Supplementary Material for Chemical Communications

Electronic Supplementary Information

A modular approach to two-photon absorbing organic nanodots: brilliant dendrimers as an alternative to semiconductor quantum dots?

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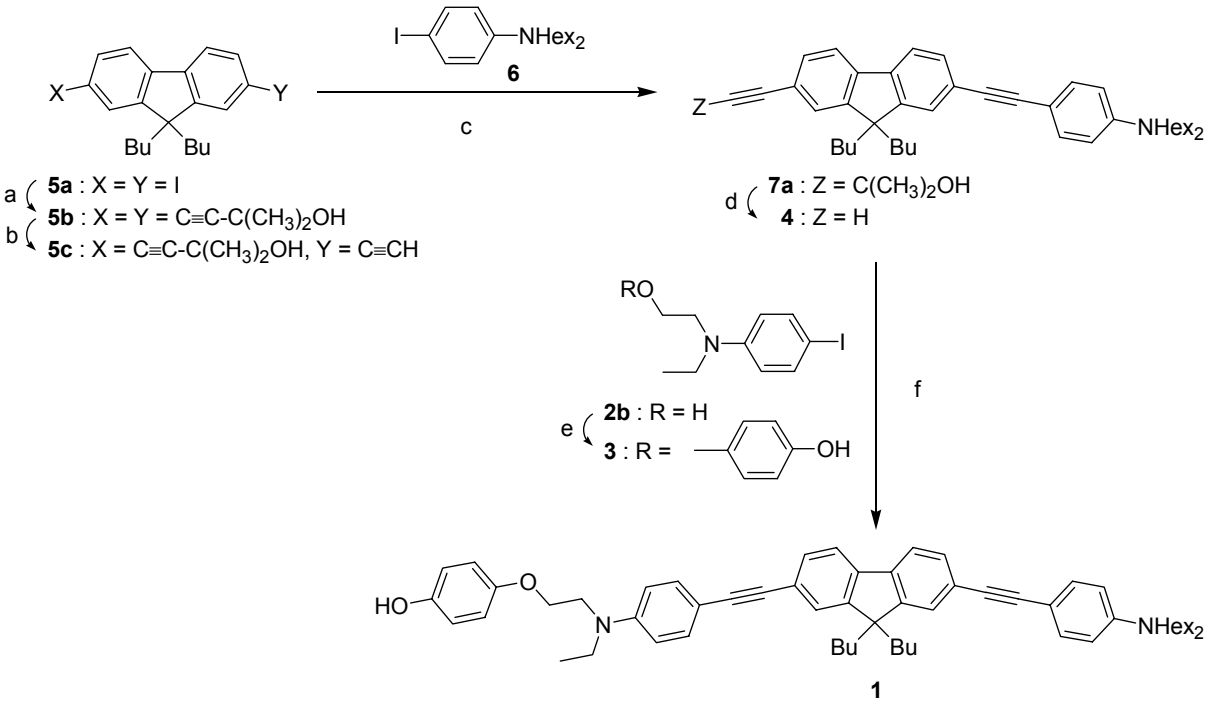
1. Synthesis of fluorophore 1.



Scheme S1: (a) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_2Cl_2$, CuI, toluene/Et_3N, 40 °C, 16 h (87%); (b) NaOH, toluene/*i*-PrOH, reflux, 0,5 h (44%); (c) $Pd(PPh_3)_2Cl_2$, CuI, toluene/Et_3N, 40 °C,

3.5 h (37%); (d) KOH, toluene/*i*-PrOH, reflux, 1 h (87%); (e) hydroquinone (3 equiv.), DEAD, PPh_3, THF, rt, 16 h (51%); (f) $Pd(PPh_3)_2Cl_2$, CuI, toluene/Et_3N, 40 °C, 16 h (57%).

4,4'-(9,9-Dibutyl-9*H*-fluorene-2,7-diyl)bis(2-methyl-3-butyn-2-ol) (5b). Air was removed from a solution of **5a**[S1] (6.00 g, 11.3 mmol) in 37.5 mL of toluene/Et_3N (5/1) by blowing argon for 20 min. Then CuI (86 mg, 0.45 mmol), $Pd(PPh_3)_2Cl_2$ (316 mg, 0.45 mmol) and 2-methyl-3-butyn-2-ol (2.84 g, 33.8 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvent, the residue was purified by column chromatography (heptane/CH_2Cl_2 30:70 then CH_2Cl_2) to yield 4.37 g (87%) of 4,4'-(9,9-dibutyl-9*H*-fluorene-2,7-diyl)bis(2-methyl-3-butyn-2-ol) (**5b**): ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.60 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.38 (s, 2H), 2.16 (s, 2H), 1.94 (m, 4H), 1.66 (s, 12H), 1.07 (m, 4H), 0.66 (t, J = 7.3, 6H), 0.52 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 150.8, 140.5, 130.7, 126.0, 121.3, 119.8, 93.9, 82.9, 65.7, 55.0, 40.1, 31.5, 25.7, 23.0, 13.8; HRMS (EI) calcd for $C_{31}H_{38}O_2$ ($M^{+\cdot}$) *m/z* 442.2872, found 442.2859. Anal. Calcd for $C_{31}H_{38}O_2$ (442.64): C, 84.12; H, 8.65. Found: C, 84.01; H, 8.71.

4-(9,9-Dibutyl-7-ethynyl-9*H*-fluorene-2-yl)-2-methyl-3-butyn-2-ol (5c). To a solution of **5b** (4.02 g, 9.09 mmol) in 50 mL of toluene/*i*-PrOH (6/1), was added solid NaOH (0.73 g). The mixture was heated under reflux for 0.5 h. After cooling, NaOH was filtered off and the solvents were evaporated. The compounds were separated by column chromatography (heptane/CH_2Cl_2 70:30 then 20:80) to yield 0.66 g (22%) of 9,9-dibutyl-2,7-diethynyl-9*H*-fluorene and 1.54 g (44%) of **5c**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.45 (m, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 3.15 (s, 1H), 2.04 (s, 1H), 1.94 (m, 4H), 1.65 (s, 6H), 1.07 (m, 4H), 0.66 (t, J =7.2 Hz, 6H), 0.52 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 150.92, 150.86, 141.0, 140.4, 131.2, 130.7, 126.4, 126.0, 121.5, 120.6, 119.9, 119.8, 94.0, 84.5, 82.9, 77.3, 65.7, 55.0, 40.1, 31.5, 25.7, 22.9, 13.7; HRMS (EI) calcd for $C_{28}H_{32}O$ ($M^{+\cdot}$) *m/z* 384.2453, found 384.2448. Anal. Calcd for $C_{28}H_{32}O$ (384.56): C, 87.45; H, 8.39. Found: C, 87.02; H, 8.51.

[9,9-Dibutyl-7-[2-[4-(dihexylamino)phenyl]ethynyl]-9*H*-fluorene-2-yl]-2-methyl-3-butyn-2-ol (7a). Air was removed from a solution of **5c** (1.304 g, 3.39 mmol) and **6**[S2] (1.71 g, 4.41 mmol) in 10.8 mL of toluene/Et_3N (5/1) by blowing argon for 20 min. Then CuI (12.9 mg, 0.068 mmol) and $Pd(PPh_3)_2Cl_2$ (48 mg, 0.068 mmol) were added, and deaeration was

continued for 10 min. Thereafter the mixture was stirred at 40 °C for 3.5 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (heptane/CH_2Cl_2 75:25 then 30:70) to yield 817 mg (37%) of **7a**; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 1H), 7.45 (m, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.39 and 6.58 (AA'XX', J_{AX} = 9.1 Hz, 4H), 7.37 (m, 1H), 3.28 (m, 4H), 2.08 (s, 1H), 1.95 (m, 4H), 1.66 (s, 6H), 1.65-1.52 (m, 4H), 1.32 (m, 12H), 1.08 (m, 4H), 0.90 (m, 6H), 0.67 (t, J =7.2 Hz, 6H), 0.56 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 150.8 (2C), 147.9, 140.9, 139.6, 132.8, 130.7, 130.3, 125.9, 125.4, 123.0, 120.9, 119.8, 119.6, 111.1, 108.6, 93.7, 91.3, 88.0, 83.0, 65.6, 55.0, 50.9, 40.2, 31.6, 31.5, 27.1, 26.7, 25.8, 23.0, 22.6, 14.0, 13.8; HRMS (ES^+) calcd for $C_{46}H_{62}NO$ ($[M+H]^+$) *m/z* 644.4831, found 644.4832. Anal. Calcd for $C_{46}H_{61}NO$ (644.00): C, 85.79; H, 9.55; N, 2.17. Found: C, 86.06; H, 9.57; N, 2.07.

4-[2-(9,9-Dibutyl-7-ethynyl-9*H*-fluoren-2-yl)ethynyl]-*N*,*N*-dihexylbenzenamine (4). To a solution of **7a** (0.798 g, 1.24 mmol) in 8.75 mL of toluene/*i*-PrOH (6/1), was added solid KOH (0.07 g). The mixture was heated under reflux for 1 h. After cooling, KOH was filtered off and the solvents were evaporated. The crude product was purified by column chromatography (heptane/CH_2Cl_2 90:10) to yield 0.632 g (87%) of **4**; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.46 (m, 2H), 7.39 and 6.58 (AA'XX', J_{AX} = 8.8 Hz, 4H), 3.28 (m, 4H), 3.14 (s, 1H), 1.96 (m, 4H), 1.60 (m, 4H), 1.32 (m, 12H), 1.08 (m, 4H), 0.90 (m, 6H), 0.67 (t, J = 7.3 Hz, 6H), 0.57 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 150.91, 150.85, 147.9, 141.4, 139.5, 132.8, 131.1, 130.3, 126.4, 125.5, 123.3, 120.3, 119.9, 119.6, 111.1, 108.6, 91.4, 88.0, 84.6, 77.1, 55.0, 50.9, 40.1, 31.7, 27.1, 26.8, 25.8, 23.0, 22.6, 14.0, 13.8; HRMS (ES^+) calcd for $C_{43}H_{56}N$ ($[M+H]^+$) *m/z* 586.4413, found 586.4411. Anal. Calcd for $C_{43}H_{55}N$ (585.92): C, 88.15; H, 9.46; N, 2.39. Found: C, 87.89; H, 9.59; N, 2.40.

4-[2-[Ethyl-(4-iodophenyl)amino]ethoxy]phenol (3). To a solution of **2b** (5.00 g, 17.2 mmol), hydroquinone (5.65 g, 51.3 mmol) and triphenylphosphine (13.50 g, 51.5 mmol) in THF (110 mL), was added dropwise a solution of DEAD (9.00 g, 51.7 mmol) in THF (40 mL). The mixture was stirred at rt for 16 h and the solvent was removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2) to yield 3.35 g (51%) of **3**; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.44 and 6.50 (AA'XX', J_{AX} = 9.3 Hz, 4H), 6.75 (s,

4H), 4.47 (s, 1H), 4.03 (t, J = 6.0 Hz, 2H), 3.65 (t, J = 6.0 Hz, 2H), 3.43 (q, J = 7.0 Hz, 2H), 1.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 152.6, 149.6, 147.1, 137.7, 116.1, 115.5, 114.1, 76.5, 65.9, 49.6, 45.5, 12.0; HRMS (ES^+) calcd for $C_{16}H_{19}INO_2$ ($[M+H]^+$) *m/z* 384.0461, found 384.0459. Anal. Calcd for $C_{16}H_{18}INO_2$ (383.23): C, 50.15; H, 4.73; N, 3.65. Found: C, 50.36; H, 4.85; N, 3.65.

4-[2-[[4-[2-[9,9-Dibutyl-7-[2-[4-(dihexylamino)phenyl]ethynyl]-9*H*-fluoren-2-yl]ethynyl]-phenyl]ethylamino]ethoxy]phenol (1). Air was removed from a solution of **4** (155.9 mg, 0.266 mmol) and **3** (132.6 mg, 0.346 mmol) in 1.2 mL of toluene/Et_3N (5/1) by blowing argon for 20 min. Then CuI (1.0 mg, 0.005 mmol) and $Pd(PPh_3)_2Cl_2$ (3.7 mg, 0.005 mmol) were added, and deaeration was continued for 10 min. Thereafter the mixture was stirred at 40 °C for 16 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (heptane/CH_2Cl_2 70:30 then 20:80) to yield 127.9 mg (57%) of **1**; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.45 (m, 2H), 7.43 and 6.72 (AA'XX', J_{AX} = 9.1 Hz, 4H), 7.39 and 6.58 (AA'XX', J_{AX} = 8.9 Hz, 4H), 6.76 (m, 4H), 4.58 (s, 1H), 4.07 (t, J = 6.1 Hz, 2H), 3.72 (t, J = 6.1 Hz), 3.50 (q, J = 6.9 Hz, 2H), 3.28 (m, 4H), 1.97 (m, 4H), 1.60 (m, 4H), 1.32 (m, 12H), 1.21 (t, J = 6.9 Hz, 3H), 1.09 (m, 4H), 0.90 (m, 6H), 0.67 (t, J = 7.2 Hz, 6H), 0.59 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 152.6, 151.0, 150.9, 149.9, 147.9, 147.4, 140.1, 139.9, 132.9, 132.8, 130.3, 125.5, 122.7, 122.5, 119.7, 119.6, 116.1, 115.5, 111.4, 111.2, 109.8, 108.7, 91.2, 90.8, 88.4, 88.2, 66.0, 55.0, 50.9, 49.6, 45.5, 40.2, 31.7, 27.1, 26.8, 25.8, 23.0, 22.6, 14.0, 13.8, 12.2; HRMS (ES^+) calcd for $C_{59}H_{73}N_2O_2$ ($[M+H]^+$) *m/z* 841.5672, found 841.5660. Anal. Calcd for $C_{59}H_{72}N_2O_2$ (841.24): C, 84.24; H, 8.63; N, 3.33. Found: C, 83.84; H, 8.52; N, 3.38.

2. Synthesis of dendrimers G1-G4.

General Procedure:

To a solution of dendrimers bearing $P(S)Cl_2$ end groups [Gn] (n = 1, 44 mg, 24 μmol; n = 2, 58 mg, 12 μmol; n = 3, 70 mg, 6.5 μmol; n = 4, 36 mg, 1.6 μmol) in 20 mL of distilled THF, was added fluorophore **1** (n = 1, 270 mg, 320 μmol; n = 2, 270 mg, 320 μmol; n = 3, 270 mg, 320 μmol; n = 4, 135 mg, 160 μmol) and Cs_2CO_3 (n = 1, 208 mg, 640 μmol; n = 2, 208 mg, 640 μmol; n = 3, 208 mg, 640 μmol; n = 4, 104 mg, 320 μmol;). The resulting mixture was

stirred at room temperature overnight, filtered and the solvent evaporated. The crude product was purified on column chromatography (SiO_2; $CHCl_3$/Hexane : 90 : 10).

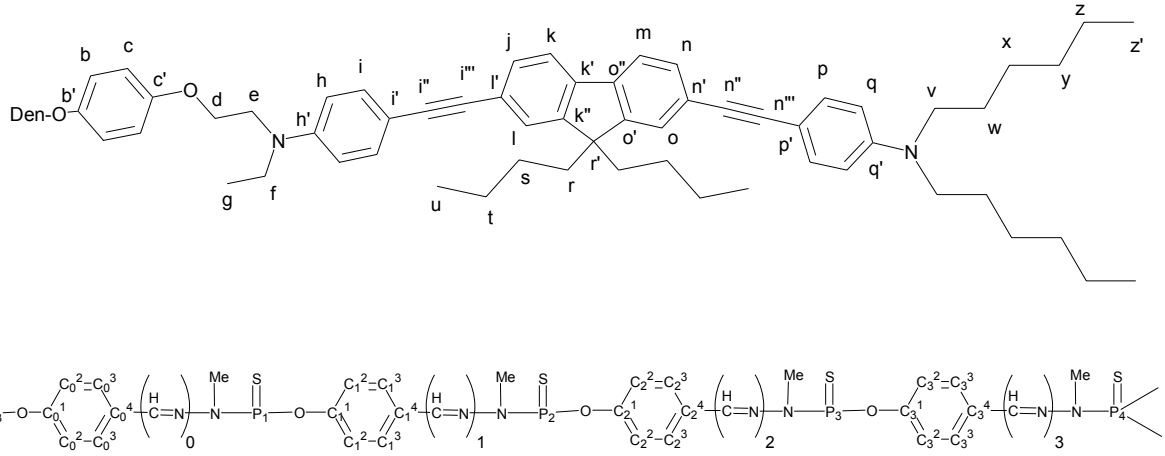


Chart S1 Notations used for characterising the dendrimers **G1**-**G4**.

Dendrimer G1. (261 mg, 95 %) (Found: C, 78.50, H, 7.80, N 4.63. $C_{756}H_{900}N_{39}O_{30}P_9S_6$ requires C 79.06, H, 7.90, N 4.76.); δ_P (202.5 MHz, $CDCl_3$) 8.8 (s, P_0), 64.4 (s, P_1); δ_H (500 MHz, $CDCl_3$) 0.59 (m, 48H, Hs), 0.67 (t, J = 7.4 Hz, 72H, Hu), 0.93 (t, J = 6.8 Hz, 72H, Hz'), 1.10 (q, J = 7.4 Hz, 48H, Ht), 1.16 (t, J = 7.0 Hz, 36H, Hg), 1.35 (br s, 144H, Hx, Hy, Hz), 1.60 (m, 48H, Hw), 1.98 (m, 48H, Hr), 3.21 (d, J = 10 Hz, 18H, P_1-N-CH_3), 3.30 (t, J = 7.7 Hz, 48H, Hv), 3.43 (q, J = 7.0 Hz, 24H, Hf), 3.66 (t, J = 6 Hz, 24H, He), 3.98 (t, J = 6 Hz, 24H, Hd), 6.60 (d, J = 8.0 Hz, 24H, Hq), 6.64 (d, J = 9.0 Hz, 24H, Hh), 6.73 (d, J = 9.1 Hz, 24H, Hc), 6.97 (d, J = 8.5 Hz, 12H, C_0^2-H), 7.08 (d, J = 9.1 Hz, 24H, Hb), 7.41 - 7.43 (m, 48H, Hi, Hp), 7.47 - 7.49 (m, 54H, C_0H=N, Hl, Ho, Hj, Hn), 7.58 - 7.65 (m, 36H, C_0^3-H, Hk, Hm); δ_C NMR (126 MHz, $CDCl_3$) 156.0 (Cc'), 151.2 (C_0^1), 151.0, 150.9 (Ck", Co'), 147.9 (Cq'), 147.3 (Ch'), 144.2 (d, J = 6.9 Hz, Cb'), 140.2, 140.0 (Cl', Cn'), 138.2 (C_0H=N), 133.0, 132.9 (Ci, Cp), 132.4 (C_0^4), 130.4, 130.3 (Cj, Cn) 128.3 (C_0^3), 125.5 (Cl, Co), 122.8, 122.5 (Ck', Co"), 122.3 (d, J = 3.9 Hz, Cb), 121.5 (C_0^2), 119.8 (Ck, Cm), 115.0 (Cc), 111.4 (Ch), 111.2 (Cq), 109.8 (Ci'), 108.7 (Cp'), 91.2 (Cn'"), 90.9 Ci"), 88.6 (Ci'"), 88.2 (Cn"), 65.7 (Cd), 55.1 (Cr'), 51.0 (Cv), 49.5 (Ce), 45.6 (Cf), 40.4 (Cr), 33.1 (d, J = 11.5 Hz, P_1-N-CH_3), 31.8 (Cy), 27.2 (Cw), 26.8 (Cx), 25.9 (Cs), 23.1 (Ct), 22.7 (Cz), 14.1 (Cz'), 13.9 (Cu), 12.2 (Cg).

Dendrimer G2. (231 mg, 80%) (Found: C, 77.22, H, 7.45, N 5.01. $C_{1560}H_{1848}N_{87}O_{66}P_{21}S_{18}$ requires C 77.74, H, 7.73, N 5.06); δ_P (101.3 MHz, $CDCl_3$) 8.7 (s, P_0), 62.4 (s, P_1), 64.8 (s,

P_2); δ_H (250 MHz,, $CDCl_3$) 0.60 - 0.73 (m, 240H, Hs, Hu), 0.97 (t, J = 6.5 Hz, 144H, Hz'), 1.08 - 1.17 (m, 168H, Ht, Hg), 1.33 - 1.38 (m, 288H, Hx, Hy, Hz), 1.65 (br s, 96H, Hw), 1.98 (br s, 96H, Hr), 3.22 (d, J = 9.4 Hz, 18H, P_1-N-CH_3), 3.31 -3.43 (m, 180H, P_2-N-CH_3, Hv, Hf), 3.66 (br s, 48H, He), 3.98 (br s, 48H, Hd), 6.62 - 6.76 (br s, 144H, Hq, Hh, Hc), 6.97 (br s, 12H, C_0^2-H), 7.09 -7.22 (m, 72H, Hb, C_1^2-H), 7.44 - 7.52 (m, 210H, Hi, Hp, Hl, Ho, Hj, Hn, C_0H=N, C_1H=N), 7.62 - 7.65 (m, 84H, C_0^3-H, C_1^3-H, Hk, Hm); δ_C (62.8 MHz, $CDCl_3$) 156.0 (Cc'), 151.2 (d, J = 6 Hz, C_1^1), 151.0, 150.9 (Ck", Co', C_0^1), 148.0 (Cq'), 147.4 (Ch'), 144.3 (d, J = 6.9 Hz, Cb'), 140.2, 140.0 (Cl', Cn'), 138.4 (m, C_0H=N, C_1H=N), 133.0, 132.9 (Ci, Cp), 132.5 (C_0^4), 131.6 (C_1^4), 130.4 (Cj, Cn), 128.4 (d, J = 7Hz, C_1^3), 127.6 (C_0^3), 125.6 (Cl, Co), 122.9, 122.6 (Ck', Co"), 122.5 (m, Cb), 121.8 (m, C_0^2, C_1^2), 119.8 (Ck, Cm), 115.1 (Cc), 111.5 (Ch), 111.3 (Cq), 109.9 (Ci'), 108.8 (Cp'), 91.3 (Cn'"), 90.9 (Ci"), 88.6 (Ci'"), 88.3 (Cn"), 65.8 (Cd), 55.0 (Cr'), 51.0 (Cv), 49.5 (Ce), 45.6 (Cf), 40.4 (Cr), 33.1 (d, J = 12.6 Hz, P_2-N-CH_3, P_1-N-CH_3), 31.8 (Cy), 27.3 (Cw), 26.9 (Cx), 25.9 (Cs), 23.1 (Ct), 22.8 (Cz), 14.1 (Cz'), 13.9 (Cu), 12.3 (Cg).

Dendrimer G3. (261 mg, 81%) (Found: C, 75.93, H, 7.51, N 5.12. $C_{3168}H_{3744}N_{183}O_{138}P_{45}S_{42}$ requires C 77.13, H, 7.65, N 5.20); δ_P (101.3 MHz, $CDCl_3$) 8.3 (s, P_0), 62.5 (m, P_1, P_2), 64.8 (s, P_3); δ_H (250 MHz, $CDCl_3$) 0.62 - 0.68 (m, 480H, Hs, Hu), 0.97 (m, 288H, Hz'), 1.09 - 1.11 (m, 336H, Ht, Hg), 1.31 - 1.35 (m, 576H, Hx, Hy, Hz), 1.61 (br s, 192H, Hw), 1.97 (br s, 192H, Hr), 3.27 - 3.30 (m, 414H, $P_{1\text{-}2\text{-}3}$-N-CH_3, Hv, Hf), 3.61 (br s, 96H, He), 3.98 (br s, 96H, Hd), 6.59 - 6.62 (m, 192H, Hq, Hh), 6.72 - 6.75 (m, 96H, Hc), 6.97 -7.22 (m, 180H, Hb, C_0^2-H, C_1^2-H, C_2^2-H), 7.41 - 7.48 (m, 426H, Hi, Hp, Hl, Ho, Hj, Hn, C_0H=N, C_1H=N, C_2H=N), 7.62 - 7.65 (m, 180H, C_0^3-H, C_1^3-H, C_2^3-H, Hk, Hm); δ_C (62.8 MHz, $CDCl_3$) 156.0 (Cc'), 151.3 (d, J = 6 Hz, C_2^1, C_1^1), 151.0, 150.9 (Ck", Co', C_0^1), 148.0 (Cq'), 147.4 (Ch'), 144.3 (d, J = 6.9 Hz, Cb'), 140.2, 140.0 (Cl', Cn'), 138.4 (m, C_0H=N, C_1H=N, C_2H=N), 132.9 (Ci, Cp), 132.5 (C_0^4, C_1^4), 131.6 (C_2^4), 130.4 (Cj, Cn), 128.4 (C_2^3, C_1^3, C_0^3), 125.6 (Cl, Co), 122.9, 122.6 (Ck', Co"), 122.5 (m, Cb), 121.9 (m, C_0^2, C_1^2, C_2^2), 119.8 (Ck, Cm), 115.1 (Cc), 111.5 (Ch), 111.3 (Cq), 109.9 (Ci'), 108.8 (Cp'), 91.3 (Cn'"), 90.9 (Ci"), 88.6 (Ci'"), 88.3 (Cn"), 65.8 (Cd), 55.0 (Cr'), 51.0 (Cv), 49.5 (Ce), 45.6 (Cf), 40.3 (Cr), 33.1 (d, J = 11.9 Hz, P_3-N-CH_3), 32.0 (m, $P_{1\text{-}2}$-N-CH_3), 31.8 (Cy), 27.3 (Cw), 26.9 (Cx), 25.7 (Cs), 23.1 (Ct), 22.7 (Cz), 14.1 (Cz'), 13.9 (Cu), 12.3 (Cg).

Dendrimer G4. (116 mg, 72 %) (Found: C, 75.12, H, 7.43, N 5.00. $C_{6384}H_{7536}N_{375}O_{282}P_{93}S_{90}$ requires C 76.83, H, 7.61, N 5.26); δ_P (101.3 MHz, $CDCl_3$) 8.3 (s, P_0), 62.3 (m, P_1, P_2, P_3), 64.5 (s, P_4); δ_H (250 MHz, $CDCl_3$) 0.64 (br s, 960H, Hs, Hu), 0.93 (br s, 576H, Hz'), 1.11 (br s, 672H, Ht, Hg), 1.31 - 1.34 (m, 1152H, Hx, Hy, Hz), 1.60 (br s, 384H, Hw), 1.97 (br s, 384H, Hr), 3.30 (m, 846H, $P_{1\text{-}2\text{-}3\text{-}4}$-N-$CH_3$, Hv, Hf), 3.60 (br s, 192H, He), 3.96 (br s, 192H, Hd), 6.59 - 6.61 (m, 384H, Hq, Hh), 6.74 (m, 192H, Hc), 6.97 -7.22 (m, 372H, Hb, C_0^2-H, C_1^2-H, C_2^2-H, C_3^2-H), 7.41 - 7.48 (m, 858H, Hi, Hp, Hl, Ho, Hj, Hn, C_0H=N, C_1H=N, C_2H=N, C_3H=N), 7.62 - 7.65 (m, 372H, C_0^3-H, C_1^3-H, C_2^3-H, C_3^3-H, Hk, Hm); δ_C (62.8 MHz, $CDCl_3$) 156.0 (Cc'), 151.3 (m, C_1^1, C_2^1, C_3^1), 151.0 (Ck'', Co', C_0^1), 148.0 (Cq'), 147.3 (Ch'), 144.3 (d, J = 6.9 Hz, Cb'), 140.2, 140.0 (Cl', Cn'), 138.4 (m, C_0H=N, C_1H=N, C_2H=N, C_3H=N), 132.9 (Ci, Cp), 132.4 (C_0^4, C_1^4, C_2^4), 131.6 (C_3^4), 130.4 (Cj, Cn), 128.3 (C_3^3, C_2^3, C_1^3, C_0^3), 125.5 (Cl, Co), 122.8 (Ck', Co''), 122.6 (m, Cb), 122.4 (m, C_0^2, C_1^2, C_2^2, C_3^2), 119.8 (Ck, Cm), 115.0 (Cc), 111.5 (Ch), 111.3 (Cq), 109.9 (Ci'), 108.8 (Cp'), 91.3 (Cn'''), 91.0 (Ci''), 88.6 (Ci'''), 88.3 (Cn''), 65.7 (Cd), 55.0 (Cr'), 51.0 (Cv), 49.5 (Ce), 45.6 (Cf), 40.3 (Cr), 33.0 (br d, J = 11.9 Hz, $P_{1\text{-}2\text{-}3\text{-}4}$-N-$CH_3$), 31.7 (Cy), 27.2 (Cw), 26.8 (Cx), 25.9 (Cs), 23.1 (Ct), 22.7 (Cz), 14.1 (Cz'), 13.9 (Cu), 12.3 (Cg).

3. Optical spectroscopy

General methods

UV/Vis spectra were recorded on a Jasco V-570 double-beam spectrophotometer.

Steady-state fluorescence measurements were performed at room temperature using an Edinburgh Instruments (FLS 920) spectrometer working in photon-counting mode. Corrected emission spectra were obtained for each compound, at $\lambda_{ex} = \lambda_{max}$(abs) with $A_{\lambda ex} < 0.1$ to minimize internal absorption. Fluorescence quantum yields were measured using standard methods on air-equilibrated samples at room temperature. Fluorescein in 0.1 M NaOH (ϕ = 0.90) was used as a reference.[S3]

TPA (two-photon absorption) measurements were conducted by investigating the TPEF (two-photon excited fluorescence) of fluorophore **1** and dendrimers **G1**-**G4** in toluene using a Ti-sapphire laser delivering 150 fs excitation pulses, according to the experimental protocol established by Xu and Webb.[S4] This experimental protocol allows avoiding contributions from excited-state absorption that are known to result in largely overestimated TPA cross-sections. Fluorescein in 0.01 M NaOH, whose TPEF action cross-sections are well-known,[S4] served as the reference, taking into account the necessary corrections for the refractive index of the solvents.[S5] The quadratic dependence of the fluorescence intensity on the excitation intensity was verified for each data point, indicating that the measurements were carried out in intensity regimes in which saturation or photodegradation do not occur. More details about the experimental setup have been previously published.[S5]

Fluorescence anisotropy: steady-state fluorescence anisotropies for the dendrimers were measured using the Edinburgh Instruments FLS920 instrument, by inserting Glan-Thompson polarizers in the excitation and emission paths. Emission anisotropies were obtained at right angles using vertically polarized excitation light. Wavelength-dependent polarization correction factors ("G-factors") were measured on the same sample under horizontally polarized excitation following standard procedures.

Absorption properties

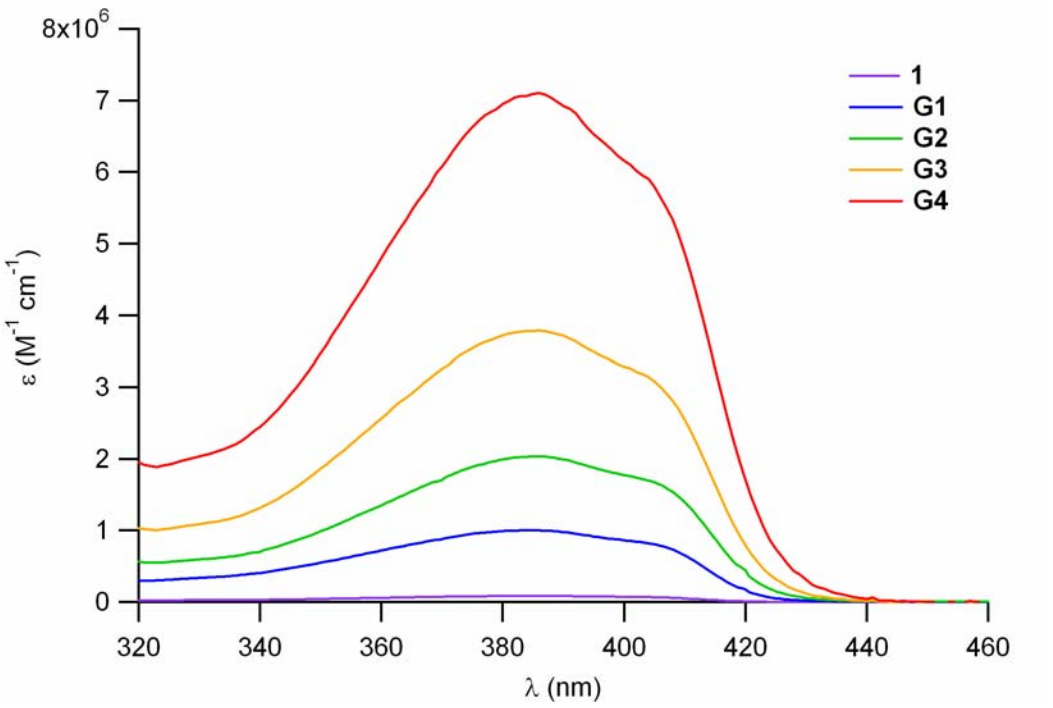


Fig. S1 Absorption spectra in toluene of dendrimers **G1-G4** and model chromophore **1**.

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