Supporting Materials and Methods

Synthesis

Proton nuclear magnetic resonance spectra were recorded on a Mercury 400 or Inova 500 NMR spectrometer using tetramethylsilane as an internal standard. Laser desorption mass spectra were obtained with a PE Voyager DE-Pro MALDI-TOF mass spectrometer using dithranol as a matrix. Solvents were purified before use according to standard protocols. All column chromatography was performed with standard 60-Å sorbent silica gel. *N*-(*n*-octyl)-1,7-bis(3',5'-di-*t*-butylphenoxy)perylene-3,4-dicarboxyanhydride-dicarboximide, **PIA**, was synthesized as reported earlier (1).

2,7-Dibromo-9,9-dihexyl-9*H*-fluorene (Br-FL-Br). 2,7-Dibromofluorene (1 g, 3.1 mmol), 1-bromohexane (1.26 g, 7.7 mmol), potassium hydroxide (730 mg, 13 mmol), and potassium iodide (50 mg, 0.3 mmol) were combined suspended in 50 ml of acetonitrile and heated at 60°C for 24 h. The solvent was removed by using a rotary evaporator. The crude product was suspended in chloroform, washed with water, dilute acetic acid, then twice more with water, and then purified by column chromatography on silica using hexanes as the mobile phase to afford (**Br-FL-Br**) (1.14g, 75%). ^{1}H NMR ($CDCl_3$) δ: 7.52 (m, 2H), 7.43 (m, 4H), 1.93 (t, *J* = 8.3 Hz, 4H), 1.32-1.00 (m, 12H), 0.79 (*t*, *J* = 7.1 Hz, 6H), 0.59 (m, 4H)

10-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)-10*H*-phenothiazine (Br-FL-PTZ). Br-FL-Br (800 mg, 1.33 mmol) and phenothiazine (**PTZ**) (242 mg, 1.2 mmol) were suspended in 60 ml of toluene, and N_2 was bubbled through for 20 min. Potassium *t*-butoxide (136 mg, 1.2 mmol), tris(dibenzylideneacetone)dipalladium(0) (30 mg, 0.26 mmol), and tri-*o*-tolylphosphine (100 mg, 0.33 mmol) were then added and the reaction was heated under nitrogen at 90°C for 24 h. The solvent was removed by rotary evaporation and the product was purified by column chromatography with silica with a 9:1 (vol/vol) combination of hexanes and chloroform to obtain the product, **Br-FL-PTZ** (230 mg, 23%). MS: 610.79 (calcd. 609.21). ^{1}H NMR ($CDCl_3$) δ: 7.82 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 (m, 2H), 7.29 (m, 2H), 6.96 (m, 2H), 6.74 (m, 4H), 6.13 (m, 2H), 1.90 (t, *J* = 8.3 Hz, 4H) 1.07-1.01 (m, 12H), 0.79 (t, *J* = 7.1 Hz, 6H), 0.67 (m, 4H).

9,9-Dihexyl-7-phenothiazin-10-yl-9*H*-fluoren-2-ylamine (PTZ-FL-NH_2). **Br-FL-PTZ** (230 mg, 0.38 mmol) was combined with benzophenone imine (83 mg, 0.46 mmol) in 5 ml of toluene, and N_2 was bubbled through the mixture for 20 min. Tris(dibenzylideneacetone)dipalladium(0) (4 mg, 0.035 mmol), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 7 mg, 0.011 mmol), and potassium *t*-butoxide (60 mg, 0.53 mmol) were then added and the reaction was heated under N_2 at 80°C for 24 h. Column chromatography with silica and a 1:1 (vol/vol) mixture of hexanes and chloroform as the mobile phase yielded a crude sample of benzhydrylidene-(9,9-dihexyl-7-phenothiazin-10-yl-9*H*-fluoren-2-yl) **(PTZ-FL-$NCPh_2$)**. MS: 710.7 (calcd. 710.37). This crude product was then dissolved in 5 ml of tetrahydrofuran and several drops of HCl were added. Further chromatography in chloroform separated out the benzophenone byproduct and yielded 9,9-dihexyl-7-phenothiazin-10-yl-9*H*-fluoren-2-

ylamine **(PTZ-FL-NH_2)** (36 mg, 17% over both steps). MS: 547.9 (calcd. 546.31). ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.20 (d + s, 2H), 6.92 (m, 2H), 6.71 (m, 4H), 6.63 (d + s, 2H), 6.15 (m, 2H), 3.79 (br, 2H), 1.83 (m, 4H), 0.99 (m, 12H), 0.67 (t, 6H, *J* = 7.1 Hz), 0.56 (m, 4H).

***N*-(*n*-octyl)-*N*-(7-phenothiazin-10-yl-9,9-dihexyl-9*H*-fluoren-2-yl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PTZ-FL-PDI).** PTZ-FL-NH_2 (36 mg, 0.066 mmol) and **PIA** (25 mg, 0.028 mmol) were combined in 6 ml of dimethylformamide with a catalytic amount of zinc acetate, sparged with N_2, and set to reflux for 24 h. Silica column chromatography was performed with a 7:3 (vol/vol) chloroform and hexanes mixture to afford the product, *N*-(*n*-octyl)-*N*-(7-phenothiazin-10-yl-9*H*-fluoren-2-yl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) **(PTZ-FL-PDI)** (16 mg, 40%). HPLC purification was performed isocratically with a 70:30 (vol/vol) acetonitrile/chloroform eluent on C_{18} reverse-phase column (Altex) for spectroscopic samples. MS: 1441.0 (calcd. 1439.77). ^{1}H NMR ($CDCl_3$) δ: 9.68 (d + d, 2H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.35 (s, 1H), 8.32 (s, 1H), 7.90 (d, *J* = 7.9 Hz), 7.83 (d, *J* = 8.7 Hz, 1H), 7.47 (m, 1H), 7.36-7.24 (m, 4H), 7.06-6.94 (m, 6H), 6.75 (m, 4H), 6.17 (m, 2H), 4.09 (t, *J* = 6.9 Hz, 2H), 2.27 (m, 2H), 1.92 (t, *J* = 7.3 Hz, 4H), 1.73 (m, 3H), 1.39-0.96 (m, 62H), 0.68 (t, *J* = 6.9 Hz, 6H).

7-Bromo-9,9-dihexyl-9*H*-fluoren-2-ylamine (Br-FL-NH_2). 2,7-Dibromofluorene **(Br-FL-Br)** (3.35 g, 6.8 mmol) was combined with benzophenone imine (1.27 g, 7.0 mmol) in 50 ml of toluene, and N_2 was bubbled through the mixture for 20 min. Tris(dibenzylideneacetone)dipalladium(0) (65 mg, 0.55 mmol), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP, 7 mg, 0.20 mmol), and potassium *t*-butoxide (980 mg, 8.7 mmol) were then added and the reaction was heated under N_2 at 80°C for 24 h. Column chromatography with silica and a 1:1 (vol/vol) mixture of hexanes and chloroform as the mobile phase yielded a crude sample of benzhydrylidene-(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)amine **(Br-FL-NCPh_2)**. This crude product was then dissolved in 10 ml of tetrahydrofuran and several drops of HCl were added. Further chromatography in chloroform separated out the benzophenone byproduct and yielded **Br-FL-NH_2** (1.38 g, 48% over both steps). ^{1}H NMR ($CDCl_3$) δ: 7.44 (d, *J* = 7.9 Hz, 1H), 7.38 (m, 3H), 6.65 (m, 2H), 3.78 (s, 2H), 1.86 (m, 4H), 1.17-0.99 (m, 12H), 0.78 (t, *J* = 7.2 Hz, 6H), 0.63 (m, 4H).

***N*-(*n*-octyl)-*N*-(7-bromo-9,9-dihexyl-9*H*-bifluoren-2-yl-)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (Br-FL-PDI). Br-FL-NH_2** (140 mg, 0.33 mmol) and **PIA** (157 mg, 0.17 mmol) were suspended in 25 ml of quinoline, and N_2 was bubbled for 20 min. Phosphorus pentoxide (10 mg) was then added and the reaction was heated under N_2 at 230°C for 2 days. After the solution was cooled, the mixture was poured onto 125 ml of 18% HCl. The product was extracted into chloroform and washed with water. The chloroform was removed under reduced pressure and column chromatography was performed with chloroform as the mobile phase to yield **Br-FL-PDI** (98 mg, 43%). MS: 1320.79 (calcd. 1320.65). ^{1}H NMR ($CDCl_3$) δ: 9.60 (d + d [appears as t], 2H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.21 (s, 1H), 7.70 (d, *J* = 8.7, 1H), 7.50 (d, *J* = 7.9, 1H), 7.41 (s, 1H), 7.28 (m, 2H), 7.22 (m,

2H), 7.17 (s, 1H), 6.96 (d, *J* = 1.5 Hz, 2H) , 6.95 (d, *J* = 1.5 Hz, 2H), 4.06 (t, *J* = 7.5 Hz, 2H), 1.89-1.75 (m, 6H), 1.63 (m, 3H), 1.32-0.99 (m, 58H), 0.78 (t, *J* = 6.8 Hz, 4H), 0.69 (m, 4H).

10-[9,9-Dihexyl-7-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9*H*-fluoren-2-yl]-10*H*-phenothiazine (PTZ-FL-BE). PTZ-FL-Br (297 mg, 0.49 mmol), 4,4,5,5-tetramethyl[1,3,2]dioxaborolane (190 mg, 1.5 mmol), and triethylamine (152 mg, 1.5 mmol) were added to 10 ml of dioxane, and N_2 was bubbled through the mixture for 20 min. 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II) (complex with dichloromethane, 60 mg, 0.074 mmol) was then added and the reaction was heated under N_2 at 95°C for 24 h. The solvent was removed by rotary evaporation and column chromatography in 1:1 hexanes/chloroform yielded **PTZ-FL-BE** (86 mg, 27%). MS: 657.6 (calcd. 657.38). ^{1}H NMR ($CDCl_3$) δ: 7.88 (d, *J* = 6.7H, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.70 (m, 2H), 7.28 (m, 2H), 6.94 (m, 2H), 6.72 (m, 4H), 6.14 (m, 2H), 1.93 (m, 4H), 1.32 (s, 12H), 1.06-0.90 (m, 12H), 0.67 (t, *J* = 7.0 Hz, 6H), 0.57 (m, 4H).

***N*-(*n*-octyl)-*N*-(7-phenothiazin-10-yl-9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2']bifluorenyl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PTZ-FL$_2$-PDI). PTZ-FL-BE** (260 mg, 0.39 mmol) and **Br-FL-PDI** (45 mg, 0.034 mmol) were combined in 10 ml of dioxane with several drops of water and potassium carbonate (41 mg, 0.30 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (≈5 mg, 0.004 mmol), was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography with a 7:3 chloroform/hexanes mixture yielded **PTZ-FL$_2$-PDI** (29 mg, 48%). MS: 1772.6 (calcd. 1772.02). ^{1}H NMR ($CDCl_3$) δ: 9.68 (d + d, 2H), 8.65 (d, *J* = 8.6 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.35 (s, 1H), 8.32 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.83-7.74 (m, 3H), 7.66-7.57 (m, 4H), 7.48-7.28 (m, 6H), 6.99 (s, 2H), 6.96 (m, 2H), 6.74 (m, 4H), 6.18 (m, 2H), 4.10 (t, *J* = 7.5 Hz, 2H), 1.98 (m, 6H), 1.84 (m, 4H), 1.66 (m, 3H), 1.30-0.90 (m, 70H), 0.70 (m, 12H), 0.51 (m, 8H). HPLC purification was performed isocratically with a 65:35 vol/vol acetonitrile/chloroform eluent on C_{18} reverse-phase column (Altex) for spectroscopic samples.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (BE-FL-BE). Br-FL-Br (1.9 g, 3.9 mmol) in 40 ml of tetrahydrofuran was put under a N_2 atmosphere and cooled to -78°C. After the solution had been cooled, 1.6 M *n*-butyl lithium in hexanes (5.35 ml, 8.56 mol) was then slowly added. 2-Isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (2.38 ml, 11.7 mmol) was then quickly added, and the reaction was allowed to warm to room temperature and was then stirred for 24 h. The reaction mixture was then poured over 200 ml of water and extracted into diethyl ether, washed with brine, and dried over magnesium sulfate. The diethyl ether was removed under reduced pressure, and column chromatography was performed with 1:1 chloroform/hexanes to afford **BE-FL-BE** (567 mg, 25%). ^{1}H NMR ($CDCl_3$) δ: 7.83 (d, *J* = 7.6 Hz, 2H), 7.78 (s, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 2.00 (m, 4H), 1.39 (s, 24H), 1.12-0.94 (m, 12H), 0.76 (t, *J* = 7.1 Hz, 6H), 0.56 (m, 4H).

10-[9,9,9',9'-Tetrahexyl-7'-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9*H*,9'*H*-[2,2']bifluorenyl-7-yl]-10*H*-phenothiazine (BE-FL$_2$-PTZ). **BE-FL-BE** (565 mg, 0.96 mmol) and **PTZ-FL-BR** (440 mg, 0.72 mmol) were combined in 40 ml of dioxane with several drops of water and potassium carbonate (200 mg, 1.4 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (5 mg, 0.004 mmol) was then added and the reaction was put at 80°C for 6 h. The solvent was removed by rotary evaporation. Column chromatography with a 1:1 chloroform/hexanes mixture yielded **BE-FL$_2$-PTZ** (214 mg, 30%). MS: 989.94 (calcd. 989.63). ^{1}H NMR ($CDCl_3$) δ: 7.97 (d, J = 7.9, 1H), 7.87-7.64 (m, 9H), 7.38 (m, 2H), 7.03 (m, 2H), 6.82 (m, 4H), 6.26 (m, 2H), 2.07 (m, 8H), 1.41 (s, 12H), 1.16-0.95 (m, 24H), 0.76 (m, 20H).

***N*-(*n*-octyl)-*N*-(7-phenothiazin-10-yl-9,9,9',9',9'',9''-hexahexyl-9*H*,9'*H*,9''*H*-[2,2',2'']terfluorenyl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PTZ-FL$_3$-PDI).** **PTZ-FL$_2$-BE** (214 mg, 0.22 mmol) and **Br-FL-PDI** (49 mg, 0.037 mmol) were combined in 10 ml of dioxane with several drops of water and potassium carbonate (30 mg, 0.22 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (≈5 mg, 0.004 mmol) was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography on silica gel with an 8:2 chloroform/hexanes mixture yielded **PTZ-FL$_3$-PDI** (43 mg, 55%). HPLC purification was performed isocratically with a 60:40 (vol/vol) acetonitrile/chloroform eluent on a C_{18} reverse-phase column (Altex) for spectroscopic samples. MS: 2105.67 (calcd. 2104.27). ^{1}H NMR ($CDCl_3$) δ: 9.66 (d + d, 2H), 8.65 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.34 (s, 1H), 8.30 (s, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.82-7.75 (m, 4H), 7.67-7.57 (m, 9H), 7.34-7.18 (m, 6H), 6.99 (m, 4H), 6.95 (m, 2H), 6.75 (m, 4H), 6.18 (m, 2H), 4.09 (t, J = 7.4 Hz, 2H), 2.08-1.93 (m, 14H), 1.66 (m, 3H), 1.32-0.98 (m, 82H), 0.70 (m, 30H).

7,7''-Dibromo-9,9,9',9',9'',9''-hexahexyl-9*H*,9'*H*,9''*H*-terfluorene (Br-FL$_3$-Br). **FL-FL-FL** (255 mg, 0.26 mmol) was dissolved in 1 ml of chloroform. Approximately 1 mg of ferric chloride was added and the solution was cooled to 0°C. Bromine (43 mg, 0.27 mmol) in 0.5 ml of chloroform was then slowly added over 1 h. The reaction was then left at room temperature overnight. The reaction mixture was then poured onto 5 ml of water and the product was extracted into the chloroform and dried over magnesium sulfate. Column chromatography in 9:1 hexanes/chloroform yielded the product, **Br-FL$_3$-Br** (251 mg, 83%). MS: 1157.11 (calcd. 1154.59). ^{1}H NMR ($CDCl_3$) δ: 7.83 (m, 2H), 7.76 (m, 2H), 7.69-7.59 (m, 7H), 7.57 (s, 1H), 7.52-7.46 (m, 6H), 2.02 (m, 12H), 0.79 (t, J = 6.4 Hz, 18H), 0.72 (m, 12H).

10-[9,9,9',9',9'',9''-Hexahexyl-7''-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9*H*,9'*H*,9''*H*-[2,2';7',2'']terfluoren-7-yl]-10*H*-phenothiazine (BE-FL$_3$-PTZ). **Br-FL$_3$-Br** (250 mg, 0.22 mmol) and **PTZ** (43 mg, 0.22 mmol) were suspended in 10 ml of toluene, and N_2 was bubbled through for 20 min. Potassium *t*-butoxide (30 mg, 0.26 mmol), tris(dibenzylideneacetone)dipalladium(0) (4 mg, 0.034 mmol), and tri-*o*-tolylphosphine (12 mg, 0.040 mmol) were then added and the reaction was heated under nitrogen at 90°C for 24 h. The solvent was removed by rotary evaporation, and column chromatography with silica with a 7:3 (vol/vol) combination of hexanes yielded a crude

mixture of the desired product, **Br-FL$_3$-PTZ**, and the disubstituted product, **PTZ-FL$_3$-PTZ**. MS: 1275.9 (calcd. 1273.71). This crude mixture, along with 4,4,5,5,4',4',5',5'-octamethyl[2,2']bi[[1,3,2]dioxaborolanyl] (140 mg, 0.53 mmol), and potassium acetate (150 mg, 1.53 mmol) was dissolved in 5 ml of dimethylformamide and sparged with N_2 for 20 min. 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II) (complex with dichloromethane, 12 mg, 0.015 mmol) was then added along with extra 1,1'-bis(diphenylphosphino)ferrocene (9 mg, 0.015 mmol), and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed under reduced pressure, and column chromatography with a 1:1 chloroform/hexanes mobile phase yielded the product, **BE-FL$_3$-PTZ** (13 mg, 4.4% over two steps). MS: 1321.94 (calcd. 1321.88). ^{1}H NMR ($CDCl_3$) δ: 7.90 (d, *J* = 7.7 Hz, 1H), 7.79-7.55 (m, 14H), 7.33 (s, 1H), 7.30 (s, *J* = 7.9 Hz, 1H), 6.96 (m, 2H), 6.75 (m, 4H), 6.18 (m, 2H), 2.00 (m, 12H), 1.33 (s, 12H), 1.09-0.95 (m, 48H), 0.69 (m, 30H).

***N*-(*n*-octyl)-*N*-(7-phenothiazin-10-yl-9,9,9',9',9'',9'',9''',9''''-octahexyl-9*H*,9'*H*,9''*H*,9''''-[2,2',2'',2''']tetrafluorenyl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PTZ-FL$_4$-PDI). PTZ-FL$_3$-BE** (13 mg, 0.0097 mmol) and **Br-FL-PDI** (13 mg, 0.0097 mmol) were combined in 5 ml of dioxane with one drop of water and potassium carbonate (2 mg, 0.014 mmol) and sparged for 15 min. Tetrakis(triphenylphosphine)palladium(0) (≈2 mg, 0.002 mmol) was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography with a 6:4 chloroform/hexanes mixture yielded **PTZ-FL$_4$-PDI** (9.3 mg, 39%). HPLC purification was performed isocratically with a 55:45 (vol/vol) acetonitrile/chloroform eluent on a C_{18} reverse-phase column (Altex) for spectroscopic samples. MS: 2438.8 (calcd 2436.52). ^{1}H NMR ($CDCl_3$) δ: 9.67 (d + d, 2H), 8.72 (d, *J* = 8.1 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.43 (s, 1H), 8.40 (s, 1H), 8.04 (m, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.91-7.81 (m, 7H), 7.74-7.64 (m, 15H), 7.53 (m, 1H), 7.42-7.30 (m, 4H), 7.09-7.02 (m, 6H), 6.82 (m, 4H), 6.25 (m, 2H), 4.17 (t, *J* = 7.4 Hz, 2H), 2.16-1.98 (m, 18H), 1.71 (m, 3H), 1.39-1.05 (m, 110H), 0.78 (m, 24H).

9,9-Dihexyl-2-nitro-9*H*-fluorene (FL-NO$_2$). 9,9-Dihexyl-9*H*-fluorene (5.1 g, 15 mmol) was dissolved in 15 ml of acetic acid and put at 60°C for 20 min. Then 3.5 ml of nitric acid was added over 30 min. The mixture was then heated at 90°C for 40 min and left to cool overnight. The product was extracted into chloroform and washed with water several times, and the solution was evaporated under reduced pressure. Column chromatography was performed in 4:1 hexanes/chloroform to obtain the product (5.7 g, 98%). ^{1}H NMR ($CDCl_3$) δ: 8.26 (d, *J* = 8.4 Hz, 1H), 8.20 (s, 1H), 7.78 (m, 2H), 7.41 (m, 3H), 2.02 (t, *J* = 8.3 Hz, 4H), 1.14-0.95 (m, 12H), 0.75 (t, *J* = 7.0 Hz, 6H), 0.57 (m, 4H).

9,9-Dihexyl-2-amino-9*H*-fluorene (FL-NH$_2$). FL-NO$_2$ (497 mg, 1.3 mmol) was dissolved in 30 ml of ethanol. Palladium (finely divided on carbon, 116 mg) was added and the mixture was put under 50 atmospheres of H_2 for 12 h. The catalyst was removed via a Celite plug and the ethanol was removed under reduced pressure to afford the product in quantitative yield. ^{1}H NMR ($CDCl_3$) δ: 7.54 (d, *J* = 7.3, 1H), 7.47 (d, *J* = 6.6, 1H), 7.27 (m, 2H), 7.19 (d, *J* = 8.0, 1H), 6.71 (m, 2H), 3.87 (br s, 2H), 1.88 (m, 4H), 1.14-0.96 (m, 12H), 0.76 (t, *J* = 7.1, 6H), 0.62 (m, 4H).

***N*-(*n*-octyl)-*N*-(9,9-dihexyl-9*H*-bifluoren-2-yl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (FL-PDI).** **FL-NH_2** (168 mg, 0.48 mmol), and **PIA** (44 mg, 0.048 mmol) were combined in 10 ml of dimethylformamide, and N_2 was bubbled through the mixture for 20 min. Zinc acetate (≈2 mg, 0.014 mmol) was added and the reaction mixture was refluxed for 24 h. After the solvent was removed by rotary evaporation, column chromatography in 7:3 dichloromethane/hexanes yielded **FL-PDI** (20 mg, 33%). MS: 1253.9 (calcd. 1242.74). ^{1}H NMR ($CDCl_3$) δ: 9.74 (d + d, 2H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.72 (m, 2H), 7.53 (m, 2H), 7.35 (m, 4H), 7.05 (s, 4H), 4.16 (t, *J* = 7.1 Hz, 2H), 2.33 (m, 6H), 1.95 (m, 3H), 1.37-1.22 (m, 58H), 0.89 (m, 6H), 0.75 (m, 4H).

2-Bromo-9,9-dihexyl-9*H*-fluorene (Br-FL). 2-Bromofluorene (1.25 g, 5.1 mmol), *n*-bromohexane (1.9 ml, 13.7 mmol), potassium hydroxide (1.25 g, 22 mmol), and potassium iodide (70 mg, 0.4 mmol) were combined in 150 ml of acetonitrile and heated at 60°C for 24 h. The solvent was then removed by rotary evaporation, and the residue was dissolved in chloroform, washed with water, dilute acetic acid, then twice more with water, and dried over magnesium sulfate. Column chromatography in hexanes yielded **Br-FL** (1.3 g, 60%). ^{1}H NMR ($CDCl_3$) δ:7.66 (m, 1H), 7.55 (m, 1H), 7.44 (m, 2H), 7.32 (m, 3H), 1.93 (t, *J* = 8.0 Hz, 4H), 1.15-0.98 (m, 12H), 0.77 (m, 6H), 0.59 (m, 4H).

2-(9,9-Dihexyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (FL-BE). **FL-Br** (0.72 g, 1.7 mmol), 4,4,5,5,4',4',5',5'-octamethyl[2,2']bi[[1,3,2]dioxaborolanyl] (680 mg, 2.57 mmol), and potassium acetate (750 mg, 7.7 mmol) was dissolved in 15 ml of DMSO and sparged with N_2 for 20 min. 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II) (complex with dichloromethane, 180 mg, 0.225 mmol) was then added along with extra 1,1'- bis(diphenylphosphino)ferrocene (45 mg, 0.075 mmol) and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed under reduced pressure and column chromatography with a 3:2 chloroform/hexanes mobile phase yielded the product, **FL-BE** (600 mg, 75%). MS: 460.90 (calcd. 460.35). ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, *J* = 7.5 Hz, 1H), 7.72 (m, 3H), 7.32 (m, 3H), 1.98 (m, 4H), 1.39 (s, 12H), 1.12-0.97 (m, 12H), 0.72 (t, *J* = 7.2 Hz, 6H), 0.58 (m, 4H).

***N*-(*n*-octyl)-*N*-(9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2']bifluorenyl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (FL_2-PDI).** **FL-BE** (137 mg, 0.30 mmol) and **Br-FL-PDI** (45 mg, 0.034 mmol) were combined in 10 ml of dioxane with several drops of water and potassium carbonate (41 mg, 0.30 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (5 mg, 0.004 mmol) was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography with a 7:3 chloroform/hexanes mixture yielded **FL_2-PDI** (23 mg, 43%). MS: 1575.97 (calcd. 1574.99). ^{1}H NMR ($CDCl_3$) δ: 9.75 (d + d, 2H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 7.87 (s, 1H), 7.82 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 1H) 7.68-7.60 (m, 5H), 7.39-7.27 (m, 7H), 7.06 (m, 4H), 4.17 (t, *J* = 7.7 Hz, 2H), 2.03 (m, 10H), 1.74 (m, 3H), 1.38-1.05 (m, 70H), 0.78 (t, *J* = 6.9 Hz, 12H), 0.51 (m, 8H).

7-Bromo-9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2']bifluorenyl (Br-FL-FL). Br-FL-Br (5.1 g, 10.4 mmol) and **FL-BE** (1.6 g, 2.94 mmol) were combined in 90 ml of dioxane with several drops of water and potassium carbonate (406 mg, 2.94 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (10 mg, 0.008 mmol) was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography with a 1:9 chloroform/hexanes mixture yielded **Br-FL-FL** (822 mg, 37%). MS: 744.44 (calcd. 744.43). ^{1}H NMR ($CDCl_3$) δ: 7.78 (m, 3H), 7.72-7.59 (m, 5H), 7.50 (m, 2H), 7.37 (m, 3H), 2.04 (m, 8H), 1.19-1.03 (m, 24H) 0.79 (m, 12H), 0.73 (m, 8H).

4,4,5,5-Tetramethyl-2-(9,9,9',9'-tetrahexyl-9*H*,9'*H*-[2,2']bifluorenyl-7-yl)-[1,3,2]dioxaborolane (BE-FL-FL). Br-FL-FL (820 mg, 1.1 mmol), 4,4,5,5,4',4',5',5'-octamethyl[2,2']bi[[1,3,2]dioxaborolanyl] (571 mg, 2.2 mmol), and potassium acetate (641 mg, 6.5 mmol) were added to 15 ml of DMSO and N_2 was bubbled through the mixture for 20 min. 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II) (complex with dichloromethane, 49 mg, 0.06 mmol) was then added along with extra 1,1'-bis(diphenylphosphino)ferrocene (35 mg, 0.06mmol), and the reaction was heated under N_2 at 95°C for 24 h. The solvent was removed by rotary evaporation, and column chromatography in 1:1 hexanes/chloroform yielded **BE-FL-FL** (121 mg, 14%). MS: 792.82 (calcd. 792.60). ^{1}H NMR ($CDCl_3$) δ: 7.77-7.64 (m, 6H), 7.56 (m, 4H), 7.27 (m, 3H), 1.97 (m, 8H), 1.06-0.94 (m, 24H), 0.62 (m, 12H), 0.62 (m, 8H).

***N*-(*n*-octyl)-*N*-(9,9,9',9',9'',9''-hexahexyl-9*H*,9'*H*,9''*H*-[2,2',2'']terfluorenyl)-(3',5'-di-*t*-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (FL_3-PDI). FL_2-BE** (120 mg, 0.15 mmol) and **Br-FL-PDI** (50 mg, 0.04 mmol) were combined in 10 ml of dioxane with several drops of water and potassium carbonate (21 mg, 0.15 mmol) and sparged for 20 min. Tetrakis(triphenylphosphine)palladium(0) (5 mg, 0.004 mmol) was then added and the reaction was heated under N_2 at 90°C for 24 h. The solvent was removed by rotary evaporation. Column chromatography with a 7:3 chloroform/hexanes mixture yielded **FL_3-PDI** (46 mg, 60%). MS: 1908.16 (calcd. 1907.24). ^{1}H NMR ($CDCl_3$) δ: 9.75 (d + d, 2H), 8.72 (d, J = 8.3 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 8.43 (s, 1H), 8.40 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.83 (m, 3H), 7.79 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.1 Hz, 1H), 7.68-7.63 (m, 4H), 7.39-7.28 (m, 9H), 7.06 (m, 4H), 4.17 (t, J = 7.6 Hz, 2H), 2.15-1.98 (m, 14H), 1.74 (m, 3H), 1.38-1.04 (m, 82H), 0.77 (m, 30H).

Spectroscopy

The kinetic data displayed in Figs. 5 and 6 are summarized in Table 3.

Computational Details

Geometries of **1-4** were optimized by using the AM1 model in the HYPERCHEM platform [the semi-empirical AM1 method was implemented in HYPERCHEM (Hypercube, Gainesville, FL)]. Internal reorganization energies were obtained by performing single-point calculations (unrestricted Hartree-Fock) on the charged forms of the component molecules in the AM1-optimized ground state and ionic geometries and subtracting the

self-consistent field energy of the relaxed ionic configuration from that of the unrelaxed ground state configuration. From the Marcus formulation for solvent reorganization energy based on the Born dielectric continuum model of the solvent, λ_S is small (≈0.05 eV) and nearly distance independent for these compounds in toluene ($\varepsilon_S = 2.38$, $\varepsilon_0 = 2.24$).

Weller-Type Expression for the Total Energy of Two Positive Ions with One-Half of a Formal Charge and One Negative Ion with a Single Formal Charge

Calculating the energies of PTZ–$FL_n^{+\bullet}$–$PDI^{-\bullet}$, the possible intermediate in the charge separation and recombination process, from the redox data in dichloromethane presents an additional complication, since our AM1 calculations show that half of the positive charge density is localized on each of the two terminal FL monomers of $FL_n^{+\bullet}$, when $n \geq 2$. Eq. **1** in the main text can be readily modified to accommodate this situation by using positive ions having half of a formal charge at each of the terminal FL monomers and a single negative charge on PDI,

$$\Delta G_{IP} = E_{ox} - E_{red} + \frac{e^2}{\varepsilon_s}\left(\frac{1}{4r_{12}} - \frac{1}{2r_{13}} - \frac{1}{2r_{23}}\right) + e^2\left(\frac{1}{8r_1} + \frac{1}{8r_2} + \frac{1}{2r_3}\right)\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_{sp}}\right), \quad \textbf{[1]}$$

where E_{ox} and E_{red} are, respectively, the oxidation and reduction potentials of the donor and acceptor in dichloromethane (Table 1), a polar solvent with dielectric constant $\varepsilon_{sp} = 8.93$, e is the charge of the electron, $r_1 = r_2 = 4.5$ Å are the ionic radii of the FL positive ions bearing one-half of a formal electronic charge, $r_3 = 7.6$ Å is the radius of $PDI^{-\bullet}$ bearing a unit formal electronic charge, r_{12} is the distance between the two FL monomers each bearing one-half of a formal electronic charge, r_{13} and r_{23} are the respective distances between these two FL units and $PDI^{-\bullet}$, and $\varepsilon_s = 2.38$ is the static dielectric constant of toluene in which the spectroscopy is performed. The energies of PTZ–$FL_n^{+\bullet}$–$PDI^{-\bullet}$ calculated in this manner are given in Table 2. The energies of component species and relevant radii of intermediates are given in Tables 4 and 5.

1. van der Boom, T., Hayes, R. T., Zhao, Y., Bushard, P. J., Weiss, E. A. & Wasielewski, M. R. (2002) *J. Am. Chem. Soc.* **124,** 9582-9590.