Supporting Information for "Detection and Mechanistic Studies of Multi-Component Assembly by Fluorescence Resonance Energy Transfer"

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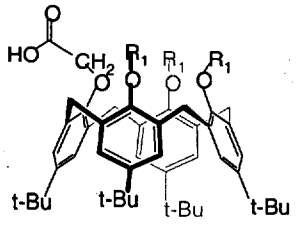
Experimental Section

General. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on a Bruker DRX-600 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000PC FT-IR spectrometer. Matrix-assisted laser desorption/ionization (MALDI) FTMS experiments were performed on an IonSpec FTMS mass spectrometer. The fast atom bombardment (FAB) positive ion mass spectra were obtained on a VG ZAB-VSE double-focusing high resolution mass spectrometer. Dichloromethane (CH_2Cl_2) was passed through columns of activated aluminum oxide as described by Grubbs and coworkers prior to use.[1] HCl (g) was bubbled through H_2SO_4 prior to use.Coumarin 2 and coumarin 343 were purchased from Acros and used without further purification. L-Valine methyl ester isocyanate was purchased from TCI America and used without further purification. All other reagents were purchased from either Aldrich or Fluka and used as received.

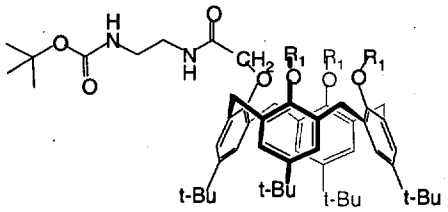
General PyBOP Coupling Procedure. The acid (1 equiv.) is dissolved in DMF and treated with PyBOP (1.2 equiv.) and NEt_3 (2–10 equivs.). To this is then added the amine (1–1.2 equivs.). The coupling reaction is monitored by TLC and is generally complete within 1 hour. The solvent is removed in vacuo and the residue is dissolved in CH_2Cl_2. After washing with 1 M HCl, 1 M NaOH, and brine, the organic phase is dried over $MgSO_4$ and evaporated to give the crude product.



$R_1 = C_{10}H_{21}$

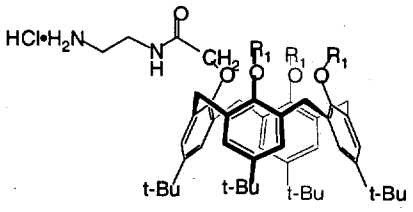
***t*-Butyl Monoacid.** The ester[2] (0.50 g, 0.43 mmol) was dissolved in a mixture of THF (20 mL) and water (5 mL). To this suspension was added $LiOH{\cdot}H_2O$ (0.18 g, 4.3 mmol) and the mixture was stirred at rt overnight. After this period, the resulting solution was poured into 50 mL of water and treated with 1 M HCl until strongly acidic. Extraction with EtOAc yielded the crude acid which was purified by chromatography on SiO_2 (1:1 hex/EtOAc) to give a clear, colorless oil (0.33 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.15 (s, 2H), 7.13 (s, 2H), 6.58 (d, 2H, J = 2.1 Hz), 6.48 (d, 2H, J = 2.2 Hz), 4.67 (s, 2H), 4.44 (d, 2H, J = 12.4 Hz), 4.22 (d, 2H, J = 12.8 Hz), 4.07 (m, 2H), 3.80–3.71 (m, 4H), 3.22 (d, 2H, J = 12.9 Hz), 3.15 (d, 2H, J = 12.5 Hz), 1.90–1.86 (m,

6H), 1.39–1.28 (m, 42H), 1.34 (s, 9H), 1.33 (s, 9H), 0.90–0.86 (m, 9H), 0.83 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 170.65, 154.24, 152.04, 151.14, 146.94, 144.97, 144.81, 135.46, 134.95, 132.57, 131.50, 125.96, 125.31, 125.10, 124.49, 76.71, 76.15, 70.91, 34.18, 34.06, 33.63, 31.97, 31.93, 31.74, 31.59, 31.23, 31.04, 30.94, 29.90, 29.87, 29.71, 29.64, 29.56, 29.42, 29.34, 26.09, 25.34, 22.72, 22.70, 14.13. IR (thin film) 3414, 2956, 2925, 2855, 1765, 1481, 1467, 1362, 1198, 1124 cm^{-1}. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{76}H_{118}O_6Na$ 1149.8826, found 1149.8788.



$R_1 = C_{10}H_{21}$

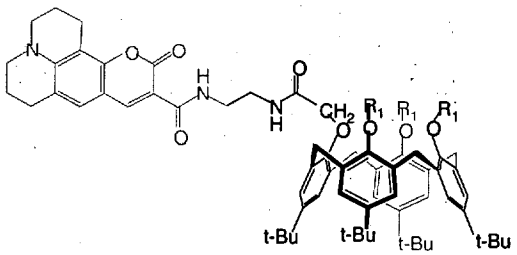
***t*-Butyl BOC Amine.** The calixarene acid (0.15 g, 0.13 mmol) was combined with mono-BOC ethylenediamine (24 μL, 0.16 mmol), PyBOP (0.081 g, 0.16 mmol), and NEt_3 (72 mL, 0.52 mmol) in a mixture of DMF (10 mL) and THF (5 mL). After 3 h the reaction was worked up in the usual fashion and the crude product was isolated as a slightly yellow oil. This material was purified by column chromatography on SiO_2 (125 mL, 4:1 hex/EtOAc) and obtained as an off-white foam (0.16 g, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (t, 1H, J = 5.3 Hz), 7.07 (s, 4H), 6.49 (s, 4H), 5.48 (t, 1H, J = 5.4 Hz), 4.85 (s, 2H), 4.36 (m, 4H), 3.92 (m, 2H), 3.86–3.76 (m, 4H), 3.60 (m, 2H), 3.45 (m, 2H), 3.25 (d, 2H, J = 13. 1 Hz), 3.13 (d, 2H, J = 12.6 Hz), 1.92 (m, 2H), 1.78 (m, 4H), 1.43 (s, 9H), 1.30–1.25 (m, 42H), 1.30 (s, 9H), 1.29 (s, 9H), 0.91–0.82 (m, 9H), 0.86 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 172.63, 156.03, 154.55, 153.84, 151.92, 145.31, 144.91, 144.52, 135.41, 133.73, 132.25, 131.48, 126.24, 125.45, 124.95, 124.42, 79.00, 76.30, 74.61, 74.05, 41.80, 39.59, 34.03, 33.97, 33.63, 31.94, 31.91, 31.83, 31.67, 31.57, 31.37, 31.13, 30.04, 30.03, 29.93, 29.79, 29.72, 29.68, 29.66, 29.61, 29.41, 29.34, 28.41, 25.97, 22.71, 22.68, 14.12. IR (thin film) 3322, 2956, 2925, 2855, 1713, 1669, 1480, 1362, 1196, 1124 cm^{-1}. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{83}H_{132}N_2O_7Na$ 1291.9927, found 1291.9991.



$R_1 = C_{10}H_{21}$

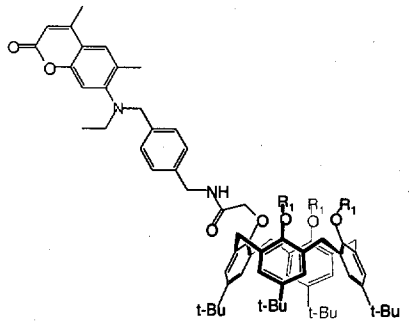
Deprotection. The protected amine (0.11 g, 0.087 mmol) was dissolved in 4 M HCl in dioxane (20 mL). After 30 min. the solution was sparged with N_2 and concentrated to dryness. The hygroscopic, off-white solid obtained was used without further purification

(quant.). HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{78}H_{124}N_2O_5Na$ 1191.9402, found 1191.9391.



$R_1 = C_{10}H_{21}$

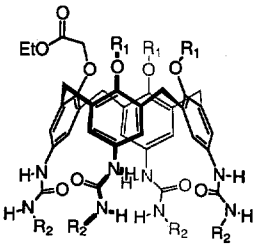
Acceptor Control (9A). The calixarene amine hydrochloride (0.11 g, 0.091 mmol) was combined with coumarin 343 (0.022 g, 0.076 mmol), PyBOP (0.047 g, 0.091 mmol), and NEt_3 (53 μL, 0.38 mmol) in DMF (10 mL). After 30 min. at rt the product partially precipitated from solution as a bright yellow solid. After the usual work-up, the crude product was purified by chromatography on SiO_2 (3:1 hex/EtOAc) to give a yellow, oily solid (0.096 g, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12 (t, 1H, J = 5.6 Hz), 8.82 (t, 1H, J = 5.6 Hz), 8.58 (s, 1H), 7.04 (s, 2H), 7.03 (s, 2H), 6.97 (s, 1H), 6.50 (m, 4H), 4.82 (s, 2H), 4.39 (d, 2H, J = 12.8 Hz), 4.37 (d, 2H, J = 12.3 Hz), 3.91 (m, 2H), 3.89-3.85 (m, 4H), 3.75 (m, 2H), 3.71 (m, 2H), 3.32 (m, 4H), 3.23 (d, 2H, J = 13.1 Hz), 3.11 (d, 2H, J = 12.6 Hz), 2.89 (t, 2H, J = 6.2 Hz), 2.76 (t, 2H, J = 6.0 Hz), 1.99-1.95 (m, 4H), 1.95–1.91 (m, 2H), 1.80-1.75 (m, 4H), 1.32–1.20 (m, 42H), 1.29 (s, 9H), 1.28 (s, 9H), 0.87–0.83 (m, 9H), 0.87 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 171.76, 163.78, 162.68, 154.48, 153.84, 152.68, 151.98, 148.00, 147.93, 145.06, 144.71, 144.35, 135.39, 133.70, 132.40, 131.83, 126.92, 126.12, 125.35, 124.84, 124.42, 119.42, 109.13, 108.20, 105.70, 76.18, 74.62, 74.13, 50.19, 49.79, 39.44, 39.35, 33.99, 33.93, 33.61, 31.92, 31.78, 31.65, 31.57, 31.41, 31.15, 30.08, 30.02, 29.93, 29.79, 29.77, 29.69, 29.63, 29.42, 29.38, 27.44, 26.04, 25.94, 22.69, 21.14, 20.20, 20.12, 14.12. IR (thin film) 3330, 2953, 2925, 2854, 1701, 1618, 1589, 1519, 1480, 1309, 1198, 1124 cm^{-1}. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{94}H_{137}N_3O_8Na$ 1459.0280, found 1459.0250.



$R_1 = C_{10}H_{21}$

Donor Control (9D). The calixarene monoacid (0.14 g, 0.12 mmol) was combined with the coumarin amine hydrochloride **6** (0.050 g, 0.12 mmol), PyBOP (0.075 g, 0.14 mmol), and NEt_3 (170 μL, 1.2 mmol) in a mixture of DMF (10 mL) and THF (5 mL). The crude

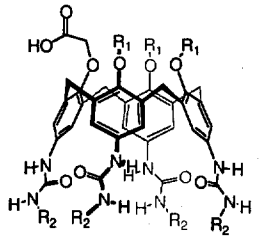
product, an orange oil, was purified by chromatography on SiO_2 (5:1 hex/EtOAc) to give a clear, colorless oil (0.12 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (t, 1H, J = 6.1 Hz), 7.33 (s, 1H), 7.31–7.26 (m, 4H), 7.05 (s, 2H), 7.04 (s, 2H), 6.95 (s, 1H), 6.51 (m, 4H), 6.13 (s, 1H), 4.91 (s, 2H), 4.74 (d, 2H, J = 6.1 Hz), 4.38 (d, 2H, J = 12.9 Hz), 4.35 (d, 2H, J = 12.5 Hz), 4.17 (s, 2H), 3.94 (m, 2H), 3.69–3.62 (m, 4H), 3.21 (d, 2H, J = 13.1 Hz), 3.11 (d, 2H, J = 12.6 Hz), 3.06–3.03 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.95 (m, 2H), 1.65-1.61 (m, 4H), 1.32–1.12 (m, 42H), 1.32 (s, 9H), 1.31 (s, 9H), 1.03 (t, 3H, J = 7.1 Hz), 0.91–0.84 (m, 9H), 0.87 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 171.43, 161.54, 154.44, 153.78, 152.63, 152.28, 151.97, 145.25, 144.85, 144.49, 137.68, 136.83, 135.29, 133.68, 132.32, 131.71, 129.57, 128.32, 126.48, 126.38, 126.19, 125.39, 124.97, 124.40, 114.76, 112.58, 109.30, 76.11, 74.63, 74.16, 56.49, 46.08, 42.49, 34.00, 33.97, 33.63, 31.95, 31.92, 31.76, 31.64, 31.57, 31.38, 31.15, 30.08, 30.06, 30.00, 29.74, 29.64, 29.62, 29.44, 29.35, 26.00, 25.84, 22.72, 22.68, 18.64, 18.54, 14.12, 11.63. IR (thin film) 3326, 2955, 2925, 2854, 1727, 1677, 1614, 1480, 1197 cm^{-1}. HRMS (MALDI-FTMS; M+H$^+$) calcd for $C_{97}H_{141}N_2O_7$ 1446.0733, found 1446.0752.



$R_1 = C_{10}H_{21}$ $R_2 = SO_2C_6H_4$-p-CH_3

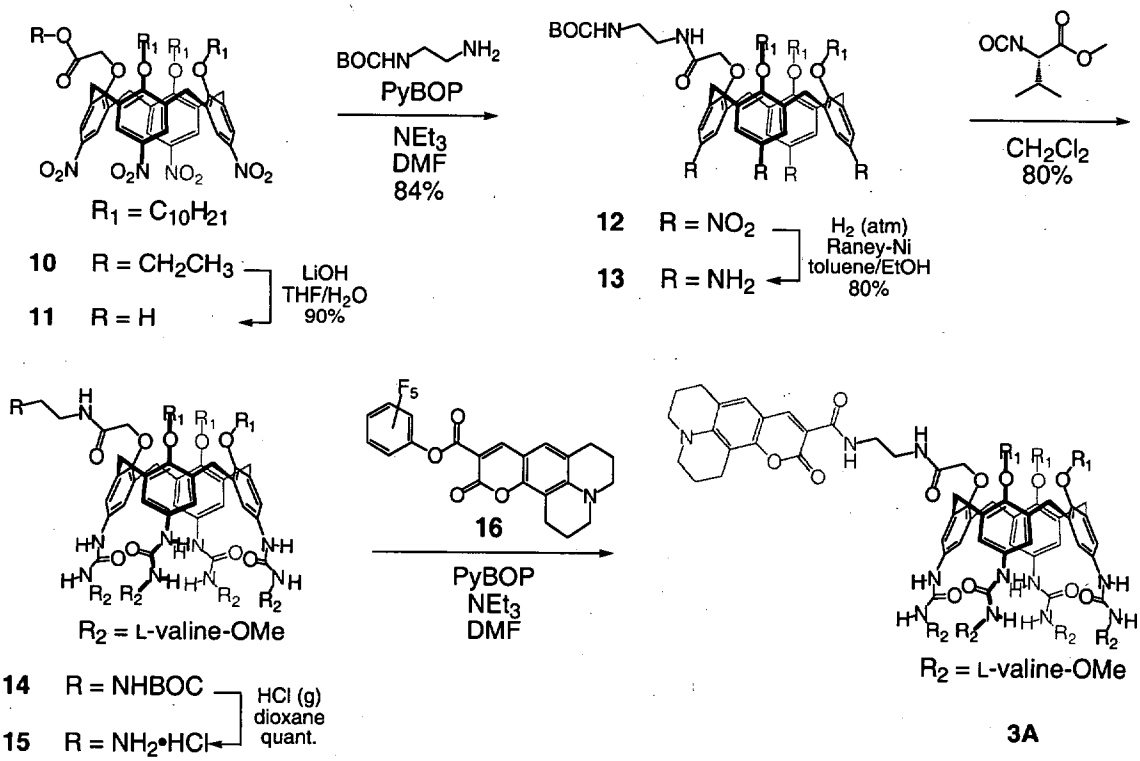
5,11,17,23-Tetrakis(tosylurea)-25,26,27-tris(decyloxy)-28-(ethoxycarbonyl)methoxycalix[4]arene. The tetraamino compound[2] (0.090 g, 0.091 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under N_2. To the homogeneous solution was added p-toluenesulfonyl isocyanate (70 μL, 0.46 mmol) and the reaction was stirred at rt for 4h. The solvent was then removed in vacuo and the resulting solid was triturated with MeOH. This process was repeated and the resulting suspension was filtered. The urea (0.145 g, 90%) was used without further purification. ^{1}H NMR (600 MHz, DMF-d_7) δ 10.39 (bs, 2H), 10.26 (bs, 2H), 8.67 (s, 1H), 8.66 (s, 1H), 8.44 (s, 2H), 7.97 (d, 4H, J = 8.2 Hz), 7.93 (d, 4H, J = 8.3 Hz), 7.49 (d, 4H, J = 8.2 Hz), 7.46 (d, 4H, J = 8.2 Hz), 6.89 (s, 2H), 6.88 (s, 2H), 6.54 (s, 4H), 4.74 (s, 2H), 4.58 (d, 2H, J = 13.3 Hz), 4.34 (d, 2H, J = 13.0 Hz), 3.84 (m, 2H), 3.81-3.72 (m, 4H), 3.08 (d, 2H, J = 14.0 Hz), 3.06 (d, 2H, J = 13.6 Hz), 2.45 (s, 6H), 2.44 (s, 6H), 1.92-1.84 (m, 6H), 1.46-1.24 (m, 44H), 1.25 (t, 3H, J = 7.2 Hz), 0.91-0.86 (m, 9H). ^{13}C NMR (DMF-d_7) δ 170.88, 153.87, 153.41, 152.99, 150.48, 145.23, 145.17, 138.77, 138.73, 136.44, 136.29, 135.40, 135.32, 133.82, 133.52, 133.20, 130.54, 130.50, 128.88, 128.84, 120.48, 120.45, 120.29, 120.24, 76.20, 71.42, 60.97, 32.67, 32.65, 32.03, 31.54, 30.97, 30.91, 30.76, 30.65, 30.60, 30.51, 30.49, 30.13, 27.17, 26.99, 23.33, 21.52, 14.66, 14.46. IR (thin film) 3350, 2924, 2854, 1762, 1694,

1599, 1550, 1464, 1343, 1218, 1162, 1091, 895, 667 cm^{-1}. LRMS (ESI; $M+Na^+$+^{13}C) calcd for $C_{94}H_{122}N_8O_{18}S_4Na$ 1752, found 1752.



$R_1 = C_{10}H_{21}$ $R_2 = SO_2C_6H_4$-*p*-CH_3

5,11,17,23-Tetrakis(tosylurea)-25,26,27-tris(decyloxy)-28-carboxymethoxycalix[4]arene (4). The ester (0.139 g, 0.0778 mmol) was dissolved in a mixture of THF (7.5 mL) and water (1.5 mL). To this suspension was added $LiOH•H_2O$ (0.065 g, 1.6 mmol) and the mixture was stirred at rt for 18 h. After this period, the resulting solution was poured into 50 mL of water and treated with 1 M HCl until strongly acidic. The tan precipitate was filtered and washed with water yielding 0.123 g (0.0702 mmol, 90%) of the crude acid. ^1H NMR (600 MHz, DMF-d_7) δ 12.65 (bs, 1H), 10.38 (bs, 2H), 10.30 (bs, 2H), 8.64 (s, 1H), 8.61 (s, 1H), 8.53 (s, 2H), 7.96 (d, 4H, J = 8.3 Hz), 7.94 (d, 4H, J = 8.3 Hz), 7.48 (d, 4H, J = 7.8 Hz), 7.47 (d, 4H, J = 7.8 Hz), 6.80 (s, 4H), 6.68 (s, 4H), 4.63 (s, 2H), 4.54 (d, 2H, J = 13.2 Hz), 4.36 (d, 2H, J = 12.9 Hz), 3.89-3.77 (m, 6H), 3.09 (d, 2H, J = 13.2 Hz), 3.07 (d, 2H, J = 12.9 Hz), 2.45 (s, 6H), 2.45 (s, 6H), 1.91-1.85 (m, 6H), 1.41-1.23 (m, 43H), 0.88-0.86 (m, 9H). ^{13}C NMR (DMF-d_7) δ 171.37, 153.08, 152.81, 152.24, 149.98, 149.95, 144.64, 138.21, 135.58, 135.40, 135.23, 135.11, 133.30, 132.93, 132.80, 129.97, 128.30, 128.29, 119.91, 119.87, 119.79, 75.80, 71.13, 32.14, 32.12, 31.44, 31.00, 30.34, 30.21, 30.15, 30.10, 30.06, 30.03, 29.94, 29.61, 26.50, 26.45, 22.79, 20.97, 13.93. IR (thin film) 3350, 2925, 2854, 1706, 1599, 1552, 1466, 1341, 1218, 1163, 1090, 1055, 894, 664 cm^{-1}. LRMS (ESI; $M+H^+$) calcd for $C_{92}H_{119}N_8O_{18}S_4$ 1752, found 1752.



Scheme 3. Preparation of the chiral urea acceptor **3A**.

Tetranitro Monoacid (11). The ester **10**[2] (1.0 g, 0.90 mmol) was dissolved in a mixture of THF (40 mL) and water (10 mL). To this was added $LiOH•H_2O$ (0.57 g, 14 mmol) and the resulting orange mixture was stirred at rt for 1h. After this period, the solution was poured into 100 mL of water and treated with 1 M HCl until strongly acidic. Extraction with EtOAc, drying over Na_2SO_4, and concentration yielded the desired acid which was used without further purification (0.93 g, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.96 (s, 2H), 7.28 (s, 2H), 7.26 (s, 2H), 4.86 (s, 2H), 4.56 (d, 2H, J = 14.2 Hz), 4.52 (d, 2H, J = 13.8 Hz), 4.06 (m, 2H), 3.97–3.89 (m, 4H), 3.52 (d, 2H, J = 14.5 Hz), 3.43 (d, 2H, J = 14.5 Hz), 1.92–1.83 (m, 6H), 1.41–1.25 (m, 42H), 0.89–0.85 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 169.28, 162.12, 160.73, 159.87, 143.59, 143.23, 143.11, 136.19, 135.29, 134.74, 133.88, 125.01, 124.60, 123.90, 123.60, 77.27, 76.83, 70.94, 31.86, 31.34, 30.99, 29.93, 29.85, 29.70, 29.63, 29.57, 29.49, 29.32, 29.29, 25.93, 25.54, 22.65, 14.07. IR (thin film) 2925, 2854, 1767, 1524, 1457, 1347, 1210, 1098 cm^{-1}. HRMS (MALDI-FTMS; $M+Na^+$) calcd for $C_{60}H_{82}N_4O_{14}Na$ 1105.5725, found 1105.5774.

Tetranitro Mono-BOC Derivative (12). The calixarene monoacid **11** (0.10 g, 0.092 mmol) was combined with mono-BOC ethylene diamine (0.018 g, 0.11 mmol), PyBOP (0.058 g, 0.11 mmol), and NEt_3 (51 μL, 0.37 mmol) in DMF (10 mL). After the standard

work-up, sans the base wash, the crude product was purified by chromatography on SiO_2 (2:1 hex/EtOAc) to give a white solid (0.095 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.79 (s, 2H), 7.67 (bt, 1H), 7.35 (s, 4H), 4.89 (t, 1H, J = 5.4 Hz), 4.69 (s, 2H), 4.59 (d, 2H, J = 14.4 Hz), 4.49 (d, 2H, J = 14.0 Hz), 4.07–4.00 (m, 4H), 3.96 (m, 2H), 3.52–3.49 (m, 4H), 3.42 (d, 2H, J = 14.2 Hz), 3.36–3.33 (m, 2H), 1.83–1.77 (m, 6H), 1.39 (s, 9H), 1.34–1.20 (m, 42H), 0.91–0.86 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 168.41, 161.66, 161.59, 160.56, 143.06, 142.99, 135.98, 135.16, 134.68, 134.31, 124.82, 124.47, 123.86, 123.79, 79.74, 76.02, 74.21, 40.35, 40.19, 31.87, 31.57, 31.32, 30.04, 29.88, 29.74, 29.69, 29.65, 29.58, 29.57, 29.31, 28.26, 25.81, 25.77, 22.66, 14.09. IR (thin film) 3393, 2925, 2854, 1694, 1524, 1456, 1347, 1097 cm^{-1}. LRMS (ESI; M+Na$^+$) calcd for $C_{67}H_{96}N_6O_{15}Na$ 1248, found 1248.

Tetraamino Mono-BOC Derivative (13). To the tetranitro compound **12** (0.086 g, 0.070 mmol) in toluene (15 mL) was added Raney nickel (cat) as a suspension in ETOH (5 mL). The mixture was heated to 50°C under H_2 (atm) for 4 h prior to filtration through a Celite pad. Concentration of the filtrate to dryness yielded the reduction product as an oil, used without further purification (0.062 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (t, 1H, J = 5.7 Hz), 6.43 (s, 2H), 6.38 (s, 2H), 5.63 (s, 4H), 5.36 (t, 1H, J = 5.0 Hz), 4.74 (s, 2H), 4.25 (d, 2H, J = 13.3 Hz), 4.24 (d, 2H, J = 13.8 Hz), 3.78–3.72 (m, 4H), 3.72–3.67 (m, 2H), 3.51 (m, 2H), 3.38 (m, 2H), 3.15 (bs, 8H), 3.03 (d, 2H, J = 13.9 Hz), 2.92 (d, 2H, J = 13.4 Hz), 1.71–1.66 (m, 6H), 1.42 (s, 9H), 1.32–1.24 (m, 42H), 0.89–0.85 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 172.55, 155.94, 151.73, 150.08, 148.08, 140.94, 140.58, 140.29, 137.42, 135.70, 135.34, 134.11, 132.82, 125.45, 116.52, 116.03, 115.90, 115.42, 78.97, 76.09, 74.46, 74.34, 41.54, 39.14, 31.87, 31.84, 31.72, 31.44, 30.24, 29.84, 29.66, 29.61, 29.57, 29.54, 29.31, 29.27, 28.34, 28.34, 25.99, 25.81, 22.63, 14.07. IR (thin film) 3393, 2925, 2854, 1694, 1524, 1456, 1347, 1097 cm^{-1}. HRMS (MALDI-FTMS; M+H$^+$) calcd for $C_{67}H_{105}N_6O_7$ 1105.8045, found 1105.8084.

Tetravaline Mono-BOC Derivative (14). The tetraamino compound **13** (0.060 g, 0.054 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under N_2. To the solution was added L-valine methyl ester isocyanate (42 μL, 0.27 mmol) and the reaction was stirred at rt for 1h. The solvent was then removed in vacuo and the resulting crude solid was purified by chromatography on SiO_2 (15:1 CH_2Cl_2/MeOH) and precipitation from EtOAc with hexanes (0.090 g). Further purification by PTLC on SiO_2 (18:1 CH_2Cl_2/MeOH) gave the urea as a white powder (0.075 g, 80%). ^{1}H NMR (600 MHz, DMF-d_7) δ 8.49 (s, 1H), 8.44 (s, 1H), 8.38 (t, 1H, J = 5.6 Hz), 8.34 (s, 1H), 8.33 (s, 1H), 7.01 (m, 2H), 6.95 (t, 1H, J = 5.6 Hz), 6.93 (m, 2H), 6.86 (m, 2H), 6.72 (m, 2H), 6.43 (m, 2H), 6.37 (d, 2H, J = 8.3 Hz), 4.53 (s, 2H), 4.45 (d, 2H, J = 12.7 Hz), 4.41 (d, 2H, J = 12.7 Hz), 4.25 (m, 2H), 4.20

(m, 2H), 4.00 (m, 2H), 3.91 (m, 2H), 3.86 (m, 2H), 3.72 (s, 6H), 3.70 (s, 6H), 3.47 (m, 2H), 3.30 (m, 2H), 3.17 (d, 2H, J = 13.1 Hz), 3.11 (d, 2H, J = 12.8 Hz), 2.12–2.04 (m, 4H), 1.91 (m, 6H), 1.45–1.20 (m, 42H), 1.42 (s, 9H), 0.99–0.88 (m, 33 H). ^{13}C NMR (DMF-d_7) δ 173.49, 169.89, 156.44, 155.81, 155.74, 155.70, 151.78, 151.16, 150.92, 135.39, 135.31, 135.00, 134.77, 134.76, 134.39, 134.29, 134.28, 119.02, 118.89, 118.82, 118.81, 118.74, 118.63, 118.57, 118.49, 78.05, 75.96, 75.13, 74.91, 58.28, 58.22, 51.66, 51.62, 40.45, 39.59, 32.16, 31.78, 31.60, 31.57, 31.07, 31.01, 30.29, 30.18, 30.16, 30.04, 30.00, 29.96, 28.21, 26.53, 26.42, 22.85, 19.07, 19.03, 17.83, 17.75, 14.00. IR (thin film) 3362, 2926, 2854, 1745, 1713, 1657, 1602, 1554, 1477, 1214, 1170 cm^{-1}. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{95}H_{148}N_{10}O_{19}Na$ 1756.0820, found 1756.0888.

Tetravaline Monoamine Hydrochloride (15). To a dioxane solution of the BOC-protected amine **14** (0.075 g, 0.043 mmol) was bubbled dry HCl (g). After 0.5 h the solution was sparged with N_2 for 1 h and evaporated to dryness. The hygroscopic amine hydrochloride (quant.) was used without further purification. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{90}H_{140}N_{10}O_{17}Na$ 1656.0296, found 1656.0316.

Pentafluorophenyl Ester of Coumarin 343 (16). Coumarin 343 (0.050 g, 0.18 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with oxalyl chloride (31 μL, 0.35 mmol) and DMF (cat.). After 0.5 h the solvent was removed and the acid chloride was dried under high vacuum. Following dissolution in CH_2Cl_2 (10 mL), pentafluorophenol (0.039 g, 0.21 mmol) and NEt_3 (49 μL, 0.35 mmol) were added. The solution was stirred for 1 h at room temperature. Following solvent evaporation, the crude ester was purified by PTLC on SiO2 (1:1 hex/EtOAc) to give the desired product as an orange powder (0.064 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 6.96 (s, 1H), 3.38 (m, 4H), 2.86 (m, 2H), 2.76 (m, 2H), 1.98 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 160.42, 158.37, 154.47, 151.23, 150.37, 142.77 (m), 141.11, 139.05 (m), 137.39 (m), 128.10, 120.32, 108.09, 106.09, 102.71, 50.87, 50.47, 27.72, 21.31, 20.31, 20.23. IR (thin film) 2948, 2852, 1777, 1728, 1621, 1585, 1518, 1445, 1312, 1199, 1175, 1002 cm^{-1}. HRMS (MALDI-FTMS; M+Na$^+$) calcd for $C_{22}H_{14}F_5NO_4$ 474.0741, found 474.0749.

Chiral Acceptor (3A). The calixarene amine hydrochloride **15** (0.072 g, 0.0 mmol) was combined with the activated ester **16** (0.019 g, 0. mmol), NEt_3 (51 μL, 0.37 mmol), and DMAP (0.005 g, 0.04 mmol) in CH_2Cl_2 (10 mL). After stirring overnight at room temperature the solvent was removed and the crude product was purified initially by PTLC on SiO_2 (5% MeOH/CH_2Cl_2) and then by preparative HPLC to give a yellow powder. ^{1}H NMR (600 MHz, DMF-d_7) δ 9.02 (t, 1H, J = 5.8 Hz), 8.58 (s, 1H), 8.47 (s, 1H), 8.44 (t, 1H, J = 5.6 Hz), 8.42 (s, 1H), 8.36 (s, 1H), 8.35 (s, 1H), 7.25 (s, 1H), 7.00

(d, 1H, J = 2.3 Hz), 6.99 (d, 1H, J = 2.3 Hz), 6.91 (d, 1H, J = 2.1 Hz), 6.89 (m, 3H), 6.76 (d, 1H, J = 2.1 Hz), 6.75 (d, 1H, J = 2.2 Hz), 6.43 (d, 1H, J = 8.6 Hz), 6.41 (d, 1H, J = 8.6 Hz), 6.38 (d, 2H, J = 8.5 Hz), 4.50 (s, 2H), 4.49 (d, 2H, J = 13.0 Hz), 4.41 (d, 2H, J = 12.7 Hz), 4.26–4.20 (m, 4H), 4.05–3.95 (m, 2H), 3.90–3.88 (m, 2H), 3.86 (m, 2H), 3.75–3.66 (m, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.70 (s, 3H), 3.62–3.58 (m, 2H), 3.41–3.38 (m, 4H), 3.16 (d, 2H, J = 13.2 Hz), 3.10 (d, 2H, J = 12.8 Hz), 2.81–2.78 (m, 4H), 2.12–2.05 (m, 4H), 1.98–1.88 (m, 10H), 1.38–1.20 (m, 42H), 1.00–0.85 (m, 33H). ^{13}C NMR (DMF-d_7) δ 173.49, 169.82, 163.58, 155.80, 155.76, 155.71, 152.96, 151.56, 151.15, 150.96, 148.66, 147.95, 135.34, 135.28, 135.21, 135.00, 134.95, 134.90, 134.88, 134.46, 134.35, 134.28, 127.60, 120.18, 118.93, 118.80, 118.75, 118.68, 118.55, 118.52, 108.78, 108.13, 105.38, 75.91, 75.21, 74.85, 58.28, 58.24, 51.63, 50.16, 49.65, 39.78, 39.30, 32.18, 31.75, 31.58, 31.06, 31.03, 30.21, 29.69, 27.44, 26.55, 26.43, 22.85, 21.21, 20.24, 20.17, 19.05, 19.03, 17.82, 17.77, 13.99.

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