Electronic Supplementary Material for CrystEngComm

Supporting Information

Title: A pyridyl functionalized cavitand: Starting point for hydrogen-bond driven assembly of heterodimeric capsules.

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Experimental Section

All chemicals were purchased from Aldrich and used without further purification. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity plus 400 MHz or 200 MHz spectrometer in $CDCl_3$ or D_6-DMSO. Compounds were prepared for infrared spectroscopic (IR) analysis as a mixture in KBr. Elemental Analysis was carried out by Atlantic Microlab Inc. Electrospray Ionization – Ion-Trap Mass Spectrometry (ESI-IT-MS) was carried out on a Bruker Daltonics Esquire 3000 plus. MALDI-TOF / TOF-MS was carried out on a Bruker Daltonics Ultraflex TOF/TOF.

Synthesis:

C-pentylcalix[4]resorcinarene was prepared according to the literature. To a solution of resorcinol (10.0 g, 0.09 mol) and hexanal (9.10 g, 0.09 mol) in ethanol (90 mL) was added conc. HCl (14.5 mL) at 0 ºC under a dinitrogen atmosphere. A condenser was attached and the mixture heated to 70 ˚C for 10 hours. The reaction was monitored by TLC and allowed to cool to room temperature upon completion, then diluted with water. A white precipitate formed which was filtered, yielding (15.1 g, 86%) of pure product. M.p. >280 ˚C; ^{1}H NMR (δ_H; 400 MHz, D_6-DMSO): 8.86 (s, 8H), 7.15 (s, 4H), 6.14 (s, 4H), 4.21 (t, J = 7.6Hz, 4H), 2.00 – 2.02 (m, 8H), 1.16 – 1.25 (m, 24H), 0.83 (t, J = 6.4Hz, 12H); ^{13}C NMR (δ_H; 200 MHz, D_6-DMSO):151.68, 124.92, 123.08, 102.37, 33.99, 33.07, 31.51, 27.49, 22.27, 13.99; IR (KBr): 3276, 2955, 2859, 1617, 1502, 1457, 1293, 1170, 1084, 841; MALDI-TOF / TOF-MS *m/z* 791 ($[M + Na]^+$).

C-pentyltetrabromocalix[4]resorcinarene was prepared according to the literature. A mixture of C-pentylcalix[4]resorcinarene (10.0 g, 0.013 mol) and N-bromosuccinimide (13.8 g, 0.078 mol) were added to a round bottom flask. 2-butanone (75 mL) was added

and stirred at room temperature for 12 hours. The precipitate from the reaction was filtered and washed with cold 2-butanone (50 mL) then cold water (3 x 100 mL). The product was dried in the oven producing (10.2 g, 72%) of a pure white solid. M.p. >280 ˚C; ^{1}H NMR (δ_H; 400 MHz, D_6-DMSO): 9.10 (s, 8H), 7.35 (s, 4H), 4.35 (t, J = 7.6Hz, 4H), 2.15 – 2.17 (m, 8H), 1.18 – 1.32 (m, 24H), 0.84 (t, J = 7Hz, 12H); ^{13}C NMR (δ_H; 200 MHz, D_6-DMSO): 148.60, 125.48, 123.64, 101.29, 35.46, 33.48, 31.35, 27.38, 22.25, 13.94; IR (KBr): 3397, 2929, 2853, 1614, 1472, 1306, 1168, 1081, 768; MALDI-TOF / TOF-MS *m/z* 1107 ($[M + Na]^+$).

C-pentyltetrabromocavitand was prepared according to the literature. A mixture of C-pentyltetrabromocalix[4]resorcinarene (1.0 g, 1.30 mmol), potassium carbonate (3.8 g, 27.7 mmol) and bromochloromethane (1.2 mL, 9.3 mmol) were added to a round bottom flask. Dry DMF (27 mL) was added and dinitrogen bubbled through the resultant mixture for 10 minutes. A condenser was attached and the mixture heated to 65 ˚C under a dinitrogen atmosphere for 4 days. Every 24 hours, more bromochloromethane (0.3 mL, 2.3 mmol) was added. The DMF was removed under vacuo to give a dark brown solid. Chloroform (20 mL) was added to the reaction mixture along with 2M HCl (30 mL). The aqueous phase was separated and extracted with more chloroform (3 x 50 mL). The organic separations were combined then washed with water (3 x 100 mL) then washed with saturated aqueous sodium chloride (1 x 100 mL) and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residue chromatographed on silica with a hexane/dichloromethane (1/2) mixture as the eluant. The product was isolated as a white solid (720 mg, 49%). M.p. >280 ˚C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 7.04 (s, 4H), 5.97 (d, J = 7.2Hz, 4H), 4.86 (t, J = 8.2Hz, 4H), 4.40 (d, J = 7.2Hz, 4H), 2.18 – 2.24 (m, 8H), 1.32 – 1.43 (m, 24H), 0.87 – 0.94 (m, 12H); ^{13}C NMR (δ_H; 400 MHz, $CDCl_3$): 152.04, 139.26, 119.01, 113.50, 98.45, 37.66, 31.84, 29.80, 27.39, 22.60, 14.03; IR (KBr): 2919, 2858, 1460, 1404, 1296, 1086, 1015, 948, 789; ESI-IT-MS *m/z* 1167 ($[\mathbf{1} + Cl]^-$).

C-pentyltetraiodocavitand **(1)** C-pentyltetrabromocavitand (2.0 g, 1.77 mmol) was added to a round-bottomed flask containing dry, freshly distilled THF (40 mL). The solution was cooled to –78 °C (dry ice / acetone bath temperature) and *n*-butyllithium (6.0 equiv., 6.63 mL, ca. 1.6 M solution in hexanes) was rapidly added. After stirring for 60 minutes, Iodine (3.6 g, 14.2 mmol, solution in THF (5 mL)) was added to the solution and the cooling bath removed allowing the reaction mixture to warm to room temperature. After 2 hours the reaction mixture was cooled to 0 ºC and quenched with a saturated aqueous sodium thiosulfate solution. The aqueous phase was extracted with ethyl acetate (3 x 75 mL), the portions washed with brine and dried with magnesium sulfate. The solvent was removed by rotary evaporator and the residue purified by column chromatography using a hexanes / dichloromethane (4:1) mixture as the eluent. The product was further purified by reprecipitation (dichloromethane:hexanes) yielding a white powder (1.46 g, 63 %). M.p. >280 ˚C; ^{1}H NMR (δ_H; 200 MHz, $CDCl_3$): 7.07 (s, 4H), 5.98 (d, J = 7.4 Hz, 4H), 4.86 (t, J = 8 Hz, 4H), 4.33 (d, 7.8 Hz, 4H), 2.20 – 2.19 (m, 8H), 1.39 (m, 24H), 0.92 (t, J = 7Hz, 12 H). ^{13}C NMR (δ_H; 200 MHz, $CDCl_3$): 154.86, 138.69, 120.65, 98.70, 93.02, 37.94, 31.84, 30.04, 27.40, 22.61, 14.03.

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C-pentyltetra(3-ethynylpyridine)cavitand **(2)**. C-pentyltetraiodocavitand **1** (400 mg, 0.303 mmol), 3-ethynylpyridine (480 mg, 4.29 mmol), *bis*(triphenylphosphine)palladium (II) dichloride (50 mg, 0.07 mmol), triphenylphosphine (20 mg, 0.08 mmol), copper(I) iodide (12 mg, 0.06 mmol) were added to a round bottom flask. Tetrahydrofuran (25 mL) and triethylamine (25 mL) were added and dinitrogen bubbled through the resultant mixture of 10 minutes. A condenser was attached and the mixture heated at 65 ºC under a dinitrogen atmosphere. The reaction was monitored by TLC and allowed to cool to room temperature upon completion (72 hours). The solution was diluted with chloroform (100 mL), washed with water (3 x 100 mL), and washed with brine (2 x 100 mL). The organic layer was separated and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the residue chromatographed on silica with an ethyl acetate/ethanol mixture (2:1) containing 1% triethylamine as the eluant. The product was isolated as an off-white solid. The product **2** was then further purified from dissolving in chloroform and then adding hexanes (250 mg, 67%). M.p. >280 ˚C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.69 (m, 4H), 8.55 (dd, J = 4.8 Hz, J = 1.6 Hz, 4H), 7.71 (dt, J = 8 Hz, J = 1.6 Hz, 4 H), 7.29 (m, 4H), 6.03 (d, J = 7.2 Hz, 4H), 4.88 (t, J = 8 Hz, 4H), 4.62 (d, 6.8 Hz, 4H), 2.28 – 2.45 (m, 8H), 1.46 – 1.35 (m, 24H), 0.96 – 0.92 (m, 12 H). ^{13}C NMR (δ_H; 200 MHz, $CDCl_3$): 155.40, 152.23, 148.93, 138.52, 138.39, 123.11, 120.65, 120.03, 112.60, 98.36, 94.07, 84.25, 36.50, 31.81, 29.46, 27.38, 22.63, 14.03.