SUPPORTING INFORMATION

Applying Reversible Chemistry of CO_2 to Supramolecular Polymers

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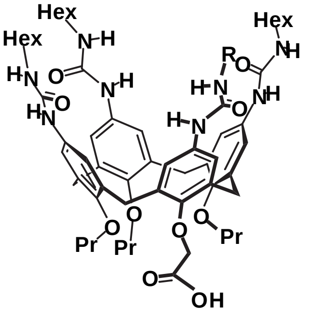
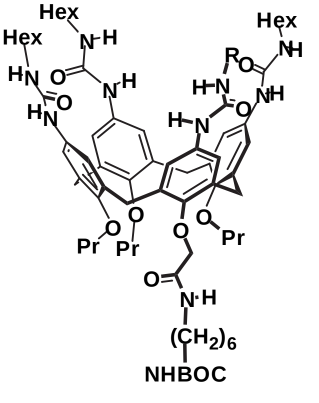
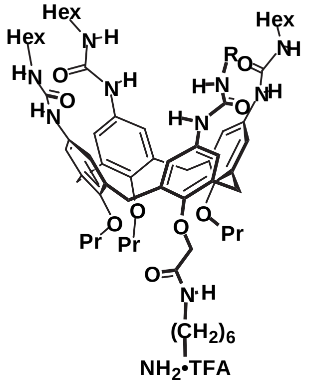
General. ^1H and ^{13}C NMR spectra were recorded at 295 ± 1 ^{O}C on JEOL Eclipse 500 MHz spectrometer. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. ESI-MS spectra were obtained on a Finnigan LCQ Ion Trap apparatus. All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen atmosphere. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used. Parent tetrahydroxycalix[4]arene and other calixarene precursors were prepared according to the published procedures.[1,2] Molecular modeling was performed using commercial MacroModel 7.1 with Amber* Force Field.



Calix[4]arene Tetraurea Acid: A mixture of tetraurea ester (1.5g, 1.2 mmol), THF-H_2O, 5:1 (60 mL) and KOH (0.67g, 12.0mmol) was refluxed overnight, after which H_2O (60 mL) was added, and the pH was adjusted to 2 with aq 1 M HCl. The product was extracted with $CHCl_3$ (3 x 60 mL), the organic layer was dried over Na_2SO_4, evaporated and recrystallized from MeOH to give the tetraurea acid as a yellow powder (1.13 g, 80%). ^{1}H NMR (DMSO-*d*$_6$): δ 8.07 (s, 1 H), 8.03 (s, 1 H), 7.83 (s, 2 H), 6.87 (s, 4 H), 6.59 (s, 4 H), 5.88 (q, *J* =5.3 Hz, 2 H), 5.72 (t, *J* = 5.0 Hz, 2 H), 4.56 (s, 2 H), 4.43 (d, *J* = 12.6 Hz, 2 H), 4.27 (d, *J* = 12.6 Hz, 2 H), 3.76 (t, *J* = 7.8 Hz, 2 H), 3.69 (t, *J* = 7.8 Hz, 2 H), 3.67 (t, *J* = 7.8 Hz, 2 H), 3.01 (m, 8 H), 2.95 (m, 4 H), 1.95-1,75(m, 6 H), 1.5-1.1 (m, 32 H), 1.0-0.8 (m, 21 H); ^{13}C NMR (DMSO-*d*$_6$): δ 171.5, 155.8, 151.1, 150.4, 150.2, 135.6, 135.3, 135.1, 134.8, 134.3, 134.1, 118.7, 77.5, 77.2, 71.2, 31.7, 30.4, 30.3, 26.7, 23.1, 23.0, 22.7, 14.4, 10.8, 10.5; IR (KBr): ν 3376, 3333, 2961, 2931, 2858, 1761, 1654, 1558, 1478, 1213.

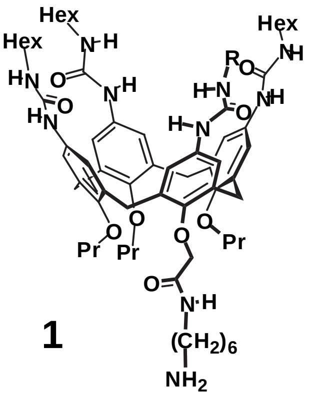


Amine (1) BOC-Derivative. To a stirred and ice-cooled solution of the tetraurea acid (1.0 g, 0.84 mmol) in DMF (30 mL) was added *N*-BOC-1,6-diaminohexane (0.38 ml,1.68 mmol), DCC (0.35 g,1.68 mmol), HOBt (0.23 g, 1.68 mmol), and Et$_3$N (0.23 mL, 1.68 mmol). The mixture was allowed to stir for 30 min at 0°C and for 24 h at rt, filtered, concentrated, diluted with CHCl$_3$, and washed successively with 1N NaHSO$_4$ (4 x 100 mL), water (3 x 100 mL), 1N NaHCO$_3$ (4 x 100 mL) and again water (3 x 100 mL). The organic layer was then dried over anhydrous Na$_2$SO$_4$ and evaporated. The residue was chromatographed on silica gel eluting with CHCl$_3$-CH$_3$OH, 95:5 to afford BOC protected amine **1** as a colorless solid. Yield 0.84 g (72%). ^{1}H NMR (DMSO-*d*$_6$): δ 8.17 (t, *J* = 5.7 Hz, 1 H), 8.02 (br s, 1 H), 7.98 (br s, 1 H), 7.83 (br s, 2 H), 6.81 (s, 2 H), 6.79 (s, 2 H), 6.76 (t, *J* = 5.5 Hz, 1 H), 6.62 (br s, 4 H), 5.82 (q, *J* = 5.7 Hz, 2 H), 5.77 (t, *J* = 5.3 Hz, 2 H), 4.35 (s, 2 H), 4.33 (d, *J* = 12.6 Hz, 2 H), 4.27 (d, *J* = 12.6 Hz, 2 H), 3.76 (t, *J* = 7.3 Hz, 4 H), 3.72 (t, *J* = 7.3 Hz, 2 H), 3.24 (m, 2 H), 3.00 (m, 12 H), 2.91 (m, 2 H), 1.36 (s, 9 H), 1.9-0.8 (m, 71 H); ^{13}C NMR (DMSO-*d*$_6$): δ 169.2, 156.1, 155.74, 155.7, 151.2, 150.7, 150.3, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.7, 118.4, 77.8, 77.3, 76.5, 74.8, 31.6, 30.4, 28.83, 28.8, 26.7, 23.0, 22.9, 22.7, 14.5, 10.63, 10.6; IR (KBr): ν 3329, 2928, 2852, 1628, 1559, 1476, 1213.



Amine (1) TFA-Salt. A solution of BOC protected **1** (0.5 g, 0.36 mmol) in THF (15 mL) was treated with TFA (5mL) and then stirred at rt for 2 h. The reaction mixture was concentrated in vacuo to afford the pure TFA salt (0.47 g, 93 %). ^{1}H NMR (DMSO-*d*$_6$): δ 8.18 (t, J = 5.5 Hz, 1 H), 8.05 (s, 1 H), 7.99 (s, 1 H), 7.84 (s, 2 H), 6.80 (s, 2 H), 6.63 (s, 2 H), 6.60 (s, 2 H), 5.88 (q, *J* = 5.9 Hz, 2 H), 5.78 (t, *J* = 5.5 Hz, 2H), 4.37 (s, 2 H), 4.32 (d, *J* = 12.8 Hz, 2 H), 4.26 (d, *J* = 12.8 Hz, 2 H), 3.75 (t, *J* = 7.2 Hz, 4 H), 3.71 (t, *J* = 7.2 Hz, 2 H), 3.26 (m, 2 H), 3.0 (m, 12 H), 2.78 (m, 2 H), 1.9-0.8 (m, 70 H); ^{13}C NMR (DMSO-*d*$_6$): δ 169.4, 155.8, 151.3, 150.7, 150.4, 135.3, 135.1, 135.0, 135.0, 134.5, 134.2, 134.0, 118.8, 11

8.54, 118.48, 77.3, 76.6, 74.8, 31.6, 30.4, 27.6, 26.6, 26.2, 22.9, (KBr): ν 3339, 2932, 2859, 1659, 1599, 1562, 1468, 1213; ESI-MS, *m/z* calcd for $C_{75}H_{115}F_{3}N_{10}O_{11}$ 1389, found 1389.



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Amine (1): The above TFA salt (0.50 g, 0.36 mmol) in $CHCl_3$ (100 mL) was washed with 10% NaOH (2 x 50 mL), then evaporated and dried in high vacuum. ^{1}H NMR (DMSO-d_6) δ 8.18 (t, *J* = 5 Hz, 1 H), 8.05 (br s, 1 H), 8.00 (br s, 1 H), 7.85 (br s, 2 H), 6.80 (2 x s, 4 H), 6.61(s, 4 H), 5.88 (m, 2 H), 5.80 (t, *J* = 5.5 Hz, 2 H), 4.36 (s, 2 H), 4.32 (d, J = 12.8 Hz, 2 H), 4.26 (d, *J* =12.8 Hz, 2 H), 3.76 (t, *J* = 7.8 Hz, 4 H), 4.26 (d, *J* = 12.8 Hz, 2 H),), 3.69 (t, *J* = 7.8 Hz, 2 H), 3.22 (m, 2 H), 2.99 (m, 12 H), 2.53 (t, *J* = 6.0 Hz, 2 H), 1.9-1.7, 1.6-1.4, 1.4-1.1, 1.0-0.8 (4 x m, 67 H); ^{13}C NMR (DMSO-d_6) δ 169.3, 155.8, 155.7, 151.2, 150.7, 150.4, 135.4, 135.1, 135.0, 134.5, 134.2, 134.1, 118.8, 118.7, 118.5, 118.47, 77.3, 76.5, 74.8, 31.6, 30.4, 26.7, 22.9, 22.7, 14.5, 10.6; IR (KBr) ν 3344, 2930, 2858, 1654, 1559, 1475, 1213; ESI MS, *m/z* calcd for $C_{73}H_{114}N_{10}O_{9}$ 1275, found 1276 (M+H^{+}), 2552 (2M+2H^{+}).

Carbamate Salt (2): Amine **1** (0.50 g, 0.39 mmol) in benzene (6 mL) was placed in a glass tube (13 x 100 mm), and dry CO_2 was then bubbled through the solution for 5min at 35 °C. Carbamate salt **2** quantitively precipitated, then filtered off and dried in high vacuum at rt. The experiment was performed at least 5 times giving reproducible results. Mp >140 ^{0}C (decomp); ^{1}H NMR (DMSO-d_6) δ 8.18 (2 x br s, 4 H), 8.11 (br s, 2 H), 7.96 (br s, 4 H), 6.89

(2 x s, 8 H), 6.66 (s, 8 H), 6.00 (br s, 2 H), 5.95 (br s, 2 H), 5.91(br s, 4 H), 5.8 (br s, 1 H), 4.42 (s, 4 H), 4.37 (d, *J* = 12.4 Hz, 4 H), 4.29 (d, *J* = 12.4 Hz, 4 H), 3.77 (m, 12 H), 3.26 (m, 4 H), 3.04 (m, 26 H), 2.58 (t, *J* = 6.4 Hz, 2 H), 19-1.7, 1.7-1.5, 1.5-1.1, 1.0-0.8(4 x m, 134H); ^{13}C NMR (DMSO-*d*$_6$): δ 169.3, 159.8, 155.8, 151.3, 150.8, 150.3, 135.5, 135.2, 135.1, 134.5, 134.2, 134.0, 134.0, 118.8, 118.6, 79.8, 77.3, 76.5, 74.8, 31.7, 31.5, 30.4, 27.1, 26.7, 23.0, 22.9, 22.7, 14.4, 10.6, 10.59.

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