

Synthesis and Photophysical Properties of Donor- and Acceptor-
Substituted 1,7-Di(arylalkynyl)perylene-3,4:9,10-
bis(dicarboximide)s

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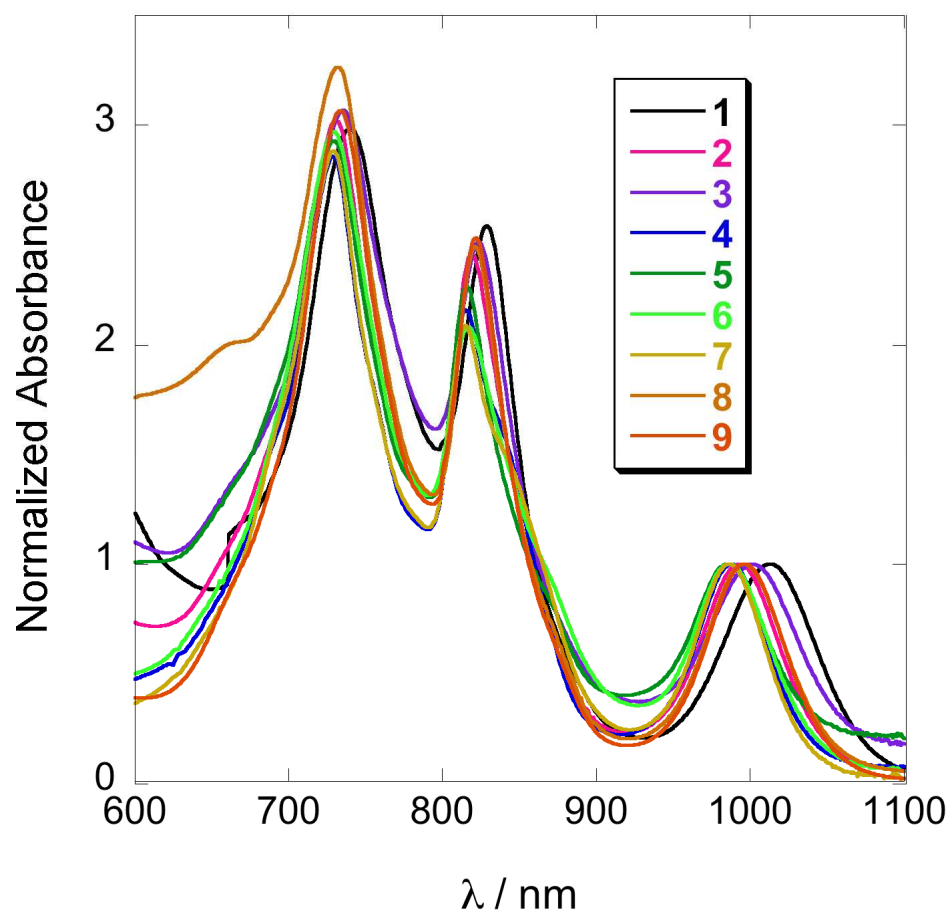


Figure S1. Normalized absorption spectra for the radical anions of **1-9** in tetrahydrofuran, generated by reduction with cobaltocene.

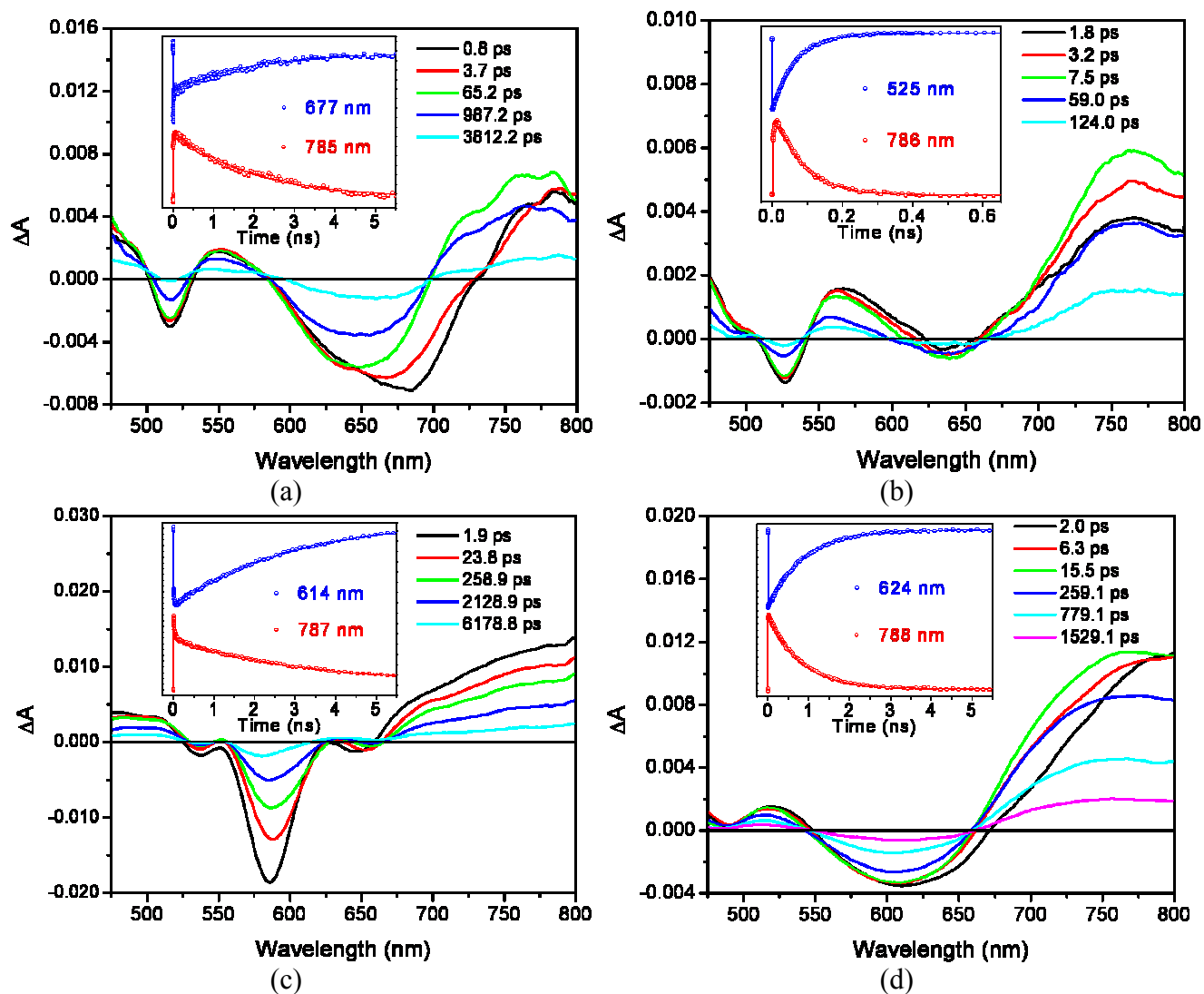


Figure S2. Transient absorption of compound 2 (a), 3 (b), 6 (c), and 9 (d) in toluene after excitation at 400 nm (left) and decay of the excited states at various wavelengths.

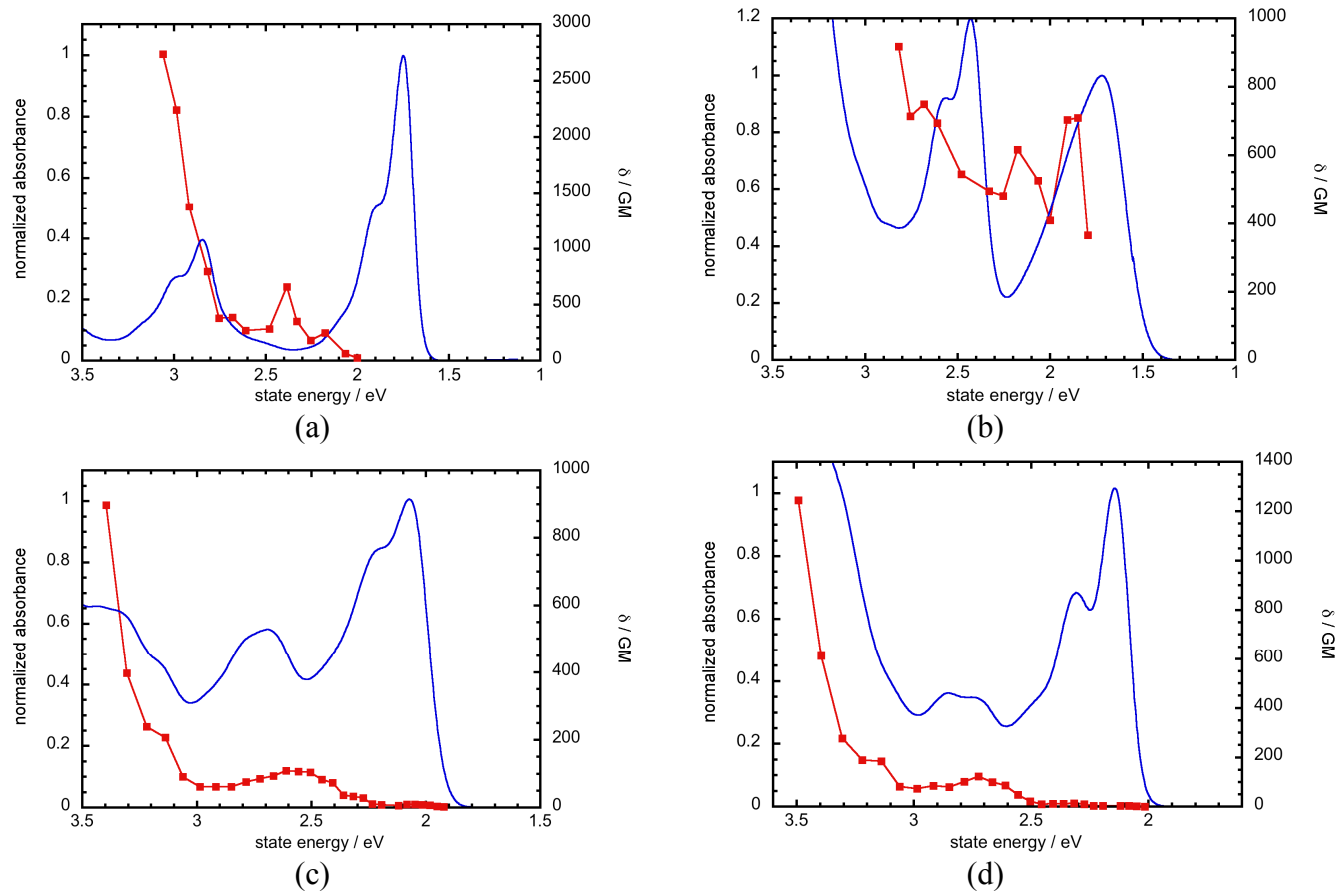


Figure S3. One-photon (blue) and two-photon (red) spectra of compounds **II** (a), **1** (b), **5** (c), and **6** (d) in dichloromethane plotted as a function of transition energy to facilitate comparison of 1P- and 2P-state energies.

Experimental Details

Transient Absorption Measurements. Femtosecond transient absorption measurements were performed with the following apparatus: a Spectra-Physics Millenium V frequency-doubled CW Nd:YVO₄ laser was used to pump a Coherent MIRA Ti:sapphire oscillator. The 110 fs, 828 nm pulses from the oscillator were stretched to ~200 ps using a four-pass, reflective, single-grating pulse stretcher and were used to seed a homemade regenerative amplifier, which includes a Clark-MXR two-step Pockels cell and driver. The amplifier was pumped at a 2 kHz repetition rate by a Quantronix 527DP frequency-doubled Nd:YLF laser (4.1 mJ/pulse). The amplified Ti:sapphire pulse (0.5 mJ/pulse) was recompressed to approximately 120 fs by a four-pass, reflective, single grating compressor. The pulse energy after compression was 320 μ J/pulse. Two 5% reflective beam splitters were placed in the output path to generate two 828 nm beams for white-light generation. The remaining 828 nm light was frequency doubled by using a 1 mm type-I LBO crystal to give 414 nm 120 fs, 75 μ J pulses. The 828 nm light from the first 5% beam splitter was passed through a waveplate-polarizer pair to control its intensity, and a few microjoules were focused into a 1 mm sapphire disk to generate white-light-continuum pulses. All reflective optics were used both to focus the 828 nm pulse into the sapphire and recollimate the white light output, thus limiting the chirp on the white light pulse to < 200 fs from 450 to 750 nm. The 828 nm light from the second 5% beam splitter was used to create a second white light continuum by focusing the 828 nm pulse into a 2 mm sapphire disk, using a 100 mm focal length (f.l.) lens. This white light was used to seed the first stage of a two-stage optical parametric amplifier, which has been described previously.¹ The first stage contains a Type-II BBO crystal, which was pumped with about 20 μ J of 414 nm light focused into the crystal with a 300 mm f.l. lens. After removal the IR idler beam and residual 414 nm pump light, the first stage produced transform-limited pulses having ca. 1.0 μ J/pulse from 460 to 750 nm. This light was then focused into the Type-I BBO of the second stage of the OPA with a 75 mm f.l. lens. The second stage amplifies the first stage light upon overlap with the

remaining 55 $\mu\text{J}/\text{pulse}$ of 414 nm pump light. The final amplified pulse energy was ca. 7.5 $\mu\text{J}/\text{pulse}$ after filtering out the residual 414 nm and IR idler light. The optical path for the probe beams and the chopping scheme used in the pump-probe experiments were described by Lukas et al..² The instrument was outfitted with a CCD array detector (Ocean Optics PC2000) for simultaneous collection of spectral and kinetic data.³ The instrument response function (IRF) for the pump-probe experiments was 180 fs. Typically 5 s of averaging was used to obtain the transient spectrum at a given delay time. Cuvettes with a 2 mm pathlength were used and the samples were irradiated with 0.5 $\mu\text{J}/\text{pulse}$ focused to a 200 μm spot. The optical density at λ_{ex} was kept between 0.2-0.4 to prevent aggregation. Analysis of the kinetic data was performed at multiple wavelengths using a Levenberg-Marquardt nonlinear least-squares fit to a general sum-of-exponentials function with an added Gaussian to account for the finite instrument response.

Two-Photon Absorption Spectroscopy. The methods used for characterization of the degenerate 2PA spectra for these molecules were single wavelength Z-scan⁴ and two-photon fluorescence (2PF) spectroscopy.⁵ The femtosecond source used as the pump beam was a Ti:sapphire regenerative amplification system (CPA2010, CLARK-MXR) which provides laser pulses at 775 nm with 140 fs duration (FWHM) at a 1 kHz repetition rate. This laser pumps an optical parametric amplifier (OPG/OPA) system (TOPAS, Light Conversion), which can be tuned from 270-11000 nm (0.11-4.6 eV) and provide up to 200 μJ of energy per pulse. This output energy was then attenuated, and 10-150 nJ was used for Z-scan measurement and 2PA cross sections determined as described in Ref. ⁴. The same system was used to excite the sample for 2PF measurements. The 2PF signals and 2PA cross sections for the molecules under investigation were measured and calibrated against well-known reference standards: fluorescein in water (pH = 11) and rhodamine B in methanol.⁵ To obtain the 2PA cross-sections from the 2PF measurements, the fluorescence quantum yields of **5** and **6** in dichloromethane were measured as 0.31 and 0.89, respectively.

Other Instrumental Methods. EI and FAB mass spectra were obtained on a VG 70SE spectrometer and MALDI mass spectra were obtained on an Applied Biosystems 4700 Proteomics Analyzer. Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer. Electrochemical measurements were carried out under nitrogen in dry deoxygenated dichloromethane solutions ca. 10^{-4} M in analyte and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate using a BAS 100W Potentiostat with a glassy carbon working electrode, a platinum auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride. Potentials were referenced to ferrocenium / ferrocene by using cobaltocenium hexafluorophosphate (−1.32 V in dichloromethane) as an internal reference. Cyclic voltammograms were recorded at a scan rate of 50 mVs^{−1}. UV-vis-NIR absorption spectra were recorded in 1 cm cells on a Varian Cary 5E UV-Vis-NIR spectrophotometer using photospectroscopic grade solvents. Absorptivities were measured on three solutions with concentrations in the range of 10^{-6} to 10^{-4} M.

General Synthetic Procedures. Starting materials were obtained from commercial sources and used without further purification or were synthesized according to the literature references given. Compounds **I**,⁶ **II**,⁷ and **III**⁸ were synthesized as previously described in the literature. Solvents were dried by passing through columns of activated alumina in a manner similar to that described in the literature (tetrahydrofuran, toluene, dichloromethane)⁹ or were obtained as anhydrous grade from Acros Organics. Flash column chromatography was performed on silica gel (32-63 μ m, 60 Å, Sorbent Technologies). Size exclusion chromatography was performed on crosslinked polystyrene beads (Bio-beads, S-X1 Support, 1% cross-linked, 40 – 80 μ m bead size, Bio-Rad) using tetrahydrofuran (freshly distilled to remove stabilizer, then deoxygenated to prevent peroxide formation) as the mobile phase. Chemical oxidations were accomplished by gradual addition of tris(4-bromophenyl)aminium hexafluoroantimonate (Aldrich) in dry dichloromethane to solutions of the PDI derivative in dry

dichloromethane. Chemical reductions were accomplished by gradual addition of cobaltocene (Aldrich) in dry tetrahydrofuran to solutions of the PDI in dry tetrahydrofuran.

1,7-Bis[4-di(*n*-butylamino)phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (1). Copper(I) iodide (0.05 g, 0.28 mmol) and tetrakis(triphenylphosphino)palladium(0) (0.07 g, 0.06 mmol) were added to a solution of **S10**¹⁰ (0.50 g, 0.57 mmol) in a deoxygenated mixture of tetrahydrofuran (20 mL) and *N,N*-di(*iso*-propyl)-*N*-ethylamine (20 mL) under argon atmosphere. After the resultant solution was further sparged with argon for 10 minutes, compound **S1**¹¹ (0.34 g, 1.5 mmol) was added. The reaction mixture was heated at 80 °C under argon for 15 hours. After cooling to room temperature, the reaction mixture was poured into 2 M aqueous hydrochloric acid (150 mL) and was extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate and was filtered. The solution was concentrated by rotary evaporation and was purified by flash chromatography on silica gel, eluting with dichloromethane / hexanes (1:1) to give the product as a dark green solid (0.60 g, 89%). ¹H NMR (CDCl₃, 300 MHz), δ 10.28 (d, *J* = 8.1 Hz, 2H), 8.96 (s, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 7.52 (m, 6H), 7.36 (d, *J* = 7.8 Hz, 4H), 6.68 (d, *J* = 8.7 Hz, 4H), 3.33 (t, *J* = 7.2 Hz, 8H), 2.79 (septet, *J* = 6.9 Hz, 4H), 1.60 (quintet, *J* = 6.3 Hz, 8H), 1.35 (sextet, *J* = 7.2 Hz, 8H), 1.19 (dd, *J* = 6.8, 1.7 Hz, 24H), 0.97 (t, *J* = 7.2 Hz, 12H). ¹³C NMR (CDCl₃, 100 MHz), δ 163.6, 163.5, 149.0, 145.7, 138.0, 134.9, 133.6, 132.9, 130.6, 130.4, 129.6, 128.3, 127.9, 126.9, 124.11, 122.5, 121.8, 121.5, 111.5, 107.3, 102.3, 90.4, 50.8, 29.3, 29.2, 24.0, 20.3, 14.0. HRMS (FAB) calcd for C₈₀H₈₄N₄O₄ (M⁺): 1164.6493. Found: 1164.6481. Anal. Calcd for C₈₀H₈₄N₄O₄: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.25; H, 7.16; N, 4.75.

1,7-Bis[4-(diphenylamino)phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (2). Compound **2** was synthesized in an analogous fashion to **1** using the following quantities of reagents: **S10** (0.61 g, 0.70 mmol), tetrakis(triphenylphosphino)palladium(0) (0.07 g, 0.06

mmol), copper(I) iodide (0.18 g, 0.96 mmol), **S2**¹² (0.45 g, 1.7 mmol), tetrahydrofuran (25 mL), *N,N*-di(*iso*-propyl)-*N*-ethylamine (25 mL). Yield: 0.78 g (89%). ¹H NMR (300 MHz, CDCl₃) δ 10.21 (d, *J* = 8.4 Hz, 2H), 8.97 (s, 2H), 8.77 (d, *J* = 8.4 Hz, 2H), 7.49 (m, 6H), 7.32 (m, 12H), 7.11 (m, 16H), 2.76 (septet, *J* = 6.7 Hz, 4H), 1.18 (d, *J* = 6.6 Hz, 24 H). ¹³C NMR (CDCl₃, 75 MHz), δ 163.4, 163.3, 149.3, 146.6, 145.7, 138.1, 134.8, 133.7, 133.0, 130.8, 130.5, 129.7, 129.6, 128.2, 128.1, 127.3, 125.6, 124.3, 124.1, 122.8, 122.0, 121.3, 120.9, 113.9, 100.2, 90.5, 29.2, 24.0. HRMS (FAB⁺) calcd for C₈₈H₆₈N₄O₄ (M⁺): 1244.5241. Found: 1244.5276. Anal. Calcd for C₈₈H₆₈N₄O₄: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.21; H, 5.52; N, 4.46.

1,7-Bis[4-{di(4-methoxyphenyl)amino}phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (3). Compound **3** was synthesized in an analogous fashion to **1** using the following quantities of reagents: **S10** (0.26 g, 0.29 mmol), tetrakis(triphenylphosphino)palladium(0) (0.04 g, 0.03 mmol), copper(I) iodide (0.08 g, 0.04 mmol), **S3**¹³ (0.34 g, 1.01 mmol), tetrahydrofuran (20 mL), *N,N*-di(*iso*-propyl)-*N*-ethylamine (20 mL). Yield: 0.25 g (62%). ¹H NMR (CDCl₃, 300 MHz) δ 10.23 (d, *J* = 8.1 Hz, 2H), 8.97 (s, 2H), 8.77 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 4 H), 7.37 (d, *J* = 7.8 Hz, 4H), 7.13 (d, *J* = 8.7 Hz, 8H), 6.89 (m, 12H), 3.82 (s, 12H), 2.78 (septet, *J* = 6.6 Hz, 4H), 1.19 (d, *J* = 6.6 Hz, 24H). ¹³C NMR (CDCl₃, 75 MHz), δ 163.5, 163.3, 156.8, 150.1, 145.7, 139.4, 138.1, 134.8, 133.5, 132.9, 130.6, 130.5, 129.7, 128.2, 128.0, 127.6, 127.2, 124.1, 122.7, 121.9, 121.1, 118.4, 115.0, 111.9, 100.8, 90.4, 55.5, 29.2, 24.0. HRMS(FAB⁺) calcd for C₉₂H₇₆N₄O₈ (M⁺): 1364.5663. Found: 1364.5690. Anal. Calcd for C₉₂H₇₆N₄O₈: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.84; H, 5.64; N, 4.13.

1,7-Bis[4'-(*N*-phenyl-*N*-*m*-tolylamino)biphenyl-4-ethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (4) and 1,7-bis[4-*n*-butoxyphenylethynyl]-

***N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (5).** We have previously published the synthesis and characterization of **4** and **5** along with that of the new intermediate, **S4**.¹⁴

4-{Di(mesityl)boronyl}phenylacetylene (S6). A 1.6 M *n*-butyllithium solution in hexane (10.2 mL, 16.3 mmol) was added dropwise under nitrogen to a solution of **S11** (3.01 g, 11.6 mmol) in dry tetrahydrofuran (40 mL) at $-78\text{ }^{\circ}\text{C}$. After the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 minutes, a solution of dimesitylboron fluoride (5.00 g, 16.8 mmol) in dry tetrahydrofuran (20 mL) was added dropwise; the resulting mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for another hour before being allowed to warm to room temperature and stir for an additional 2 hours. The reaction was quenched with water (20 mL), and the reaction mixture was extracted with diethyl ether. The organic solution was dried over anhydrous magnesium sulfate, was filtered, and the solvent was removed by rotary evaporation. The residue was purified by flash chromatography on silica gel, eluting with hexanes. After removal of solvent by rotary evaporation, a white solid was obtained and was dissolved in tetrahydrofuran (25 mL) and treated with $^n\text{Bu}_4\text{NF}$ in tetrahydrofuran (25 mL of a 1.0 M solution). After stirring for 1 hour, 3 M aqueous hydrochloric acid (20 mL) was added, and the resulting mixture was stirred for 15 minutes before extraction with diethyl ether. The organic solution was dried over anhydrous magnesium sulfate and was filtered through a pad of silica gel. The solvent was removed by rotary evaporation, and the residue was recrystallized from a mixture of methanol and ethanol to give the product as a white solid (2.61 g, 64%). ^1H NMR (500 MHz, CDCl_3) δ 7.47 (s, 4H), 6.83 (s, 4H), 3.17 (s, 1H), 2.32 (s, 6H), 2.00 (s, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 146.5, 141.5, 140.8, 138.9, 135.9, 131.6, 128.2, 125.3, 83.9, 79.0, 23.4, 21.2. HRMS(EI) calcd for $\text{C}_{26}\text{H}_{27}\text{B}$ (M^+): 350.2206. Found: 350.2222. Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{B}$: C, 89.15; H, 7.77. Found: C, 89.06; H, 7.88.

1,7-Bis[4-{di(mesityl)boronyl}phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (6). Compound **6** was synthesized in an analogous fashion to **1** using the following reagents and quantities: **S10** (0.51 g, 0.57 mmol), **S6** (0.45 g, 1.28 mmol), $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (0.022 g,

0.057 mmol), copper(I) iodide (0.022 g, 0.12 mmol), tri(*tert*-butyl)phosphine (0.23 g, 0.12 mmol, 10% wt. in hexanes), dioxane (15 mL), *N,N*-di(*iso*-propyl)-*N*-ethylamine (15 mL). Yield: 0.40 g (56%). ¹H NMR (500 MHz, CDCl₃) δ 10.23 (d, *J* = 8.5 Hz, 2H), 9.03 (s, 2H), 8.83 (d, *J* = 8.5 Hz, 2H), 7.62 (m, 8H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 4H), 6.83 (s, 4H), 2.80 (m, 4H), 2.30 (s, 12H), 2.05 (s, 24H), 1.20 (d, *J* = 7.5 Hz, 24H). ¹³C NMR (CDCl₃, 75 MHz), δ 163.3, 163.1, 145.7, 141.4, 140.8, 139.1, 138.2, 136.3, 134.6, 134.5, 131.3, 130.3, 129.8, 128.4, 128.2, 128.1, 127.8, 125.0, 124.2, 123.2, 122.3, 120.3, 99.0, 92.2, 29.7, 29.3, 24.0, 23.5, 21.2. HRMS (MALDI) calcd for C₁₀₀H₉₂B₂N₂O₄ (M⁺): 1406.7243. Found: 1406.7338. Anal. Calcd for C₃₂H₃₁B: C, 90.14; H, 7.33. Found: C, 90.12; H, 7.40.

4'-(Dimesitylboronyl)biphenyl-4-acetylene (S7). Compound **S7** was synthesized in an analogous fashion to **S6** using the following reagents and quantities: **S12**¹⁵ (4.23 g, 12.85 mmol), *n*-butyllithium (9.0 mL, 2.0 M in hexane, 18 mmol), dimesitylboron fluoride (4.50 g, 16.8 mmol), tetrabutylammonium fluoride (38 mL, 1.0 M in tetrahydrofuran). Yield: 3.57 g (66%). ¹H NMR (500 MHz, CDCl₃) δ 7.58 (m, 8H), 6.84 (s, 4H), 3.13 (s, 1H), 2.32 (s, 6H), 2.04 (s, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 143.2, 141.7, 141.0, 140.8, 138.7, 137.1, 132.6, 128.2, 127.1 (2C), 126.4, 121.4, 83.5, 78.0, 23.5, 21.2. HRMS (EI) calcd for C₃₂H₃₁B (M⁺): 426.2519. Found: 426.2529. Anal. Calcd for C₁₁₂H₁₀₀B₂N₂O₄: C, 86.25; H, 6.46; N, 1.80. Found: C, 86.02; H, 6.46; N, 1.76.

1,7-Bis[4-{di(mesityl)boronyl}phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (7). Compound **7** was synthesized in an analogous fashion to **2** using the following reagents and quantities: **S1** (0.25 g, 0.29 mmol), **S7** (0.27 g, 0.63 mmol), Pd(PhCN)₂Cl₂ (0.022 g, 0.057 mmol), *N,N*-di(*iso*-propyl)-*N*-ethylamine (10 mL). Yield: 0.37 g (90%). ¹H NMR (500 MHz, CDCl₃) δ 10.23 (d, *J* = 8.5 Hz, 2H), 9.04 (s, 2H), 8.86 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 4H), 7.76 (d, *J* = 9.0 Hz, 4H), 7.63 (d, *J* = 8.5 Hz, 4H), 7.61 (d, *J* = 8.5 Hz, 4H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 4H), 6.83 (s, 8H), 2.78 (septet, *J* = 7.0 Hz, 4H), 2.30 (s, 12H), 2.03 (s, 24H), 1.20 (d, *J* = 6.5 Hz,

24H). ^{13}C NMR (CDCl_3 , 75 MHz), 163.4, 163.2, 145.7, 142.9, 142.0, 141.6, 140.8, 138.7, 138.2, 137.1, 134.7, 134.4, 132.4, 131.1, 130.4, 129.8, 128.4, 128.2, 127.6, 126.5, 124.2, 123.2, 122.3, 121.3, 120.5, 98.8, 91.6, 29.3, 24.0, 23.5, 21.2 (one aromatic peak missing, presumably due to overlap). HRMS (MALDI) calcd for $\text{C}_{112}\text{H}_{100}\text{B}_2\text{N}_2\text{O}_4$ (M^+): 1558.7869. Found: 1558.8043. Anal. Calcd for $\text{C}_{112}\text{H}_{100}\text{B}_2\text{N}_2\text{O}_4$: C, 86.25; H, 6.46, N, 1.80. Found: C, 86.02; H, 6.46; N, 1.76.

1-(4-Iodophenyl)-4-(4-methoxyphenyl)piperazine (S14). A mixture of copper(I) iodide (0.14 g, 0.73 mmol), potassium phosphate (6.6 g, 49 mmol), ethylene glycol (1.86 g, 30.0 mmol), 1,4-diiodobenzene (8.30 g, 25.1 mmol), and **S13** (1.92 g, 10.0 mmol) was stirred in isopropanol (30 mL) for 18 hours at 90 °C under nitrogen in a 100 mL round-bottomed flask with a reflux condenser attached. Water (100 mL) was added, and the resulting precipitate was filtered and washed with water and methanol. The solid was then dissolved in hot chloroform and was passed through a short pad of silica gel, eluting with chloroform, followed by chloroform / ethyl acetate (8:1) to give, after removal of solvent by rotary evaporation, a white solid (2.41 g, 61%). ^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.73 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H) 3.30–3.28 (m, 4H), 3.20–3.18 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.6, 151.3, 145.9, 138.3, 119.0, 118.7, 114.9, 82.1, 56.0, 51.2, 49.5. HRMS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{IN}_2\text{O}$ (M^+): 394.0542. Found: 394.0514. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{IN}_2\text{O}$: C, 51.79; H, 4.86; N, 7.11. Found: C, 51.93; H, 4.94; N, 7.10.

4-[4-{4-(4-Methoxyphenyl)piperazin-1-yl}phenyl]-2-methylbut-3-yn-2-ol (S15). 2-Methyl-3-butyn-2-ol (2.0 g, 24 mmol) was added to a deoxygenated mixture of **S14** (1.6 g, 4.1 mmol), copper(I) iodide (0.030 g, 0.16 mmol), and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.11 g, 0.16 mmol) in triethylamine (30 mL) in a 100 mL 2-neck round-bottomed flask with a reflux condenser attached. The reaction mixture was heated to 90 °C for 18 hours and was then allowed to cool to room temperature. The resulting precipitate was collected by filtration, washing with water and methanol. The solid was then dissolved in minimum amount of chloroform and was run through a short pad of silica gel. The solvent was removed by rotary

evaporation, and the resulting solid was then heated to reflux in methanol for 1 hour, then filtered to give the product as a pale yellow solid (0.93 g, 65%). ^1H NMR (500 MHz, CDCl_3) δ 7.32 (d, J = 8.5 Hz, 2H), 6.92-6.84 (m, 6H), 3.77 (s, 3H), 3.36 (m, 4H), 3.20 (m, 4H), 1.98 (s, 1H), 1.59 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.6, 151.2, 145.9, 133.1, 119.0, 115.7, 114.9, 113.5, 92.6, 82.8, 66.1, 56.0, 51.2, 49.1, 30.0. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$ (M^+): 350.1994. Found: 350.1974. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.40; H, 7.41; N, 7.95.

1-(4-Ethynylphenyl)-4-(4-methoxyphenyl)piperazine (S8). A mixture of **S15** (0.70 g, 2.0 mmol) and sodium *tert*-butoxide (0.10 g, 1.8 mmol) in toluene (10 mL) were heated to reflux for 4 hours under nitrogen atmosphere. The reaction mixture was passed through a short pad of silica gel, eluting with hot chloroform. The solvent was removed by rotary evaporation, and the solid was heated in refluxing methanol for 1 hour and was recovered by filtration as a pale yellow solid (0.60 g, 97%). ^1H NMR (500 MHz, CDCl_3) δ 7.40 (d, 2H, J = 9.0 Hz), 6.94-6.84 (m, 6H), 3.76 (s, 3H), 3.37 (m, 4H), 3.20 (m, 4H), 2.98 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 154.1 (two peaks separated by 0.02 ppm), 145.4, 133.2, 118.6, 115.2, 114.5, 112.3, 84.2, 75.5, 55.6, 50.7, 48.5. HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ (M^+): 292.1576. Found: 292.1586. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$: C, 78.05; H, 6.89; N, 9.58. Found: C, 77.82; H, 6.93; N, 9.29.

1,7-Bis[4-(4-methoxyphenyl)piperazinyl-phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4:9,10-bis(dicarboximide) (8). A deoxygenated mixture of **S10** (0.30 g, 35 mmol), **S8** (0.36 g, 1.1 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.028 g, 0.035 mmol), and copper(I) iodide (0.007 g, 0.035 mmol) in toluene (8 mL) and triethylamine (2 mL) was heated to 80 °C for 18 hours in a 50 mL 2-neck round-bottomed flask with a reflux condenser attached. After allowing the reaction mixture to cool to room temperature, the reaction mixture was poured into methanol (200 mL), and the resulting black solid was collected by filtration and purified twice by column chromatography on silica gel, eluting with dichloromethane / ethyl acetate (20:1), yielding the product as a black solid (0.308 g, 68%). ^1H NMR

(500 MHz, CDCl₃) δ 10.26-10.23 (m, 2H), 8.98 (s, 1.5H, major isomer), 8.95 (s, 0.7H, minor isomer), 8.86 (d, J = 8.5Hz, 0.7H, minor isomer), 8.82 (d, J = 8.0 Hz, 1.5H, major isomer), 7.60 (d, J = 8.5Hz, 4H), 7.53 (m, 2H), 7.37 (d, J = 8.0Hz, 4H), 7.03 (d, J = 9.0Hz, 4H), 6.97 (m, 4H), 6.87 (m, 4H), 3.77 (s, 6H), 3.49 (m, 8H), 3.24 (m, 8H), 2.81 (m, 4H), 1.20 (m, 24H). Satisfactory ¹³C NMR data were not obtained due to the low solubility of this compound. HRMS (MALDI) calcd for C₈₆H₇₈N₆O₆ (M⁺): 1290.598. Found: 1290.608. Anal. Calcd for C₈₆H₇₈N₆O₆: C, 79.97; H, 6.09; N, 6.51. Found: C, 80.22; H, 6.06; N, 6.45.

[4-{Bis(4-methoxyphenyl)amino}phenyl][4-(4-iodophenyl)piperazin-1-yl]methanone (S17). A solution of *N,N'*-dicyclohexylcarbodiimide (1.0 g, 4.9 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.06 g, 0.5 mmol) in dichloromethane (10 mL) was added to a solution of 1-(4-iodophenyl)piperazine (1.0 g, 3.5 mmol) and **S16**¹⁶ (1.21 g 3.47 mmol) in dichloromethane (40 mL) under nitrogen. After stirring for 18 hours at room temperature, the reaction mixture was run through a column of silica gel, eluting with chloroform / ethyl acetate (2:1). After concentration by rotary evaporation, the crude product was run through a second column of silica gel, eluting with hexane / ethyl acetate (4:1), yielding the product as a white solid (1.74 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, J = 8.5 Hz, 2H) 7.25 (m, 2H), 7.41 (m, 4H), 6.85 (m, 6H), 6.67 (d, J = 9.0 Hz, 2H), 3.80 (s, br, 10H), 3.14 (s, br, 4H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 170.7, 157.1, 151.2, 150.8, 140.4, 138.2, 129.1, 127.8, 126.4, 118.8, 118.4, 115.2, 82.0, 55.8, 49.4. This spectrum is missing one alkyl carbon peak, presumably due to overlap with the solvent peak. HRMS (ESI) calcd for C₃₁H₃₁IN₃O₃ (MH⁺): 620.1410. Found: 620.1398. Anal. Calcd for C₃₁H₃₀IN₃O₃, C, 60.10; H, 4.88; N, 6.78. Found: C, 59.97; H, 4.89; N, 6.61.

[4-{Bis(4-methoxyphenyl)amino}phenyl][4-(4-((trimethylsilyl)ethynyl)phenyl)piperazin-1-yl]methanone (S18). (Trimethylsilyl)acetylene (1.0 mL, 90 mmol) was added to a deoxygenated mixture of **S17** (0.62 g, 1.0 mmol), copper(I) iodide (0.0055 g, 0.029 mmol), and Pd(PPh₃)₂Cl₂ (0.02 g, 0.03 mmol) in toluene (20 mL) and triethylamine (5 mL) under nitrogen in a 50 mL 2-neck round-

bottomed flask with a reflux condenser attached. The reaction mixture was then heated to 80 °C for 18 hours. After cooling to room temperature, the mixture was washed with water (2 × 20 mL) and was dried with anhydrous magnesium sulfate. After filtration and solvent removal by rotary evaporation, the residue was purified using column chromatography on silica gel, eluting with hexane / ethyl acetate (4:1) to give the product as a pale yellow solid (0.47 g, 79%). ¹H NMR (500 MHz, CD₂Cl₂) δ 7.34 (d, *J* = 9.0 Hz, 2H) 7.24 (d, *J* = 9.0 Hz, 2H), 7.10 (m, 4H), 6.88 (m, 8H), 3.79 (s, 6H), 3.74 (s, b, 4H), 3.23 (s, b, 4H), 0.21 (s, 9H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 170.1, 157.1, 151.3, 150.8, 140.4, 133.3, 129.1, 127.8, 126.4, 118.4, 115.6, 115.2, 113.9, 105.9, 92.5, 55.8, 48.9, 0.1. The ¹³C NMR spectrum is missing one alkyl peak, presumably due to overlap with the solvent peaks. HRMS (ESI) calcd for C₃₆H₃₉N₃O₃Si: 589.2761. Found: 589.2843. Anal. Calcd for C₃₆H₃₉N₃O₃Si: C, 73.31; H, 6.66; N, 7.12. Found: C, 73.10; H, 6.71; N, 6.85.

[4-{Bis(4-methoxyphenyl)amino}phenyl][4-(4-ethynylphenyl)piperazin-1-yl]methanone (S9) and 1,7-bis[4-{4-(4-{bis(4-methoxyphenyl)amino}benzoyl)piperazin-1-yl}phenylethynyl]-*N,N'*-di[2,6-di(*iso*-propyl)phenyl]perylene-3,4,9,10-bis(dicarboximide) (9). Potassium carbonate (6 drops of a saturated aqueous solution) and methanol (10 mL) were added to a solution of **S18** (0.59 g, 1.0 mmol) in tetrahydrofuran (4 mL) in a 50 mL round-bottomed flask. The reaction mixture was stirred under nitrogen for 3 hours, after which the solvent was removed by rotary evaporation. The residue was dissolved in chloroform (50 mL); the solution was washed with water and was then dried over anhydrous magnesium sulfate. The crude product (**S9**) obtained after rotary evaporation was used in the next reaction without further purification or characterization. A deoxygenated mixture of the crude **S9** (0.52 g, 1.0 mmol), **S10** (0.27 g, 0.30 mmol), copper(I) iodide (0.008 g, 0.04 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol), toluene (20 mL), and triethylamine (5 mL) were heated to 80 °C for 18 hours under nitrogen in 50 mL 2-neck round-bottomed flask with a reflux condenser attached. After cooling to room temperature, the mixture was washed with water and was dried over anhydrous magnesium sulfate.

After filtration and concentration by rotary evaporation, purification with one column of silica gel, eluting with toluene / ethyl acetate (4:1), and five times through a size-exclusion chromatography column (1.2 meters in length and 6 cm in diameter), eluting with fresh distilled tetrahydrofuran, afforded the product as a black solid (0.33 g, 38% calculated from amount of **S18**). In contrast to **1-8**, **9** is rather unstable as a solid at room temperature. ^1H NMR (500 MHz, CD_2Cl_2) δ 10.33 (m, 2H), 8.98 (s, 1.4H, major isomer), 8.95 (s, 0.6H, minor isomer), 8.80 (d, $J = 8.5$ Hz, 0.7H, minor isomer), 8.37 (d, $J = 8.5$ Hz, 1.56H, major isomer), 7.65 (d, $J = 8.5$ Hz, 4H), 7.58 (t, $J = 7.5$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 4H), 7.11 (d, $J = 9.0$ Hz, 8H), 7.00 (d, $J = 9.0$ Hz, 4H), 6.88 (m, 12H), 3.79 (s, 6H), 3.79 (s, br, 20H), 3.36 (s, br, 8H), 2.82 (septet, $J = 7.0$ Hz, 4H), 1.18 (d, $J = 6.5$ Hz, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 170.7, 164.0, 163.8, 157.1, 152.0, 146.5, 140.3, 138.3, 135.2, 134.0, 133.7, 131.4, 131.0, 130.0, 129.1, 128.5, 127.8, 126.2, 124.5, 123.2, 122.4, 121.4, 118.3, 115.6, 115.2, 112.2, 100.8, 90.6, 55.8, 48.3, 29.5, 24.1. HRMS (MALDI) calcd for $\text{C}_{114}\text{H}_{100}\text{N}_8\text{O}_{10}$ (M^+): 1740.7562. Found: 1740.7481. Anal. Calcd for $\text{C}_{114}\text{H}_{100}\text{N}_8\text{O}_{10}$: C, 78.60; H, 5.79; N, 6.43. Found: C, 78.22; H, 6.11; N, 6.15.

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