SUPPORTING INFORMATION

A NEW CRYPTAND: SYNTHESIS & COMPLEXATION WITH PARAQUAT

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3,5-Bis(11-chloro-3,6,9-trioxaundecyloxy)benzyloxybenzene. NaH (3.55 g, 88.8 mmol, 60% in mineral oil) was added to a solution of 5-benzyloxyresorcinol[1] (9.15 g, 42.3 mmol) in DMF (90 mL). The mixture was stirred for 2h at 70°C and cooled to RT. Tetra(ethylene glycol) dichloride[2] (150 g, 649 mmol) was added and the mixture was stirred for 5 days at 50°C, filtered and evaporated. Flash silica gel column chromatography with Et_2O gave 17.45 g (68%) of an oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.62 (t, J = 5.8Hz, 4H), 3.70 (m, 20H, 3.83 (t, J = 4.8 Hz, 4H), 4.07 (t, J = .8 Hz, 4H), 4.99 (s, 2H), 6.12 (t, J = 2.2 Hz, 1H), 6.18 (d, J = 2.2 Hz, 2H) and 7.36 (m, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 42.70, 67.40, 69.61, 70.02, 70.59, 70.61, 70.65, 70.76, 94.40, 94.54, 115.51, 127.49, 127.95, 128.53, 136.78 and 160.50. FAB MS (3-nitrobenzyl alcohol, NBA) m/z (rel int): 605.2 {$[M(^{35}Cl_2)]^+$, 100%}, 569.2 {$[M(^{35}Cl_2)$ - HCl]$^+$, 21%}, 498.2 {$[M(^{35}Cl_2)$ - $C_6H_5CH_2]^+$, 19%} and 375.2 {$[M(^{35}Cl_2)$ - $C_6H_5CH_2O$ - $Cl(CH_2CH_2O)_2]^+$, 13%}. HR FAB MS (NBA): m/z 605.2290 [calcd. for $C_{29}H_{43}{}^{35}Cl_2O_9$ m/z 605.2284].

Bis(5-benzyloxy-1,3-phenylene)-32-crown-10 (2c). A solution of 5-benzyloxyresorcinol[1] (18.12 g, 29.92 mmol) and 3,5-bis(11-chloro-3,6,9-trioxaundecyloxy)benzyloxybenzene (6.49 g, 30.01 mmol) in DMF (52 mL) was added via a syringe pump at 0.75 mL/h to a suspension of K_2CO_3 (41.91 g, 303.2 mmol) and *n*-$Bu_4N^+I^-$ (50 mg) in DMF (1.45 L) at 110°C. After complete addition, the mixture was stirred at 110°C for 5 days, cooled, evaporated, treated with CH_2Cl_2 and filtered. Removal of CH_2Cl_2 followed by flash column chromatography using diethyl ether gave **2c** (11.62 g, 52%), mp 94.3-95.8°C. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H, 3.81 (t, J = 4.8 Hz, 8H), 4.03 (t, J = 4.8 Hz, 8H), 4.96 (s, 4H), 6.12 (t, J = 2.2 Hz, 2H), 6.16 (d, J = 2.2 Hz, 4H) and 7.36 (m, 10H). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.48, 69.59, 69.98, 70.80, 94.31, 94.63, 127.50, 127.91, 128.52, 136.85, 160.47 and 160.54. FAB MS (NBA) m/z (rel int): 749 [$(M)^+$, 100%], and 657 [$(M - C_6H_5CH_2)^+$, 5%]. HR FAB MS (NBA): m/z 749.3569 [calcd. for $C_{42}H_{53}O_{12}$ m/z 749.3537].

Bis(5-hydroxy-1,3-phenylene)-32-crown-10 (2d). A solution of **2c** (7.45 g, 9.95 mmol) in 1:1 $CHCl_3$:MeOH (30 mL) was subjected to hydrogenolysis at RT in the presence of 150 mg 10% Pd/C. The reaction mixture was filtered and the solvent was removed under vacuum. Recrystallization of the solid from MeOH:H_2O (8.5:1) gave **2d** (5.37 g, 95%), a white solid, mp 171.3-172.7°C. ^{1}H NMR (DMSO) δ (ppm): 3.55 (m, 16H, 3.68 (t, J = 4.6 Hz, 8H), 3.96 (t, J = 4.6 Hz, 8H), 5.91 (t, J = 2.2 Hz, 4H), 5.97 (d, J = 2.2 Hz, 2H) and 9.37 (s, 2H). ^{13}C NMR (DMSO) δ (ppm): 66.97, 68.91, 70.00, 92.15, 94.60, 158.98 and 160.27. FAB MS (NBA) m/z (rel int): 569.5 $[(M)^+$, 100%]. HR FAB MS (NBA): 569.2576 [calcd. for $C_{28}H_{41}O_{12}$ m/z 569.2598].

Bis(1,3,5-phenylene)tri(1,4,7,10,13-pentaoxatridecyl) (3). A solution of **2d** (2.031 g, 3.572 mmol) and tetra(ethylene glycol) ditosylate[3] (1.796 g, 3.573 mmol) in DMF (20

mL) was addded via a syringe pump at 0.75 mL/h to a suspension of K_2CO_3 (4.95 g, 35.8 mmol) and *n*-$Bu_4N^+I^-$ (20 mg) in DMF (250 mL) at 110°C. After addition, the mixture was stirred at 110°C for 5 days, cooled, evaporated, treated with CH_2Cl_2 and filtered. Removal of CH_2Cl_2 followed by flash silica gel column chromatography using EtOAc gave pure **3** (0.986 g, 38%), mp 77.5-78.0°C.

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