Supporting Information for:

Segregated assemblies in bridged electron-rich and electron-poor π-conjugated moities

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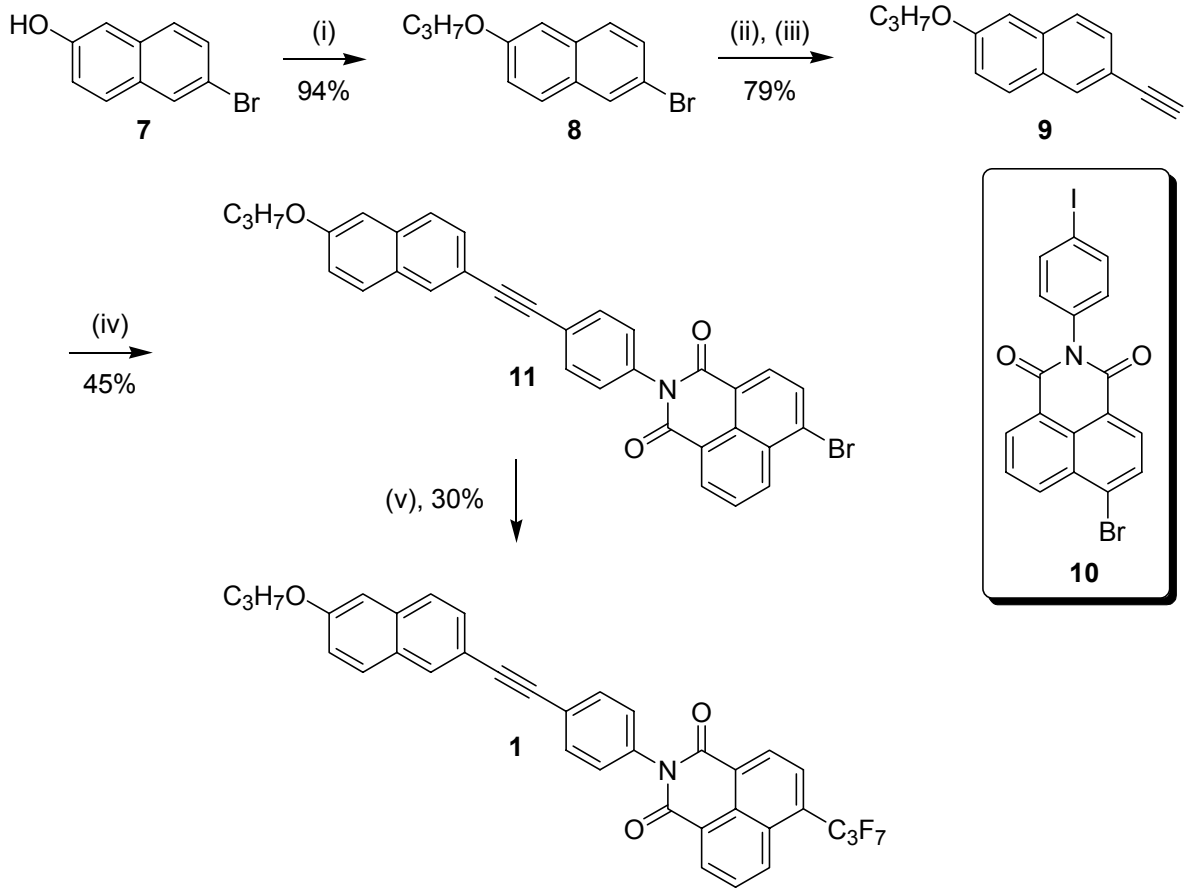
I. General Procedures

All chemicals were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, and TCI) and used without further purification unless otherwise noted. Copper catalysts [Cu(phen)(PPh_3)Br] and [Cu(phen)(PPh_3)$_2$]NO_3 were prepared and used according to methods previously reported by our group[1]. Toluene was distilled from sodium-benzophenone ketyl. Common solvents were purchased from EMD (through VWR). Routine monitoring of the reactions were carried out on glass-supported EMD silica gel 60 F_{254} TLC plates. Flash chromatography was performed using silica gel from either ICN (230-400 mesh) or Sorbent Technologies (Standard Grade, 60 Å, 32-63 μm). All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance400 spectrometer. ^{19}F NMR spectra were recorded on a Bruker DPX300 spectrometer. Chemical shifts and coupling constants are reported in parts per million (δ) and Hertz, respectively. Elemental analyses were performed in the Microanalysis Laboratory, University of Massachusetts at Amherst, by Dr. Greg Dabkowski. Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Facility which is supported, in part, by the National Science Foundation. X-ray data were collected using a Nonius kappa-CCD diffractometer with MoKα (λ=0.71073 Å) as the incident radiation. Diffraction data were collected at ambient temperature. The raw data were integrated, refined, scaled, and corrected for Lorentz polarization and absorption effects, if necessary, using the programs DENZO and SCALEPAK, supplied by Nonius. Structure solutions and refinements were done (on F_o^2) using programs such as SIR97, LSQ, SHELXS and SHELXL that are contained within the Nonius MAXUS module and the WinGX suite (L.J.

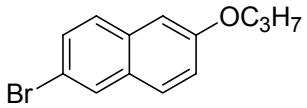
Farrugia (1999) *J. Appl. Cryst.* **32**, 837-838). All structures were checked for any missing symmetry using MISSYM of PLATON.

II. Experimental Details for the Synthesis of All Compounds

Synthesis of Compound **1**

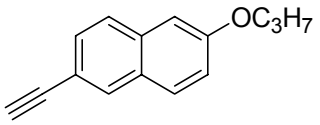


Reagents: (i) C_3H_7Br, Cs_2CO_3, DMSO, rt; (ii) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 80 °C; (iii) K_2CO_3, MeOH, CH_2Cl_2, rt; (iv) **10**, [Cu(phen)(PPh_3)Br], K_2CO_3, toluene, 110 °C; (v) C_3F_7I, Cu-bronze, 2,2'-bipyridine, fluorobenzene, DMSO, 75 °C.

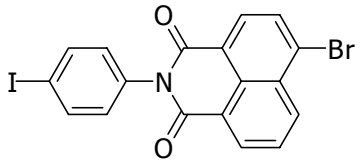


2-Bromo-6-propoxy-naphthalene (8): To a stirred solution of 6-bromo-2-naphthol (**7**, 2.23 g, 10.00 mmol) and cesium carbonate (6.52 g, 20.00 mmol) in DMSO (100 mL) was added 1-bromopropane (1.37 mL, 15.00 mmol). After stirring overnight at room temperature, the reaction mixture was diluted with water (150 mL). The resulting solution was extracted with ethyl acetate (3x). The combined extracts were washed with saturated NaCl solution (4x), dried over sodium sulfate, filtered, and rotovaped. The crude product was purified via silica gel chromatography (100% hexanes to 5:95 ethyl acetate/hexanes) to yield a white solid (2.50 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.8,

1H), 7.63 (d, J = 9.1, 1H), 7.57 (d, J = 8.8, 1H), 7.48 (dd, J = 8.8, 2.0, 1H), 7.16 (dd, J = 8.8, 2.5, 1H), 7.07 (d, J = 2.5, 1H), 4.02 (t, J = 6.6, 2H), 1.87 (m, J = 7.4, 2H), 1.07 (t, J = 7.5, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.43, 133.13, 129.95, 129.64, 129.54, 128.42, 128.34, 120.09, 116.89, 106.56, 69.61, 22.56, 10.59. Anal. calcd for $C_{13}H_{13}BrO$: C, 58.89; H, 4.94; Br, 30.14. Found: C, 59.04; H, 5.01; Br, 30.0.

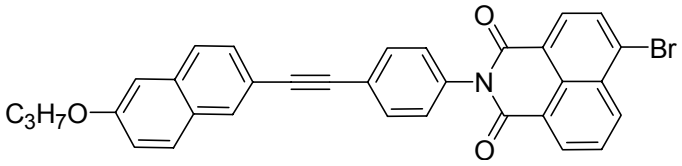


2-Ethynyl-6-propoxy-naphthalene (9): To a 200 mL Schlenk flask with Teflon stir bar was added 2-bromo-6-propoxy-naphthalene (**8**, 2.65 g, 10.00 mmol), $PdCl_2(PPh_3)_2$ (281 mg, 0.400 mmol), and copper iodide (76.1 mg, 0.400 mmol). The flask was sealed with a rubber septum then evacuated and backfilled with nitrogen 3 times. Triethylamine (100 mL) and trimethylsilylacetylene (2.04 mL, 20.00 mmol) were added and the reaction mixture was stirred and heated to 75 ºC. After 16 h, the solvent was removed *in vacuo* and the residue was dispersed in diethyl ether. The resulting dispersion was filtered through a pad of silica gel and the filtrate was rotovaped to afford an orange solid. The crude TMS-protected product was dissolved in a 1:1 mixture of CH_2Cl_2/MeOH (100 mL) and stirred at rt overnight in the presence of excess K_2CO_3. The mixture was filtered and the filtrate was rotovaped onto silica gel. Purification via silica gel chromatography (100% hexanes to 1:99 ethyl acetate/hexanes) afforded a yellow solid which was used for future reactions (1.65 g, 79%). Recrystallization from EtOH/water yielded analytically pure material as fluffy yellow crystals (1.39 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.68 (d, J = 8.8, 1H), 7.64 (d, J = 8.6, 1H), 7.47 (dd, J = 8.3, 1.5, 1H), 7.15 (dd, J = 8.8, 2.3, 1H), 7.08 (d, J = 2.3, 1H), 3.09 (s, 1H), 4.03 (t, J = 6.6, 2H), 1.87 (m, J = 7.3, 2H), 1.08 (t, J = 7.6, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.03, 134.48, 132.09, 129.27, 129.09, 128.23, 126.79, 119.81, 116.80, 106.57, 84.29, 76.62, 69.61, 22.55, 10.58. Anal. calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.49; H, 6.73.

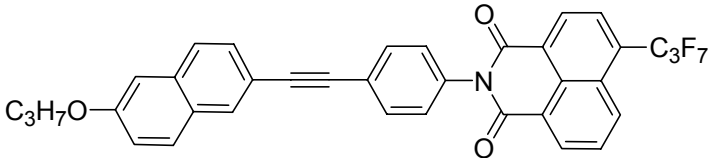


Compound (10): To a 100 mL round bottom flask with Teflon stir bar was added 4-bromo-1,8-naphthalic anhydride (1.94 g, 7.00 mmol), 4-iodoaniline (3.12 g, 14.20 mmol), imidazole[2] (10.13 g, 148.7 mmol), and chloroform (50 mL). The slightly yellow solution was stirred and heated to 75 ºC. After 1.5 h, the reaction was cooled to room temperature. The solvent was removed *in vacuo* and the residue was taken up in absolute ethanol. The resulting suspension was sonicated for 15 min and then filtered through a Buchner funnel. The cake was washed with cold ethanol, air-dried, and purified via

column chromatography to afford a white solid (2.76 g, 82%). $C_{18}H_9BrINO_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.66 (d, *J* = 7.3, 1H), 8.63-8.61 (d, *J* = 8.5, 1H), 8.43-8.41 (d, *J* = 7.8, 1H), 8.07-8.05 (d, *J* = 7.9, 1H), 7.88-7.84 (m, 3H), 7.05-7.03 (d, *J* = 8.6, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.52, 163.49, 138.61, 134.80, 133.83, 132.56, 131.69, 131.25, 130.92, 130.81, 130.55, 129.30, 128.21, 122.99, 122.10, 94.60.



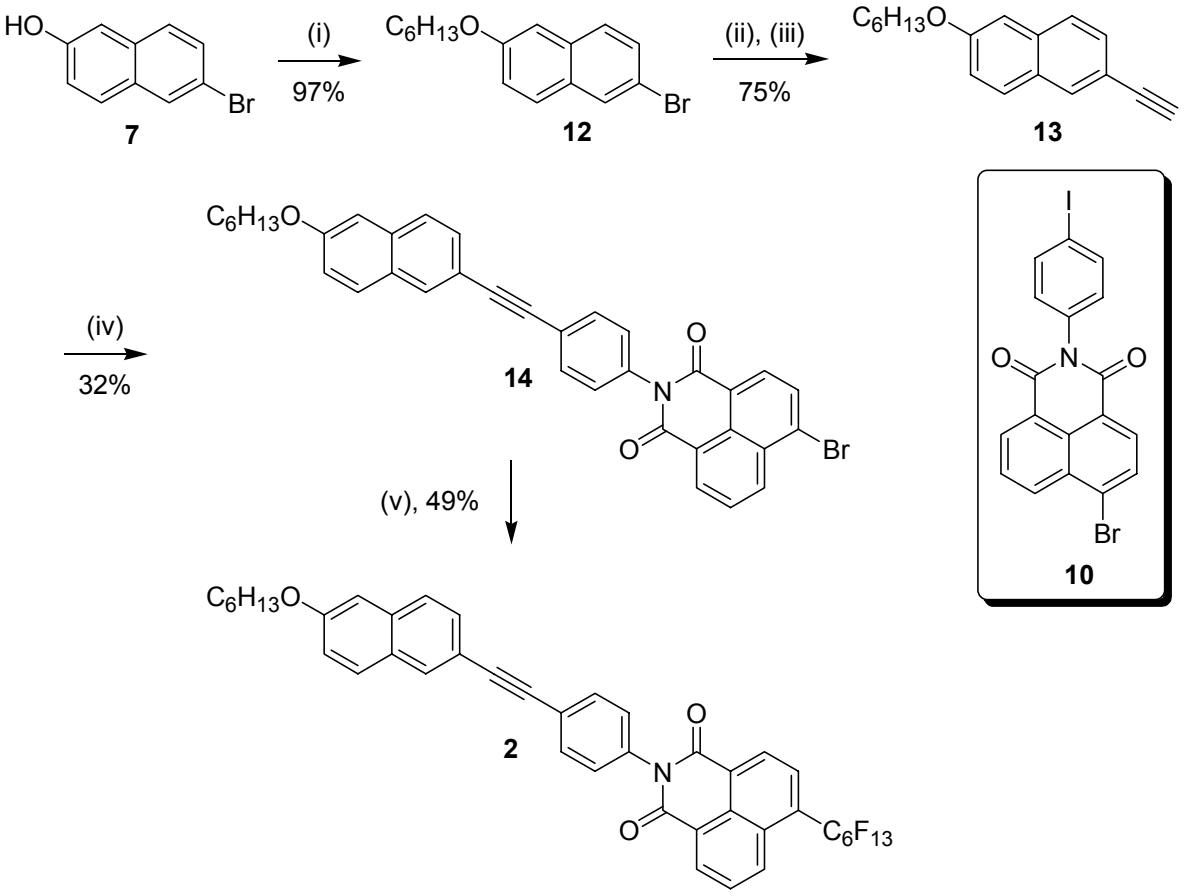
Compound (11): In an argon-filled glove box, a 100 mL round bottom flask equipped with Teflon stir bar was charged with 2-ethynyl-6-propoxy-naphthalene (**9**, 0.420 g, 2.00 mmol), **10** (0.956 g, 2.00 mmol), [Cu(phen)(PPh_3)Br] (0.234 g, 0.40 mmol), and potassium carbonate (0.552 g, 4.00 mmol). The flask was then sealed with a rubber septum, taken out of the glove box, and 40 mL of toluene was added through the septum. The mixture was stirred at 110 °C for 24 h. The mixture was then cooled to room temperature and filtered to remove insoluble materials. The ppt was washed with dichloromethane and the resulting combined filtrate was concentrated. Purification by column chromatography afforded a slightly yellow solid (0.503 g, 45%). $C_{33}H_{22}BrNO_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.70 (d, *J* = 6.8, 1H), 8.66-8.63 (d, *J* = 7.8, 1H), 8.46-8.44 (d, *J* = 8.4, 1H), 8.10-8.08 (d, *J* = 7.8, 1H), 8.00 (s, 1H), 7.92-7.88 (t, *J* = 7.3, 1H), 7.74-7.68 (m, 4H), 7.57-7.54 (d, *J* = 7.8, 1H), 7.32-7.30 (d, *J* = 8.4, 2H), 7.19-7.16 (d, *J* = 8.9, 1H), 7.12 (s, 1H), 4.07-4.04 (t, *J* = 6.7, 2H), 1.93-1.84 (m, 2H), 1.11-1.07 (t, *J* = 7.7, 3H).



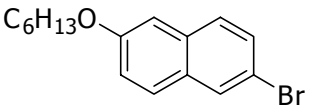
Molecule (1): To a 200 mL round bottom flask with Teflon stir bar, was added **11** (0.500 g, 0.89 mmol), copper bronze (0.17 g, 2.67 mmol), and 2,2'-bipyridine (0.07 g, 0.45 mmol). The flask was sealed with a rubber septum then evacuated and backfilled with nitrogen 3 times. DMSO/fluorobenzene (18 + 12 mL) and perfluoropropyl iodide (0.18 mL, 1.16 mmol) were added. The reaction mixture was then stirred at 75 °C. After 39 h, the reaction was cooled to room temperature and filtered to remove insoluble material. The ppt was washed with dichloromethane. The combined filtrate was then diluted with chloroform, washed with water (3x), and concentrated *in vacuo*. Purification via column chromatography afforded a slightly yellow solid (0.171 g, 30%). $C_{36}H_{22}F_7NO_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76-8.74 (dd, *J* = 6.4, 3.8, 2H), 8.64-8.62 (d, *J* = 8.4, 1H), 8.13-8.11 (d, *J* = 8.4, 1H), 8.00 (s, 1H), 7.95-7.91 (dd, *J* = 9.6, 6.4, 1H), 7.75-7.68 (m, 4H), 7.56-

7.54 (d, J = 8.4, 1H), 7.32-7.30 (d, J = 9.0, 2H), 7.19-7.16 (dd, J = 9.2, 3.2, 1H), 7.12 (s, 1H), 4.07-4.03 (t, J = 7.1, 2H), 1.93-1.84 (m, 2H), 1.11-1.07 (t, J = 7.1, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.68 (3F), -105.79 (2F), -124.39 (2F).

Synthesis of Compound **2**

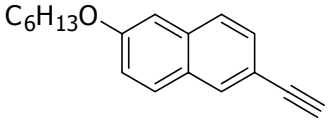


Reagents: (i) $C_6H_{13}I$, NaOH, DMSO, rt; (ii) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 80 °C; (iii) K_2CO_3, MeOH, CH_2Cl_2, rt; (iv) **10**, [Cu(phen)(PPh_3)Br], K_2CO_3, toluene, 110 °C; (v) $C_6F_{13}I$, Cu-bronze, 2,2'-bipyridine, fluorobenzene, DMSO, 75 °C.

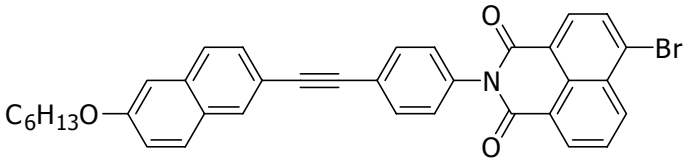


2-Bromo-6-hexyloxy-naphthalene (12): To a stirred solution of 6-bromo-2-naphthol (**7**, 2.22 g, 9.95 mmol) in DMSO (20 mL) was slowly added sodium hydroxide (2.5 M aqueous, 4.8 mL, 12.0 mmol), maintaining the temperature at 20-25 ºC. The cold bath was removed and 1-iodohexane (1.7 mL, 11.46 mmol) was added in one portion. The resulting yellow solution was stirred at room temperature. After 12 h, the solution was diluted with dichloromethane and washed with water (3x) and saturated NaCl solution. The resulting solution was dried over sodium sulfate, filtered, and rotovaped. The residue was purified by column chromatography to afford a white solid (2.97 g, 97%). $C_{16}H_{19}BrO$: ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.60-7.44 (m, 3H), 7.14-7.12 (d, *J* = 8.8, 1H), 7.04 (s, 1H), 4.00 (t, *J* = 6.4, 2H), 1.81 (m, 2H), 1.54-1.34 (m, 6H), 0.91 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.37, 133.05, 129.86, 129.57, 129.46, 128.35, 128.28, 120.03, 116.82, 106.42, 68.04, 31.58, 29.15, 25.76, 22.60, 14.04.

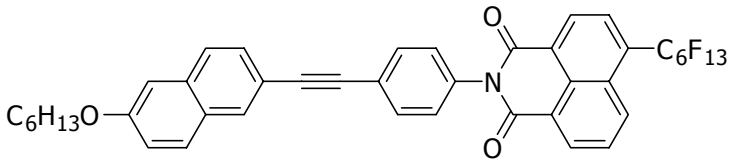


2-Ethynyl-6-hexyloxy-naphthalene (13): To a 50 mL Schlenk flask with Teflon stir bar was added 2-bromo-6-hexyloxy-naphthalene (**12**, 2.82 g, 9.16 mmol), $PdCl_2(PPh_3)_2$ (0.128 g, 0.182 mmol), and copper iodide (0.034 g, 0.182 mmol). The flask was sealed with a rubber septum, evacuated, and backfilled with nitrogen 3 times. Triethylamine (8 mL) and trimethylsilylacetylene (1.4 mL, 13.7 mmol) were added and the reaction mixture was stirred and heated to 60 ºC. After 2 h, the reaction mixture was cooled to room temperature and filtered through a Buchner funnel. The cake was washed with ether until the filtrate was clear. The combined filtrate was concentrated and the residue was purified by column chromatography to afford a white solid (2.48 g, 83%). A portion of the TMS-protected acetylene was deprotected by adding an excess of potassium carbonate to a solution of the protected acetylene dissolved in a dichloromethane/methanol (1:1) solution. The mixture was stirred at room temperature until deprotection was complete (monitored by TLC). Then the reaction mixture was filtered through a Buchner funnel and the filter cake was washed with dichloromethane until the filtrate was clear. The filtrate was rotovaped down and the resulting product was purified by column chromatography to afford a white solid (1.12 g, 90%). $C_{18}H_{20}O$: ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.69-7.66 (d, *J* = 9.0, 1H), 7.65-7.63 (d, *J* = 8.5, 1H), 7.48-7.46 (d, *J* = 8.4, 1H), 7.16-7.14 (dd, *J* = 8.9, 2.5, 1H), 7.08 (m, 1H), 4.07-4.04 (t, *J* = 6.5, 2H), 3.09 (s, 1H), 1.87-1.80 (m, 2H), 1.53-1.46 (m, 2H), 1.38-1.34 (m, 4H), 0.93-0.89 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.99, 134.43, 132.06, 129.23, 129.05, 128.17, 126.75, 119.79, 116.73, 106.47, 84.25, 76.60, 68.08, 31.59, 29.15, 25.77, 22.61, 14.04.



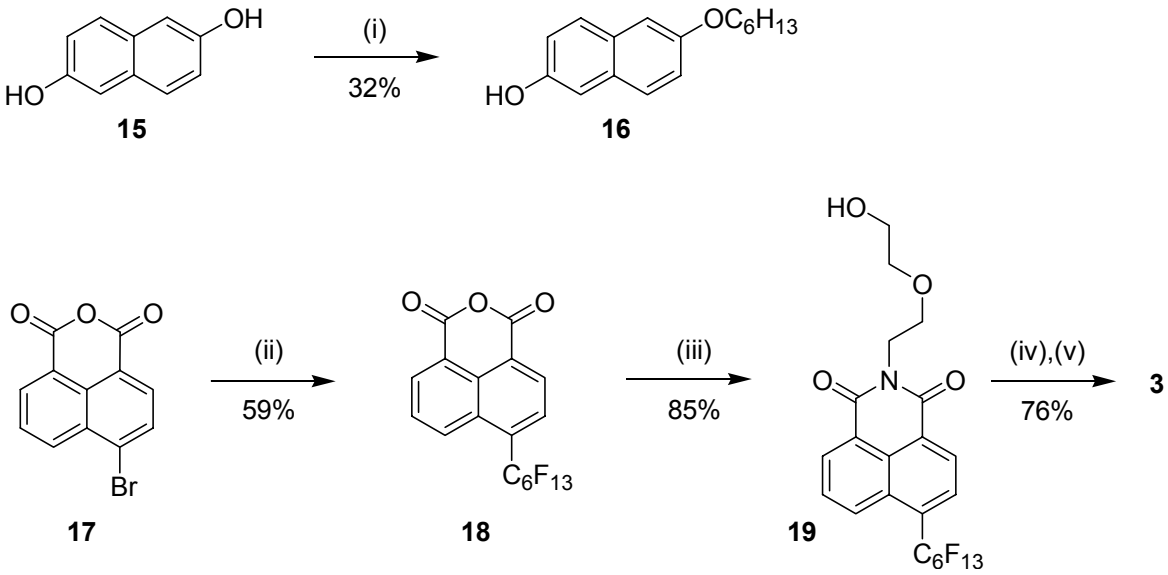
Compound (14): In an argon-filled glove box, a 50 mL round bottom flask equipped with a Teflon stir bar was charged with 2-ethynyl-6-hexyloxy-naphthalene (**13**, 0.378 g, 1.5 mmol), **10** (0.717 g, 1.5 mmol), [Cu(phen)(PPh_3)Br] (0.176 g, 0.3 mmol), and potassium carbonate (0.414 g, 3.0 mmol). The flask was then sealed with a rubber septum, taken out of the glove box, and 30 mL of toluene was added through the septum. After stirring at 110 ºC for 4 days, the mixture was cooled to room

temperature and filtered to remove insolubles. The cake was washed well with dichloromethane and the resulting combined filtrate was concentrated. Purification of the residue by column chromatography afforded a slightly yellow solid (0.295 g, 32%). $C_{36}H_{28}BrNO_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.66 (d, *J* = 7.2, 1H), 8.61-8.59 (d, *J* = 7.4, 1H), 8.43-8.41 (d, *J* = 7.8, 1H), 8.06-8.03 (d, *J* = 7.8, 1H), 7.97 (s, 1H), 7.87-7.83 (t, *J* = 7.4, 1H), 7.73-7.65 (m, 4H), 7.54-7.52 (d, *J* = 9.9, 1H), 7.31-7.29 (d, *J* = 8.6, 2H), 7.16-7.13 (d, *J* = 8.9, 1H), 7.09 (s, 1H), 4.08-4.04 (t, *J* = 6.6, 2H), 1.88-1.80 (m, 2H), 1.53-1.46 (m, 2H), 1.38-1.34 (m, 4H), 0.93-0.90 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.56, 163.52, 157.88, 134.61, 134.22, 133.64, 132.47, 132.41, 131.55, 131.39, 131.17, 130.73, 130.71, 129.25, 129.24, 128.89, 128.71, 128.31, 128.13, 126.73, 124.24, 123.04, 122.16, 119.68, 117.70, 106.50, 91.00, 88.34, 68.06, 31.58, 29.15, 25.76, 22.60, 14.04.

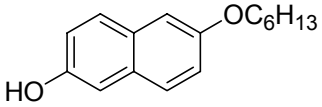


Molecule (2): To a 100 mL round bottom flask equipped with a Teflon stir bar was added **14** (0.295 g, 0.48 mmol), copper bronze (0.093 g, 1.47 mmol), and 2,2'-bipyridine (0.037 g, 0.24 mmol). The flask was sealed with a rubber septum, evacuated, and backfilled with nitrogen 3 times. DMSO (3 mL), fluorobenzene (2 mL), and perfluorohexyl iodide (0.14 mL, 0.64 mmol) were added. The reaction mixture was stirred at 75 ºC for 42 h. Then the reaction mixture was cooled to room temperature, filtered, and the filter cake was washed with well with dichloromethane. The combined filtrate was then diluted with chloroform, washed with water (3x), and concentrated *in vacuo*. The residue was purified by column chromatography to afford a slightly yellow solid (0.198 g, 49%). $C_{42}H_{28}F_{13}NO_3$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.74 (d, *J* = 7.0, 2H), 8.66-8.63 (d, *J* = 8.5, 1H), 8.16-8.13 (d, *J* = 7.8, 1H), 8.01 (s, 1H), 7.97-7.92 (d, *J* = 7.4, 1H), 7.76-7.68 (m, 4H), 7.58-7.54 (d, *J* = 8.4, 1H), 7.34-7.31 (d, *J* = 8.3, 2H), 7.19-7.16 (d, *J* = 8.8, 1H), 7.12 (s, 1H), 4.11-4.07 (t, *J* = 6.5, 2H), 1.91-1.81 (m, 2H), 1.54-1.47 (m, 2H), 1.40-1.36 (m, 4H), 0.95-0.90 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.67 (3F), -104.80 (2F), -119.89 (2F), -121.32 (2F), -122.59 (2F), -126.02 (2F). HRMS calcd for $C_{42}H_{28}F_{13}NO_3$: 841.1862; Found 841.1838.

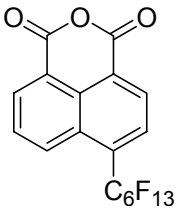
Synthesis of Compound **3**



Reagents: (i) $C_6H_{13}I$, Cs_2CO_3, DMSO, rt; (ii) $C_6F_{13}I$, Cu-bronze, 2,2'-bipyridine, fluorobenzene, DMSO, 80 °C; (iii) 2-(2-aminoethoxy)ethanol, EtOH, reflux; (iv) MsCl, Et_3N, CH_2Cl_2, 0 °C to rt; (v) **16**, Cs_2CO_3, DMF, 100 °C.

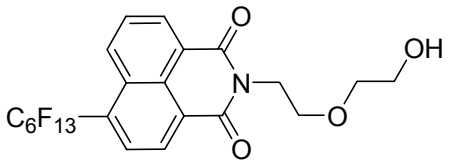


6-Hexyloxy-naphthalen-2-ol (16): To a stirred solution of 2,6-dihydroxynaphthalene (**15**, 1.60 g, 10.00 mmol) and cesium carbonate (3.58 g, 10.00 mmol) in DMSO (50 mL) under nitrogen, was added 1-iodohexane (1.48 mL, 10.00 mmol). After stirring at rt overnight, the reaction mixture was diluted with water and acidified (to pH 3) with 10% (v/v) HCl. The resulting mixture was extracted with ethyl acetate (3x). The combined extracts were washed with water (1x) and saturated NaCl solution (3x) and dried over sodium sulfate. The resulting dispersion was filtered and rotovaped onto silica gel. Purification via silica gel chromatography (25:75 ethyl acetate/hexanes) yielded and off-white solid (780 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.8, 1H), 7.56 (d, J = 8.8, 1H), 7.15-7.03 (m, 4H), 4.90 (s, 1H), 4.04 (t, J = 6.6, 2H), 1.83 (m, J = 7.1, 2H), 1.55-1.44 (m, 2H), 1.41-1.30 (m, 4H), 0.91 (t, J = 7.1, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.54, 151.68, 129.86, 129.85, 128.52, 127.86, 119.65, 118.12, 109.88, 107.12, 68.30, 31.68, 29.30, 25.85, 22.68, 14.12. Anal. calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.85; H, 8.20.

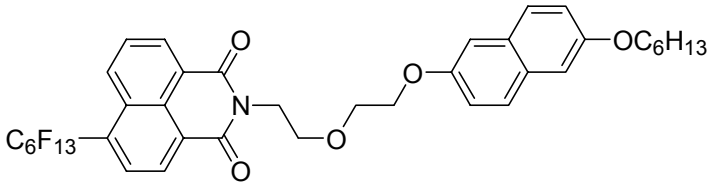


4-Perfluorohexyl-1,8-naphthalic anhydride (18): 4-bromo-1,8-naphthalic anhydride (**17**, 2.77 g, 10.00 mmol), copper bronze powder (3.69 g, 20.00 mmol), 2,2'-bipyridine (156 mg, 1.00 mmol),

fluorobenzene (20 mL), and DMSO (30 mL) were combined in a Schlenk flask. The vessel was purged with nitrogen and 1-iodoperfluorohexane (2.39 mL, 11.00 mmol) was added. The reaction mixture was stirred at 80 ºC for 3 days. After cooling to rt, the mixture was diluted with water (100 mL) and ethyl acetate (100 mL). The resulting insoluble material was filtered off and the filter cake was rinsed well with fresh ethyl acetate. The organic layer of the filtrate was collected and the aqueous layer was extracted with ethyl acetate (2x). The combined extracts were washed with saturated NaCl solution (3x), dried over sodium sulfate, filtered, and rotovaped down to afford a yellow solid. Recrystallization from 500 mL ethyl acetate/hexanes (1:1) yielded the desired product as fluffy white needles (3.02 g, 59%). Concentration of the filtrate yielded 870 mg of a second crop of light yellow material that NMR revealed to be a 1.0:1.3 mixture of the desired product and 1,8-naphthalic anhydride. **(18)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.72 (m, *J* = 6.8, 2H), 8.69 (d, *J* = 8.6, 1H), 8.17 (d, *J* = 7.8, 1H), 7.98 (dd, *J* = 8.8, 7.3, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.67 (3F), -105.07 (2F), -119.89 (2F), -121.27 (2F), -122.59 (2F), -126.02 (2F). Anal. calcd for $C_{18}H_5F_{13}O_3$: C, 41.88; H, 0.98; F, 47.84. Found: C, 41.70; H, 0.92; F, 48.1.



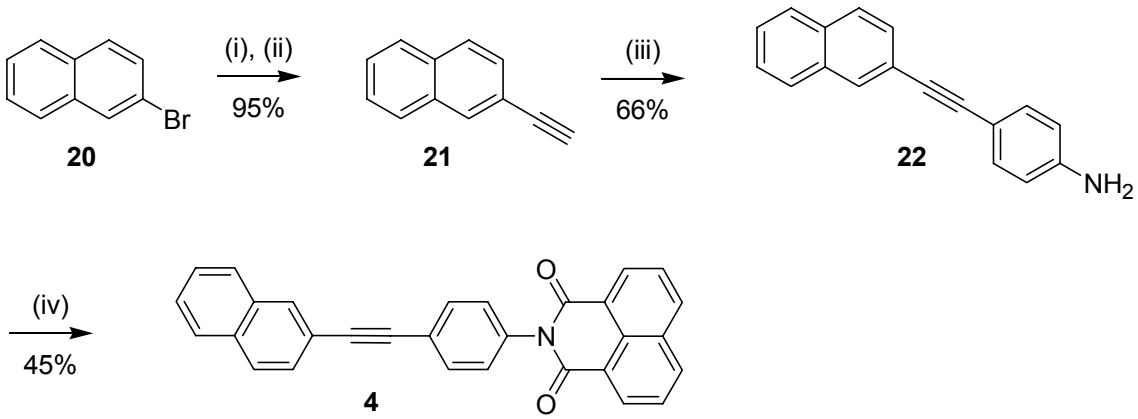
Compound (19): To a stirred solution of 4-perfluorohexyl-1,8-naphthalic anhydride (**18**, 2.58 g, 5.00 mmol) in absolute ethanol (50 mL) was added 2-(2-aminoethoxy)ethanol (0.55 mL, 5.50 mmol). The resulting dispersion was heated to reflux and formed a clear yellow solution. After 2 h, the reaction mixture was cooled to rt and concentrated *in vacuo*. Purification of the residue via silica gel chromatography (10:90 acetone/methylene chloride) yielded the desired product as a white solid (2.57 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 7.3, 1H), 8.69 (d, *J* = 7.8, 1H), 8.56 (d, *J* = 8.8, 1H), 8.08 (d, *J* = 7.8, 1H), 7.88 (m, *J* = 8.7, 7.4, 1H), 4.46 (t, *J* = 5.8, 2H), 3.87 (t, *J* = 5.8, 2H), 3.73-3.62 (m, 4H), 2.52 (t, *J* = 5.6, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.80 (3F), -104.93 (2F), -120.04 (2F), -121.42 (2F), -122.73 (2F), -126.16 (2F). Anal. calcd for $C_{22}H_{14}F_{13}NO_4$: C, 43.80; H, 2.34; N, 2.32; F, 40.94. Found: C, 43.78; H, 2.34; N, 2.26; F, 40.6.



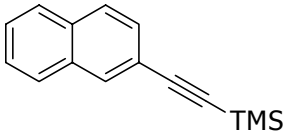
Molecule (3): A stirred solution of **19** (2.41 g, 4.00 mmol) in methylene chloride (40 mL) was cooled under nitrogen in an ice bath. Triethylamine (1.69 mL, 12.00 mmol) was added and the resulting mixture was stirred for 5 minutes at 0 ºC. Methanesulfonyl chloride (0.46 mL, 6.00 mmol) was added

dropwise and the mixture was allowed to warm to rt. After 1 h, the reaction mixture was rinsed with water (2x) and saturated NaCl solution. The organic phase was dried over sodium sulfate, filtered, and concentrated *in vacuo* to provide a quantitative yield of the mesylate as an off-white solid. The mesylate was combined with 6-hexyloxy-naphthalen-2-ol (**16**, 1.08 g, 4.40 mmol), cesium carbonate (2.89 g, 8.80 mmol), and DMF (80 mL). The resulting mixture was purged with nitrogen and heated to 100 ºC. After stirring overnight, the reaction mixture was cooled to rt and diluted with water. The resulting mixture was extracted with ethyl acetate (4x). The combined extracts were washed with water (1x) and saturated NaCl solution (2x), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified via silica gel chromatography (1% acetone in methylene chloride) to yield the desired product as a light orange solid (2.53 g, 76% from **19**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 7.1, 1H), 8.61 (d, *J* = 7.8, 1H), 8.47 (d, *J* = 8.6, 1H), 7.99 (d, *J* = 7.8, 1H), 7.79 (dd, *J* = 8.8, 7.3, 1H), 7.50 (d, *J* = 9.1, 1H), 7.42 (d, *J* = 8.8, 1H), 7.07 (dd, *J* = 9.0, 2.4, 1H), 7.00 (d, *J* = 2.3, 1H), 6.94 (d, *J* = 2.5, 1H), 6.89 (dd, *J* = 8.8, 2.5, 1H), 4.48 (t, *J* = 5.8, 2H), 4.12 (t, *J* = 4.3, 2H), 4.02 (t, *J* = 6.6, 2H), 3.97 (t, *J* = 5.6, 2H), 3.93 (t, *J* = 5.1, 2H), 1.83 (m, *J* = 7.1, 2H), 1.56-1.44 (m, 2H), 1.41-1.31 (m, 4H), 0.92 (t, *J* = 7.1, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.67 (3F), -105.06 (2F), -119.89 (2F), -121.27 (2F), -122.60 (2F), -126.02 (2F). Anal. calcd for $C_{38}H_{32}F_{13}NO_5$: C, 55.01; H, 3.89; N, 1.69; F, 29.77. Found: C, 54.98; H, 3.85; N, 1.62; F, 29.9.

Synthesis of Compound **4**

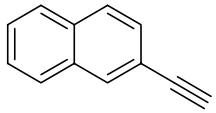


Reagents: (i) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 80 °C; (ii) K_2CO_3, MeOH, CH_2Cl_2, rt; (iii) iodoaniline, $[Cu(phen)(PPh_3)_2]NO_3$, Cs_2CO_3, toluene, 110 °C; (iv) 1,8-naphthalic anhydride, imidazole, $CHCl_3$, 75 °C.

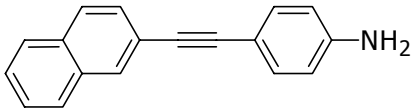


2-Naphthyl-1-trimethylsilyl acetylene: To a 10 mL Schlenk flask with a Teflon stir bar was added 2-bromo-naphthalene (**20**, 1.04 g, 5.00 mmol), $PdCl_2(PPh_3)_2$ (0.035 g, 0.05 mmol), and copper iodide

(0.009 g, 0.05 mmol). The flask was sealed with a rubber septum, evacuated, and backfilled with nitrogen 3 times. Triethylamine (5 mL) and trimethylsilylacetylene (0.8 mL, 7.5 mmol) were added and the reaction mixture was stirred at 70 ºC. After 24 h, the reaction mixture was cooled to room temperature and filtered through a Buchner funnel. The filter cake was washed with ether until the filtrate was clear. The combined filtrate was concentrated and the residue was purified by column chromatography to afford a white solid (1.08 g, 96%). $C_{15}H_{16}Si$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72-6.67 (m, 3H), 7.50-7.48 (d, J = 8.5, 1H), 7.41-7.39 (m, 2H), 0.30 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.82, 132.80, 131.95, 128.50, 127.82, 127.70, 127.66, 126.67, 126.45, 120.37, 105.52, 94.47, 0.04.

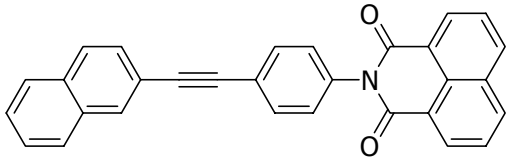


2-Ethynyl-naphthalene (21): Deprotection of the trimethylsilyl group was accomplished by adding an excess amount of potassium carbonate to a solution of 2-naphthyl-1-trimethylsilyl acetylene (1.08 g, 4.8 mmol) dissolved in a dichloromethane/methanol (1:1) solution. The reaction mixture was stirred at room temperature until deprotection was complete (monitored by TLC). Then the reaction mixture was filtered through a Buchner funnel and the cake was washed with dichloromethane until the filtrate was clear. The filtrate was rotovaped down and the resulting residue was purified by column chromatography to afford a white solid (0.73 g, 99%). $C_{12}H_8$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.85-7.80 (m, 3H), 7.59-7.57 (d, J = 8.5, 1H), 7.55-7.51 (m, 2H), 3.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.96, 132.75, 132.25, 128.48, 127.97, 127.72, 127.70, 126.84, 126.55, 119.31, 83.98, 77.44.



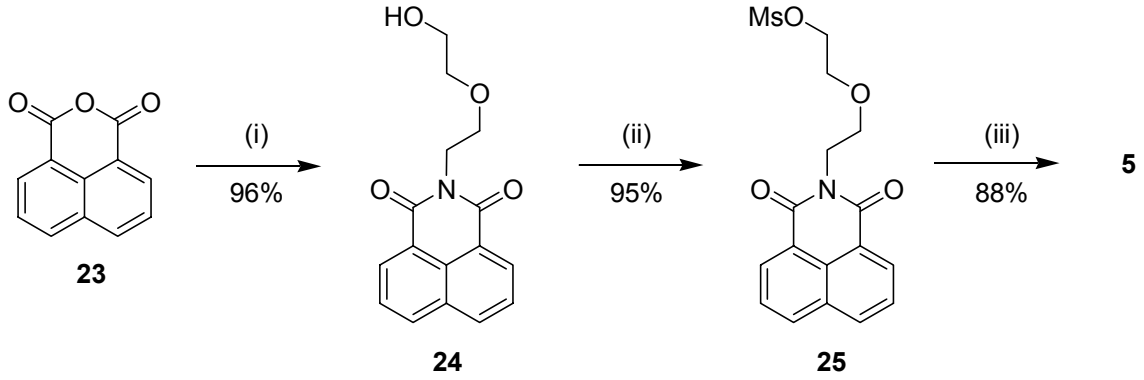
4-Naphthalen-2-ylethynyl-phenylamine (22): In an argon-filled glove box, a 50 mL round bottom flask equipped with Teflon stir bar was charged with 2-ethynyl-naphthalene (**21**, 0.77 g, 5.00 mmol), 4-iodoaniline (1.05 g, 4.80 mmol), $[Cu(phen)(PPh_3)_2]NO_3$ (0.797 g, 0.96 mmol), and cesium carbonate (3.13 g, 9.60 mmol). The flask was then sealed with a rubber septum, taken out of the glove box, and 15 mL of toluene was added through the septum. The mixture was stirred at 110 ºC for 36 h. After cooling to room temperature, the mixture was filtered to remove insoluble materials and the cake was washed with ethyl acetate. The combined filtrate was concentrated *in vacuo* and the residue purified by column chromatography to afford a slightly yellow solid (0.76 g, 66%). $C_{18}H_{13}N$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.81-7.76 (m, 3H), 7.56-7.54 (d, J = 8.4, 1H), 7.49-7.43 (m, 2H), 7.39-7.37 (d, J = 8.5, 2H), 6.64-6.62 (d, J = 8.5, 2H), 3.80 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.67,

133.06, 132.99, 132.48, 130.80, 128.43, 127.84, 127.70, 127.64, 126.39, 126.30, 121.21, 114.74, 112.54, 90.54, 87.75.

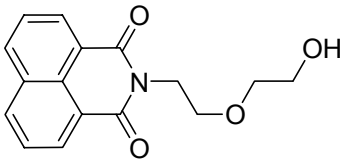


Molecule (4): To a 50 mL round bottom flask equipped with a Teflon stir bar was added 1,8-naphthalic anhydride (0.41 g, 2.08 mmol), 4-naphthalen-2-ylethynyl-phenylamine (**22**, 0.76 g, 3.12 mmol), imidazole[2] (3.11 g, 45.76 mmol), and chloroform (20 mL). The resulting slightly yellow solution was heated to 75 ºC. After 1 h, the reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was taken up in absolute ethanol. The suspension was sonicated 15 min and then filtered through a Buchner funnel. The filter cake was washed with cold ethanol, air dried, and purified by column chromatography to afford a white solid (0.392 g, 45%). $C_{30}H_{17}NO_2$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65-8.64 (d, *J* = 7.2, 2H), 8.27-8.25 (d, *J* = 8.3, 2H), 8.08 (s, 1H), 7.83-7.77 (m, 5H), 7.75-7.73 (d, *J* = 8.6, 2H), 7.61-7.59 (d, *J* = 8.4, 1H), 7.51-7.48 (m, 2H), 7.34-7.32 (d, *J* = 8.6, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.22, 135.22, 134.40, 132.99, 132.86, 132.58, 131.76, 131.70, 131.61, 128.85, 128.53, 128.43, 128.01, 127.82, 127.77, 127.06, 126.71, 126.55, 123.90, 122.69, 120.39, 90.60, 89.15.

Synthesis of Compound **5**

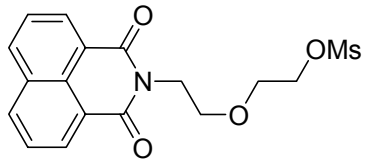


Reagents: (i) 2-(2-aminoethoxy)ethanol, EtOH, reflux; (ii) MsCl, Et_3N, CH_2Cl_2, 0 °C to rt; (iii) 2-naphthol, Cs_2CO_3, DMF, 100 °C.

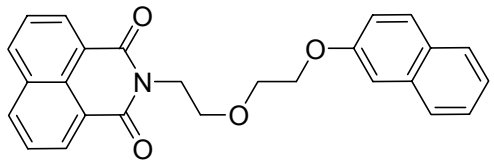


Compound (24): To a stirred solution of 1,8-naphthalic anhydride (**23**, 1.98 g, 10.00 mmol) in absolute ethanol (100 mL) was added 2-(2-aminoethoxy)ethanol (1.11 mL, 11.00 mmol). The mixture

was refluxed for 2 h, then cooled to rt and concentrated *in vacuo*. Purification of the residue via silica gel chromatography (5:95 to 20:80 acetone/methylene chloride) yielded the desired product as a clear oil that solidified upon standing (2.73 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 7.3, 1.0, 2H), 8.21 (dd, *J* = 8.3, 1.0, 2H), 7.75 (dd, *J* = 8.2, 7.3, 2H), 4.45 (t, *J* = 5.7, 2H), 3.87 (t, *J* = 5.7, 2H), 3.73-3.64 (m, 4H), 2.52 (t, *J* = 5.0, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.45, 134.06, 131.53, 131.39, 128.14, 126.94, 122.45, 72.24, 68.42, 61.85, 39.48. Anal. calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.17; H, 5.24; N, 4.82.



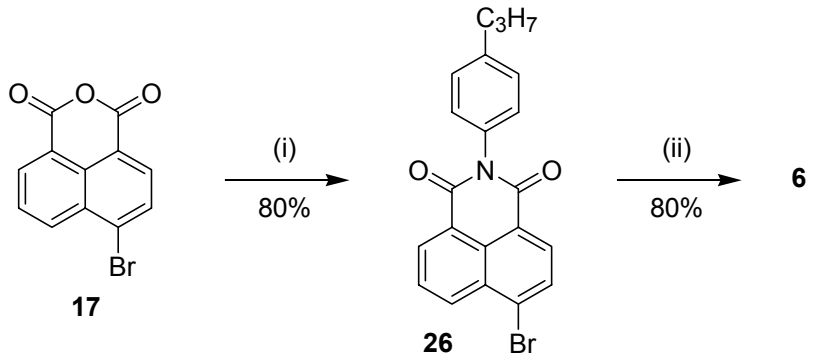
Compound (25): A solution of **24** (1.43 g, 5.00 mmol) in methylene chloride (50 mL) under nitrogen was cooled in an ice bath. Triethylamine (2.11 mL, 15.00 mmol) was added and the resulting solution was stirred at 0 ºC for 5 minutes. Methanesulfonyl chloride (0.58 mL, 7.50 mmol) was added dropwise and the reaction mixture was warmed to rt. After 2 h, the reaction mixture was rinsed with water (2x) and saturated NaCl solution (1x). The organic phase was dried over sodium sulfate, filtered, and concentrated *in vacuo*. Purification via silica gel chromatography yielded the desired mesylate as a light yellow solid (1.72 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 7.3, 1.0, 2H), 8.21 (dd, *J* = 8.3, 0.9, 2H), 7.75 (dd, *J* = 8.1, 7.4, 2H), 4.44 (t, *J* = 5.9, 2H), 4.36-4.31 (m, 2H), 3.86 (t, *J* = 5.9, 2H), 3.82-3.77 (m, 2H), 2.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.25, 134.14, 131.62, 131.35, 128.19, 126.99, 122.48, 69.31, 68.48, 68.28, 39.05, 37.54. Anal. calcd for $C_{17}H_{17}NO_6S$: C, 56.19; H, 4.72; N, 3.85. Found: C, 55.93; H, 4.65; N, 3.80.



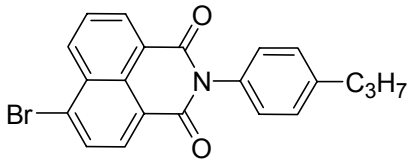
Molecule (5): To a stirred mixture of 2-naphthol (1.44 g, 10.00 mmol) and cesium carbonate (6.52 g, 20.00 mmol) in DMF (100 mL) was added mesylate **25** (3.63 g, 10.00 mmol). The reaction mixture was purged with nitrogen and heated to 100 ºC. After 1 h, the reaction was cooled to rt and diluted with water. The resulting solution was extracted with ethyl acetate (3x). The combined extracts were washed well with saturated NaCl solution (3x), dried over sodium sulfate, and concentrated *in vacuo*. Recrystallization from ethyl acetate/hexanes afforded two crops of the desired product as fluffy white crystals (3.63 g, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 7.2, 1.1, 2H), 8.13 (dd, *J* = 8.2, 0.9, 2H), 7.73-7.66 (m, 3H), 7.65-7.57 (m, 2H), 7.39 (ddd, *J* = 8.1, 7.0, 1.2, 1H), 7.30 (ddd, *J* = 8.0, 6.9, 1.2, 1H), 7.03-6.98 (m, 2H), 4.49 (t, *J* = 6.1, 2H), 4.20-4.15 (m, 2H), 3.99-3.93 (m, 4H), . ^{13}C NMR

(75 MHz, $CDCl_3$) δ 164.31, 156.69, 134.41, 133.91, 131.54, 131.25, 129.17, 128.93, 128.19, 127.56, 126.86, 126.76, 126.19, 123.53, 122.57, 118.90, 106.61, 69.13, 68.21, 67.47, 39.16. Anal. calcd for $C_{26}H_{21}NO_4$: C, 75.90; H, 5.14; N, 3.40. Found: C, 75.75; H, 5.03; N, 3.34.

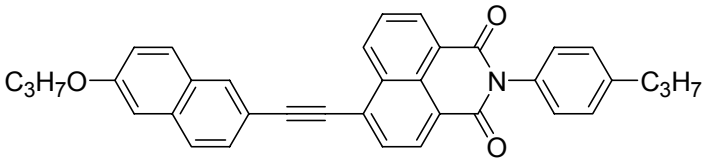
Synthesis of Compound **6**



Reagents: (i) *n*-propylaniline, imidazole, $CHCl_3$, reflux; (ii) **9**, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 80 °C.

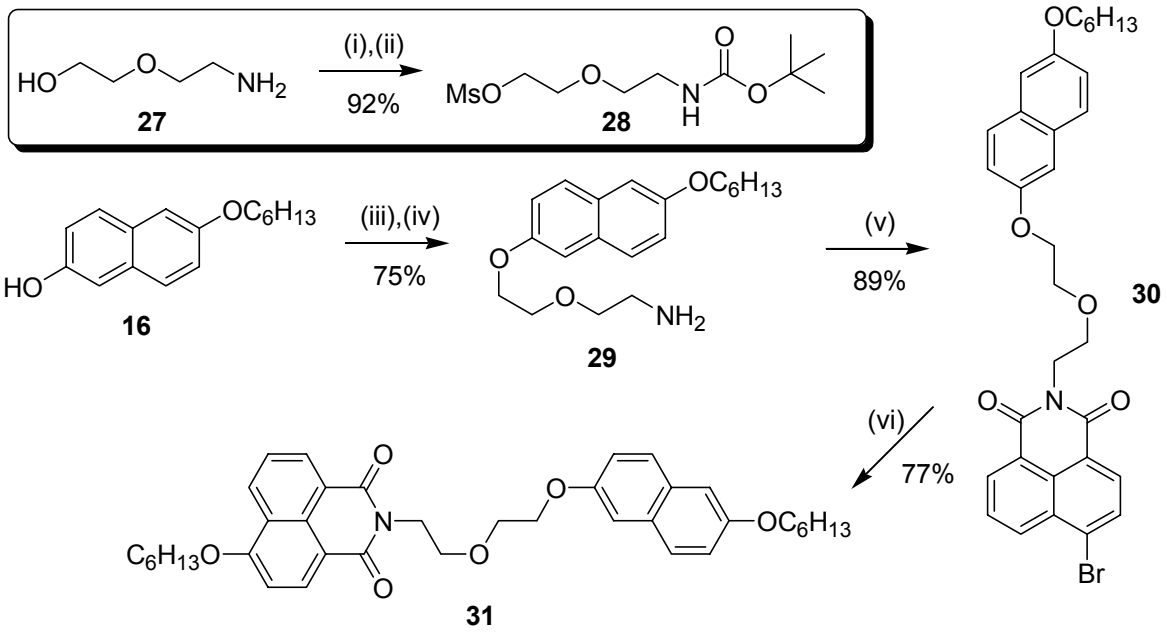


Compound (26): To a stirred solution of 4-bromo-1,8-naphthalic anhydride (**17**, 2.77 g, 10.00 mmol) and imidazole[2] (14.98 g, 220.00 mmol) in chloroform, was added 4-*n*-propylaniline (2.94 mL, 20.00 mmol). Upon heating to reflux, the reaction mixture formed a clear orange solution. After 1 h, the reaction mixture was cooled to rt and concentrated *in vacuo*. The residue was dissolved in ethyl acetate (600 mL) and the resulting mixture was washed with 10% (v/v) HCl (3x), water (1x), and saturated NaCl solution (1x). The organic phase was dried over sodium sulfate, filtered, and concentrated in vacuo to yield about 12 g of an orange mixture of imidazole and the desired product. Recrystallization from ethanol (500 mL) afforded the desired product as a light yellow solid (3.15 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 7.07, 1H), 8.62 (d, J = 8.3, 1H), 8.45 (d, J = 7.8, 1H), 8.07 (d, J = 7.8, 1H), 7.88 (dd, J = 7.9, 7.9, 1H), 7.36 (d, J = 7.8, 2H), 7.21 (d, J = 8.1, 2H), 2.68 (t, J = 7.7, 2H), 1.72 (m, J = 7.5, 2H), 1.00 (t, J = 7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.88, 163.85, 143.41, 133.56, 132.55, 132.42, 131.57, 131.21, 130.80, 130.58, 129.50, 129.37, 128.19, 128.15, 123.34, 122.47, 37.86, 24.35, 13.98. Anal. calcd for $C_{21}H_{16}BrNO_2$: C, 63.97; H, 4.09; N, 3.55; Br, 20.27. Found: C, 63.78; H, 4.15; N, 3.51; Br, 20.5.

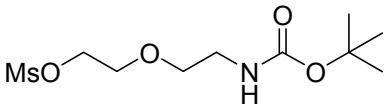


Molecule (6): A mixture of **26** (1.18 g, 3.00 mmol), 2-ethynyl-6-propoxy-naphthalene (**9**, 631 mg, 3.00 mmol), $Pd(PPh_3)_2Cl_2$ (42.1 mg, 0.060 mmol), copper iodide (11.4 mg, 0.060 mmol), and triethylamine (30 mL) were stirred overnight under nitrogen in a Schlenk flask at 80 ºC. After cooling to rt, the mixture was concentrated *in vacuo*. The residue was adsorbed onto silica gel and purified via silica gel chromatography (70:30 methylene chloride/hexanes) to afford the desired product as a highly fluorescent yellow solid (1.24 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 8.3, 0.8, 1H), 8.66 (dd, *J* = 7.3, 1.0, 1H), 8.57 (d, *J* = 7.6, 1H), 8.11 (s, 1H), 7.97 (d, *J* = 7.6, 1H), 7.86 (dd, *J* = 8.2, 7.5), 7.75 (d, *J* = 9.1, 1H), 7.73 (d, *J* = 8.6, 1H), 7.65 (dd, *J* = 8.3, 1.5, 1H), 7.35 (d, *J* = 8.3, 2H), 7.25-7.18 (m, 3H), 7.13 (d, *J* = 2.3, 1H), 4.06 (t, *J* = 6.7, 2H), 2.67 (t, *J* = 7.7, 2H), 1.90 (m, *J* = 7.1, 2H), 1.72 (m, *J* = 7.5, 2H), 1.10 (t, *J* = 7.5, 3H), 1.01 (t, *J* = 7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.29, 164.01, 158.44, 143.25, 134.87, 132.81, 132.78, 132.14, 131.94, 131.74, 130.79, 130.63, 129.51, 129.46, 128.73, 128.48, 128.33, 128.25, 127.44, 127.15, 123.16, 122.00, 120.12, 116.83, 106.67, 100.41, 86.14. 69.69, 37.89, 24.38, 22.56, 14.01, 10.62. Anal. calcd for $C_{36}H_{29}NO_3$: C, 82.58; H, 5.58; N, 2.67. Found: C, 82.33; H, 5.63; N, 2.59.

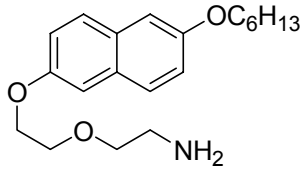
Synthesis of Compound **31**



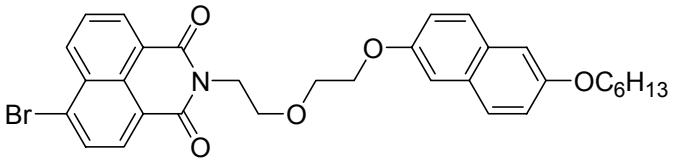
Reagents: (i) (*t*-BOC)$_2$O, CH_2Cl_2, rt; (ii) MsCl, CH_2Cl_2, rt; (iii) **28**, Cs_2CO_3, DMSO, rt; (iv) TFA, CH_2Cl_2, rt; (v) 4-bromo-1,8-naphthalic anhydride, EtOH, reflux; (vi) hexyl alcohol, CuI, 1,10-phenanthroline, Cs_2CO_3, 110 ºC.



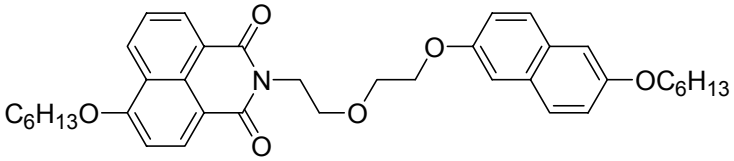
Compound (28): To a stirred solution of 2-(2-aminoethoxy)ethanol (**27**, 1.00 mL, 10.00 mmol) in methylene chloride (50 mL) was slowly added a solution of (*t*-BOC)$_2$O (2.18 g, 10.00 mmol) dissolved in methylene chloride (50 mL). The resulting mixture was stirred at room temperature overnight. Next, triethylamine (4.22 mL, 30.00 mmol) was added, followed by the dropwise addition of methanesulfonyl chloride (1.55 mL, 20.00 mmol). The resulting light yellow solution was stirred at rt for 4 h and then quenched with water (100 mL). The layers were separated and the aqueous phase was extracted again with methylene chloride. The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a yellow oil. The crude product was dispersed in diethyl ether and filtered through a pad of silica gel. The filtrate was concentrated to afford the desired product as a clear oil (2.59 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) agreed with that reported in the literature[3]. The material was used without further purification.



Compound (29): A mixture of 6-hexyloxy-naphthalen-2-ol (**16**, 1.83 g, 7.50 mmol), **28** (2.66 g, 9.38 mmol), and cesium carbonate (2.44 g, 7.50 mmol) in DMSO (75 mL) was purged with nitrogen and stirred at rt overnight. After being diluted with water, the resulting mixture was extracted with ethyl acetate (4x). The combined extracts were washed with water (2x), saturated NaCl solution (2x), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The residue was purified via silica gel chromatography (25:75 ethyl acetate/hexanes) to yield the BOC-protected amine as an off-white solid (2.44 g, 75%). The BOC-protected amine was dissolved in methylene chloride (75 mL) and trifluoroacetic acid (2.79 mL, 37.5 mmol) was added. After stirring at rt overnight, the solution was washed with 2M NaOH (2x), water (2x), and saturated NaCl solution. The organic phase was dried over sodium sulfate, filtered, and concentrated *in vacuo* to afford the free amine as an off-white solid (1.87 g, 100% yield deprotection, 75% yield from **16**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 1.3, 1H), 7.60 (d, J = 1.3, 1H), 7.18-7.16 (m, 4H), 4.23 (t, J = 4.7, 2H), 4.04 (t, J = 6.6, 2H), 3.88 (t, J = 4.8, 2H), 3.60 (t, J = 5.2, 2H), 2.91 (bs, 2H), 1.83 (m, J = 7.1, 2H), 1.56-1.30 (m, 8H), 0.92 (t, J = 7.1, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.71, 155.16, 129.94, 129.56, 128.13, 128.08, 119.31, 119.15, 107.18, 106.90, 73.58, 69.54, 68.06, 67.45, 41.80, 31.64, 29.28, 25.82, 22.64, 14.08. Anal. calcd for $C_{20}H_{29}NO_3$: C, 72.47; H, 8.82; N, 4.23. Found: C, 71.92; H, 8.86; N, 4.07.



Compound (30): A mixture of 4-bromo-1,8-naphthalic anhydride (1.52 g, 5.50 mmol) and **29** (1.82 g, 5.50 mmol) in absolute ethanol was heated to reflux. After 2 h, the resulting yellow slurry was cooled in an ice bath. The precipitate was filtered off and dried *in vacuo* to yield the desired product as a light yellow solid (2.88 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 7.2, 0.9, 1H), 8.39 (dd, *J* = 8.6, 0.8, 1H), 8.29 (d, *J* = 7.8, 1H), 7.89 (d, *J* = 7.8, 1H), 7.70 (dd, *J* = 7.3, 8.3, 1H), 7.46 (d, *J* = 8.8, 1H), 7.40 (d, *J* = 8.8, 1H), 7.06 (dd, *J* = 9.0, 2.4, 1H), 6.99 (d, *J* = 2.5, 1H), 6.90-6.85 (m, 2H), 4.45 (t, *J* = 5.8, 2H), 4.10 (t, *J* = 4.7, 2H), 4.02 (t, *J* = 6.6, 2H), 3.98-3.89 (m, 4H), 1.83 (m, *J* = 7.1, 2H), 1.55-1.44 (m 2H), 1.41-1.31 (m, 4H), 0.92 (t, *J* = 7.1, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.70, 163.65, 155.57, 155.01, 133.07, 131.96, 131.14, 130.93, 130.43, 130.18, 129.69, 129.37, 128.88, 127.98, 127.88, 127.78, 122.86, 122.03, 119.12, 118.87, 106.84, 69.24, 68.05, 67.44, 39.38, 31.66, 29.30, 25.84, 22.66, 14.10. Anal. calcd for $C_{32}H_{32}BrNO_5$: C, 65.09; H, 5.46; N, 2.37. Found: C, 65.13; H, 5.57; N, 2.27.



Compound (31): Prepared according to a literature procedure for the cross-coupling of aryl iodides with aliphatic alcohols[4]. A mixture of **30** (591 mg, 1.00 mmol), copper iodide (38.1 mg, 0.200 mmol), 1,10-phenanthroline (36.0 mg, 0.200 mmol), cesium carbonate (652 mg, 2.00 mmol), and hexyl alcohol (4.0 mL) was combined in a sealed tube. The reaction mixture was stirred at 110 ºC for 24 h. After cooling to rt, the solvent was removed *in vacuo* and the residue was partitioned between water and ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic phase was rinsed with water (1x), saturated NaCl solution (1x), dried over sodium sulfate, filtered, and rotovaped onto silica gel. Purification via silica gel chromatography (1.5% acetone in methylene chloride) afforded the desired product as a light yellow solid (470 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 7.3, 0.8, 1H), 8.51-8.44 (m, 2H), 7.63 (t, *J* = 7.8, 1H), 7.52 (d, *J* = 8.8, 1H), 7.48 (d, *J* = 9.1, 1H), 7.07 (dd, *J* = 8.8, 2.3, 1H), 7.02 (d, *J* = 2.3, 1H), 6.99 (dd, *J* = 8.8, 2.5, 1H), 6.96 (d, *J* = 2.3, 1H), 6.91 (d, *J* = 8.3, 1H), 4.46 (t, *J* = 6.1, 2H), 4.19 (t, *J* = 6.4, 2H), 4.14 (t, *J* = 4.8, 2H), 4.02 (t, *J* = 6.6, 2H), 3.98-3.90 (m, 4H), 1.95 (m, *J* = 7.0, 2H), 1.82 (m, *J* = 7.1, 2H), 1.62-1.44 (m, 4H), 1.44-1.30 (m, 8H), 0.94 (t, *J* = 7.1, 3H), 0.91 (t, *J* = 6.9, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.67, 164.04, 160.35, 155.56, 155.15, 133.57, 131.52, 129.75, 129.50, 129.45,

128.71, 128.06, 127.85, 125.71, 123.53, 122.25, 119.10, 119.05, 114.60, 106.99, 106.84, 105.73, 69.18, 69.04, 68.25, 68.05, 67.50, 38.99, 31.66, 31.57, 29.31, 28.97, 25.83, 22.65, 22.62, 14.08, 14.06. Anal. calcd for $C_{38}H_{45}NO_6$: C, 74.60; H, 7.41; N, 2.29. Found: C, 74.52; H, 7.57; N, 2.23.

III. Calculated Electrostatic Potential Surfaces for 2-6

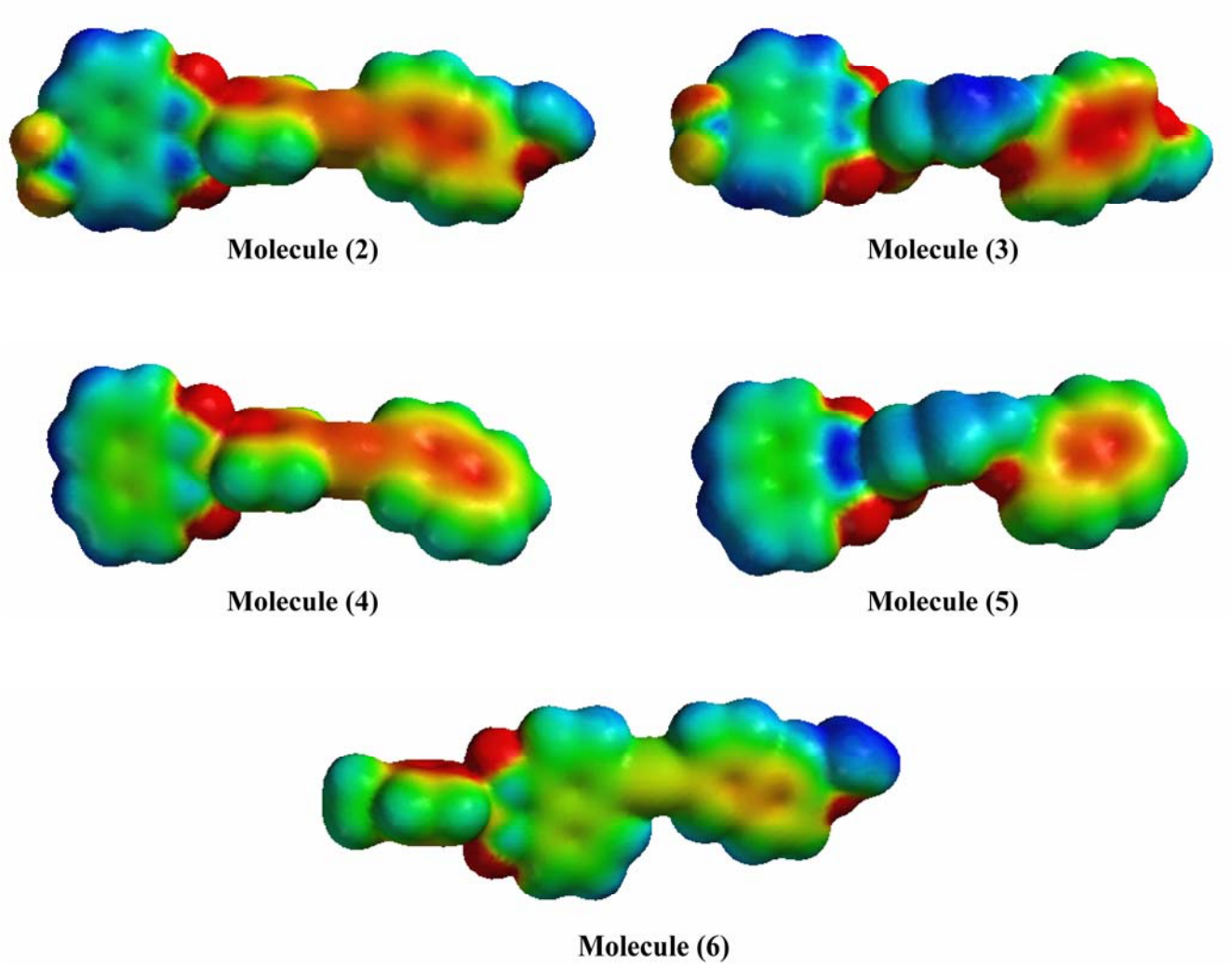


Figure S1. Electrostatic potential surfaces calculated at the AM1 level using SPARTAN '02. (Red) more negative; (blue) more positive. Structures were imported from the crystal structures of the compounds. Side-chains, where present, were truncated at the first carbon. These calculations and the color scaling are intended for qualitative comparisons only.

IV. Crystal Growth Procedures for Compounds 1-6

Molecule **1**: Crystals of compound **1** were grown by liquid-liquid diffusion of diethyl ether into a solution of **1** in methylene chloride. This resulted in yellow crystals which were suitable for x-ray diffraction.

Table S1. Crystal data and structure refinement for Molecule **1**.

Identification code	Molecule 1	
Empirical formula	C36 H22 F7 N O3	
Formula weight	649.55	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.6784(8) Å	α= 87.186(6)°.
	b = 8.4377(11) Å	β= 87.102(5)°.
	c = 31.313(5) Å	γ = 79.417(8)°.
Volume	1471.7(4) $Å^3$	
Z	2	
Density (calculated)	1.466 Mg/m^3	
Absorption coefficient	0.123 mm^{-1}	
F(000)	664	
Crystal size	0.5 x 0.5 x 0.025 mm^3	
Theta range for data collection	1.30 to 25.75°.	
Index ranges	0<=h<=6, -9<=k<=10, -37<=l<=38	
Reflections collected	5147	
Independent reflections	5147 [R(int) = 0.0000]	
Completeness to theta = 25.75°	91.4 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5147 / 18 / 469	
Goodness-of-fit on F^2	1.151	
Final R indices [I>2sigma(I)]	R1 = 0.0924, wR2 = 0.1918	
R indices (all data)	R1 = 0.1842, wR2 = 0.2428	
Largest diff. peak and hole	0.337 and -0.234 $e.Å^{-3}$	

Refinement of disordered Fluorine atoms:‡ The Fourier difference map indicated that the fluorine atoms were disordered. The fluorine atoms on the terminal carbon and the penultimate carbon of the fluorocarbon chain were modeled as disordered over two sites; the occupancy factor was set to 0.5 on

‡ In structure that involve fluorine disorder (molecule **1**-**3**), we observed that the refinements will not converge without restraints on bond lengths and angles. In all cases, we first used SADI command as a soft restraint on distances. In cases where SADI afforded unreasonable bond lengths and angles, DFIX was used with default standard deviations. If default standard deviations did not work, then the standard deviations were reduced in steps until the bonds lengths were reasonable. We had to reduce the default standard deviation only on one occasion, for a terminal –CF3 in molecule **3**. For anisotropic refinements, SIMU used as a soft restraint instead of DELU or EADP. We recognize that SIMU and ISOR are only rough approximations when compared to DELU but used them since the data-to-parameter ratio was low for these structures.

each site and was not refined. The bond length of the carbon-fluorine bond was restrained to be 1.35 A using the DFIX command in SHELXL with a standard deviation of 0.02. The distance between the fluorines on carbon C35 (penultimate carbon of the chain) was restrained to be 2.20 A using DANG command with 0.04 as the standard deviation. The distance between the fluorine atoms on the terminal carbon were restrained to be the same using SADI command with 0.02 as standard deviation. No restraints were placed on the anisoptropic refinement of the fluorine atoms. SHELXL output (.LST) suggests further disorder in the fluorine atoms of the terminal and penultimate carbon atoms but were not included in the final model.

Molecule **2**: Crystals of compound **2** were grown by liquid-liquid diffusion of diethyl ether into a solution of **2** in methylene chloride. This resulted in yellow crystals which were suitable for x-ray diffraction.

Table S2. Crystal data and structure refinement for Molecule **2**.

Identification code	Molecule 2	
Empirical formula	C42 H28 F13 N O3	
Formula weight	841.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.8313(3) Å	α= 90.655(2)°.
	b = 8.9482(5) Å	β= 91.406(2)°.
	c = 36.8720(19) Å	γ = 104.355(2)°.
Volume	1863.03(17) $Å^3$	
Z	2	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	0.138 mm^{-1}	
F(000)	856	
Crystal size	0.5 x 0.5 x 0.05 mm^3	
Theta range for data collection	1.66 to 25.23°.	
Index ranges	0<=h<=6, -10<=k<=10, -43<=l<=43	
Reflections collected	6363	
Independent reflections	6363 [R(int) = 0.0000]	
Completeness to theta = 25.23°	94.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6363 / 78 / 586	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.1008, wR2 = 0.2332	
R indices (all data)	R1 = 0.1775, wR2 = 0.2773	

Largest diff. peak and hole	0.372 and -0.344 e.Å^{-3}

The Fourier difference map indicated that the fluorine atoms were disordered. The carbon-carbon bond lengths in the fluorocarbon chain were restrained using DFIX command with a distance of 1.55 A (0.02 as standard deviation). The C-F bond length was restrained at a distance of 1.35 A using DFIX with 0.02 as standard deviation. The distance between the geminal fluorines were restrained using DANG 2.20 with 0.04 as standard deviation. In the anisotropic refinement, F9, F9A, F10, F10A F11, F12 F13, F11A, F12A and F13A atoms were restrained using SIMU command with 0.05 as standard deviation. The fluorine atoms on C41 and C42 were modeled as disordered over two sites with equal occupancies. C42 was also modeled as disordered over two sites with equal occupancy. We did not model the disorder on other fluorine and carbon atoms of the fluorocarbon chain due to lack of good quality data. The refinements did not converge if disorders were introduced at these sites.

Molecule **3**: Compound **3** (1.00 g) was dispersed in a 9:1 (acetonitrile/water) mixture and heated to reflux. The resulting solution was slowly cooled to rt in a water bath. Amber platelets formed which were suitable for x-ray diffraction.

Table 3. Crystal data and structure refinement for Molecule **3**.

Identification code	Molecule 3	
Empirical formula	C38 H32 F13 N O5	
Formula weight	829.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.9502(3) Å	α= 88.7490(10)°.
	b = 9.5259(4) Å	β= 90.2360(10)°.
	c = 49.289(2) Å	γ = 87.669(2)°.
Volume	3728.8(3) Å^3	
Z	4	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	0.140 mm^{-1}	
F(000)	1696	
Crystal size	0.6 x 0.25 x 0.25 mm^3	
Theta range for data collection	3.29 to 19.98°.	
Index ranges	0<=h<=7, -9<=k<=9, -46<=l<=47	
Reflections collected	6097	
Independent reflections	6097 [R(int) = 0.0000]	
Completeness to theta = 19.98°	87.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	6097 / 325 / 1024
Goodness-of-fit on F^2	1.439
Final R indices [I>2sigma(I)]	R1 = 0.1089, wR2 = 0.3120
R indices (all data)	R1 = 0.1479, wR2 = 0.3541
Largest diff. peak and hole	0.629 and -0.357 e.$Å^{-3}$

The Fourier difference map indicated that the fluorine atoms were disordered. The C-F distances of the fluorocarbon chains were restrained to be at 1.35 A using the DFIX command with 0.02 as standard deviation. The geminal F-F distances were restrained at 2.200 A using DANG command with 0.04 standard deviation. The C-F distance on the terminal carbon (C38) of one of the fluorocarbon chain was restrained using DFIX 1.35 with a standard deviation of 0.005. The DANG command for the fluorine atoms on C38 had a standard deviation of 0.01. The carbon-carbon distances were restrained to be the same using SADI command with 0.02 as standard deviation. In anisotropic refinement, the carbons on the each fluorocarbon chain were restrained using SIMU command with 0.04 as standard deviation and ISOR default values. The fluorines were also restrained with SIMU command with 0.04 as standard deviation and with ISOR command. The following models were tried :(a)fluorine disordered over two sites on carbons C71, C72, C73, C74, C75 and C76 and fluorines isotropic thermal factors (b) fluorines and carbons disorderd over two sites for carbons C71, C72, C73, C74, C75 and C76 and fluorines isotropic thermal factors. Both refinements were unstable, did not converge and led to chemically unacceptable bond distances and angles. Therefore, we have now modeled the fluorines as ordered but with large thermal ellipsoids. We believe that since the disorder is large and the data/parameter ratio is low, we cannot further refine the disorder. We have attempted to collect data at low temperature but it does not improve the quality of the data. The model presented here is consistent the general conclusions of the paper.

Molecule **4**: Crystals of compound **4** were grown by liquid-liquid diffusion of hexanes into a solution of **4** in methylene chloride. This resulted in colorless crystals which were suitable for x-ray diffraction.

Table S4. Crystal data and structure refinement for Molecule **4**.

Identification code	orig	
Empirical formula	C30 H17 N O2	
Formula weight	423.45	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	P c a b	
Unit cell dimensions	a = 9.329(5) Å	α= 90.000(5)°.
	b = 17.981(5) Å	β= 90.000(5)°.
	c = 25.306(5) Å	γ = 90.000(5)°.
Volume	4245(3) $Å^3$	
Z	8	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	

F(000)	1760
Crystal size	0.05 x 0.05 x 0.05 mm^3
Theta range for data collection	2.94 to 27.48°.
Index ranges	-12<=h<=12, -23<=k<=23, -32<=l<=32
Reflections collected	9140
Independent reflections	4850 [R(int) = 0.0497]
Completeness to theta = 27.48°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4850 / 0 / 298
Goodness-of-fit on F^2	0.989
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1236
R indices (all data)	R1 = 0.1310, wR2 = 0.1538
Largest diff. peak and hole	0.135 and -0.203 e.$Å^{-3}$

Molecule **5**: Compound **5** (500 mg) was dispersed in 50 mL of a 9:1 mixture of acetonitrile/water. The mixture was heated to reflux and allowed to cool slowly to rt, resulting in thick amber needles which were suitable for x-ray diffraction.

Table 5. Crystal data and structure refinement for Molecule **5**.

Identification code	import	
Empirical formula	C26 H21 N O4	
Formula weight	411.44	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.140(5) Å	α= 90.000(5)°.
	b = 5.718(5) Å	β= 96.673(5)°.
	c = 29.183(5) Å	γ = 90.000(5)°.
Volume	2012(2) $Å^3$	
Z	4	
Density (calculated)	1.358 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	864	
Crystal size	0.6 x 0.3 x 0.2 mm^3	
Theta range for data collection	3.11 to 25.03°.	
Index ranges	-14<=h<=14, -6<=k<=6, -34<=l<=34	
Reflections collected	6298	

Independent reflections	3513 [R(int) = 0.0204]
Completeness to theta = 25.03°	98.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3513 / 0 / 280
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1065
R indices (all data)	R1 = 0.0655, wR2 = 0.1211
Largest diff. peak and hole	0.151 and -0.223 e.Å^{-3}

Molecule **6**: Compound **6** (5.0 mg) was dissolved in 1.0 mL of 1:1 (CH_2Cl_2/acetone). The resulting solution was filtered into a clean vial and allowed to slowly evaporate. Bright yellow crystals (flat needles) formed which were used for x-ray diffraction.

Table S6. Crystal data and structure refinement for Molecule 6.

Identification code	Molecule 6	
Empirical formula	C36 H29 N O3	
Formula weight	523.60	
Temperature	570(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 24.8660(6) Å	α= 90°.
	b = 5.2750(2) Å	β= 101.0280(10)°.
	c = 21.6140(11) Å	γ = 90°.
Volume	2782.72(19) Å^3	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1104	
Crystal size	0.60 x 0.20 x 0.05 mm^3	
Theta range for data collection	1.92 to 25.05°.	
Index ranges	-29<=h<=29, -6<=k<=0, 0<=l<=25	
Reflections collected	4894	
Independent reflections	4894 [R(int) = 0.0000]	
Completeness to theta = 25.05°	99.1 %	
Absorption correction	None	
Max. and min. transmission	0.9961 and 0.9542	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	4894 / 0 / 477
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0646, wR2 = 0.1227
R indices (all data)	R1 = 0.1623, wR2 = 0.1642
Largest diff. peak and hole	0.143 and -0.202 e.Å^{-3}

V. References

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