Two-Photon Absorption Properties of Proquinoidal D-A-D and A-D-A Quadrupolar Chromophores

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Synthesis and Characterization

4-Iodo-*N*,*N*-dihexylaniline (1). 4-Iodoaniline (15.05 g, 6.87×10^{-2} mol), K_2CO_3 (19.00 g, 0.137 mol), 1-iodohexane (32.0 ml, 0.217 mol) and dry DMF (170 ml) were added to a 500-ml two-neck round-bottom flask. Ar was bubbled into the reaction mixture for 10 min. The reaction mixture was stirred at 90 °C for 16 h and at 100 °C for 2.5 h under Ar. After cooling, the reaction mixture was filtered to remove inorganic solids. Solvents were removed in vacuo, and water was added to the reaction mixture. The organic layer was extracted with $CHCl_3$, washed with aq. $NaHCO_3$ and water, and dried over Na_2SO_4. The residue was chromatographed on silica gel 4:1 hexane:$CHCl_3$ as the eluent. Yield = 20.47 g (77 % based on 15.05 g of 4-iodoaniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.41 (d, 2H, *J* = 8.8 Hz, Ph), 6.40 (d, 2H, *J* = 9.1 Hz, Ph), 3.20 (t, 4H, *J* = 7.6 Hz, -NCH_2-), 1.43–1.61 (m, 4H, -NCH_2CH_2-), 1.18–1.37 (m, 12H, -CH_2-), 0.89 (t, 6H, *J* = 6.5 Hz, -CH_3). CI MS *m/z* : 388.149 ($(M+H)^+$) (calcd 388.150).

4-[(Trimethylsilyl)ethynyl]-*N*,*N*-dihexylaniline (2). 4-Iodo-*N*,*N*-dihexylaniline (**1**) (3.150 g, 8.13×10^{-3} mol), $Pd(PPh_3)_2Cl_2$ (0.332 g, 4.73×10^{-4} mol), CuI (0.130 g, 6.83×10^{-4} mol) and Et_3N (20 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before (trimethylsilyl)acetylene (2.40 ml, 1.70×10^{-2} mol) was added. The reaction mixture was stirred at 45 °C for 18 h under Ar. After the solvent was removed in vacuo, the residue was chromatographed on silica gel 4:1 hexane:$CHCl_3$ as the eluent. Yield = 2.861 g (98 % based on 3.150 g of 4-iodo-*N*,*N*-

dihexylaniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.29 (d, 2H, *J* = 9.0 Hz, Ph), 6.50 (d, 2H, *J* = 9.0 Hz, Ph), 3.24 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 1.43–1.65 (m, 4H, -NCH_2CH_2-), 1.19–1.41 (m, 12H, -CH_2-), 0.89 (t, 6H, *J* = 6.5 Hz, -CH_3), 0.22 (s, 9H, Si-CH_3). CI MS *m/z* : 358.292 ($(M+H)^+$) (calcd 358.293).

4-Ethynyl-*N*,*N*-dihexylaniline (3). 4-[(Trimethylsilyl)ethynyl]-*N,N*-dihexylaniline (**2**) (1.206 g, 3.37×10^{-3} mol), K_2CO_3 (0.558 g, 4.04×10^{-3} mol), THF (20 ml) and MeOH (20 ml) were added to a 100-ml round-bottom flask. The reaction mixture was stirred at room temperature for 4.5 h under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel with 4:1 hexane:$CHCl_3$ as the eluent. Yield = 0.858 g (89 % based on 1.206 g of 4-[(trimethylsilyl)ethynyl]-*N,N*-dihexylaniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.32 (d, 2H, *J* = 8.9 Hz, Ph), 6.52 (d, 2H, *J* = 8.9 Hz, Ph), 3.25 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 2.96 (s, 1H, ethynyl-H), 1.46–1.64 (m, 4H, -NCH_2CH_2-), 1.20–1.42 (m, 12H, -CH_2-), 0.90 (t, 6H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 286.253 ($(M+H)^+$) (calcd 286.253).

4,7-Bis[4′-(*N*,*N*-dihexylamino)phenylethyn-1′-yl]benzo[c][1,2,5]thiadiazole (4) [$(DHAt)_2BTD$)]. 4,7-Dibromobenzo[c][1,2,5]thiadiazole[1] (0.1009 g, 3.43×10^{-4} mol), 4-Ethynyl-*N,N*-dihexylaniline (**3**) (0.2089 g, 7.32×10^{-4} mol), Pd_2dba_3 (66.9 mg, 7.31×10^{-5} mol), $AsPh_3$ (0.1071 g, 3.50×10^{-4} mol) and dry THF (20 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 10 min before *i*-Pr_2EtN (0.30 ml) was added. The reaction mixture was stirred at 43 °C for 20.5 h under

Ar. After the solvent was evaporated, the reaction mixture was chromatographed on silica gel with 80:10:1 hexane:THF:Et_3N. The product was further purified by size exclusion column chromatography (BioRad Bio-Beads SX-1 packed in THF, gravity flow). Yield = 0.1488 g (62 % based on 0.1009 g of 4,7-Dibromobenzo[c][1,2,5]thiadiazole). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.68 (s, 2H, Ph), 7.49 (d, 4H, *J* = 8.8 Hz, Ph), 6.59 (d, 4H, *J* = 9.0 Hz, Ph), 3.29 (t, 8H, *J* = 7.6 Hz, -NCH_2-), 1.50–1.70 (m, 8H, -NCH_2CH_2-), 1.19–1.45 (m, 24H, -CH_2-), 0.91 (t, 12H, *J* = 6.6 Hz, -CH_3). MALDI-TOF MS *m/z* : 704.13 (M^+) (calcd 702.470).

***N,N*-Dihexylaniline (5)**. A mixture of aniline (5.90 ml, 6.47×10^{-2} mol), 1-iodohexane (20.0 ml, 0.136 mol) and K_2CO_3 (18.80 g, 0.136 mol) in 80 ml of EtOH was refluxed for 27 h under Ar. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate was washed with water and dried over Na_2SO_4. The residue was chromatographed on silica gel with 4:1 hexane:$CHCl_3$ as the eluent. Yield = 14.735 g (87 % based on 5.90 ml of aniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20 (dd, 2H, *J* = 7.1, 8.8 Hz, Ph), 6.57–6.66 (m, 3H, Ph), 3.24 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 1.48–1.65 (m, 4H, -NCH_2CH_2-), 1.22–1.40 (m, 12H, -CH_2-), 0.90 (t, 6H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 262.253 ($(M+H)^+$) (calcd 262.253).

4-(*N,N*-Dihexylamino)benzaldehyde (6). To a solution of *N,N*-dihexylaniline (**5**) (12.02 g, 4.60×10^{-2} mol) in anhydrous 1,2-dichloroethane (200 ml) at room temperature

were successively added anhydrous DMF (3.60 ml, 4.65×10^{-2} mol) and $POCl_3$ (5.20 ml, 5.58×10^{-2} mol), and the mixture was refluxed for 5.5 h. After cooling, 2M aqueous NaOAc solution (200 ml) was added and the reaction mixture was stirred overnight. The product was extracted three times with $CHCl_3$ and the combined organic layers were dried over Na_2SO_4. The residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$ as the eluent. Yield = 10.793 g (81 % based on 12.02 g of *N,N*-dihexylaniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.69 (s, 1H, -CHO), 7.70 (dd, 2H, *J* = 8.9 Hz, Ph), 6.63 (d, 2H, *J* = 9.0 Hz, Ph), 3.34 (t, 4H, *J* = 7.8 Hz, -NCH_2-), 1.48–1.70 (m, 4H, -NCH_2CH_2-), 1.19–1.41 (m, 12H, -CH_2-), 0.91 (t, 6H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 290.247 ($(M+H)^+$) (calcd 290.248).

***N,N*-Dihexyl-4-vinylaniline (7)**. To methyltriphenylphosphonium bromide (3.07 g, 8.59×10^{-3} mol) in 50 ml of dry THF was added *n*-BuLi (2.2 M solution in hexane, 4.00 ml, 8.80×10^{-3} mol) dropwise at –78 °C. After 2.5 h, the reaction mixture was gradually warmed up to 0 °C, and again cooled to –78 °C. 4-(*N,N*-Dihexylamino)benzaldehyde (**6**) (2.26 g, 7.81×10^{-3} mol) in 15 ml of dry THF was slowly added to the reaction mixture. The reaction mixture was stirred overnight and meanwhile gradually warmed up to 10 °C. Aqueous NaCl was added to the reaction mixture. The organic layer was extracted with petroleum ether and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$. Yield = 0.775 g (35 % based on 2.26 g of *N,N*-dihexyl-4-formylaniline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.27 (d,

2H, *J* = 8.8 Hz, Ph-H), 6.61 (dd, 1H, *J* = 10.9, 17.8 Hz, vinyl-H), 6.58 (d, 2H, *J* = 8.9 Hz, Ph-H), 5.49 (dd, 1H, *J* = 1.1, 17.6 Hz, vinyl-H), 4.97 (dd, 1H, *J* = 0.9, 10.8 Hz, vinyl-H), 3.25 (t, 4H, *J* = 7.7 Hz, NCH_2), 1.48–1.66 (m, 4H, NCH_2CH_2-), 1.20–1.42 (m, 12H, -CH_2-), 0.89 (t, 6H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 288.269 ($(M+H)^+$) (calcd 288.269).

4,7-Bis[4′-(*N*,*N*-dihexylamino)phenylethen-1′-yl]benzo[c][1,2,5]thiadiazole (8) [(DHAd)$_2$BTD]. 4,7-Dibromobenzo[c][1,2,5]thiadiazole[1] (50.3 mg, 1.71×10^{-4} mol), *N*,*N*-dihexyl-4-vinylaniline (**7**) (120.0 mg, 4.17×10^{-4} mol), Pd_2dba_3 (41.7 mg, 4.55×10^{-5} mol) and dry THF (10 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before *i*-Pr_2EtN (0.30 ml) and P(*t*-Bu)$_3$ (10 wt% in hexane, 0.50 ml, 1.6×10^{-4} mol) were added. The reaction mixture was stirred at 39 °C for 21 h under Ar. After the solvent was evaporated, the reaction mixture was chromatographed on silica gel with 30:15:1 hexane:$CHCl_3$:Et_3N. Yield = 0.035 g (29 % based on 50.3 mg of 4,7-dibromobenzo[c][1,2,5]thiadiazole). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.83 (d, 2H, *J* = 16.2 Hz, vinyl-H), 7.61 (s, 2H, Ph), 7.51 (d, 4H, *J* = 8.8 Hz, Ph), 7.45 (d, 2H, *J* = 16.3 Hz, vinyl-H), 6.64 (d, 4H, *J* = 8.8 Hz, Ph), 3.30 (t, 8H, *J* = 7.6 Hz, -NCH_2-), 1.46–1.69 (m, 8H, -NCH_2CH_2-), 1.16–1.40 (m, 24H, -CH_2-), 0.88 (t, 12H, *J* = 6.8 Hz, -CH_3). MALDI-TOF MS *m/z* : 707.55 (M^+) (calcd 706.501).

3,7-Dimethyloctyl bromide (9). To a solution of 3,7-dimethyl-1-octanol (50.0 ml, 0.264 mol) and triphenylphosphine (86.9 g, 0.331 mol) in 300 ml of CH_2Cl_2 were added

N-bromosuccinimide (56.6 g, 0.318 mol) in portions at 0 °C. After stirring at 0 °C for 2 h, the solvent was evaporated. The residue was treated with hexane and filtered. The solids were washed thoroughly with hexane, and the combined hexane extracts were evaporated. The residue was chromatographed on silica gel with hexane. Yield = 54.13 g (93 % based on 50.0 ml of 3,7-dimethyl-1-octanol). ^{1}H NMR (360 MHz, $CDCl_3$): δ 3.37–3.50 (m, 2H, -CH_2Br), 1.07–1.94 (m, 10H, (CH_3)$_2$C*H*CH_2CH_2CH_2C*H*(CH_3)CH_2CH_2Br), 0.89 (d, 3H, *J* = 6.5 Hz, -CH_3), 0.87 (d, 6H, *J* = 6.8 Hz, -CH_3). CI MS *m/z* : 220.048 (M^+) (calcd 220.083).

2,6,13,17-Tetramethyloctadecane-9,10-dione (10). To a suspension of 1,4-dimethylpiperazine-2,3-dione[2] (2.08 g, 1.46×10^{-2} mol) in 50 ml of dry Et_2O was added 3,7-dimethyloctyl lithium (0.45M solution in Et_2O, 65 ml, 2.9×10^{-2} mol, freshly prepared from 3,7-dimethyloctyl bromide (**9**) and lithium) by a syringe. After 40 min of stirring at room temperature under N_2, the solution was hydrolyzed with 100 ml of 10% HCl and extracted with $CHCl_3$. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. The product was chromatographed on silica gel with 3:1 hexane:$CHCl_3$ as the eluent. Yield = 4.446 g (91 % based on 65 ml of 0.45M 3,7-dimethyloctyl lithium in Et_2O). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.69–2.78 (m, 4H, -CH_2CO), 1.06–1.65 (m, 20H, (CH_3)$_2$C*H*CH_2CH_2CH_2C*H*(CH_3)CH_2CH_2CO), 0.87 (d, 6H, *J* = 9.0 Hz, -CH_3), 0.86 (d, 12H, *J* = 9.5 Hz, -CH_3). CI MS *m/z* : 338.3175 (M^+) (calcd 338.318).

4,9-Dibromo-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (11). 5,6-Diamino-4,7-dibromobenzo[c][1,2,5]thiadiazole[3] (0.224 g, 6.91×10^{-4} mol) was dissolved in acetic acid (40 ml). 2,6,13,17-Tetramethyloctadecane-9,10-dione (**10**) (0.261 g, 7.71×10^{-4} mol) was added, and the reaction mixture was stirred for 71 h at room temperature under N_2. After the solvent was evaporated, water was added, and the mixture was extracted with $CHCl_3$. The combined organic layers were washed with water, aq. $NaHCO_3$ and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with $CHCl_3$ and further purified by size exclusion column chromatography (BioRad Bio-Beads SX-1 packed in THF, gravity flow). Yield = 0.360 g (83 % based on 0.224 g of 5,6-diamino-4,7-dibromobenzo[c][1,2,5]thiadiazole). ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.01–3.22 (m, 4H, Ar-CH_2), 1.11–2.09 (m, 20H, $(CH_3)_2CHCH_2CH_2CH_2CH(CH_3)CH_2CH_2Ar$), 1.03 (d, 6H, J = 6.5 Hz, -CH_3), 0.88 (d, 12H, J = 6.6 Hz, -CH_3). CI MS m/z : 625.157 ($(M+H)^+$) (calcd 625.158).

4-(*n*-Dodecyloxy)iodobenzene (12). 4-Iodophenol (3.03 g, 1.38×10^{-2} mol), 1-bromododecane (6.65 ml, 2.77×10^{-2} mol) and K_2CO_3 (3.81 g, 2.76×10^{-2} mol) were dissolved in 50 ml of dry DMF and refluxed for 3.5 h under N_2. After cooling, the solution was diluted with 2M HCl, and extracted with CH_2Cl_2. The combined organic layers were washed with saturated aq. $NaHCO_3$, water, and dried over Na_2SO_4. The product was chromatographed on silica gel with 3:1 hexane:$CHCl_3$ as the eluent. Yield =

5.274 g (98 % based on 3.03 g of 4-iodophenol). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.53 (d, 2H, *J* = 8.8 Hz, Ph), 6.67 (d, 2H, *J* = 9.0 Hz, Ph), 3.90 (t, 2H, *J* = 6.5 Hz, -OCH_2-), 1.76 (quint, 2H, *J* = 6.6 Hz, -OCH_2CH_2-), 1.13–1.48 (m, 18H, -CH_2-), 0.88 (t, 3H, *J* = 6.4 Hz, -CH_3). CI MS *m/z* : 388.125 (M^+) (calcd 388.126).

4-*n*-Dodecyloxy[(trimethylsilyl)ethynyl]benzene (13). 4-(Dodecyloxy)iodobenzene (**12**) (4.04 g, 1.04×10^{-2} mol), triphenylphosphine (0.165 g, 6.29×10^{-4} mol), CuI (0.108 g, 5.67×10^{-4} mol) and $Pd(PPh_3)_2Cl_2$ (0.153 g, 2.18×10^{-4} mol) were dissolved in 40 ml of dry piperidine under N_2. (Trimethylsilyl)acetylene (3.00 ml, 2.12×10^{-2} mol) was added and the mixture was stirred at 50 °C for 6 h under N_2. After cooling, the reaction mixture was poured into aq. NH_4Cl and extracted with CH_2Cl_2 (three times). The combined organic layers were washed with aq. NH_4Cl, water, and dried over Na_2SO_4. The crude product was chromatographed on silica gel with 4:1 hexane:CH_2Cl_2 as the eluent. Yield = 3.633 g (97 % based on 4.04 g of 4-(dodecyloxy)iodobenzene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 8.9 Hz, Ph), 6.80 (d, 2H, *J* = 9.0 Hz, Ph), 3.94 (t, 2H, *J* = 6.6 Hz, -OCH_2-), 1.77 (quint, 2H, *J* = 6.6 Hz, -OCH_2CH_2-), 1.17–1.50 (m, 18H, -CH_2-), 0.88 (t, 3H, *J* = 6.6 Hz, -CH_3), 0.24 (s, 9H, Si-CH_3). CI MS *m/z* : 358.268 (M^+) (calcd 358.269).

4-*n*-Dodecyloxyethynylbenzene (14). 4-Dodecyloxy[(trimethylsilyl)ethynyl]benzene (**13**) (3.09 g, 8.62×10^{-3} mol) was dissolved in a mixture of 20 ml of MeOH and 20 ml of THF. 5N NaOH (2.1 ml, 1.05×10^{-2} mol) was

added and the solution was stirred for 3.5 h at room temperature under N_2. Water was added to the reaction mixture. The aqueous mixture was extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$. The product was chromatographed on silica gel with 4:1 hexane:CH_2Cl_2 as the eluent. Yield = 2.430 g (98 % based on 3.09 g of 4-dodecyloxy[(trimethylsilyl)ethynyl]benzene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.41 (d, 2H, *J* = 8.8 Hz, Ph), 6.83 (d, 2H, *J* = 8.7 Hz, Ph), 3.95 (t, 2H, *J* = 6.6 Hz, -OCH_2-), 2.99 (s, 1H, ethynyl-H), 1.78 (quint, 2H, *J* = 6.9 Hz, -OCH_2CH_2-), 1.10–1.51 (m, 18H, -CH_2-), 0.88 (t, 3H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 287.236 ($(M+H)^+$) (calcd 287.237).

4,9-bis[(4′′-*n*-dodecyloxy)phenylethyn-1′′-yl]-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (15) [(ROPht)$_2$TDQ]. 4,9-Dibromo-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (**11**) (82.3 mg, 1.31×10^{-4} mol), 4-dodecyloxyethynylbenzene (**14**) (50.0 mg, 1.7×10^{-4} mol), Pd_2dba_3 (25.4 mg, 2.77×10^{-5} mol), $AsPh_3$ (60.4 mg, 1.97×10^{-4} mol) and dry THF (10 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before *i*-Pr_2NH (0.50 ml) was added. The reaction mixture was stirred at 40 °C for 37 h under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel with 2:3 hexane:$CHCl_3$ as the eluent. Yield = 0.037 g (42 % based on 50 mg of 4-dodecyloxyethynylbenzene). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.74 (d, 4H, *J* = 8.8 Hz, Ph), 6.94 (d, 4H, *J* = 8.9 Hz, Ph), 4.01 (t, 4H, *J* = 6.6 Hz, -OCH_2-), 3.00–3.23 (m, 4H, Ar-CH_2),

1.1–2.2 (m, 60H, -CH_2-), 1.06 (d, 6H, *J* = 6.6 Hz, -CH_2-), 0.89 (t, 6H, *J* = 6.6 Hz, -CH_3), 0.86 (d, 12H, *J* = 6.6 Hz, -CH_3). MALDI-TOF MS *m/z* : 1037.7 (M^+) (calcd 1036.757).

4-*n*-Dodecyloxybenzaldehyde (16). 4-Hydroxybenzaldehyde (8.00 g, 6.55×10^{-2} mol), 1-bromododecane (16.50 ml, 6.87×10^{-2} mol), K_2CO_3 (9.05 g, 6.55×10^{-2} mol) and dry DMF (100 ml) were added to a two-neck round-bottom flask. The reaction mixture was stirred at 105 °C for 21.5 h under Ar. After cooling, the solution was diluted with 2M HCl and extracted three times with CH_2Cl_2. The combined organic layers were washed with aqueous $NaHCO_3$, H_2O and dried over Na_2SO_4. The product was chromatographed on silica gel with 1:1 hexane:CH_2Cl_2 as the eluent. Yield = 19.02 g (~100 % based on 8.00 g of 4-hydroxybenzaldehyde). ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.88 (s, 1H, -CHO), 7.83 (d, 2H, *J* = 8.8 Hz, Ph), 6.99 (d, 2H, *J* = 8.7 Hz, Ph), 4.04 (t, 2H, *J* = 6.5 Hz, OCH_2), 1.82 (quint, 2H, *J* = 6.9 Hz, OCH_2CH_2), 1.40–1.54 (m, 2H, -CH_2-), 1.16–1.40 (m, 16H, -CH_2-), 0.88 (t, 3H, *J* = 6.5 Hz, -CH_3). CI MS *m/z* : 291.232 ($(M+H)^+$) (calcd 291.232).

4-*n*-Dodecyloxystyrene (17). To methyltriphenylphosphonium bromide (8.13 g, 2.28×10^{-2} mol) in 60 ml of dry THF was added *n*-BuLi (1.6 M solution in hexane, 15.8 ml, 2.53×10^{-2} mol) dropwise at –78 °C. After 2.5 h, the reaction mixture was gradually warmed up to 0 °C, and again cooled to –78 °C. 4-Dodecyloxybenzaldehyde (**16**) (6.00 g, 2.07×10^{-2} mol) in 20 ml of dry THF was slowly added to the reaction mixture. The

reaction mixture was stirred overnight and meanwhile gradually warmed up to 10 °C. Aqueous NaCl was added to the reaction mixture. The organic layer was extracted with petroleum ether and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with 1:1 hexane:CH_2Cl_2. Yield = 5.358 g (90 % based on 6.00 g of 4-dodecyloxybenzaldehyde). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.33 (d, 2H, *J* = 8.7 Hz, Ph), 6.85 (d, 2H, *J* = 8.7 Hz, Ph), 6.66 (dd, 1H, *J* = 10.8, 17.6 Hz, vinyl-H), 5.60 (d, 1H, *J* = 17.5 Hz, vinyl-H), 5.11 (d, 1H, *J* = 10.6 Hz, vinyl-H), 3.95 (t, 2H, *J* = 6.6 Hz, OCH_2), 1.78 (quint, 2H, *J* = 7.0 Hz, OCH_2CH_2), 1.38–1.52 (m, 2H, -CH_2-), 1.16–1.38 (m, 16H, -CH_2-), 0.88 (t, 3H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 288.245 (M^+) (calcd 288.245).

4,9-bis[(4′′-*n*-dodecyloxy)phenylethen-1′′-yl]-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (18) [(ROPhd)$_2$TDQ]. 4,9-Dibromo-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (**11**) (75.9 mg, 1.21×10^{-4} mol), 4-*n*-dodecyloxystyrene **(17)** (77.0 mg, 2.67×10^{-4} mol), Pd_2dba_3 (29.5 mg, 3.2×10^{-5} mol) and dry THF (15 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 10 min before *i*-Pr_2EtN (0.30 ml) and P(*t*-Bu)$_3$ (10 wt% solution in hexane, 0.37 ml, 1.2×10^{-4} mol) were added. The reaction mixture was stirred at 40 °C for 15 h under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel with 80:10:1 hexane:THF:Et_3N as the eluent. The product was further purified by size exclusion column chromatography (BioRad Bio-Beads SX-1 packed in THF, gravity flow). Yield = 0.065 g (52 % based on 75.9 mg of 4,9-

dibromo-6,7-bis(3′,7′-dimethyloctyl)[1,2,5]thiadiazolo[3,4-g]quinoxaline). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.78 (s, 4H, vinyl-H), 7.72 (d, 4H, *J* = 8.7 Hz, Ph), 6.96 (d, 4H, *J* = 8.7 Hz, Ph), 4.02 (t, 4H, *J* = 6.6 Hz, -OCH_2-), 2.98–3.20 (m, 4H, Ar-CH_2), 1.1–2.2 (m, 60H, -CH_2-), 1.07 (d, 6H, *J* = 6.5 Hz, -CH_2-), 0.88 (t, 6H, *J* = 6.7 Hz, -CH_3), 0.87 (d, 12H, *J* = 6.7 Hz, -CH_3). MALDI-TOF MS *m/z* : 1040.2 (M^+) (calcd 1040.788).

4-Bromo-7-(*N,N*-dihexylamino)benzo[c][1,2,5]thiadiazole (19). 4,7-Dibromobenzo[c][1,2,5]thiadiazole[1] (0.500 g, 1.70×10^{-3} mol), *N,N*-dihexylamine (0.50 ml, 2.1×10^{-3} mol), Pd_2dba_3 (45 mg, 4.9×10^{-5} mol), 2-(di-*t*-butylphosphino)biphenyl (30 mg, 1.0×10^{-4} mol), NaO*t*-Bu (0.242 g, 2.5×10^{-3} mol), toluene (4.0 ml) and DMF (0.40 ml) were added to a reaction vial. The reaction mixture was stirred at 160 °C for 15 min under microwave irradiation. After the reaction mixture was filtered and the solvent was evaporated, the resudie was chromatographed on silica gel with 1:1 hexane:CH_2Cl_2. Yield = 0.271 g (40 % based on 0.500 g of 4,7-dibromobenzo[c][1,2,5]thiadiazole). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.59 (d, 1H, *J* = 8.4 Hz, Ph-H), 6.31 (d, 1H, *J* = 8.5 Hz, Ph-H), 3.68 (t, 4H, *J* = 7.7 Hz, -NCH_2), 1.51–1.75 (m, 4H, -NCH_2CH_2-), 1.20–1.44 (m, 12H, -CH_2-), 0.89 (t, 6H, *J* = 6.7 Hz, -CH_3). CI MS *m/z* : 398.125 ($(M+H)^+$) (calcd 398.127).

4,7-Bis[4′-(*N,N*-dihexylamino)benzo[c][1,2,5]thiadiazolylethyn-7′-yl] benzo[c][1,2,5]thiadiazole (20) [(DHA-BTDt)$_2$BTD]. 4-Bromo-7-(*N,N*-dihexylamino)benzo[c][1,2,5]thiadiazole (**19**) (0.493 g, 1.24×10^{-3} mol), 4,7-bis[(trimethylsilyl)ethynyl]benzo[c][1,2,5]thiadiazole[4] (0.169 g, 5.14×10^{-4} mol),

$Pd(PPh_3)_4$ (73.6 mg, 6.4×10^{-5} mol), CuI (1.3 mg, 6.8×10^{-6} mol), K_2CO_3 (0.334 g, 2.4×10^{-3} mol) and dry THF (20 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 10 min before piperidine (1.0 ml) and MeOH (2.0 ml) were added. The reaction mixture was stirred at 50 °C for 24 h under Ar. After the solvent was evaporated, the residue was chromatographed on silica gel with 1:2 hexane:$CHCl_3$ as the eluent. Yield = quantitative. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.85 (s, 2H, Ph-H), 7.80 (d, 2H, *J* = 8.3 Hz, Ph-H), 6.41 (d, 2H, *J* = 8.4 Hz, Ph-H), 3.81 (t, 8H, *J* = 7.8 Hz, -NCH_2), 1.62–1.80 (m, 8H, -NCH_2CH_2-), 1.20–1.49 (m, 24H, -CH_2-), 0.91 (t, 12H, *J* = 7.0 Hz, -CH_3). MALDI-TOF MS *m/z* : 820.78 (M^+) (calcd 818.395).

1,4-Di-*n*-octyloxybenzene (21). Hydroquinone (10.00 g, 9.08×10^{-2} mol) was dissolved in 100 ml of ethanol. After addition of KOH (10.79 g, 0.192 mol), the solution was stirred under reflux for 20 min. 1-Bromooctane (33.0 ml, 0.191 mol) was added dropwise to the light brown solution over 1 h, followed by stirring under reflux for 3 h. After cooling, $CHCl_3$ and H_2O were added to the reaction mixture and the organic layer was collected. The aqueous layer was further washed with $CHCl_3$. The combined organic layers were washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$ as the eluent. Yield = 27.33 g (90 % based on 10.00 g of hydroquinone). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82 (s, 4H, Ph-H), 3.90 (t, 4H, *J* = 6.6 Hz, -OCH_2-), 1.75 (quint, 4H, *J* = 7.0 Hz, -$OCCH_2$-), 1.37–1.51 (m, 4H, -$OCCCH_2$-), 1.17–1.37 (m, 16H, -CH_2-

), 1.20–1.49 (m, 24H, -CH_2-), 0.88 (t, 6H, J = 6.6 Hz, -CH_3). CI MS m/z : 334.287 (M^+) (calcd 334.287).

1,4-Diiodo-2,5-di-*n*-octyloxybenzene (22). 1,4-Di-*n*-octyloxybenzene (**21**) (19.282 g, 5.76×10^{-2} mol) was dissolved in acetic acid (60 ml) and CCl_4 (20 ml). To this solution were added iodine (32.2 g, 0.127 mol), conc. H_2SO_4 (7.0 ml), distilled water (4.0 ml), and finally potassium iodate (12.4 g, 5.79×10^{-2} mol). The reaction mixture was stirred for 28 h under reflux. After cooling, aqueous Na_2SO_4 was added until the brown color of iodine disappeared, and the reaction mixture was poured into ice water. The organic layer was extracted with CH_2Cl_2, and the combined organic layers were washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with 4:1 hexane:$CHCl_3$ as the eluent. Yield = 12.399 g (37 % based on 19.286 g of 1,4-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 2H, Ph-H), 3.92 (t, 4H, J = 6.4 Hz, -OCH_2-), 1.80 (quint, 4H, J = 6.9 Hz, -$OCH_2C\mathit{H}_2$-), 1.42–1.57 (m, 4H, -$OCH_2CH_2C\mathit{H}_2$-), 1.18–1.42 (m, 16H, -CH_2-), 0.89 (t, 6H, J = 6.8 Hz, -CH_3). CI MS m/z : 586.078 (M^+) (calcd 586.080).

1,4-Bis(trimethylsilylethynyl)-2,5-di-*n*-octyloxybenzene (23). 1,4-Diiodo-2,5-di-*n*-octyloxybenzene (**22**) (4.01 g, 6.84×10^{-3} mol), $Pd(PPh_3)_2Cl_2$ (0.248 g, 3.53×10^{-4} mol), PPh_3 (0.179 g, 6.82×10^{-4} mol), CuI (0.072 g, 3.8×10^{-4} mol) and piperidine (40 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5

min before (trimethylsilyl)acetylene (3.0 ml, 2.1×10^{-2} mol) was added. The reaction mixture was stirred at 60 °C for 2 h under Ar. After cooling, the solvent was evaporated. $CHCl_3$ was added to the residue, and the organic solution was washed with aqueous NH_4Cl (3 times), water, and dried over Na_2SO_4. After the solvent was evaporated, the residue was chromatographed on silica gel with 2:1 hexane:$CHCl_3$ as the eluent. Yield = 3.455 g (96 % based on 4.01 g of 1,4-diiodo-2,5-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (s, 2H, Ph-H), 3.94 (t, 4H, *J* = 6.4 Hz, -OCH_2), 1.78 (quint, 4H, *J* = 6.9 Hz, -OCH_2CH_2-), 1.42–1.60 (m, 4H, -$OCH_2CH_2CH_2$-), 1.16–1.42 (m, 16H, -CH_2-), 0.88 (t, 6H, *J* = 6.7 Hz, -CH_3), 0.25 (s, 18H, -Si-CH_3). CI MS *m/z* : 526.366 (M^+) (calcd 526.366).

1,4-Diethynyl-2,5-di-*n*-octyloxybenzene (24). 1,4-Bis(trimethylsilylethynyl)-2,5-di-*n*-octyloxybenzene (**23**) (2.331 g, 4.42×10^{-3} mol) was dissolved in a mixture of THF (25 ml) and MeOH (25 ml). 5N NaOH (2.0 ml, 1.0×10^{-2} mol) was added and the solution was stirred for 3 h under Ar. Water was added to the reaction mixture. The organic layer was extracted three times with $CHCl_3$. The combined organic layers were dried over Na_2SO_4. The residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$ as the eluent. Yield = 1.419 g (84 % based on 2.331 g of 1,4-bis(trimethylsilylethynyl)-2,5-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95 (s, 2H, Ph-H), 3.97 (t, 8H, *J* = 6.6 Hz, -OCH_2-), 3.33 (s, 2H, -CC-H), 1.80 (quint, 4H, *J* = 7.0 Hz, -OCH_2CH_2-), 1.39–1.52

(m, 4H, -$OCH_2CH_2CH_2$-), 1.15–1.39 (m, 16H, -CH_2-), 0.88 (t, 6H, *J* = 6.7 Hz, -CH_3). CI MS *m/z* : 382.285 (M^+) (calcd 382.287).

1,4-Bis[(4′-benzo[c][1,2,5]thiadiazolyl)ethynyl]-2,5-di-*n*-octyloxybenzene (25) [(BTDt)$_2$ROPh]. 4-Bromobenzo[c][1,2,5]thiadiazole[1] (0.151 g, 7.02×10^{-4} mol), 1,4-diethynyl-2,5-di-*n*-octyloxybenzene (**24**) (0.121 g, 3.16×10^{-4} mol), $Pd(PPh_3)_4$ (80.0 mg, 6.92×10^{-5} mol), CuI (5.6 mg, 2.9×10^{-5} mol) and dry THF (10 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before piperidine (0.50 ml) was added. The reaction mixture was stirred at 53 °C for 12 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 4:1 $CHCl_3$:hexane as the eluent. Yield = 0.145 g (70 % based on 0.121 g of 1,4-diethynyl-2,5-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (dd, 2H, *J* = 1.0, 8.8 Hz, Ph-H), 7.81 (dd, 2H, *J* = 1.0, 7.0 Hz, Ph-H), 7.60 (dd, 2H, *J* = 7.0, 8.8 Hz, Ph-H), 7.17 (s, 2H, Ph-H), 4.11 (t, 4H, *J* = 6.4 Hz, -OCH_2-), 1.91 (quint, 4H, *J* = 7.0 Hz, -OCH_2CH_2-), 1.50–1.65 (m, 4H, -$OCH_2CH_2CH_2$-), 1.12–1.47 (m, 16H, -CH_2-), 0.84 (t, 12H, *J* = 6.8 Hz, -CH_3). MALDI-TOF MS *m/z* : 649.97 (M^+) (calcd 650.275).

1-(4′-*N*,*N*-dihexylaminophenylethyn-1′-yl)-4-iodobenzene (26). (4-*N*,*N*-dihexylaminophenyl)ethyne (**3**) (0.694 g, 2.43×10^{-3} mol), 1,4-diiodobenzene (3.04 g, 9.21×10^{-3} mol), $Pd(PPh_3)_2Cl_2$ (0.176 g, 2.51×10^{-4} mol), CuI (27.7 mg, 1.45×10^{-4} mol) and

Et_3N (25 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min. The reaction mixture was stirred at 45 °C for 14.5 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 3:1 hexane:$CHCl_3$ as the eluent. Yield = 0.644 g (54 % based on 0.694 g of (4-*N,N*-dihexylaminophenyl)ethyne). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, 2H, *J* = 8.3 Hz, Ph-H), 7.34 (d, 2H, *J* = 8.8 Hz, Ph-H), 7.20 (d, 2H, *J* = 8.3 Hz, Ph-H), 6.56 (d, 2H, *J* = 8.9 Hz, Ph-H), 3.26 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 1.45–1.68 (m, 4H, -NCH_2CH_2-), 1.18–1.42 (m, 12H, -CH_2-), 0.90 (t, 12H, *J* = 6.5 Hz, -CH_3). CI MS *m/z* : 487.172 (M^+) (calcd 487.174).

1-(4′-*N,N*-dihexylaminophenylethyn-1′-yl)-4-(trimethylsilylethynyl)benzene (27). 1-(4-*N,N*-dihexylaminophenylethyn-1′-yl)-4-iodobenzene (**26**) (0.530 g, 1.09×10^{-3} mol), $Pd(PPh_3)_2Cl_2$ (81 mg, 1.2×10^{-4} mol), CuI (11 mg, 5.8×10^{-5} mol) and Et_3N (20 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before (trimethylsilyl)acetylene (0.62 ml, 4.4×10^{-3} mol) was added. The reaction mixture was stirred at 45 °C for 3 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 3:1 hexane:CH_2Cl_2 as the eluent. Yield = 0.484 g (97 % based on 0.530 g of 1-(4-*N,N*-dihexylaminophenylethyn-1′-yl)-4-iodobenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 4H, Ph-H), 7.34 (d, 2H, *J* = 8.9 Hz, Ph-H), 6.56 (d, 2H, *J* = 9.0 Hz, Ph-H), 3.27 (t, 4H, *J* = 7.7 Hz, -NCH_2), 1.47–1.65 (m, 4H, -NCH_2CH_2-), 1.19–1.38 (m, 12H, -CH_2-), 0.90 (t, 6H, *J* = 6.6 Hz, -CH_3), 0.25 (s, 9H, -Si-CH_3). CI MS *m/z* : 458.323 ($(M+H)^+$) (calcd 458.324).

1-(4-*N*,*N*-dihexylaminophenylethyn-1′-yl)-4-ethynylbenzene (28). 1-(4′-*N*,*N*-dihexylaminophenylethyn-1′-yl)-4-(trimethylsilylethynyl)benzene (**27**) (0.262 g, 5.72×10^{-4} mol), K_2CO_3 (0.109 g, 7.89×10^{-4} mol), THF (5.0 ml) and MeOH (3.0 ml) were added to a 100-ml round bottom flask. The reaction mixture was stirred at room temperature for 2 h under Ar. Subsequently, the reaction mixture was filtered and the filtrate was evaporated. Yield = 0.220 g (~100 % based on 0.262 g of 1-(4′-*N*,*N*-dihexylaminophenylethyn-1′-yl)-4-(trimethylsilylethynyl)benzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (s, 4H, Ph-H), 7.35 (d, 2H, *J* = 9.0 Hz, Ph-H), 6.57 (d, 2H, *J* = 9.1 Hz, Ph-H), 3.27 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 3.14 (s, 1H, -CC-H), 1.45–1.65 (m, 4H, -NCH_2CH_2-), 1.18–1.40 (m, 12H, -CH_2-), 0.90 (t, 6H, *J* = 6.6 Hz, -CH_3). CI MS *m/z* : 386.284 ($(M+H)^+$) (calcd 386.285)

1,4-Bis[4′-(4′′-*N*,*N*-dihexylaminophenylethyn-1′′-yl)phenylethyn-1′-yl]-2,5-di-*n*-octyloxybenzene (29) [(DHAtPht)$_2$ROPh]. 1-(4′-*N*,*N*-dihexylaminophenylethyn-1′-yl)-4-ethynylbenzene (**28**) (63.6 mg, 1.65×10^{-4} mol), 1,4-diiodo-2,5-di-*n*-octyloxybenzene (**22**) (46.4 mg, 7.91×10^{-5} mol), $Pd(PPh_3)_4$ (20.0 mg, 1.73×10^{-5} mol), CuI (1.6 mg, 8.4×10^{-6} mol) and dry THF (6.0 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before piperidine (0.50 ml) was added. The reaction mixture was stirred at 50 °C for 17 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$ as

the eluent. The crude product was further purified by size exclusion column chromatography (BioRad Bio-Beads SX-1 packed in THF, gravity flow). Yield = 51.5 mg (59 % based on 46.4 mg of 1,4-diiodo-2,5-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (dd, 8H, *J* = 8.4, 9.6 Hz, Ph-H), 7.36 (d, 4H, *J* = 8.8 Hz, Ph-H), 7.01 (s, 2H, Ph-H), 6.57 (d, 4H, *J* = 8.7 Hz, Ph-H), 4.03 (t, 4H, *J* = 6.5 Hz, -OCH_2-), 3.28 (t, 8H, *J* = 7.6 Hz, -OCH_2-), 1.86 (quint, 4H, *J* = 6.8 Hz, -OCH_2CH_2-), 1.47–1.65 (m, 12H, -CH_2-), 1.16–1.43 (m, 40H, -CH_2-), 0.77–0.98 (m, 18H, -CH_3). MALDI-TOF MS *m/z* : 1100.78 (M^+) (calcd 1100.810).

4-(4′-*N*,*N*-Dihexylaminophenylethyn-1′-yl)-7-iodobenzo[c][1,2,5]thiadiazole (30). (4-*N*,*N*-Dihexylaminophenyl)ethyne (**3**) (0.251 g, 8.79×10^{-4} mol), 4,7-diiodobenzo[c][1,2,5]thiadiazole[5] (0.584 g, 1.51×10^{-3} mol), Pd_2dba_3 (99.4 mg, 1.1×10^{-4} mol), $AsPh_3$ (0.283 g, 9.2×10^{-4} mol) and dry THF (15 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before *i*-Pr_2EtN (1.0 ml) was added. The reaction mixture was stirred at 46 °C for 19 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 1:1 hexane:$CHCl_3$ as the eluent. Yield = 0.241 g (50 % based on 0.251 g of (4-*N*,*N*-dihexylaminophenyl)ethyne). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, 1H, *J* = 7.5 Hz, Ph-H), 7.49 (d, 2H, *J* = 8.9 Hz, Ph-H), 7.45 (d, 1H, *J* = 7.5 Hz, Ph-H), 6.59 (d, 2H, *J* = 8.9 Hz, Ph-H), 3.29 (t, 4H, *J* = 7.7 Hz, -NCH_2-), 1.51–1.66 (m, 4H, -NCH_2CH_2-), 1.19–1.40 (m,

12H, -CH_2-), 0.91 (t, 6H, *J* = 6.7 Hz, -CH_3). MALDI-TOF MS *m/z* : 546.147 ($(M+H)^+$) (calcd 546.144).

1,4-Bis{[7′-(4′′-*N,N*-dihexylaminophenylethyn-1′′-yl)benzo[c][1,2,5]thiadiazol-4′-yl]ethynyl}-2,5-di-*n*-octyloxybenzene (31) [$(DHAtBTDt)_2$ROPh]. 4-(4′-*N,N*-Dihexylaminophenylethyn-1′-yl)-7-iodobenzo[c][1,2,5]thiadiazole (**30**) (0.102 g, 1.87×10^{-4} mol), 1,4-diethynyl-2,5-di-*n*-octyloxybenzene (**24**) (33.1 mg, 8.65×10^{-5} mol), $Pd(PPh_3)_4$ (23.2 mg, 2.01×10^{-5} mol), CuI (1.6 mg, 8.4×10^{-6} mol) and dry THF (6.0 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before piperidine (0.50 ml) was added. The reaction mixture was stirred at 40 °C for 12 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 5:1 hexane:THF as the eluent. Yield = 0.101 g (96 % based on 33.1 mg of 1,4-diethynyl-2,5-di-*n*-octyloxybenzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, 2H, *J* = 7.5 Hz, Ph-H), 7.71 (d, 2H, *J* = 7.4 Hz, Ph-H), 7.51 (d, 4H, *J* = 8.3 Hz, Ph-H), 7.16 (s, 2H, Ph-H), 6.60 (d, 4H, Ph-H), 4.11 (t, 4H, *J* = 6.5 Hz, -OCH_2-), 3.30 (t, 8H, *J* = 7.5 Hz, -NCH_2-), 1.92 (quint, 4H, *J* = 7.5 Hz, -CH_2-), 1.46–1.72 (m, 12H, -CH_2-), 1.14–1.46 (m, 40H, -CH_2-), 0.74–1.00 (m, 18H, -CH_3). MALDI-TOF MS *m/z* : 1217.02 (M^+) (calcd 1216.735).

1-(4′-*N,N*-dihexylaminophenylethyn-1′-yl)-4-iodo-2,5-di-*n*-octyloxybenzene (32). (4-*N,N*-Dihexylaminophenyl)ethyne (**3**) (0.3317 g, 1.16×10^{-3} mol), 1,4-diiodo-2,5-di-*n*-

octyloxybenzene (**22**) (2.046 g, 3.49×10^{-3} mol), $Pd(PPh_3)_2Cl_2$ (90.4 mg, 1.29×10^{-4} mol), CuI (9.2 mg, 4.8×10^{-5} mol) and triethylamine (16.0 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min and the reaction mixture was stirred at 48 °C for 16.5 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 3:1 hexane:CH_2Cl_2 as the eluent. Yield = 0.502 g (58 % based on 0.3317 g of 4-ethynyl-*N,N*-dihexylaniline). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, 2H, *J* = 8.7 Hz, Ph-H), 7.26 (s, 1H, Ph-H), 6.89 (s, 1H, Ph-H), 6.55 (d, 2H, *J* = 8.7 Hz, Ph-H), 3.90–4.01 (m, 4H, -OCH_2-), 3.26 (t, 4H, *J* = 7.5 Hz, -NCH_2-), 1.73–1.88 (m, 4H, -CH_2-), 1.43–1.61 (m, 4H, -CH_2-), 1.16–1.43 (m, 32H, -CH_2-), 0.76–1.00 (m, 12H, -CH_3). ESI MS *m/z* : 744.41 ($(M+H)^+$) (calcd 743.410).

4,7-diethynylbenzo[c][1,2,5]thiadiazole (33). 4,7-Bis(trimethylsilylethynyl)benzo[c][1,2,5]thiadiazole[4] (0.126 g, 3.83×10^{-4} mol), K_2CO_3 (0.214 g, 1.55×10^{-3} mol), CH_2Cl_2 (5.0 ml) and MeOH (5.0 ml) were added to a 100-ml round-bottom flask. The reaction mixture was stirred at room temperature for 2.5 h under Ar. The reaction mixture was filtered and the solvent was evaporated. The residue was chromatographed on short silica gel column with CH_2Cl_2 as the eluent. Yield = 0.0663 g (94 % based on 0.126 g of 4,7-bis(trimethylsilylethynyl)benzo[c][1,2,5]thiadiazole). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (s, 2H, Ph-H), 3.70 (s, 2H, ethynyl-H). CI MS *m/z* : 184.010 (M^+) (calcd 184.010).

4,7-Bis{[4′-(4′′-*N*,*N*-dihexylaminophenylethyn-1′′-yl)-2′,5′-di-*n*-octyloxyphenyl]ethyn-1′-yl}benzo[c][1,2,5]thiadiazole (34) [(DHAtROPht)$_2$BTD]. 1-(4′-*N*,*N*-Dihexylaminophenylethyn-1′-yl)-4-iodo-2,5-di-*n*-octyloxybenzene (**32**) (0.2952 g, 3.97×10^{-4} mol), 4,7-diethynylbenzo[c][1,2,5]thiadiazole (**33**) (35.7 mg, 1.94×10^{-4} mol), $Pd(PPh_3)_4$ (49.2 mg, 4.26×10^{-5} mol), CuI (4.1 mg, 2.2×10^{-5} mol) and dry THF (6.0 ml) were added to a 100-ml round-bottom flask. Ar was bubbled into the reaction mixture for 5 min before piperidine (0.50 ml) was added. The reaction mixture was stirred at 48 °C for 3 h under Ar. After cooling, the solvent was evaporated. The residue was chromatographed on silica gel with 8:1 hexane:THF as the eluent. Yield = 0.2187 g (80 % based on 35.7 mg of 4,7-diethynylbenzo[c][1,2,5]thiadiazole). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (s, 2H, Ph-H), 7.38 (d, 4H, *J* = 8.9 Hz, Ph-H), 7.11 (s, 2H, Ph-H), 7.02 (s, 2H, Ph-H), 6.57 (d, 4H, *J* = 9.1 Hz, Ph-H), 4.08 (t, 4H, *J* = 6.5 Hz, -OCH_2-), 4.05 (t, 4H, *J* = 6.4 Hz, -OCH_2-), 3.28 (t, 8H, *J* = 7.5 Hz, -NCH_2-), 1.89 (quint, 8H, *J* = 7.4 Hz, -CH_2-), 1.48–1.69 (m, 8H, -CH_2-), 1.16–1.47 (m, 64H, -CH_2-), 0.78–1.01 (m, 24H, -CH_3). MALDI-TOF MS *m/z* : 1415.0 (M^+) (calcd 1415.013).

Table S1. Absorption Maxima (nm) of Proquinoidal D-A-D and A-D-A Chromophores in Cyclohexane, Toluene, THF, CH_2Cl_2, Acetone, and DMF Solvents.

	cyclohexane	toluene	THF	CH_2Cl_2	Acetone	DMF
(DHAt)$_2$BTD	264, 324, 356, 492	328, 501	328, 507	329, 512	504	330, 513
(DHAd)$_2$BTD	269, 330, 375, 528	335, 380, 540	273, 332, 381, 543	272, 334, 383, 546	382, 542	275, 334, 386, 551
(ROPht)$_2$TDQ	280, 331, 375, 562	331, 377, 562	277, 331, 561	277, 331, 560	553	
(ROPhd)$_2$TDQ	292, 364, 626	365, 626	288, 364, 622	288, 364, 620		
(DHA-BTDt)$_2$BTD	263, 309, 546	316, 549	267, 317, 555	269, 319, 557	550	319, 558
(BTDt)$_2$ROPh	310, 318, 424	312, 319, 424	310, 318, 419	310, 318, 419	414	
(DHAtPht)$_2$ROPh	300, 317, 396	311, 318, 401	318, 403	320, 406	402	320, 407
(DHAtBTDt)$_2$ROPh	326, 518	330, 515	328, 517	328, 520	511	329, 518
(DHAtROPht)$_2$BTD	376, 491	381, 494	379, 494	383, 495	379, 486	383, 491

Table S2. Fluorescence Maxima (nm) of Proquinoidal D-A-D and A-D-A Chromophores in Cyclohexane, Toluene, THF, CH_2Cl_2, Acetone, and DMF Solvents.

	cyclohexane	toluene	THF	CH_2Cl_2	Acetone	DMF
(DHAt)$_2$BTD	551	598	646	669	668	703
(DHAd)$_2$BTD	605	651	684	705	708	720
(ROPht)$_2$TDQ	635	655	663	667	666	
(ROPhd)$_2$TDQ	714	727	731	732		
(DHA-BTDt)$_2$BTD	587	612	641	660	681	699
(BTDt)$_2$ROPh	468	501	537	554	575	
(DHAtPht)$_2$ROPh	433	445	495	507	552	576
(DHAtBTDt)$_2$ROPh	550	590	664	676	698	
(DHAtROPht)$_2$BTD	554	587	667	689		

Table S3. Full Width at Half Maximum (cm^{-1}) of the Lowest Energy Absorption Bands of Proquinoidal D-A-D and A-D-A Chromophores in Cyclohexane, Toluene, THF, CH_2Cl_2, Acetone, and DMF Solvents.

	cyclohexane	toluene	THF	CH_2Cl_2	Acetone	DMF
(DHAt)$_2$BTD	3576.1	3698.1	3870.5	3850.7	4034.2	4086.6
(DHAd)$_2$BTD	3877.9	3848.4	3980.6	3967.5	4066.9	4074.5
(ROPht)$_2$TDQ	3416.8	3620.6	3673.5	3686.8	3714.0	
(ROPhd)$_2$TDQ	3434.1	3563.8	3602.2	3584.4		
(DHA-BTDt)$_2$BTD	3383.6	3394.5	3411.6	3382.8	3516.8	3521.5
(BTDt)$_2$ROPh	4290.7	4364.9	4568.0	4833.6	5240.4	
(DHAtPht)$_2$ROPh	4650.9	4729.8	4647.4	4607.9	4676.2	4689.9
(DHAtBTDt)$_2$ROPh	3520.3	3707.5	3879.6	3882.3	4084.9	4160.7
(DHAtROPht)$_2$BTD	4018.3	4241.0	4489.3	4551.2	4757.6	4917.1

Table S4. Full Width at Half Maximum (cm^{-1}) of the Fluorescence Bands of Proquinoidal D-A-D and A-D-A Chromophores in Cyclohexane, Toluene, THF, CH_2Cl_2, Acetone, and DMF Solvents.

	cyclohexane	toluene	THF	CH_2Cl_2	Acetone	DMF
(DHAt)$_2$BTD	2339.3	2441.1	2520.1	2370.3	2523.9	2241.6
(DHAd)$_2$BTD	2266.1	2159.2	1994.5	1944.8	1909.0	1783.8
(ROPht)$_2$TDQ	1743.4	1832.2	1852.7	1904.5	1964.9	
(ROPhd)$_2$TDQ	1123.9	1259.5	1292.4	1354.6		
(DHA-BTDt)$_2$BTD	1842.6	1938.8	2299.7	2307.6	2480.3	2402.1
(BTDt)$_2$ROPh	2865.8	3356.5	3712.0	3955.0	4038.4	
(DHAtPht)$_2$ROPh	3531.5	2771.7	4272.7	4299.9	4545.7	4556.7
(DHAtBTDt)$_2$ROPh	1229.0	2432.3	2480.9	2385.4	2487.2	
(DHAtROPht)$_2$BTD	1972.1	2312.7	2880.9	2749.0		

Table S5. Stokes Shifts (cm^{-1}) of Proquinoidal D-A-D and A-D-A Chromophores in Cyclohexane, Toluene, THF, CH_2Cl_2, Acetone, and DMF Solvents.

	cyclohexane	toluene	THF	CH_2Cl_2	Acetone	DMF
(DHAt)$_2$BTD	2176	3238	4244	4584	5306	4918
(DHAd)$_2$BTD	2410	2433	3796	4131	4326	4260
(ROPht)$_2$TDQ	2046	2526	2742	2865	3068	
(ROPhd)$_2$TDQ	1969	2219	2397	2468		
(DHA-BTDt)$_2$BTD	1279	1875	2417	2802	3498	2985
(BTDt)$_2$ROPh	2217	3625	5244	5816	6763	
(DHAtPht)$_2$ROPh	2158	2466	4612	4907	6760	7209
(DHAtBTDt)$_2$ROPh	1123	2468	4282	4438	5243	
(DHAtROPht)$_2$BTD	2316	3207	5250	5688		

References

(1) Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629–633.
(2) Mueller-Westerhof, U. T.; Zhou, M. *J. Org. Chem.* **1994**, *59*, 4988–4992.
(3) Tsubata, Y.; Suzuki, T.; Yamashita, Y.; Mukai, T.; Miyashi, T. *Heterocycles* **1992**, *33*, 337–348.
(4) Susumu, K.; Duncan, T. V.; Therien, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 5186–5195.
(5) Therien, M. J.; Susumu, K. PCT Int. Appl. WO 2007/081991 A2, 2007.