Supplementary Information for:

Practical synthesis and guest–guest communication in multi-hemicarceplexes

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Contents (10 pages):

General Experimental Methods

^{1}H NMR spectra were recorded at 298 K unless otherwise stated using a Varian Unity INOVA 500 MHz, Bruker DPX/DRX 400 MHz, Varian Unity INOVA 300 MHz or Avance DPX 300 MHz spectrometer. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual protio solvent as an internal reference and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). Residual chloroform (δ 7.26 ppm) and 1,1,2,2-tetrachloroethane (δ 6.00 ppm), were used as internal references for ^{1}H NMR spectra measured in these solvents.

^{13}C NMR spectra were recorded on a Varian Unity INOVA 125 MHz, Bruker DPX/DRX 100 MHz, Varian Unity INOVA 75 MHz or Avance DPX 75 MHz spectrometer at 298 K, unless otherwise stated, with complete proton decoupling. Data is expressed in parts per million (ppm) shift relative internal references and is reported as position (δ). Residual chloroform (δ 77.1 ppm) was used as internal reference for ^{13}C NMR spectra.

Compounds were prepared for IR spectroscopic analysis as mixtures in KBr and the spectra collected by measurement of reflectance on a BioRad FTS-40 Spectrophotometer or were recorded on a Perkin–Elmer Spectrum One as KBr discs. Elemental analyses were obtained at the Campbell Microanalytical Laboratory at the Department of Chemistry, University of Otago, New Zealand or at the Research School of Chemistry, Australian National University. All compounds were dried before analysis at *ca*. 50 °C and 0.1 mm Hg for 72 h.

Mass spectra were recorded on a VG ZAB-2SEQ instrument or a ThermoQuest MAT95XL high resolution mass spectrometer using a cesium ion gun at *ca*. 25 kV or 20 kV respectively to produce a beam of fast Cs^+ ions. Melting points were recorded on a Reichert heating stage with microscope and are uncorrected.

_O_-xylyloxytethered-hemicarceplex•pyrazine 11

Prepared by modification of the procedure of Sherman *et al.*[1] A slurry of bis-cavitandtetraphenol **8** (59 mg, 32 μmol), pyrazine (144 mg, 1.8 mmol), K_2CO_3 (207 mg, 1.5 mmol) and bromochloromethane (10 μL, 150 μmol) in NMP (16 mL) was stirred under N_2 for 24 h. Additional bromochloromethane (10 μL, 150 μmol) was added and stirring was continued for a further 24 h. The solvent was removed by distillation under vacuum, water was added, the slurry was acidified with 2 M aq. HCl and extracted into chloroform. The combined organic phases were washed with sat. aq. $NHCO_3$, and sat. aq. NaCl, dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude material was purified by flash chromatography (5 g SiO_2, 1:1 hexane/dichloromethane) to afford the title compound **11** as a white solid (55 mg, 89%): R_f = 0.44 (6:4 dichloromethane/hexane); m.p. 327 °C decomp. (dichloromethane/ethanol); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 12H), 0.94 (t, J = 7.3 Hz, 12H), 1.32–1.46 (m, 48H), 2.17–2.24 (m, 16H), 3.97 (d, J = 7.8 Hz, 4H), 4.07 (s, 4H), 4.17 (d, J = 7.3 Hz, 4H), 4.69 (t, J = 8.3 Hz, 4H), 4.74 (t, J = 7.8 Hz, 4H), 5.17 (s, 4H), 5.67 (d, J = 7.8 Hz, 4H), 5.79 (d, J = 7.3 Hz, 4H), 6.22 (d, J = 6.3 Hz, 2H), 6.25 (d, J = 6.4 Hz, 2H), 6.58 (s, 2H), 6.86 (s, 4H), 6.93 (s, 2H), 7.19 (s, 2H) 7.29–7.32 (m, 2H), 7.34–7.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 22.8, 27.7, 30.2, 30.4, 32.1, 36.8, 37.1, 74.3, 90.3, 100.4,

101.0, 111.8, 114.5, 116.7, 121.3, 129.0, 131.4, 137.5, 139.3, 139.7 (2 coincident resonances), 139.9, 141.0, 141.7, 143.2, 143.7, 144.7, 155.1; IR (KBr) 975, 1312, 2929, 3009 cm^{-1}; FAB-MS *m/z* 1935.6 (M^+, 100%); Anal. Calcd. for $C_{118}H_{138}N_2O_{22}$: C, 73.19; H, 7.18; N, 1.45; found: C, 73.07; H, 7.21, N, 1.29.

Bis-hemicarceplex•2pyrazine 12

A slurry of octaphenol **9** (126 mg, 35 μmol), pyrazine (336 mg, 4.2 mmol), K_2CO_3 (484 mg, 3.5 mmol) and bromochloromethane (23 μL, 350 μmol) in NMP (17.5 mL) was stirred under N_2 for 24 h. Additional bromochloromethane (23 μL, 350 μmol) was added and stirring was continued for a further 24 h. The solvent was removed by distillation under vacuum, water was added, the slurry was acidified with 2 M aq. HCl and extracted into chloroform. The combined organic phases were washed with sat. aq. $NHCO_3$ and sat. aq. NaCl, dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude material was purified by recrystallisation (chloroform) to afford the bis-hemicarceplex **12** as a white solid (89 mg, 67%): R_f = 0.23 (7:3 dichloromethane/hexane); m.p. > 300 °C decomp. (chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 24H), 0.93 (t, J = 6.8 Hz, 24H), 1.34–1.45 (m, 96H), 2.17–2.24 (m, 32H), 3.96 (d, J = 7.3 Hz, 8H), 4.06 (s, 8H), 4.16 (d, J = 6.8 Hz, 8H), 4.68 (t, J = 7.8 Hz, 8H), 4.73 (t, J = 8.3 Hz, 8H), 5.19 (bs, 8H), 5.65 (bs, 8H), 5.79 (d, J = 7.3 Hz, 8H), 6.22 (d, J = 6.4 Hz, 4H), 6.23 (d, J = 6.4 Hz, 4H), 6.58 (s, 4H), 6.85 (s, 8H), 6.92 (s, 4H), 7.19 (s, 4H) 7.25 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (2 coincident resonances), 22.8, 27.7, 29.8, 30.2, 30.3, 36.8, 37.0, 73.9, 90.2, 100.4, 100.9, 111.8, 114.4, 116.7, 121.3, 137.9, 139.3, 139.7 (2 coincident resonances), 140.0, 141.0, 141.7, 143.2, 143.6, 144.7, 149.0, 155.1; IR (KBr) 1466, 2864, 2930, cm^{-1}; FAB-MS *m/z* 3794.0 (M^+, 100%).

Tris-hemicarceplex•3pyrazine 13

To a slurry of dodecaphenolhexacavitand **10** (123 mg, 23 μmol), pyrazine (331 mg, 4.1 mmol) and K_2CO_3 (477 mg, 3.5 mmol) in NMP (12 mL) was added bromochloromethane (23 μL, 345 μmol). The mixture was stirred at 60 °C under N_2 for 24 h. Additional bromochloromethane (23 μL, 345 μmol) was added and stirring was continued for a further 24 h. The solvent was removed by distillation, water was added, the slurry was

acidified with 2 M aq. HCl and extracted with chloroform. The combined organic phases were washed with sat. $NaHCO_3$, sat. aq. NaCl and dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude material was purified by column chromatography (10 g SiO_2, 6:4 dichloromethane/hexane) to afford the title compound **13** as a white solid (63 mg, 48%): R_f = 0.61 (7:3 dichloromethane/hexane); m.p. 316 °C decomp. (dichloromethane/ethanol); ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 90 °C) δ 0.94–0.98 (m, 72H), 1.32–1.51 (m, 144H), 2.21–2.33 (m, 48H), 4.03 (d, J = 6.0 Hz, 12H), 4.17 (s, 12H), 4.24 (d, J = 6.0 Hz, 12H), 4.77–4.80 (m, 24H), 5.31 (bs, 12H), 5.81–5.84 (m, 24H), 6.23 (bs, 12H), 6.59 (s, 6H), 6.92 (s, 12H), 7.00 (s, 6H), 7.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 14.3, 22.8, 27.7, 27.8, 30.2, 30.4, 32.1, 32.2, 36.7, 37.1, 69.2, 90.3, 100.4, 101.0, 111.7, 114.3, 116.6, 121.3, 138.4, 139.3, 139.4, 139.6, 140.0, 141.7, 143.2, 143.8, 144.4, 148.9, 155.0; IR (KBr) 975, 1313, 1465, 2929 cm^{-1}; FAB-MS m/z 5652.2 (M^+, 100%); Anal. Calcd. for $C_{342}H_{402}N_6O_{66}$: C, 72.67; H, 7.17; N, 1.49; found: C, 72.85; H, 7.63; N, 1.38.

Charged hydrogen bonded capsule 8-CHB.

To a 2 mM solution of bis-cavitand **8** in $CDCl_3$ was added 2.1 molar equivalents of DBU. ^{1}H NMR samples were prepared by adding 500 μL of this stock solution to NMR tubes containing molecular sieves. 25 molar equivalents of pyrazine were added as a stock solution in $CDCl_3$. The resulting samples were allowed to equilibrate at room temperature for 24 h prior to insertion into the NMR spectrometer. Samples were then allowed to equilibrate in the spectrometer for 20 min at each temperature prior to data acquisition.

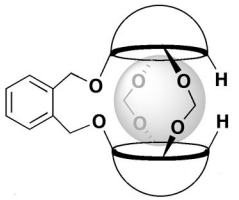
Charged hydrogen bonded capsule 9-CHB.

To a 2 mM solution of cavitand tetramer **9** in $CDCl_3$ was added 4.1 molar equivalents of DBU. ^{1}H NMR samples were then prepared in an analogous fashion to that described above, with the addition of 50 molar equivalents of pyrazine.

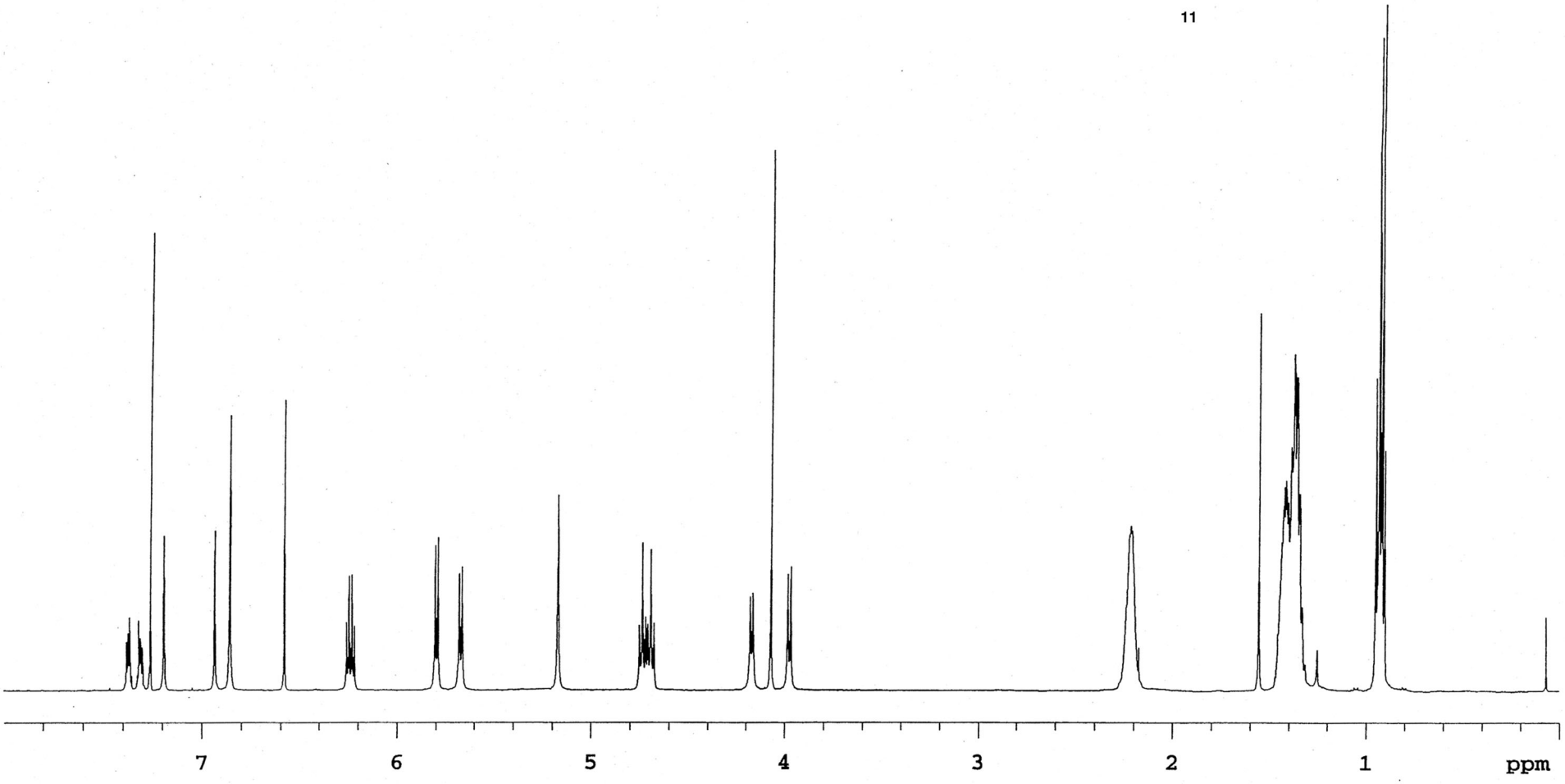
References

1. R. G. Chapman and J. C. Sherman, *J. Am. Chem. Soc.*, 1998, **120**, 9818–9826.

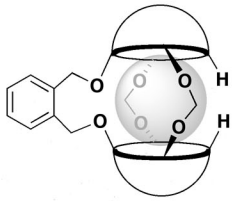
500 MHz ^{1}H NMR spectrum in $CDCl_3$ at 25 °C



11

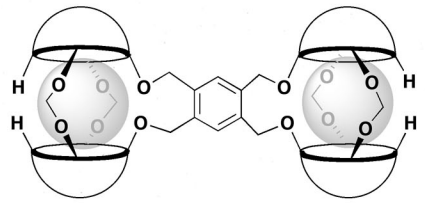


75 MHz ^{13}C NMR spectrum in $CDCl_3$ at 25 °C



11

500 MHz ^{1}H NMR spectrum in $CDCl_3$ at 25 °C



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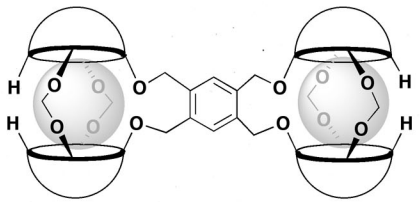

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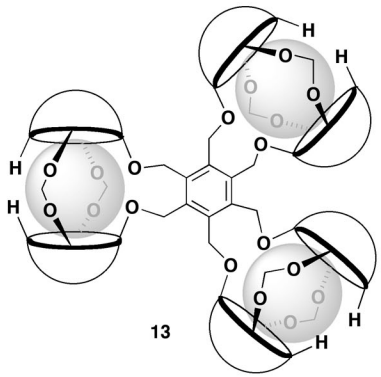
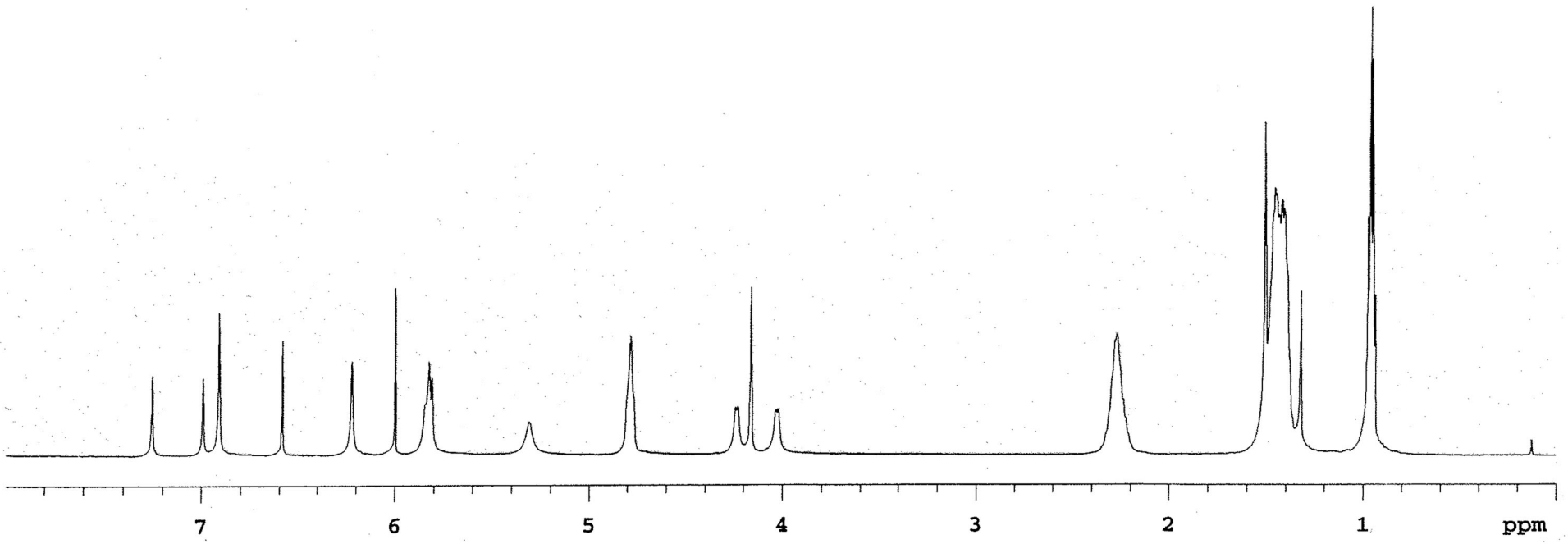
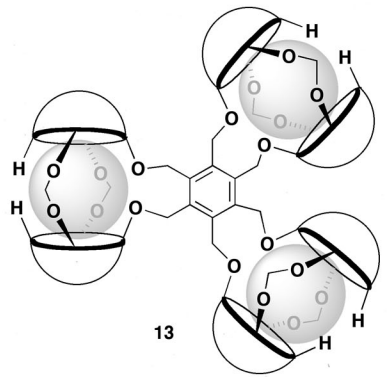




75 MHz ^{13}C NMR spectrum in $CDCl_3$ at 25 °C



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