CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Synthesis, Fluorescence and Two-Photon Absorption of a Series of Elongated Rod-like and Banana-shaped Quadrupolar Fluorophores: a Comprehensive Study of Structure-Property Relationships

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Supporting Information gathers complementary synthetic details as well as absorption and emission spectra.

Synthetic Procedures.

4-[4-(Dihexylamino)phenyl]-2-methyl-3-butyn-2-ol (1c): Air was removed from a solution of *N*,*N*-dihexyl-4-iodobenzenamine (**1b**)[S1] (0.775 g, 2 mmol) in Et_3N (10 mL) by blowing argon for 20 min. Then CuI (15 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and 2-methyl-3-butyn-2-ol (0.254 mL, 2.6 mmol) were added, and the mixture was stirred at 40 °C for 12 h. After evaporation of the solvent, the residue was purified by column chromatography (CH_2Cl_2) to yield 0.566 g (82%) of **1c**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.24 and 6.52 (AA'XX', J_{AX} = 9.0, 4H), 3.25 (m, 4H), 2.12 (s, 1H), 1.60 (s, 6H), 1.75-1.49 (m, 4H), 1.32 (m, 12H), 0.90 (t, *J* = 6.5, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 147.9, 132.8, 111.1, 108.1, 91.2, 83.1, 65.7, 50.9, 31.7, 31.6, 27.1, 26.7, 22.6, 14.0; HRMS (EI) calcd for $C_{23}H_{37}NO$ (M^+?) *m/z* 343.2875, found 343.2879; elemental analysis calcd (%) for $C_{23}H_{37}NO$ (343.55): C 80.41, H 10.85, N 4.08; found: C 80.14, H 10.61, N 3.95.

4-Ethynyl-*N*,*N*-dihexylbenzenamine (1d): To a solution of **1c** (0.457g, 1.387 mmol) in 25 mL of toluene/*i*PrOH (4/1), was added solid NaOH (0.14 g). The mixture was heated under reflux for 1 h. After cooling, the remaining NaOH was filtered off and the solvents were evaporated. The crude product was filtered through a pad of silica gel (CH_2Cl_2) to yield 0.330 g (87%) of **1d**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.32 and 6.52 (AA'XX', J_{AX} = 9.0, 4H), 3.25 (m, 4H), 2.95 (s, 1H), 1.65-1.47 (m, 4H), 1.32 (m, 12H), 0.89 (t, *J* = 6.5, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 148.2, 133.3, 111.0, 107.3, 85.1, 74.4, 50.9, 31.7, 27.1, 26.8, 22.7, 14.0; HRMS (EI) calcd for $C_{20}H_{31}N$ (M^+?) *m/z* 285.2457, found 285.2465; elemental analysis calcd (%) for $C_{20}H_{31}N$ (285.47): C 84.15, H 10.94, N 4.91; found: C 84.04, H 10.77, N 4.71.

***N*,*N*-Dihexyl-4-[(4-iodophenyl)ethynyl]benzenamine (2a):** Air was removed from a solution of **1d** (0.162 g, 0.568 mmol) and 1,4-diiodobenzene (0.562 g, 1.702 mmol) in 6 mL of toluene/Et_3N (5/1) by blowing argon for 20 min. Then CuI (2.2 mg, 0.012 mmol) and $Pd(PPh_3)_2Cl_2$ (8.1 mg, 0.012 mmol) were added, and the mixture was stirred at 30 °C for 6 h. After evaporation of the solvent, the crude product was purified by column chromatography (heptane/CH_2Cl_2, gradient from 100:0 to 90:10) to yield 0.197 g (71%) of **2a**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.64 and 7.21 (AA'XX', J_{AX} = 8.5, 4H), 7.34 and 6.56 (AA'XX', J_{AX}

= 9.0, 4H), 3.27 (m, 4H), 1.67-1.46 (m, 4H), 1.31 (m, 12H), 0.90 (t, J = 6.5, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 148.0, 137.3, 132.9, 132.7, 123.9, 111.1, 108.1, 92.7, 92.5, 86.2, 50.9, 31.7, 27.1, 26.8, 22.7, 14.0; HRMS (LSIMS$^+$, mNBA) calcd for $C_{26}H_{34}IN$ (M^+?) *m/z* 487.1736, found 487.1738.

4-[[4-(Dihexylamino)phenyl]ethynyl]benzaldehyde (2b): Air was removed from a solution of **1d** (0.158 g, 0.553 mmol) and 4-bromobenzaldehyde (0.123 g, 0.664 mmol) in 6 mL of toluene/Et_3N (5/1) by blowing argon for 20 min. Then CuI (2.1 mg, 0.011 mmol) and $Pd(PPh_3)_2Cl_2$ (7.8 mg, 0.011 mmol) were added, and the mixture was stirred at 40 °C for 15 h. After evaporation of the solvent, the crude product was purified by column chromatography (basic alumina, heptane/CH_2Cl_2, gradient from 100:0 to 60:40) to yield 0.160 g (74%) of **2b**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 9.98 (s, 1H), 7.82 and 7.60 (AA'XX', J_{AX} = 8.4, 4H), 7.38 and 6.57 (AA'XX', J_{AX} = 9.0, 4H), 3.28 (m, 4H), 1.71-1.48 (m, 4H), 1.32 (m, 12H), 0.90 (t, J = 6.5, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 191.4, 148.4, 134.5, 133.2, 131.4, 130.9, 129.5, 111.1, 107.6, 95.9, 86.9, 50.9, 31.7, 27.1, 26.7, 22.6, 14.0; HRMS (LSIMS$^+$, mNBA) calcd for $C_{27}H_{35}NO$ (M^+?) *m/z* 389.2719, found 389.2722; elemental analysis calcd (%) for $C_{27}H_{35}NO$ (389.58): C 83.24, H 9.06, N 3.60; found: C 83.06, H 9.17, N 3.34.

4-[(1*E*)-2-(4-Iodophenyl)ethenyl]-*N*,*N*-dioctylbenzenamine (4a): To a solution of **3c**[S2] (8.826 g, 12.3 mmol) and 4-iodobenzaldehyde[S3] (2.85 g, 12.3 mmol) in anhyd CH_2Cl_2 (45 mL), was added *t*BuOK (2.07 g, 18.4 mmol). The mixture was stirred at 20 °C for 5 h. After addition of water (60 mL), extraction with CH_2Cl_2, and drying (Na_2SO_4), the solvent was evaporated. The residue was purified by filtration through a short pad of silica gel (heptane/CH_2Cl_2 50:50), to afford a mixture of isomers, which was dissolved in Et_2O (80 mL). A catalytic amount of I_2 was then added and the solution was stirred at 20 °C for 2 h under light exposure (75 W lamp). The organic layer was washed with aq $Na_2S_2O_3$ and dried (Na_2SO_4). After evaporation of the solvent, the crude product was purified by filtration through a pad of silica gel (CH_2Cl_2/heptane 90:10) to yield 5.696 g (85%) of **4a**: mp 50-51 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.61 and 7.19 (AA'XX', J_{AX} = 8.4, 4H), 7.35 and 6.60 (AA'XX', J_{AX} = 8.9, 4H), 7.02 (d, J = 16.3, 1H), 6.76 (d, J = 16.3, 1H), 3.27 (m, 4H), 1.67-1.48 (m, 4H), 1.42-1.22 (m, 20H), 0.89 (t, J = 6.5, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 147.9, 137.9, 137.5, 129.7, 127.9, 127.6, 123.9, 122.2, 111.5, 91.0, 51.0, 31.8, 29.5, 29.3, 27.3, 27.1, 22.6, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{30}H_{44}IN$ (M^+?) *m/z* 545.2519, found 545.2518; elemental analysis calcd (%) for $C_{30}H_{44}IN$ (545.59): C 66.04, H 8.13, N 2.57; found: C 66.09, H 8.28, N 2.46.

4-[(1*E*)-2-[4-(Dihexylamino)phenyl]ethenyl]benzaldehyde (4b): To a solution of **3b**[S2] (1.045 g, 1.57 mmol) and terephthalaldehyde mono-(diethylacetal) (0.329 g, 1.58 mmol) in anhyd CH_2Cl_2 (15 mL), was added *t*BuOK (0.185 g, 1.65 mmol). The mixture was stirred at 20 °C for 24 h, then filtered through a short pad of silica gel. Evaporation of the solvents afforded the crude acetal, which was hydrolyzed at 20 °C for 1 h, using 10% HCl (25 mL) in THF (50 mL). Thereafter, THF was evaporated and CH_2Cl_2 was added. The two layers were separated and the organic layer was washed with aq $NaHCO_3$, dried (Na_2SO_4) and evaporated. The residue was dissolved in CH_2Cl_2, a catalytic amount of I_2 was added, and the solution was stirred at 20 °C for 3 h under light exposure (75 W lamp). The organic layer was washed with aq $Na_2S_2O_3$ and dried (Na_2SO_4). After evaporation of the solvent, the crude product was purified by column chromatography (cyclohexane/CH_2Cl_2 20:80) to yield 0.517 g (84%) of **4b**,[S4] mp 72-73 °C; ^{1}H NMR (250.13 MHz, $CDCl_3$) *d* 9.96 (s, 1H), 7.83 and 7.59 (AA'XX', J_{AX} = 8.2 Hz, 4H), 7.41 and 6.63 (AA'XX', J_{AX} = 8.8 Hz, 4H), 7.20 (d, *J* = 16.2 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 3.29 (t, *J* = 7.7 Hz, 4H), 1.60 (m, 4H), 1.32 (m, 12H), 0.91 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (62.90 MHz ,$CDCl_3$) *d* 191.6, 148.5, 144.8, 134.4, 132.7, 130.3, 128.4, 126.1, 123.6, 121.9, 111.6, 51.1, 31.7, 27.3, 26.8, 22.7, 14.1; HRMS (CI, CH_4) calcd for $C_{27}H_{38}NO$ ($[M+H]^+$) *m/z* 392.2953, found 392.2951.

5-[(1*E*)-2-[4-(Dioctylamino)phenyl]ethenyl]-2-furanecarboxaldehyde (6a): Reaction of **5a**[S5] (336 mg, 2 mmol) with **3c**[S2] (1.44 g, 2 mmol), as described for **4b**, for 15 h, with subsequent purification by column chromatography (heptane/CH_2Cl_2 50:50), afforded 832 mg (95%) of **6a**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 9.51 (s, 1H), 7.37 and 6.60 (AA'XX', J_{AX} = 8.9, 4H), 7.32 (d, *J* = 16.1, 1H), 7.23 (d, *J* = 3.7, 1H), 6.68 (d, *J* = 16.1, 1H), 6.41 (d, *J* = 3.7, 1H), 3.29 (m, 4H), 1.59 (m, 4H), 1.30 (m, 20H), 0.89 (t, *J* = 6.5, 6H); ^{13}C NMR (75.48 MHz, $CDCl_3$) *d* 176.2, 160.5, 151.1, 148.7, 134.2, 130.5, 128.7, 122.7, 111.4, 109.5, 108.7, 51.0, 31.8, 29.5, 29.3, 27.3, 27.1, 22.6, 14.1.

5-[(1*E*)-2-[4-(Dioctylamino)phenyl]ethenyl]-2-thiophenecarboxaldehyde (6b): Reaction of **5b**[S6] (366 mg, 1.99 mmol) with **3c**[S2] (1.56 g, 2.17 mmol), as described for **4b**, for 14 h, with subsequent purification by column chromatography (heptane/CH_2Cl_2 50:50), afforded 715 mg (79%) of **6b**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 9.81 (s, 1H), 7.62 (d, *J* = 4.1, 1H), 7.36 and 6.60 (AA'XX', J_{AX} = 8.5, 4H), 7.09 (d, *J* = 16.3, 1H), 7.04 (d, *J* = 4.1, 1H), 6.95 (d, *J* = 16.3, 1H), 3.29 (m, 4H), 1.56 (m, 4H), 1.30 (m, 20H), 0.89 (t, *J* = 6.3, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 182.3, 154.6, 148.7, 139.9, 137.6, 133.7, 128.6, 124.7, 122.7, 115.4, 111.5, 51.0, 31.8, 29.5, 29.3, 27.3, 27.1, 22.6, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{29}H_{43}NOS$ (M^+?)

m/z 453.3065, found 453.3068; elemental analysis calcd (%) for $C_{29}H_{43}NOS$ (453.72): C 76.77, H 9.55, N 3.09; found: C 76.78, H 9.49, N 2.96.

5-[(1*E*)-2-[4-(Dihexylamino)phenyl]ethenyl]-2-thiophenecarboxaldehyde (6c): Reaction of **5b**[S6] (368 mg, 2 mmol) with **3b**[S2] (1.425 g, 2.15 mmol), as described for **4b**, for 14 h, with subsequent purification by column chromatography (heptane/CH_2Cl_2 50:50), afforded 677 mg (85%) of **6c**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 9.80 (s, 1H), 7.62 (d, *J* = 4.3, 1H), 7.36 and 6.60 (AA'XX', J_{AX} = 8.8, 4H), 7.09 (d, *J* = 16.2, 1H), 7.03 (d, *J* = 4.3, 1H), 6.95 (d, *J* = 16.2, 1H), 3.29 (m, 4H), 1.60 (m, 4H), 1.32 (m, 12H), 0.90 (t, *J* = 6.3, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 182.3, 154.6, 148.7, 139.9, 137.6, 133.7, 128.6, 124.7, 122.7, 115.4, 111.5, 51.0, 31.7, 27.2, 26.8, 22.7, 14.0; HRMS (LSIMS$^+$, mNBA) calcd for $C_{25}H_{35}NOS$ (M^+?) *m/z* 397.2439, found 397.2435; elemental analysis calcd (%) for $C_{25}H_{35}NOS$ (397.62): C 75.52, H 8.87, N 3.52; found: C 75.64, H 9.06, N 3.28.

1-Bromo-4-(octylsulfonyl)benzene (8a): To a solution of 1-bromo-4-(octylthio)benzene (**7a**)[S7] (700 mg, 2.32 mmol) and Na_2WO_4-$2H_2O$ (12 mg, 0.036 mmol) in 7.5 mL of EtOH/water (5:1), was slowly added, at 40 °C, 35% aq H_2O_2 (0.4 mL). Then, the mixture was heated at 80 °C and H_2O_2 (0.4 mL) was again slowly added. The mixture was refluxed for 1 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2, washed with 10% Na_2CO_3, water and dried (Na_2SO_4). The solvent was removed to yield 720 mg (93%) of **8a**: mp 38-39 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.78 and 7.71 (AA'XX', J_{AX} = 8.8, 4H), 3.07 (m, 2H), 1.69 (m, 2H), 1.24 (m, 10H), 0.86 (t, *J* = 6.5, 3H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 138.2, 132.6, 129.6, 128.9, 56.3, 31.6, 28.92, 28.86, 28.2, 22.6, 22.5, 14.0; HRMS (EI) calcd for $C_{14}H_{21}{}^{79}BrO_2S$ (M^+?) *m/z* 332.0446, found 332.0418.

1-Bromo-4-[(trifluoromethyl)sulfonyl]benzene (8b): A solution of 1-bromo-4-[(trifluoromethyl)thio]benzene (**7b**) (922 mg, 3.59 mmol) in 35% aq H_2O_2 (12 mL) and glacial acetic acid (36 mL) was refluxed for 3 h. After addition of CH_2Cl_2, the organic layer was washed with $NaHCO_3$, then with water and dried (Na_2SO_4). The solvent was evaporated and the crude product was purified by column chromatography (heptane/CH_2Cl_2 70:30) to yield 912 mg (89%) of **8b**: mp 63 °C (lit.[S8] mp 59.5-61.5 °C); ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.91 and 7.83 (AA'XX', J_{AX} = 8.9, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 133.4, 132.8, 132.0, 130.2, 119.6 (q, *J* = 325.8); HRMS (EI) calcd for $C_7H_4{}^{79}BrF_3O_2S$ (M^+?) *m/z* 287.9067, found 287.9066.

Trimethyl[[4-[(trifluoromethyl)sulfonyl]phenyl]ethynyl]silane (8c): Air was removed from a solution of **8b** (390.0 mg, 1.35 mmol) in 5 mL of Et_3N by blowing argon for 20 min. Then CuI (5.1 mg, 27.0 µmol), $Pd(PPh_3)_2Cl_2$ (18.9 mg, 27.0 µmol), and trimethylsilylacetylene (288 µL, 2.02 mmol) were added under deaeration. Thereafter, the mixture was stirred at 40 °C for 3 h. The solvent was removed and the residue was purified by column chromatography (heptane/CH_2Cl_2 75:25) to yield 364.0 mg (88%) of **8c**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.94 and 7.68 (AA'XX', J_{AX} = 8.6, 4H), 0.25 (s, 9H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 132.9, 132.0, 130.5, 130.2, 119.7 (q, *J* = 325.8), 102.2, 101.9, -0.6.

1-Ethynyl-4-[(trifluoromethyl)sulfonyl]benzene (8d): To a solution of **8c** (356.6 mg, 1.16 mmol) in 3 mL of THF, was added TBAF (1 M in THF, 1.16 mL, 1.16 mmol) and the mixture was stirred for 2 min at 20 °C. After addition of $CaCl_2$, the solvent was removed and the mixture was purified by column chromatography (heptane/CH_2Cl_2 75:25) to yield 175.2 mg (64%) of **8d**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 8.02 and 7.76 (AA'XX', J_{AX} = 8.4, 4H), 3.45 (s, 1H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 133.2, 131.0, 130.8, 130.6, 119.7 (q, *J* = 325.9), 83.4, 81.2; elemental analysis calcd (%) for $C_9H_5F_3O_2S$ (234.20): C 46.16, H 2.15, S 13.69; found: C 45.88, H 2.09, S 13.66.

1-Iodo-4-[(1*E*)-2-[4-(octylsulfonyl)phenyl]ethenyl]benzene (10): To a solution of **9b** (1.702 g, 4.208 mmol) and 4-iodobenzaldehyde (1.057 g, 4.556 mmol) in anhyd THF (16 mL), was added NaH (273 mg, 60% dispersion in mineral oil). The mixture was stirred at 20 °C for 15 h. After addition of water, the product was extracted with CH_2Cl_2 and was then purified by column chromatography (heptane/CH_2Cl_2 30:70) to yield 1.242 g (61%) of **10**: mp 158-159 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.88 and 7.66 (AA'XX', J_{AX} = 8.5, 4H), 7.72 and 7.27 (AA'XX', J_{AX} = 8.5, 4H), 7.15 (s, 2H), 3.09 (m, 2H), 1.72 (m, 2H), 1.24 (m, 10H), 0.86 (t, *J* = 5.7, 3H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 142.1, 137.8, 137.6, 135.7, 131.2, 128.4, 127.2, 126.9, 94.0, 56.3, 31.5, 29.6, 28.84, 28.77, 22.6, 22.4, 14.0; HRMS (LSIMS$^+$, mNBA) calcd for $C_{22}H_{28}IO_2S$ ($[M+H]^+$) *m/z* 483.0855, found 483.0864.

[(1,1'-Biphenyl)-4,4'-diylbis(methylene)]bisphosphonic acid tetraethyl ester (15b): A solution of **15a**[S9] (10.20 g, 30.0 mmol) and $P(OEt)_3$ (13.34 g, 80 mmol) in toluene (60 mL) was refluxed for 60 h. Filtration of the precipitate obtained after cooling at 0 °C gave 11.7 g (86%) of **15b**: mp 109 °C (lit.[S10] mp 109-110 °C); ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.45 (d, *J* = 8.0, 4H), 7.28 (dd, *J* = 8.0, 2.1, 4H), 3.96 (dq, *J* = 7.8, 7.1, 8H), 3.10 (d, *J* = 21.6, 4H), 1.18 (t, *J* = 7.0, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 139.2, 130.7 (d, *J* = 9.2), 130.1 (d, *J* =

6.5), 127.1 (d, *J* = 2.3), 62.1 (d, *J* = 6.7), 33.4 (d, *J* = 137.3), 16.4 (d, *J* = 6.0); ^{31}P NMR (101.25 MHz, $CDCl_3$) *d* 26.20; HRMS (CI, CH_4) calcd for $C_{22}H_{33}O_6P_2$ $[M + H]^+$ *m/z* 455.1752, found 455.1749.

2,7-Diiodo-9,9-dinonyl-9*H*-fluorene (18b): To a mixture of **18a** (10.0 g, 23.88 mmol), AcOH (25 mL), concd H_2SO_4 (0.75 mL) and water (5 mL) at 75 °C, were added H_5IO_6 (1.09 g) and I_2 (2.42 g). The solution was heated at 75 °C for 1 h, then AcOH (25 mL), H_5IO_6 (1.09 g) and I_2 (2.42 g) were again added and the heating was continued at 75 °C for 1 h. The reaction mixture was cooled, diluted with CH_2Cl_2 and a solution of $Na_2S_2O_3$ was added. The two layers were separated and the organic layer was washed with 1 N NaOH, then with water and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by column chromatography (heptane) to yield 11.02 g (69%) of **18b**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.65 (d, *J* = 8.5, 2H), 7.40 (d, *J* = 8.5, 2H), 7.63 (s, 2H), 1.89 (m, 4H), 1.29-1.01 (m, 24H), 0.85 (t, *J* = 6.7, 6H), 0.57 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 152.5, 139.7, 136.0, 132.0, 121.5, 93.1, 55.5, 40.0, 31.8, 29.8, 29.4, 29.2, 29.1, 23.6, 22.6, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{31}H_{44}I_2$ (M^+?) *m/z* 670.1533, found 670.1527; elemental analysis calcd (%) for $C_{31}H_{44}I_2$ (670.50): C 55.53, H 6.61; found: C 55.74, H 6.89.

4,4'-(9,9-Dinonyl-9*H*-fluorene-2,7-diyl)bis(2-methyl-3-butyn-2-ol) (18c): Air was removed from a solution of **18b** (4.19 g, 6.25 mmol) in 20 mL of Et_3N by blowing argon for 20 min. Then CuI (48.1 mg, 0.253 mmol), $Pd(PPh_3)_2Cl_2$ (176.0 mg, 0.251 mmol) and 2-methyl-3-butyn-2-ol (1.868 mL, 19.12 mmol) were added, and the mixture was stirred at 20 °C for 16 h. The precipitate which separated was filtered off and washed with Et_2O. The filtrate was evaporated to dryness and the residue was purified by column chromatography (heptane/CH_2Cl_2 30:70) to yield 2.64 g (72%) of **18c**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.59 (d, *J* = 8.5, 2H), 7.39 (d, *J* = 8.5, 2H), 7.37 (s, 2H), 2.10 (s, 2H), 1.92 (m, 4H), 1.66 (s, 12H), 1.28-0.98 (m, 24H), 0.84 (t, *J* = 6.7, 6H), 0.54 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 150.8, 140.4, 130.6, 125.9, 121.4, 119.7, 94.0, 82.9, 65.6, 55.0, 40.3, 31.7, 31.4, 29.9, 29.4, 29.2, 29.1, 23.6, 22.5, 14.0; MS (LSIMS$^+$, mNBA) *m/z* 582.4 ([M^+?], 63), 565.4 ([M+H^+-H_2O], 100); HRMS (LSIMS$^+$, mNBA) calcd for $C_{41}H_{58}O_2$ ($M^{+\cdot}$) *m/z* 582.4437, found 582.4432.

2,7-Diethynyl-9,9-dinonyl-9*H*-fluorene (18d): To a refluxing solution of **18c** (1.72 g, 2.95 mmol) in 30 mL of toluene/*i*PrOH (4/1), was added solid KOH (0.494 g, 8.8 mmol). The mixture was stirred under reflux for 0.5 h. After cooling, the mixture was filtered through

Celite® and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were dried (Na_2SO_4) and evaporated to give a crude product, which was purified by column chromatography (heptane) to yield 1.21 g (88%) of **18d**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.63 (d, *J* = 8.6, 2H), 7.48 (d, *J* = 8.6, 2H), 7.46 (s, 2H), 3.14 (s, 2H), 1.93 (m, 4H), 1.27-0.99 (m, 24H), 0.84 (t, *J* = 6.7, 6H), 0.56 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 151.0, 141.0, 131.2, 126.5, 120.8, 119.9, 84.5, 77.3, 55.2, 40.2, 31.8, 29.9, 29.5, 29.2, 29.1, 23.6, 22.6, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{35}H_{46}$ (M^{+}?) *m/z* 466.3600, found 466.3602.

2,7-Dibromo-9,9-dinonyl-9*H*-fluorene (22a): To 300 mL of a CH_2Cl_2 solution of **18a** (18 g, 43 mmol) and iodine (22 mg, 0.087 mmol), was added dropwise a solution of bromine (4.41 mL, 86 mmol), and the mixture was stirred for 15 h at 20 °C. The organic layer was washed with aq $Na_2S_2O_3$ and dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography (heptane) to yield 24.16 g (97%) of **22a**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.52 (d, *J* = 8.6, 2H), 7.45 (dd, *J* = 8.6, 1.8, 2H), 7.44 (d, *J* = 1.8, 2H), 1.90 (m, 4H), 1.32-0.99 (m, 24H), 0.84 (t, *J* = 6.8, 6H), 0.57 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 152.5, 139.0, 130.1, 126.1, 121.4, 121.1, 55.6, 40.1, 31.8, 29.8, 29.4, 29.2, 23.6, 22.6, 14.1; HRMS (LSIMS$^+$, mNBA) calcd for $C_{31}H_{44}{}^{79}Br_2$ (M^{+}?) *m/z* 574.1810, found 574.1820; elemental analysis calcd (%) for $C_{31}H_{44}Br_2$ (576.50): C 64.59, H 7.69; found: C 64.96, H 7.95.

9,9-Dinonyl-9*H*-fluorene-2,7-dicarboxaldehyde (22b): A solution of 11.65 g (20.21 mmol) of **22a** in 340 mL of anhyd benzene was cooled to 0 °C before 48.5 mL of a solution of *n*-butyllithium (2.5 M in hexane, 121.25 mmol) was added dropwise. After the addition was complete, the reaction mixture was stirred at 60 °C for 4 h, cooled to 0 °C, and *N*-formylpiperidine (32 g, 282.8 mmol) was added and allowed to react at 20 °C for 14 h. Thereafter, 3 M HCl (240 mL) was added. The two layers were separated and the organic layer was washed with water. The solvents were removed under reduced pressure, and the residue was purified by column chromatography (heptane/CH_2Cl_2, gradient from 95:5 to 70:30) to yield 4.65 g (48%) of **22b**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 10.10 (s, 2H), 7.92 (m, 6H), 2.07 (m, 4H), 1.32-0.97 (m, 24H), 0.82 (t, *J* = 6.7, 6H), 0.56 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 191.6, 152.5, 145.3, 136.2, 129.8, 123.2, 121.0, 55.2, 39.7, 31.4, 29.5, 29.1, 28.9, 28.8, 23.5, 22.3, 13.7; HRMS (LSIMS$^+$, mNBA) calcd for $C_{33}H_{47}O_2$ ($[M+H]^+$) *m/z* 475.3576, found 475.3576; elemental analysis calcd (%) for $C_{33}H_{46}O_2$ (474.73): C 83.49, H 9.77; found: C 83.65, H 9.86.

2,7-Diethenyl-9,9-dinonyl-9*H*-fluorene (27): To a solution of **22b** (670.0 mg, 1.41 mmol) and methyltriphenylphosphonium iodide (1.46 g, 3.62 mmol) in anhyd THF (32 mL), was added NaH (310 mg, 60% dispersion in mineral oil). The mixture was stirred at 20 °C for 48 h and then filtered through Celite® (heptane). After evaporation of the solvent, the crude product was purified by column chromatography (heptane) to yield 417.0 mg (63%) of **27**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.66 (d, *J* = 7.9, 2H), 7.44 (dd, *J* = 7.9, *J* = 1.7, 2H), 7.39 (d, *J* = 1.7, 2H), 6.84 (dd, *J* = 17.6, *J* = 10.9, 2H), 5.84 (dd, *J* = 17.6, *J* = 0.9, 2H), 5.30 (dd, *J* = 10.9, *J* = 0.9, 2H), 1.58 (m, 4H), 1.29-1.08 (m, 24H), 0.87 (t, *J* = 6.4, 6H), 0.65 (s, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 151.8, 141.1, 137.9, 136.9, 125.7, 120.9, 120.1, 113.4, 55.3, 40.8, 32.3, 30.5, 29.9, 29.7, 24.1, 23.0, 14.5. HRMS (EI) calcd for $C_{35}H_{50}$ (M^{+}?) *m/z* 470.3913, found 470.3909.

9,9-Dinonyl-9*H*-fluorene-2,7-dimethanol (29a): To a solution of **22b** (1.018 g, 2.14 mmol) in 38 mL of EtOH/CH_2Cl_2 (2/1), was added KBH_4 (346 mg, 6.42 mmol). The mixture was stirred at 20 °C for 14 h. After addition of water, the solvent was evaporated. The residue was filtered and washed with water. The crude product was purified by column chromatography (CH_2Cl_2) to yield 0.994 g (97%) of **29a**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.67 (d, *J* = 8.3, 2H), 7.34 (s, 2H), 7.32 (d, *J* = 8.3, 2H), 4.78 (d, *J* = 5.8, 4H), 1.95 (m, 4H), 1.68 (t, *J* = 5.8, 2H), 1.24-1.03 (m, 24H), 0.83 (t, *J* = 6.7, 6H), 0.60 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 151.3, 140.3, 139.7, 125.7, 121.5, 119.6, 65.7, 55.0, 40.3, 31.8, 30.0, 29.5, 29.3, 29.2, 23.8, 22.6, 14.0; HRMS (LSIMS^{+}, mNBA) calcd for $C_{33}H_{50}O_2$ (M^{+}?) *m/z* 478.3811, found 478.3814; elemental analysis calcd (%) for $C_{33}H_{50}O_2$ (478.76): C 82.79, H 10.53; found: C 82.81, H 10.56.

2,7-Bis(bromomethyl)-9,9-dinonyl-9*H*-fluorene (29b): A solution of **29a** (1.05 g, 2.19 mmol) in 48% aq HBr (5.2 mL) was refluxed for 3 h. After addition of aq $NaHCO_3$, extraction with CH_2Cl_2, and drying (Na_2SO_4), the solvent was evaporated to yield 1.19 g (90%) of **29b**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.64 (d, *J* = 8.2, 2H), 7.36 (d, *J* = 8.2, 2H), 7.34 (s, 2H), 4.60 (s, 4H), 1.94 (m, 4H), 1.25-1.04 (m, 24H), 0.83 (t, *J* = 6.7, 6H), 0.61 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 151.6, 140.6, 136.8, 127.9, 123.6, 120.0, 55.1, 40.0, 34.3, 31.8, 29.8, 29.4, 29.1, 23.6, 22.6, 14.1; HRMS (LSIMS^{+}, mNBA) calcd for $C_{33}H_{47}{}^{79}Br_2$ ($[M-H]^{+}$) *m/z* 601.2045, found 601.2026.

[(9,9-Dinonyl-9*H*-fluorene-2,7-diyl)bis(methylene)]bisphosphonic acid tetraethyl ester (29c): A solution of **29b** (1.18 g, 1.96 mmol) in $P(OEt)_3$ (20 mL) was refluxed for 60 h. Then

$P(OEt)_3$ was removed by distillation under vacuum. The crude product was purified by column chromatography (CH_2Cl_2/AcOEt, gradient from 85:15 to 50:50) to yield 870 mg (62%) of **29c**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 7.61 (d, *J* = 8.1, 2H), 7.26 (m, 4H), 4.00 (m, 8H), 3.24 (d, *J* = 21.7, 4H), 1.94 (m, 4H), 1.23 (t, *J* = 7.1, 12H), 1.19-0.98 (m, 24H), 0.83 (t, *J* = 6.7, 6H), 0.57 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) *d* 151.0, 139.6, 130.2 (d, *J* = 9.1), 128.4 (d, *J* = 6.3), 124.2 (d, *J* = 6.6), 119.6, 62.1 (d, *J* = 7.1), 54.9, 40.4, 34.1 (d, *J* = 137.6), 31.7, 30.1, 29.5, 29.4, 29.2, 23.9, 22.6, 16.1 (d, *J* = 6.1), 14.0; ^{31}P NMR (121.50 MHz, $CDCl_3$) *d* 27.15; HRMS (LSIMS$^+$, mNBA) calcd for $C_{41}H_{69}O_6P_2$ ($[M+H]^+$) *m/z* 719.4569, found 719.4554.

5,5'-[(9,9-Dinonyl-9*H*-fluorene-2,7-diyl)di-(1*E*)-2,1-ethenediyl]bis-2-thiophene-carboxaldehyde (33): To a solution of **22b** (170 mg, 0.237 mmol) and **5b** (100.4 mg, 0.545 mmol) in anhyd THF (22 mL), was added NaH (75 mg, 60% dispersion in mineral oil). The mixture was stirred at 20 °C for 15 h, then at 60 °C for 2 h. After addition of water, extraction with CH_2Cl_2, and drying (Na_2SO_4), the solvents were evaporated. Purification of the residue by column chromatography (heptane/AcOEt 70:30) afforded the crude acetal, which was hydrolyzed at 20 °C for 2 h, using 10% HCl (4 mL) in THF (8 mL). Thereafter, THF was evaporated and CH_2Cl_2 was added. The two layers were separated and the organic layer was washed with aq $NaHCO_3$, dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography (heptane/AcOEt 80:20) to yield 90 mg (55%) of **33**; ^{1}H NMR (200.13 MHz, $CDCl_3$) *d* 9.87 (s, 2H), 7.70 (d, *J* = 7.8, 2H), 7.69 (d, *J* = 4.1, 2H), 7.50 (d, *J* = 7.8, 2H), 7.46 (s, 2H), 7.26 (m, 4H), 7.19 (d, *J* = 4.1, 2H), 2.02 (m, 4H), 1.26-1.04 (m, 24 H), 0.80 (t, *J* = 6.5, 6H), 0.61 (m, 4H); ^{1}H NMR (200.13 MHz, C_6D_6) δ 9.51 (s, 2H), 7.55 (d, *J* = 8.0, 2H), 7.43 (s, 2H), 7.24 (d, *J* = 8.0, 2H), 7.10 (d, *J* = 16.1, 2H), 6.98 (d, *J* = 16.1, 2H), 6.88 (d, *J* = 3.9, 2H), 6.56 (d, *J* = 3.9, 2H), 2.14 (m, 4H), 1.46-0.76 (m, 28H), 0.81 (t, *J* = 6.5, 6H).

Absorption and emission spectra.

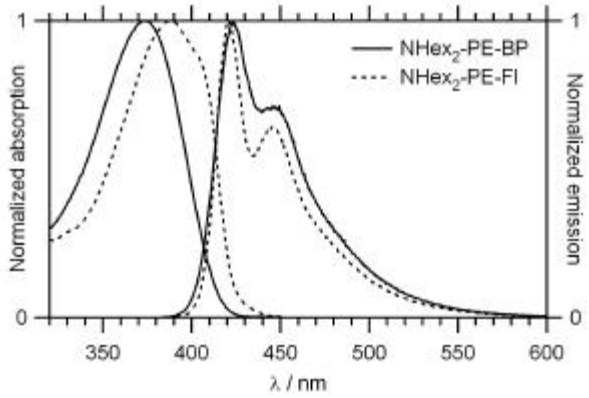

Figure S1. Absorption and emission of **13a** and **19a** in toluene: core effect.

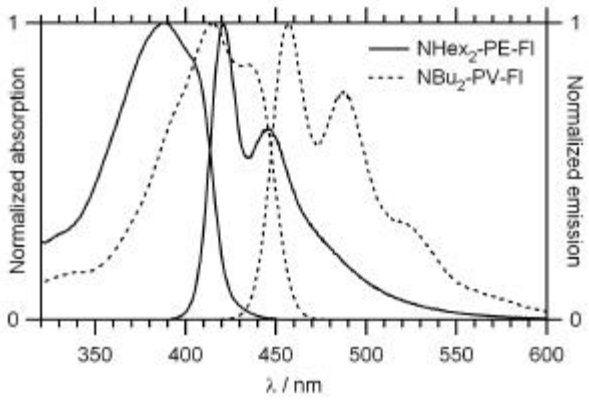

Figure S2. Absorption and emission of **19a** and **24** in toluene: linker effect.

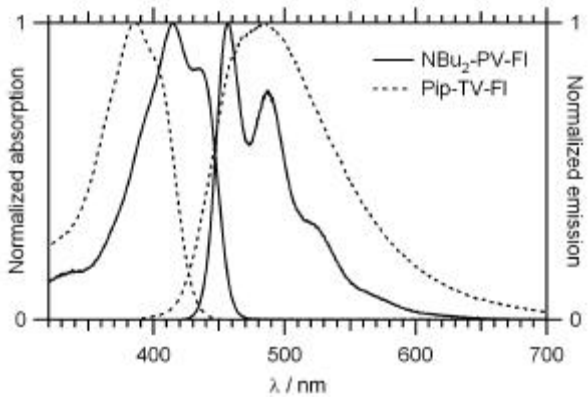

Figure S3a

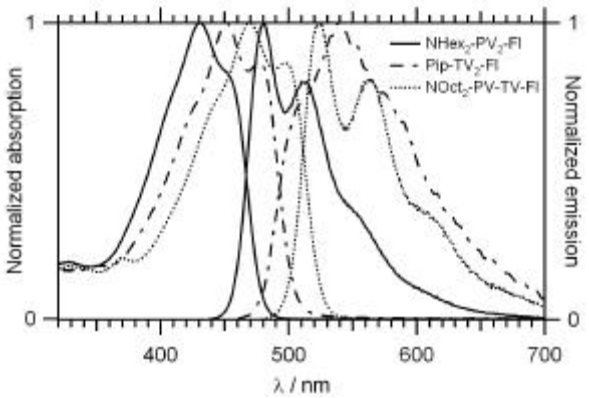

Figure S3b

Figure S3. Absorption and emission in toluene of (a) **24** and **34a**; (b) **30**, **34b** and **31**: connector effects.

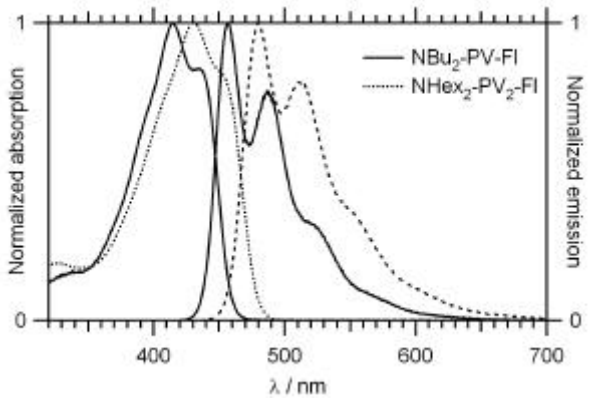

Figure S4a

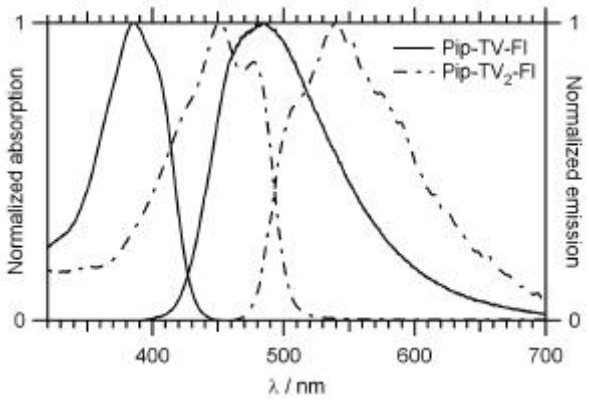

Figure S4b

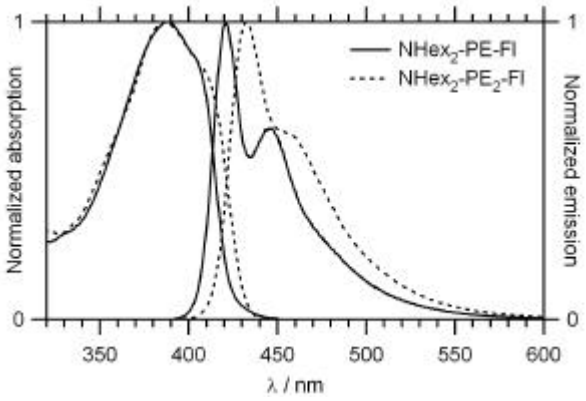

Figure S4c

Figure S4. Absorption and emission spectra in toluene of (a) **24** and **30**; (b) **34a** and **34b**; (c) **19a** and **19b**: length effects.

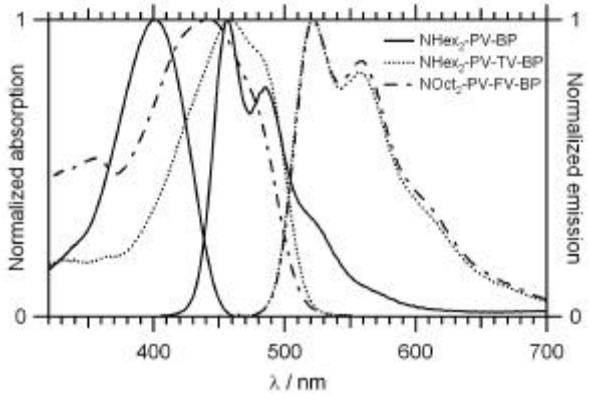

Figure S5a

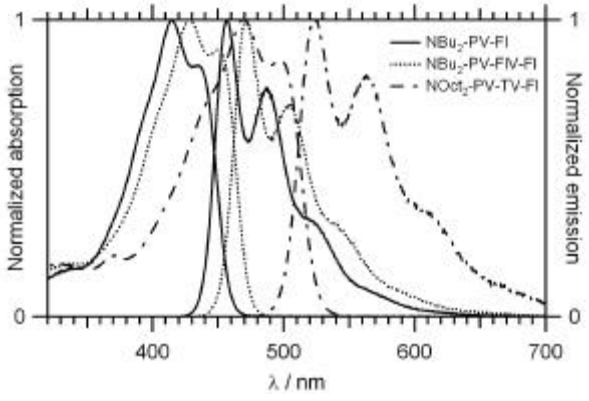

Figure S5b

Figure S5. Absorption and emission spectra in toluene of (a) **16a**, **17b** and **17a**; (b) **24**, **32** and **31**: length effects.

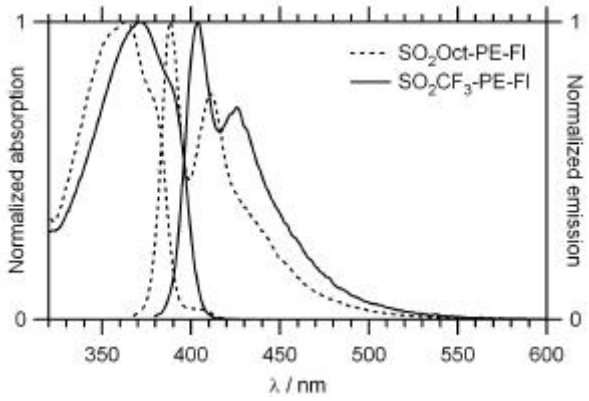

Figure S6a

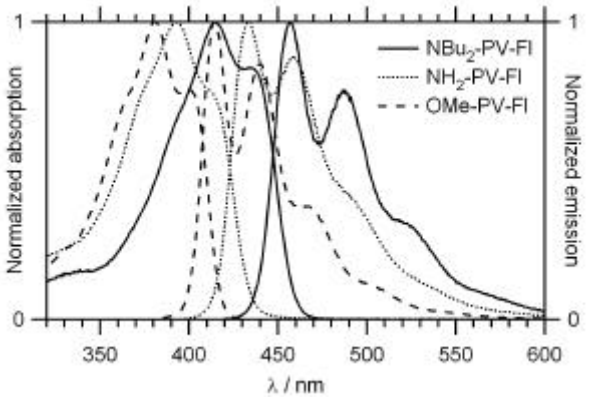

Figure S6b

Figure S6. Absorption and emission spectra in toluene of (a) **21a** and **21b**; (b) **24**, **28** and **23**: end-groups' effect.

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