Electronic Supplementary Information

Excimer Formation in Cofacial and Slip-Stacked Perylene-3,4:9,10-bis(dicarboximide) Dimers on a Redox-Inactive Triptycene Scaffold

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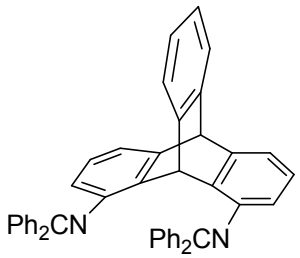
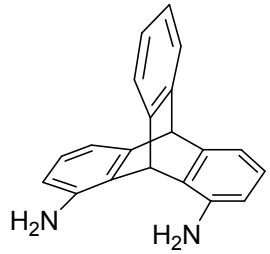
Synthesis

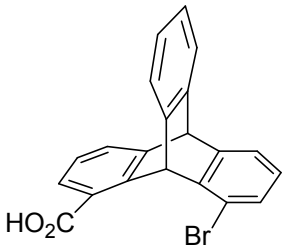
All reagents and solvents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Flash chromatography was performed using Sorbent Technologies (Atlanta, GA) silica gel. ^{1}H and ^{13}C NMR spectra were acquired at 500 MHz and 126 MHz, respectively, on a Bruker Avance III spectrometer. Low resolution mass spectrometry was performed on a Thermo Finnegan LCQ (ESI) spectrometer or a Bruker Autoflex III MALDI spectrometer. High resolution mass spectrometry was performed on an Agilent 6210 LC-TOF mass spectrometer. Characterization studies were performed at the Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern University.



Compound P1. In a glovebox, a microwave reaction vial was charged with 1,8-dibromotriptycene (500 mg, 1.2 mmol), tris(dibenzylideneacetone)dipalladium(0) (22 mg, 0.024 mmol), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (28 mg, 0.049 mmol), and sodium tert-butoxide (350 mg, 3.6 mmol) in 10 mL anhydrous toluene. The vial was then sealed, and the mixture was degassed with N_2 for 30 minutes, after which benzophenone imine (0.24 mL, 1.5 mmol) was injected and the mixture was heated to 100 °C for 24 hr. The mixture was allowed to cool to room temperature then was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL) and separated. The aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was purified on silica (hexanes/EtOAc) to afford the product as a white solid (590 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (m, 6H), 7.74 (d, J = 7.6 Hz, 2H), 7.52-7.45 (m, 4H), 7.45-7.39 (m, 8H), 7.23 (t, J = 7.5 Hz, 4H), 7.13-7.07 (m, 2H), 6.96 (d, J = 7.3 Hz, 2H), 6.65 (t, J = 7.5 Hz, 2H), 6.00 (s, 1H), 5.33 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) 168.82, 146.49, 146.35, 139.19, 136.30, 135.84, 132.45, 130.68, 130.49, 130.09, 129.95, 129.53, 129.34, 129.27, 129.14, 129.02, 128.51, 128.29, 128.25, 128.18, 128.11, 127.84, 127.79, 127.59, 124.71, 124.66, 123.99, 123.33, 118.64, 116.86, 77.24, 77.15, 54.45, 53.47, 43.79, 31.00. MS (ESI): *m/z* 613.64 $[M+H]^+$

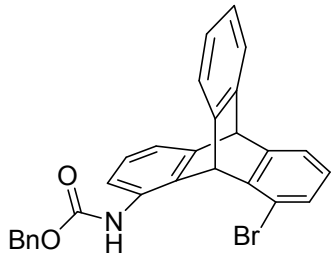


Compound P2. A 10 mL round bottom flask was flame-dried and charged with **P1** (200 mg, 0.33 mmol) and 4 mL MeOH. To this was added NaOAc (213 mg, 1.6 mmol) and $NH_2OH \cdot HCl$ (82 mg, 1.2 mmol) at once. The resulting mixture was stirred at room temperature for 12 hr then was partitioned between CH_2Cl_2 (25 mL) and H_2O (25 mL) and separated. The aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was purified on silica (hexanes/EtOAc) to afford the product as a white solid (65 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.42 (m, 2H), 7.41-7.33 (m, 4H), 6.98 (m, 1H), 6.89 (d, J = 7.3 Hz, 1H), 6.78 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 5.58 (s, 1H), 5.32 (s, 1H), 2.40 (br s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.92, 140.33, 136.20, 132.61, 130.21, 129.50, 128.32, 127.82, 125.74, 125.16, 124.91, 123.64, 115.40, 113.99, 54.75, 41.73. MS (ESI): *m/z* 285.28 $[M+H]^+$



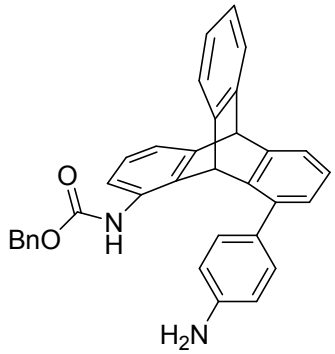
Compound P3. To a solution of 1,8-dibromotriptycene (500 mg, 1.2 mmol) in 10 mL anhydrous THF cooled to -78 °C was added was added a 1.6 M solution of n-butyllithium in hexanes (0.75 mL, 1.2 mmol) dropwise. After stirring for 1 hr at -78 °C, the reaction was

bubbled with dry CO_2 (from sublimed dry ice) for 1 hr. Afterwards, the solution was bubbled for an additional 1 hr while being allowed to warm up to room temperature. The reaction was then quenched with ~2 mL of 1 N aqueous HCl and partitioned between CH_2Cl_2 (25 mL) and H_2O (25 mL) which was acidified to pH < 1 with 1 N HCl. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified on silica (hexanes/CH_2Cl_2 then CH_2Cl_2/MeOH) to afford the product as a white solid (270 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.1 Hz, 2H), 7.46 (s, 1H), 7.42 (m, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.07 (m, 2H), 6.88 (t, J = 7.7 Hz, 1H), 5.51 (s, 1H), 4.36 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.58, 147.67, 144.99, 144.13, 143.58, 129.21, 128.53, 127.86, 126.89, 126.56, 125.77, 125.29, 125.05, 124.82, 123.63, 122.71, 120.02, 77.24, 76.91, 68.01, 57.71, 49.42, 25.64. MS (ESI): *m/z* 374.93 $[M-H]^-$



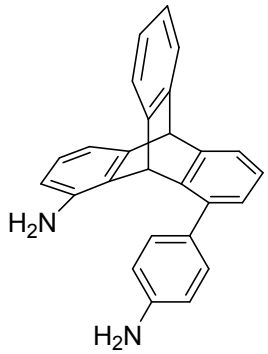
Compound P4. A flame-dried 25 mL round bottom flask was charged with **P3** (204 mg, 0.54 mmol) in 3 mL anhydrous toluene. To this suspension was added diphenylphosphoryl azide (0.15 mL, 0.70 mmol), dropwise, over 5 min. Triethylamine (0.098 mL, 0.70 mmol) was then added, dropwise, over 3 min, clearing up the suspension. After 15 min of stirring, benzyl alcohol (0.084 mL, 0.81 mmol) was added, dropwise, over 5 min and the resulting solution was heated to

85 °C. After stirring at 85 °C for 12 hr, the reaction mixture was allowed to cool then concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc) to afford the product as a white solid (227 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.33 (m, 7H), 7.30 (d, J = 7.2 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.03 (m, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.80 (br s, 1H), 6.02 (s, 1H), 5.44 (s, 1H), 5.28 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.00, 146.35, 144.86, 143.93, 143.08, 136.19, 128.68, 128.38, 126.84, 126.50, 126.03, 125.76, 125.72, 125.53, 125.51, 124.46, 124.43, 123.73, 123.70, 122.77, 122.11, 119.22, 66.32, 54.55, 47.74. MS (ESI): *m/z* 481.97 $[M+H]^+$

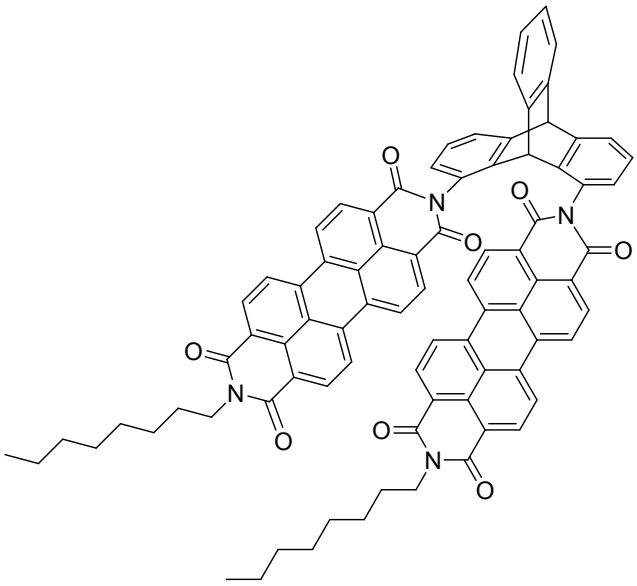


Compound P5. A flame-dried 50 mL round bottom flask was charged with **P4** (501 mg, 1.04 mmol) and 4-aminophenylboronic acid pinacol ester (341 mg, 1.56 mmol) in 13.5 mL toluene, 2.7 mL EtOH, and 5.4 mL 0.5 M aqueous K_2CO_3. The resulting suspension was then degassed by bubbling N_2 for 30 min followed by addition of tetrakis(triphenylphosphine)palladium(0) (60 mg, 0.052 mmol). After stirring for 8 hr at 85 °C, the reaction mixture was cooled to room temperature and partitioned between CH_2Cl_2 (25 mL) and H_2O (25 mL). The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc) to afford the

product as a white solid (390 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.40 (m, 7H), 7.36 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.3 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.02 (m, 3H), 6.96 (m, 2H), 6.81 (br s, 1H), 6.63 (br d, J = 6.1 Hz, 2H), 5.74 (s, 1H), 5.50 (s, 1H), 5.38 (d, J = 12 Hz, 1H), 5.17 (d, J = 12 Hz, 1H), 3.54 (br s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.02, 145.65, 145.57, 144.22, 141.88, 137.88, 136.34, 131.90, 130.49, 130.14, 128.76, 128.48, 126.22, 125.83, 125.43, 125.13, 124.91, 123.93, 123.66, 122.39, 115.06, 67.30, 54.63, 45.22. MS (ESI): *m/z* 495.33 $[M+H]^+$

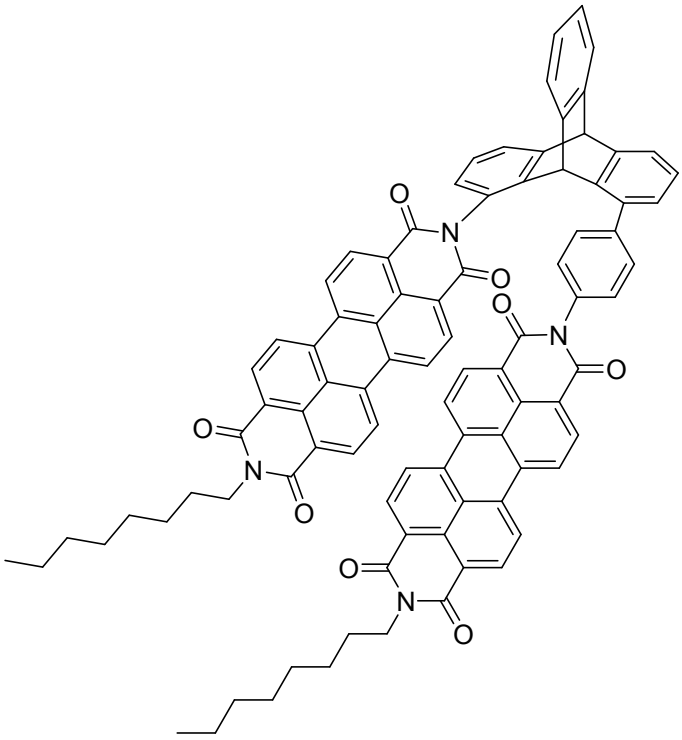


Compound P6. A Parr bottle was charged with **P5** (303 mg, 6.1 mmol) and 10% Pd/C (35 mg) in EtOAc (20 mL) and MeOH (15 mL). The bottle was then mounted to a Parr Shaker Hydrogenation Apparatus and flushed with H_2 (3 times at 40 psi), and then set to shake under H_2 (45 psi) for 8 hr. The resulting solution was pass through celite and rinsed with EtOAc, then concentrated *in vacuo* to afford a crude yellow oil (290 mg) which was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.1 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 8.3 Hz, 2H), 7.01-6.92 (m, 4H), 6.90 (d, J = 7.1 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 6.39 (m, 1H), 5.69 (s, 1H), 5.41 (s, 1H), 3.73 (br s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.82, 130.44, 126.13, 125.86, 125.12, 124.94, 124.61, 123.62, 123.42, 122.34, 115.10, 114.89, 113.51, 54.81, 44.63. MS (ESI): *m/z* 361.49 $[M+H]^+$



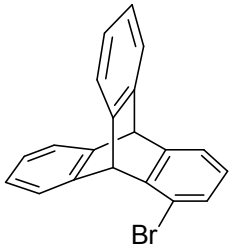
Compound 1. A mixture of **P2** (60 mg, 0.21 mmol), **Octyl-PIA**[1] (534 mg, 1.05 mmol) and imidazole (5 g) was heated to 140 °C for 18 hr. The mixture was then cooled and partitioned between CH_2Cl_2 (100 mL) and 2 N aqueous HCl (100 mL). The organic layer was separated and the aqueous layer was extracted four times with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (CH_2Cl_2/acetone) followed by chromatography on alumina (CH_2Cl_2/MeOH) to afford a dark red solid product (114 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, J = 7.9 Hz, 2H), 8.32 (d, J = 7.8 Hz, 2H), 8.29 (appar dd, J = 7.8, 5.1 Hz, 4H), 8.23 (appar dd, J = 8.0, 2.4 Hz, 4H), 8.13 (d, J = 8.3 Hz, 4H), 7.53 (d, J = 7.4 Hz, 2H), 7.48 (d, J = 7.0 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.15 (m, 3H), 6.96 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.9 Hz, 1H), 5.69 (s, 1H), 5.02 (s, 1H), 4.22 (m, 4H), 1.74 (m, 4H), 1.39 (m, 4H), 1.30-1.25 (br s, 16H), 0.89 (m, 6H). ^{13}C NMR (126 MHz, $C_2Cl_4D_2$) δ 162.72, 162.42, 137.20, 132.38, 131.58, 130.51, 130.31, 130.11, 128.68, 128.53, 127.76, 127.55, 127.36, 125.90, 125.45, 123.67, 122.95, 122.89, 122.72, 122.47, 120.44,

54.96, 32.00, 31.22, 29.88, 29.56, 29.52, 29.46, 28.20, 27.40, 22.86, 14.42. MS (MALDI): *m/z* 1254.540 [M^-]

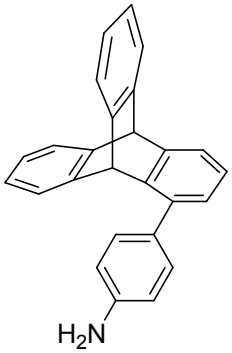


Compound 2. A mixture of **P6** (50 mg, 0.14 mmol), **Octyl-PIA**[1] (279 mg, 0.55 mmol) and imidazole (3 g) was heated to 140 ^oC for 18 hr. The mixture was then cooled and partitioned between CH_2Cl_2 (100 mL) and 2 N aqueous HCl (100 mL). The organic layer was separated and the aqueous layer was extracted four times with CH_2Cl_2 (50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (CH_2Cl_2/acetone) followed by chromatography on alumina (CH_2Cl_2/MeOH) to afford a dark red solid product (88 mg, 48%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.83 (t, J = 7.9 Hz, 2H), 8.78 (d, J = 7.9 Hz, 2H), 8.61 (d, J = 8.1 Hz, 2H), 8.50 (d, J = 8.0 Hz, 2H), 8.48 (d, J = 8.1 Hz, 2H), 8.18 (br s, 4H), 7.97 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 7.21 (m, 4H), 7.09-7.03 (m, 4H), 7.02 (d, J = 7.9 Hz, 1H), 6.98 (d,

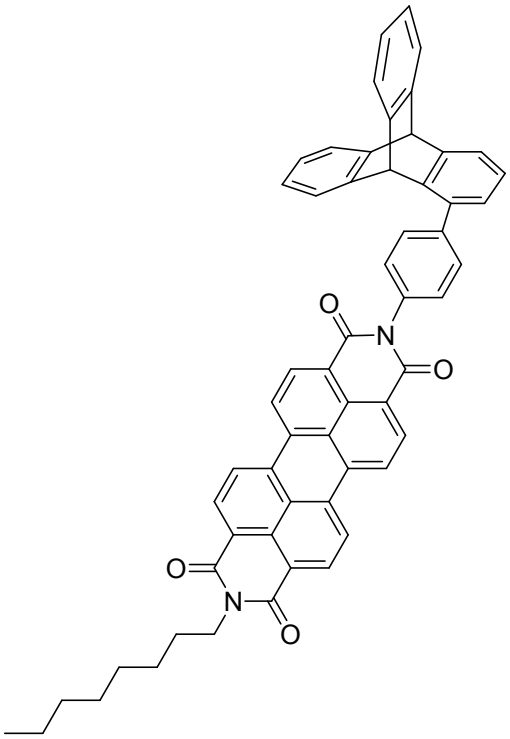
J = 7.6 Hz, 1H), 6.64 (br s, 1H), 5.64 (s, 1H), 5.12 (s, 1H), 4.27 (m, 2H), 2.22 (m, 2H), 2.01 (m, 4H), 1.83 (m, 4H), 1.31-1.16 (m, 24H), 0.94-0.79 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.16, 162.18, 145.25, 134.42, 133.72, 131.79, 131.46, 129.31, 127.75, 125.40, 123.36, 123.13, 122.12, 53.46, 47.10, 40.78, 39.64, 39.64, 31.91, 31.85, 31.78, 29.43, 29.35, 29.13, 28.33, 27.68, 27.28, 26.89, 22.72, 22.65, 14.17, 14.11. MS (MALDI): *m/z* 1330.727 [M^-]



Compound P7. To a solution of 1,8-dibromotriptycene (300 mg, 0.73 mmol) in 2 mL anhydrous THF cooled to -78 °C was added was added a 1.6 M solution of n-butyllithium in hexanes (0.455 mL, 0.73 mmol) dropwise. After stirring for 2 hr at -78 °C, the reaction was allowed to warm. The reaction was then quenched with ~3 mL of 1 N aqueous HCl and partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified on silica (hexanes/CH_2Cl_2) to afford the product as a white solid (102 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.40 (m, 2H), 7.30 (d, J = 7.3 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.02 (m, 4H), 6.85 (appar q, J = 7.5 Hz, 1H), 5.89 (s, 1H), 5.43 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.27, 145.71, 144.51, 143.18, 129.02, 127.68, 126.89, 126.56, 125.77, 125.29, 125.05, 124.82, 123.63, 122.71, 120.02, 77.24, 76.91, 68.01, 57.71, 49.42, 25.64.



Compound P8. A flame-dried 50 mL round bottom flask was charged with **P7** (100 mg, 0.30 mmol) and 4-aminophenylboronic acid pinacol ester (99 mg, 0.45 mmol) in 3.7 mL toluene, 0.75 mL EtOH, and 1.5 mL 0.5 M aqueous K_2CO_3. The resulting suspension was then degassed by bubbling N_2 for 30 min followed by addition of tetrakis(triphenylphosphine)palladium(0) (18 mg, 0.015 mmol). After stirring for 8 hr at 85 ^oC, the reaction mixture was cooled to room temperature and partitioned between CH_2Cl_2 (15 mL) and H_2O (15 mL). The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (hexanes/EtOAc) to afford the product as a white solid (72 mg, 69%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.4 Hz, 1H), 7.35 (d, J = 7.4 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 7.14 (m, 1H), 6.95 (m, 4H), 6.81 (t, , J = 7.8 Hz 1H), 6.78 (br s, 2H), 6.60 (br d, J = 7.5 Hz, 2H), 6.09 (s, 1H), 5.44 (s, 1H). MS (ESI): *m/z* 346.51 $[M+H]^+$.



Compound 3. A mixture of **P8** (3.7 mg, 0.010 mmol), **Octyl-PIA**[1] (10 mg, 0.022 mmol) and imidazole (0.15 g) was heated to 140 °C for 18 hr. The mixture was then cooled and partitioned between CH_2Cl_2 (10 mL) and 2 N aqueous HCl (10 mL). The organic layer was separated and the aqueous layer was extracted four times with CH_2Cl_2 (5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (CH_2Cl_2/acetone) followed by chromatography on alumina (CH_2Cl_2/MeOH) to afford a spectroscopic quantity of the dark red solid product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, J = 7.8 Hz, 2H), 8.73 (m, 4H), 8.70 (m, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.44 (m, 3H), 7.35 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.12 (m, 2H), 7.03 (m, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.23 (s, 1H), 5.52 (s, 1H), 4.21 (m, 2H), 2.01 (m, 2H), 1.77 (m, 2H), 1.38-1.27 (m, 8H), 0.90-0.85 (m, 3H). ^{13}C NMR (126 MHz, $C_2Cl_4D_2$) δ 162.72, 132.38, 130.51, 130.31, 130.11, 127.76, 127.55, 127.36, 125.45, 122.95, 120.44, 69.96, 54.96, 32.00, 29.88, 29.56, 29.46, 28.20, 27.40, 22.86, 14.42. MS (MALDI): *m/z* 830.377 [M^-].

Steady-state Spectroscopy. Toluene and non-stabilized HPLC grade dichloromethane were dried on a Glass Contour solvent system. Steady-state absorption spectra were acquired at ambient temperature on a Shimadzu 1601 UV/Vis spectrometer. Steady-state fluorescence spectra were acquired at ambient temperature on a PTI Quantamaster 40 with an emission correction file generated using a Newport Corporation radiometric power supply and calibrated 45 watt quartz tungsten halogen lamp.

Time Resolved Fluorescence. Picosecond time-resolved fluorescence (TRF) measurements were made using a streak camera system (Hamamatsu C4780 Streakscope). Excitation pulses at 415 nm were generated using a laboratory-built, cavity-dumped, Ti:sapphire laser system (center wavelength, 832 nm; spectral width, 55 nm; pulse duration, 25 fs; repetition rate, 820 kHz) followed by frequency doubling in a 200 μm thick lithium triborate crystal. A parabolic mirror was used to focus the excitation beam into the sample, and the subsequent fluorescence was collected in a backscattering geometry using the same parabolic mirror. Magic angle detection was used to avoid polarization effects. The IRFs were 750, 370, 180, 85, 44, and 30 ps (fwhm) in the 50, 20, 10, 5, 2, and 1 ns full scale time ranges, respectively. All data were acquired in single-photon counting mode using the Hamamatsu HPD-TA software.

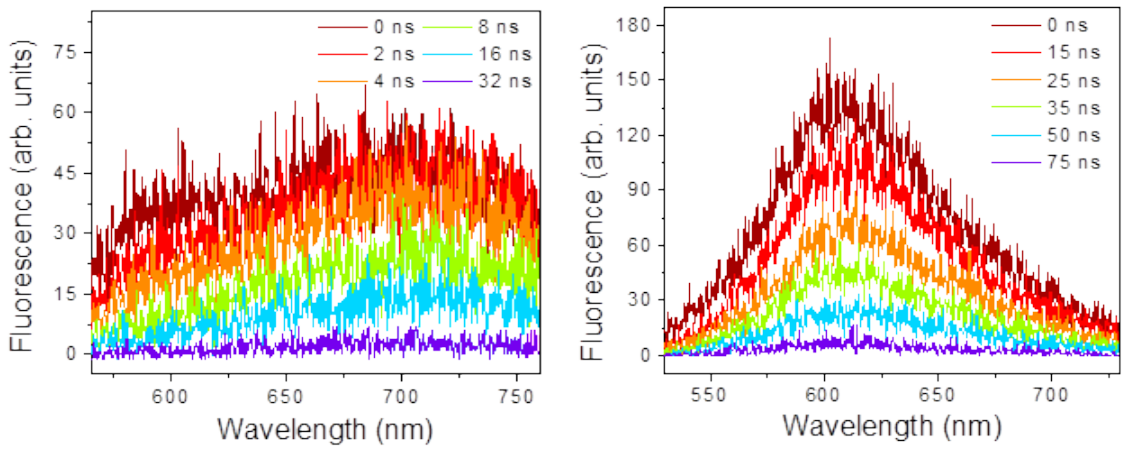


Figure S1: Time-resolved fluorescence spectra of **1** (left) and **2** (right) in dichloromethane.

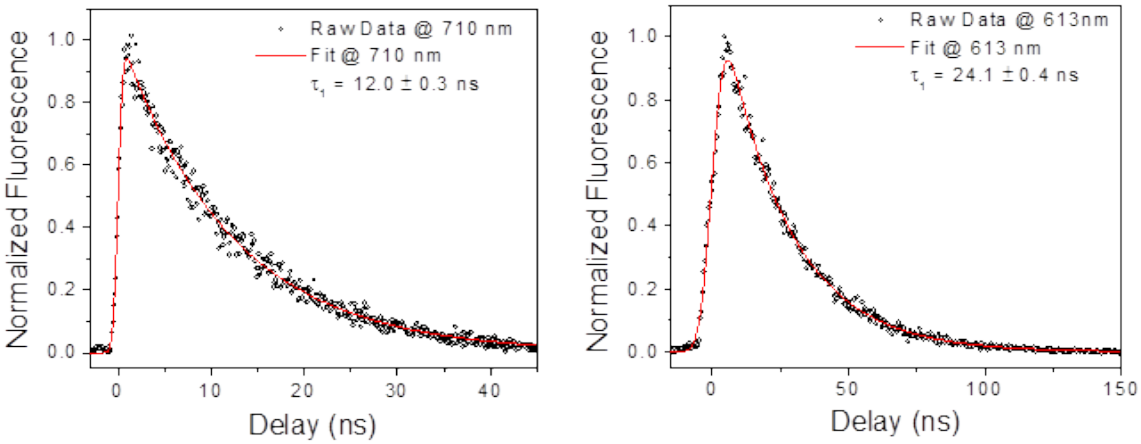


Figure S2: Time-resolved fluorescence kinetic decays of **1** (left) at 710 nm and **2** (right) at 613 nm in dichloromethane.

Femtosecond Transient Absorption Spectroscopy. Femtosecond transient absorption (fsTA) measurements were made using a regeneratively amplified titanium sapphire laser system operating at a 1 kHz repetition rate.[2] The frequency-doubled output of the amplifier was used to pump a two-stage optical parametric amplifier to generate variable-wavelength, 130 fs laser pulses. A small portion of the fundamental was focused either onto a sapphire disk to generate the white-light probe, spanning 450-800 nm, or onto a proprietary crystal (Ultrafast Systems,

LLC) to generate the near--IR probe, spanning 850-1640 nm. Spectral and kinetic data were collected with a CMOS detector (visible) or InGaAs array detector (NIR, customized Helios detector, Ultrafast Systems, LLC) and a 7 ns delay stage. Samples in solution with an absorbance of 0.4-0.8 at the excitation wavelength were irradiated in 2 mm quartz cuvettes with variable-power pulses focused to a 0.2 mm diameter spot. The total instrument response function was 180 fs. Samples were averaged for 10 seconds per time increment. Kinetic analysis was performed at several wavelengths using a Levenberg-Marquardt nonlinear least squares fit to a sum of exponentials convoluted with a Gaussian instrument response function.

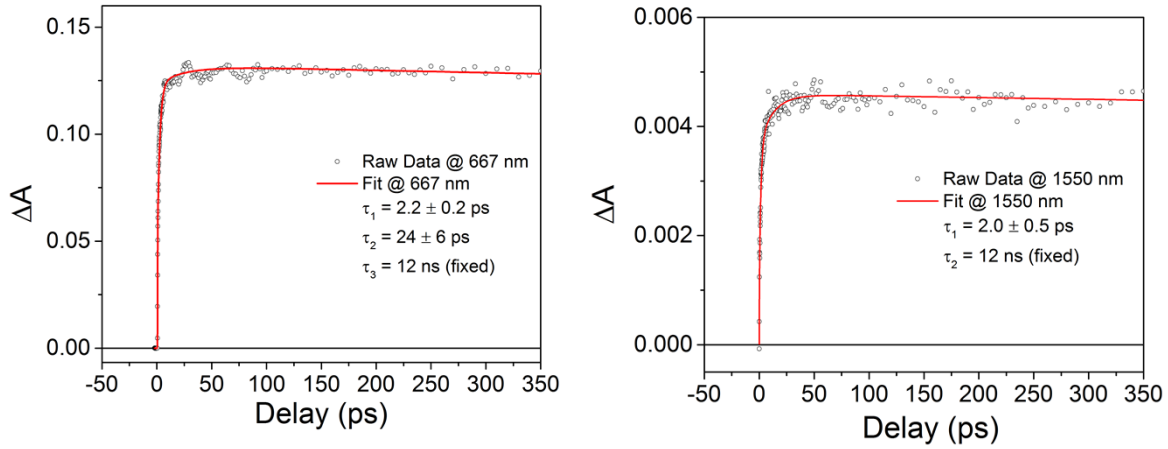


Figure S3: fsTA kinetics of **1** at 667 nm (left) and 1550 nm (right) in dichloromethane following 530 nm excitation.

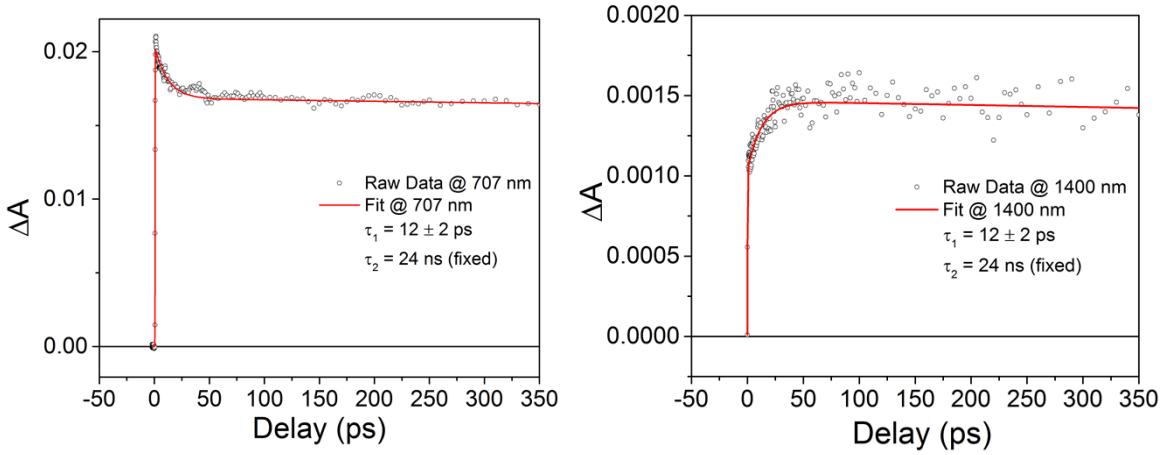


Figure S4: fsTA kinetics of **2** at 707 nm (left) and 1400 nm (right) in dichloromethane following 530 nm excitation.

Nanosecond Transient Absorption Spectroscopy. Nanosecond transient absorption (nsTA) experiments were performed by exciting the sample with 7 ns, 1.8 mJ, 416 nm pulses using the frequency-tripled output of a Continuum Precision II 8000 Nd-YAG laser pumping a Continuum Panther OPO. The probe pulse, generated using a xenon flashlamp (EG&G Electro-Optics FX-200), and pump pulse are overlapped on the sample with the pump being focused to a spot size slightly larger than the probe. Solutions were deoxygenated by four freeze-pump-thaw cycles in a 10 mm path length quartz cuvette. Kinetic traces are observed from 425-800 nm every 5 nm using a 416 nm long-pass filter, a monochromator, and photomultiplier tube (Hamamatsu R928) with high voltage applied to only 4 dynodes. Kinetic traces are recorded with a LeCroy Wavesurfer 42Xs oscilloscope interfaced to a customized Labview program (Labview v. 8.6.1). Spectra are built from the single wavelength kinetic traces taken every 5 nm. Each kinetic trace is representative of an average of 500 shots over a five microsecond time window. To increase the signal to noise ratio of the spectral profiles, 5-10 ns segments of data are averaged together and the median time reported as the time of the spectral slice.

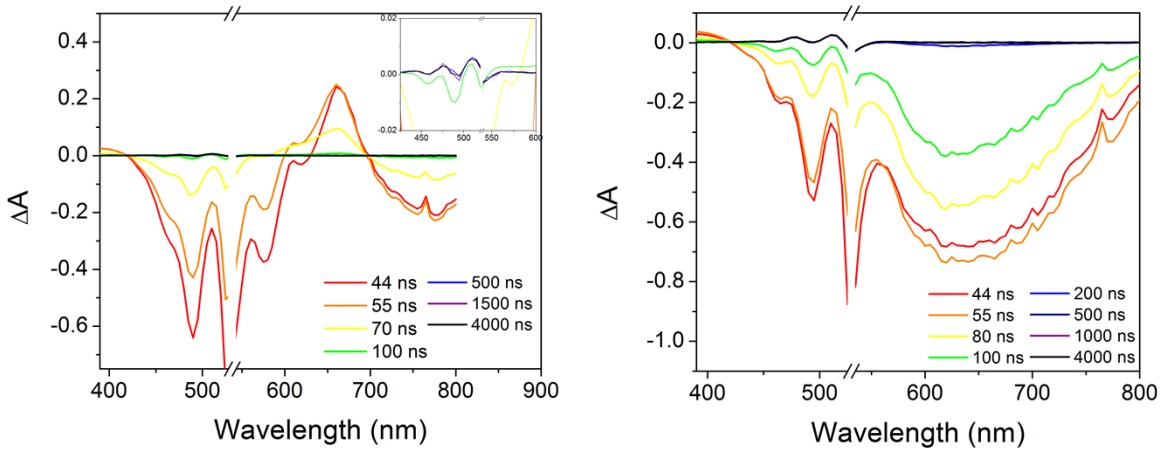


Figure S5: Nanosecond transient absorption spectra of **1** (left) and **2** (right) in dichloromethane.

References:

1. H. Langhals and W. Lona, *Eur. J. Org. Chem.*, 1998, **1998**, 847-851.

2. R. M. Young, S. M. Dyar, J. C. Barnes, M. Juríček, J. F. Stoddart, D. T. Co and M. R. Wasielewski, *J. Phys. Chem. A*, 2013, **117**, 12438-12448.