoxygenated for 10 min. P^tBu₃ (0.59 g of 10% wt. solution in hexane, ca. 0.30 mmol) was added and the mixture was further deoxygenated for 15 min. Me₃SiC≡CH (1.0 mL, 7.1 mmol) was added and the reaction mixture was heated to 50 °C for 5 h. The mixture was then poured into 2 M aqueous hydrochloric acid (75 mL) and was extracted with ethyl acetate. The combined organic extracts were washed with 2 M aqueous hydrochloric acid (50 mL) and water (100 mL), dried over anhydrous magnesium sulfate and filtered. After removal of solvent, the residue was purified by column chromatography, eluting with hexane. After removal of solvent, the resulting solid (1.90 g) was dissolved in THF (10 mL) and 1.0 M ⁿBu₄NF

THF solution (10 mL) was added. The resulting mixture was stirred at room temperature under nitrogen for 3 h. After 2 M aqueous hydrochloric acid (5 mL) was added, the mixture was further stirred for 10 min and was extracted with CH₂Cl₂. The organic extracts were dried over anhydrous magnesium sulfate and filtered; the solvent was removed under reduced pressure and the residue was recrystallized from ethyl acetate. 1.26 g (76%) of a brown solid was obtained. ¹H NMR (500 MHz, CDCl₃) δ 7.52 (s, 4H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.10 (m, 4 H), 7.02 (t, *J* = 7.5 Hz), 6.94 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 3.09 (s, 1H), 2.26 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 147.6, 147.4, 147.3, 140.9, 139.1, 133.4, 132.4, 129.2, 129.0, 127.5, 126.2, 125.3, 124.4, 124.0, 122.9, 121.8, 120.2, 83.7, 77.6, 21.5 (one peak missing from the aromatic region, presumably due to overlap). HRMS (EI): calcd. for C₂₇H₂₁N *m/z*: 359.1674; found 359.1661. Elemental analysis: calcd. for C₂₇H₂₁N, C 90.21, H 5.89, N 3.90; found C 89.94, H 5.88, N 3.90.

2. Compound **2** was synthesized in an analogous fashion to **1** using the following quantities of reagents: **I** (0.22 g, 0.25 mmol), **IV** (0.22 g, 0.61 mmol), toluene (10 mL), dioxane (5 mL), ¹Pr₂EtN (10 mL), Pd(PhCN)₂Cl₂ (0.02 g, 0.05 mmol), CuI (0.01 g, 0.05 mmol), P^tBu₃ (0.21 g, 10% wt. solution in hexane, ca. 0.10 mmol). Yield: 0.27 g (76%). ¹H NMR (500 MHz, CDCl₃): δ 10.25 (d, *J* = 8.0 Hz, 2H), 9.03 (s, 2H), 8.85 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 4H), 7.68 (d, *J* = 8.5 Hz, 4H), 7.52 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.27 (m, 4H), 7.15 (m, 10H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 2.79 (septet, *J* = 6.5 Hz, 4H), 2.27 (s, 6H), 1.20 (d, *J* = 6.5 Hz, 24H). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 163.9, 163.6, 148.5, 147.9, 147.8, 146.1, 142.5, 139.7, 138.7, 135.2, 134.6, 133.5, 132.8, 131.5, 130.9, 130.2, 129.7, 129.6, 128.8, 128.6, 128.1, 127.3, 126.0, 125.1, 124.8, 124.6, 123.7, 123.6, 122.7, 122.4, 121.1, 120.5, 99.7, 91.8, 29.7, 24.4, 21.8, (four peaks missing from aromatic region, presumably due to overlap). HRMS (MALDI): *m/z* calcd. for C₁₀₂H₈₀N₄O₄: 1424.6180; found: 1424.6104. Elemental Analysis: calcd. for C₁₀₂H₈₀N₄O₄, C 85.93, H 5.66, N 3.93; found C 85.88, H 5.66 N 3.91.

Absorption Spectra

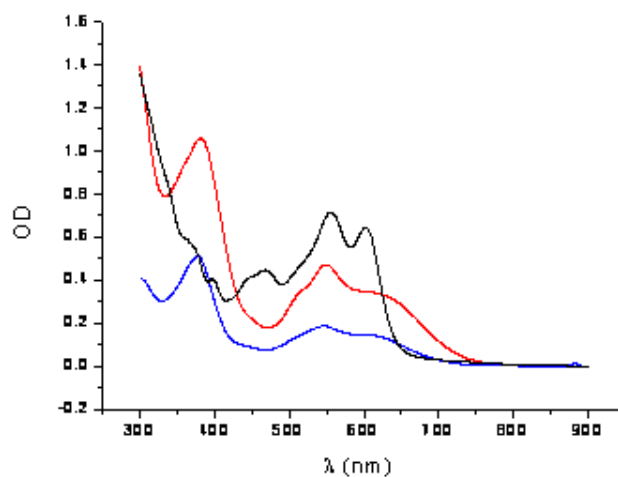


Figure S1: The UV-visible spectra of as-prepared film of **2** (red) and in chloroform (blue), and **1** film (black); films were spin-coated on untreated glass substrates at 500 rpm for 60 s.

Emission Spectra

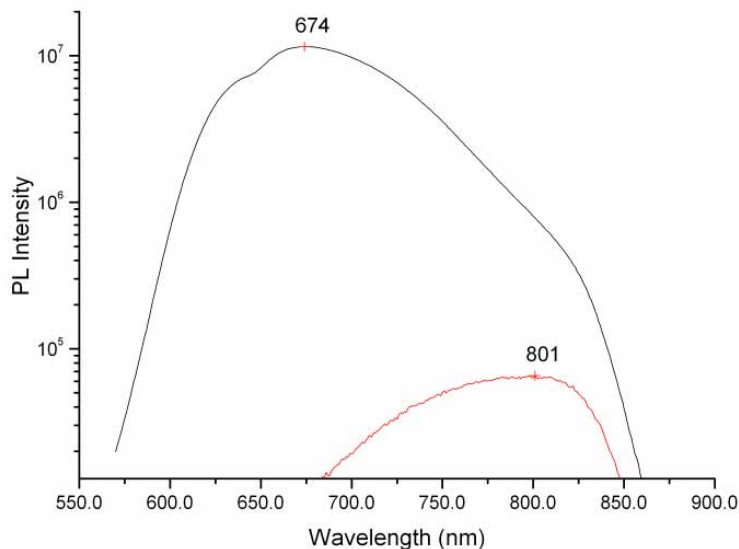


Figure S2: Steady state emission of as-prepared **1** and **2** films, excited at 500 nm, spin coated at 500 rpm for 60 s on glass substrates.

Quantum Chemical Calculations

The calculations were performed using the Gaussian 03 suite³ at the B3LYP/6-31G(d) level of theory. Both the TPA-PDI-TPA triad (**2**) and the PDI reference compound (**1**) were geometry optimized with C_2 symmetry constraints. The optimized structures were used for frequency calculations, which confirmed a full optimization (i.e. no virtual frequencies). TD-DFT calculations revealed that for the lowest excited state, for both systems, the dominant singly excited configuration is HOMO \rightarrow LUMO. Thus, the lowest transition in **2** has a much larger donor-to-acceptor charge-transfer character than that of the reference compound (**1**) (see Scheme 1). According to Hush-theory the relatively high oscillator strength and energy of the transition suggest a considerable electronic coupling between the donor (TPA) and acceptor (PDI).⁴ This is most probably due to the triple bond attached to the PDI core, which allows for an efficient extension of the core orbitals towards the donor. Design criteria to consider when improving the charge dissociation in films of TPA-PDA-TPA could involve inserting a phenyl instead

of the triple bond and removing some bulky substituents. This would potentially balance the *intra* and *intermolecular* electronic coupling for more efficient dissociation.

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