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Supporting Information

for

Template Effect Where 1-3 Molecules Drive Formation of a Trimer Carceplex

Darren A. Makeiff and John C. Sherman

General Experimental. All reactions were conducted under an N_2 atmosphere unless stated otherwise. Triethyl-1,3,5-benzenetricarboxylate and 2,4,6-tris(bromomethyl)mesitylene were used as purchased from Aldrich. 10 % Pd/C was purchased from Aldrich. DMSO, DMF, and NFP were distilled at reduced pressure and stored over activated 4 Å molecular sieves prior to use. NMP was stored over activated 4 Å molecular sieves prior to use. THF used was BDH glass distilled grade and was distilled and dried over sodium/benzophenone ketyl prior to use. All other reagents and chromatography solvents were used as purchased without further treatment. Computer modeling on carceplexes **5**•guest(s) was done using the software CS Chem 3D Pro (ver. 3.5).

MALDI Mass Spectrometry. Mass spectra were recorded on a Kratos Concept II HQ (DCI) and a VG Tofspec in reflectron mode (MALDI). For our compounds, positive molecular ions are usually detected as sodium or potassium adducts, unless other additives are present in the matrix (e.g., H^+ or Ag^+ cations). 2,5-dihydroxybenzoic acid (DHB) was used as the matrix for all of the compounds. Masses reported as silver adducts were generated from samples ionized using DHB doped with silver trifluoroacetate (~100 equiv. per mole of analyte).

Synthesis and Characterization

A,C-diol 2. Tetrol **1** (7.25g, 7.13 mmol) was dissolved in 725 mL of acetone and stirred in a 1L, single neck round bottom flask. DBU (3.20 ml, mmol, equiv.) was added and the solution was

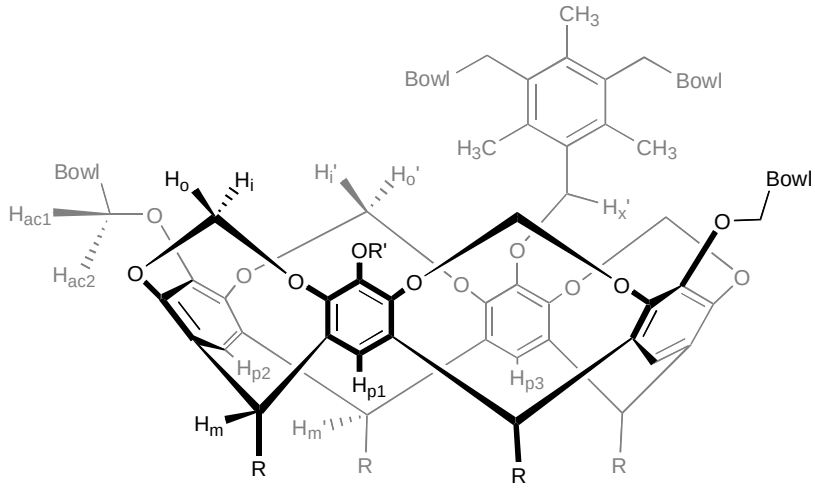
stirred. After 2 h, a thick white precipitate formed, and excess benzyl bromide was added (4.20 mL, 29.4 mmol, 4.1 equiv.). After ~30 min, the reaction mixture turned to a clear solution and was allowed to stir overnight, before the solvent and excess benzyl bromide were removed by rotary evaporation *in vacuo*. The yellow-brown crude syrup was resuspended in 2 M HCl and extracted with $CHCl_3$ (3 × 100 mL). $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and the $CHCl_3$ was removed by rotary evaporation. The crude syrup was purified by flash chromatography on silica gel (230-400 mesh) eluting with ethyl acetate:hexanes (1:8 then 1:2), to afford A,C-diol **2** as a glassy white solid that was recrystallized from acetone/hexanes to give white crystals (1.09 g, 13 %). ^{1}H NMR spectroscopic and MALDI MS spectrometric data were identical to previously data reported.[1]

Hexa-benzyl trimer 3. Solution A: 1.09 g of A,C-diol **2** was dissolved in 40 mL of DMSO (degassed only). Solution B: 0.600 mL of bromochloromethane was dissolved in 20 mL of DMSO. Solutions A and B were slowly added to a stirring suspension of K_2CO_3 (4.23g, mmol) in 540 mL of DMSO at 60 °C over a period of 48 h, after which the reaction was stirred for an additional 24 h, before removing the solvent *in vacuo*. The crude yellow syrup obtained was resuspended in 2 M HCl (100 mL) and extracted with $CHCl_3$ (3 × 100 mL). The combined extracts were dried over $MgSO_4$, filtered, and the $CHCl_3$ removed by rotary evaporation. $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and then the $CHCl_3$ was removed by rotary evaporation. The crude yellow oil was recrystallized from CH_2Cl_2/ethyl acetate to give a white crystalline solid, which was purified by flash chromatography on silica gel (10-40 μm, "TLC grade"), eluting with $CHCl_3$:hexanes (2:1). A,C-trimer **3** was isolated as a glassy white solid that was recrystallized from CH_2Cl_2/ethyl acetate to give a white crystalline solid (452 mg, 42 % after drying in vacuo overnight in a toluene reflux pistol). ^{1}H NMR spectroscopic and MALDI MS spectrometric data were identical to previously reported data.[1]

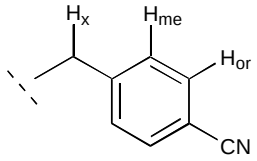
Hexa-hydroxyl A,C-trimer 4. Hexa-benzyl A,C-trimer **3** (410 mg, 0.113 mmol) was dissolved in benzene (25 mL) in a 250 mL round bottom flask. Methanol (20 mL) and 10 % Pd/C (117.3 mg) were added and the flask was sealed with a rubber septum. H_2 gas was then bubbled through the solution for ten minutes and the vessel was sealed under H_2 (gas) at 1 atm. The reaction was allow to stir for three h, after which a white precipitate (trimer **4**) was observed. The flask was opened to air and THF was added to completely dissolve the white precipitate before filtering the mixture through Celite. Rotary evaporation gave hexa-hydroxyl trimer **4** as a

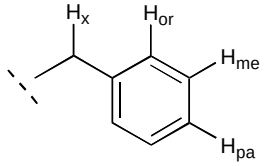
pale yellow solid, which was precipitated from THF/methanol to give a white powder (315 mg, 90 %). ^{1}H NMR spectroscopic and MALDI MS spectrometric data were identical to previously reported data.[1]

Tris-hydroxyl trimer cavitand, 14. Procedure i. Hexa-hydroxyl trimer **4** (106.8 mg, 34.6 μmol), K_2CO_3 (269.5 mg, 1.95 mmol), and KI (336.0 mg, 2.02 mmol) were mixed in DMF (50 mL) in a round bottom flask. 2,4,6-tris(bromomethyl)mesitylene (27.9 mg, 70.0 μmol) in 2.8 mL of DMF was then added over 12 h by syringe pump, followed by stirring for an additional 24 h before removing the solvent *in vacuo*. The crude yellow solid was then suspended in 2 M HCl and extracted with $CHCl_3$. The extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Tris-hydroxyl trimer cavitand was purified by flash chromatography on silica gel (230-400 mesh) eluting with $CHCl_3$:hexanes (4:1) and then $CHCl_3$:MeOH (98:2) and then precipitated from $CHCl_3$/MeOH to give a white solid (28.3 mg, 25 %). ^{1}H NMR spectroscopic and MALDI MS spectrometric data were identical to previously reported data.[2]



14, R' = H

15, R' = 

16, R' = 

^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.27-7.10 (m, 60H, ArH (feet)), 6.93 (s, 3H, H_p (cap)), 6.83 (s, 6H, H_p (interbowl acetal), 6.65 (s, 3H, H_p (OH)), 6.04 (d, 6H, H_o or H_o'), 5.90 (d, 6H, H_o or H_o'), 5.88 (d, 3H, H_{ac1} or H_{ac2}), 5.88 (d, 3H, H_{ac1} or H_{ac2}), 5.44 (brs, 3H, OH), 5.20 (s, 6H, H_x'), 4.93 (t, 6H, H_m or H_m'), 4.81 (t, 6H, H_m or H_m'), 4.43 (d, 6H, H_i or H_i'), 4.41 (d, 6H, H_i or H_i'), 2.89 (s, 9H, CH_3 (cap)), 2.75-2.38 (m, 24H, $CH_2CH_2C_6H_5$ and $CH_2CH_2C_6H_5$).

Procedure ii. A mixture containing **5**•$(DMF)_3$ and other trimer carceplex reaction byproducts (140 mg) was dissolved in TFA:CH_2Cl_2 (1:1) and allowed to stir for 30 min, before removing the solvent by rotary evaporation. Tris-hydroxyl trimer cavitand **14** was then purified by column chromatography on silica gel (230-400 mesh) eluting with $CHCl_3$ and then $CHCl_3$:MeOH (98:2), and then precipitated from $CHCl_3$/MeOH to give a white solid (26.1 mg, 21 %).

Tris-benzyl trimer cavitand 15. Tris-hydroxyl trimer cavitand **14** (29.1 mg, 8.97 μmol) and Cs_2CO_3 (103.3 mg, 317 μmol) were mixed in DMF (2 mL) for at least 2 h at 60 °C before adding benzyl bromide (20 μL, 168 μmol). After stirring for another 12 h at the same temperature, the solvent was removed *in vacuo*. The crude yellow solid was then suspended in 2 M HCl and extracted with $CHCl_3$. The extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Tris-benzyl trimer cavitand **15** was purified by flash chromatography on silica gel (230-400 mesh) eluting with $CHCl_3$:hexanes (4:1) and then recrystallized from CH_2Cl_2/EtOAc to give a white solid (18.0 mg, 56 %).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.29-7.04 (m, 75H, ArH (feet) and ArH (benzyl)), 6.90 (s, 3H, H_{p2}), 6.82 (s, 9H, H_{p1} and H_{p3}), 6.01 (d, 6H, H_o or H_o'), 5.81 (d, 3H, H_{ac1} or H_{ac2}), 5.80 (d, 6H, H_o or H_o'), 5.68 (d, 3H, H_{ac1} or H_{ac2}), 5.18 (s, 6H, H_x'), 4.92 (t, 6H, H_m or H_m'), 4.89 (s, 6H, H_x), 4.80 (t, 6H, H_m or H_m'), 4.40 (d, 6H, H_i or H_i'), 4.37 (d, 6H, H_i or H_i'), 2.88 (s, 9H, C*H*$_3$ (cap)), 2.75-2.61 (m, 24H, $CH_2CH_2C_6H_5$), 2.56-2.40 (m, 24H, $CH_2CH_2C_6H_5$). 2D NOESY and COSY spectra were also recorded.

MS (MALDI) *m/z* (rel intensity) 3537 (($M•C_{228}H_{198}O_{36} + Na^+)^+$; 100), calcd for $C_{228}H_{198}O_{36}•Na^+$ = 3537.

Tris-cyanobenzyl trimer cavitand 16. Tris-hydroxyl trimer cavitand **14** (38.9 mg, 12.0 μmol) and Cs_2CO_3 (125 mg, 385 μmol) were mixed in 2 mL of DMF at 60 °C for 2 h before *para*-bromotoluonitrile (22.8 mg, 116.3 μmol) was added. After stirring for another 12 h at the same temperature, the solvent was removed *in vacuo*. The crude yellow solid was then suspended in 2 M HCl and extracted with $CHCl_3$. The $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Tris-cyanobenzyl trimer cavitand

16 was purified by flash chromatography on silica gel (230-400 mesh) eluting with $CHCl_3$ and then recrystallized from CH_2Cl_2/EtOAc to give a white solid (10.3 mg, 24 %).

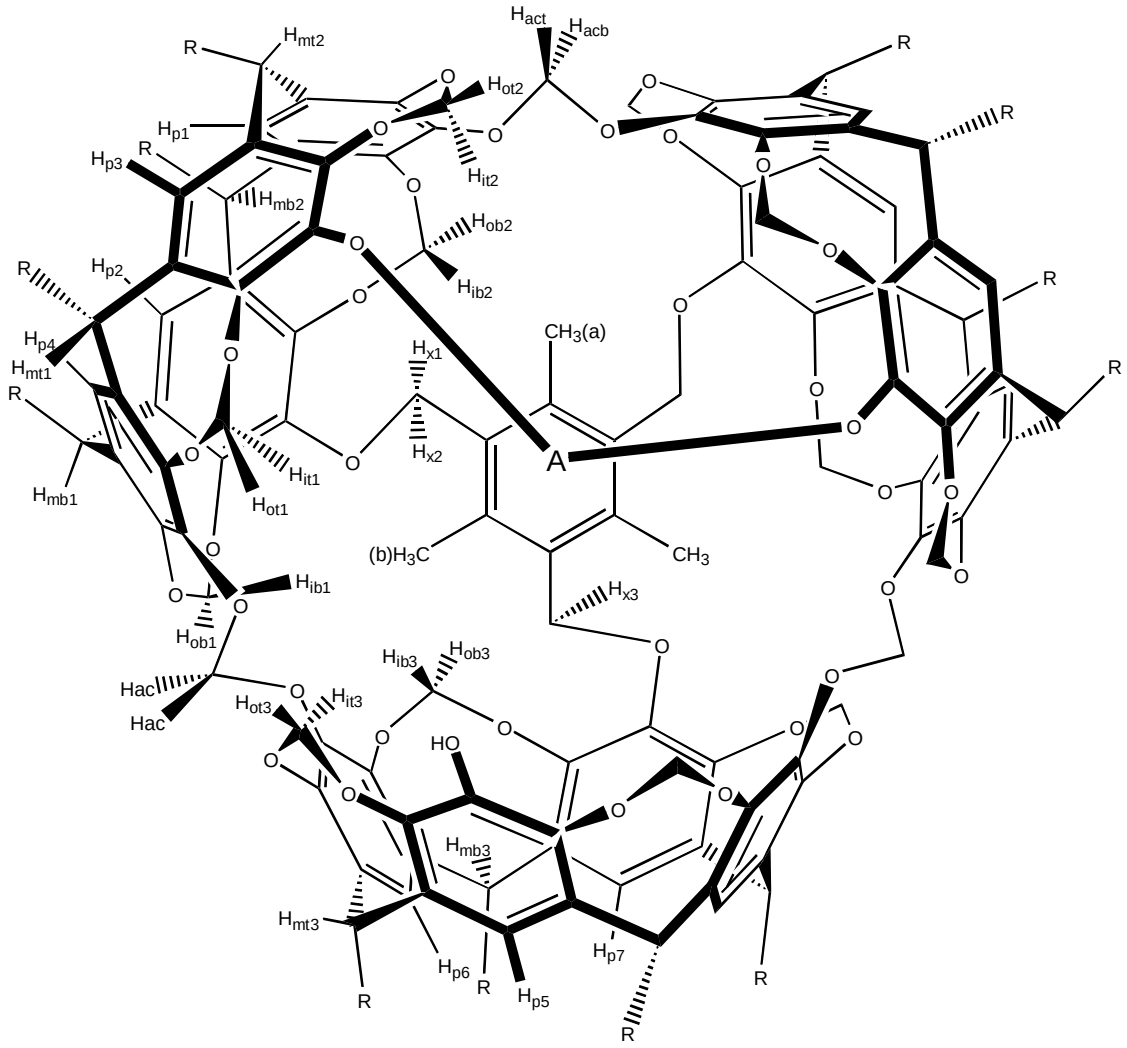
^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.37 (d, 6H, H_2)), 7.30 (d, 6H, H_1)), 7.27-7.10 (m, 60H, ArH (feet)), 6.91 (s, 3H, H_{p1} or H_{p3}), 6.86 (s, 3H, H_{p1} or H_{p3}), 6.83 (s, 6H, H_{p2}), 6.03 (d, 6H, H_o or H_o'), 5.90 (d, 6H, H_o or H_o'), 5.82 (d, 3H, H_{ac1} or H_{ac2}), 5.72 (d, 3H, H_{ac1} or H_{ac2}), 5.19 (s, 6H, H_x or H_x'), 4.96 (s, 6H, H_x or H_x'), 4.93 (t, 6H, H_m or H_m'), 4.80 (t, 6H, H_m or H_m'), 4.39 (d, 6H, H_i or H_i'), 4.38 (d, 6H, H_i or H_i'), 2.89 (s, 9H, C*H*$_3$ (cap)), 2.71 (brm, 12H, $CH_2CH_2C_6H_5$), 2.65 (brm, 12H, $CH_2CH_2C_6H_5$), 2.59-2.41 (m, 24H, $CH_2CH_2C_6H_5$). 2D NOESY and COSY spectra were also recorded.

MS (MALDI) *m/z* (rel intensity) 3612 (($M\bullet C_{231}H_{195}O_{36}N_3 + Na^+)^+$; 100), calcd for $C_{231}H_{195}O_{36}N_3\bullet Na^+$ = 3612.

(Bis *meta*-xylyl) Trimer cavitand, 17. Trimer cavitand **14** (26.1mg, 8.05 μmol), K_2CO_3 (99.0 mg, 717 μmol), KI (90.4 mg, 545 μmol) and **6** (20.0 mg, 133 μmol) were mixed in 20 mL of NFP for 2 h α,α'-Dibromo-*meta*-xylene (2.1 mg, 7.96 μmol) was then added in 1 mL of NFP and the reaction was stirred for 12 h The crude yellow-orange solid was suspended in 2 M HCl and extracted with $CHCl_3$. The $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Bis *meta*-xylyl trimer cavitand **17** was then purified by flash chromatography on silica gel (10-40 μm, "TLC grade") eluting with $CHCl_3$ and then precipitated from $CHCl_3$/hexanes to give a white solid (5.2 mg, 19 %).

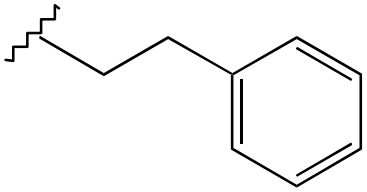
^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.46 (s, 1H, H_{mx1}), 7.36 (t, 1H, H_{mx3}), 7.32-7.08 (m, 62H, ArH (feet) and H_{mx2}), 6.94 (s, 2H, H_{p2}), 6.93 (s, 1H, H_{p7}), 6.88 (s, 2H, H_{p3}), 6.85 (s, 2H, H_{p6}), 6.80 (s, 2H, H_{p4}), 6.77 (s, 2H, H_{p1}), 6.69 (s, 1H, H_{p5}), 6.28 (d, 1H, H_{act}), 6.11 (d, 2H, H_{ob1}), 6.01 (d, 2H, H_{ot3}) , 5.99 (d, 2H, H_{ob2}), 5.96 (d, 2H, H_{ot2}), 5.92 (d, 2H, H_{ob3}), 5.73 (s, 4H, H_{ac}), 5.68 (d, 2H, H_{ot2}), 5.56 (d, 1H, H_{acb}), 5.50 (s, 1H, OH), 5.35 (d, 2H, H_{x1}), 5.21 (d, 2H, H_{x2}), 5.01 (s, 2H, H_{x3}), 4.97 (d, 2H, H_{mx4}), 4.97 (t, 2H, H_{mb1}), 4.92 (t, 2H, H_{mb2}), 4.89 (t, 2H, H_{mb3}), 4.87 (t, 4H, H_{mt3} and H_{mt2}), 4.83 (t, 2H, H_{mt1}), 4.78 (d, 2H, H_{mx5}), 4.59 (d, 2H, H_{ib1}),4.58 (d, 2H, H_{it3}), 4.46 (d, 2H, H_{it2}), 4.39 (d, 2H, H_{ib2}), 4.29 (d, 2H, H_{it1}), 4.14 (d, 2H, H_{ib3}), 2.89 (s, 6H, C*H*$_3$ (b) cap),

2.81 (s, 3H, CH_3 (a) cap), 2.77-2.60 (brm, 12H, $CH_2CH_2C_6H_5$), 2.60-2.39 (brm, 12H, $CH_2CH_2C_6H_5$).

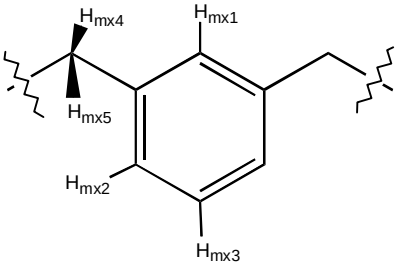


17

R=



A=

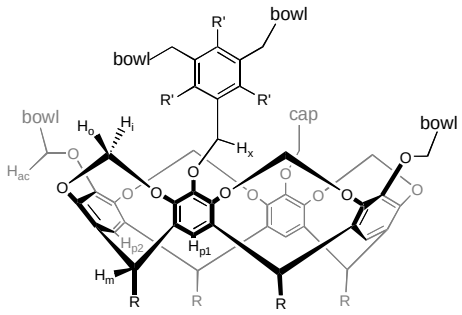


t = top. b = bottom

Proton assignments were made with the help of 2D NOESY, COSY, and long range COSY spectra recorded. $H_{p1\text{-}p7}$ were assigned from long range coupling correlations to $H_{mt1\text{-}3}$ and

H_{mb1-3}. H_{ib1-3} were assigned based on NOESY correlations with the methyl protons (a and b) of the mesityl cap.

MS (MALDI) *m/z* (rel intensity) 3366 (($M \bullet C_{215}H_{186}O_{36} + Na^+)^+$; 100), calcd for $C_{215}H_{186}O_{36} \bullet Na^+$ = 3365.

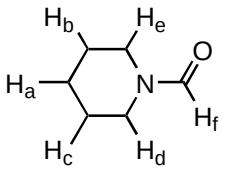


5, R' = CH_3, R = $CH_2CH_2C_6H_5$
13, R' = H, R = $CH_2CH_2C_6H_5$

5•NFP**.** Procedure A. Tris-hydroxyl trimer **4** (10.2 mg, 3.30 μmol), K_2CO_3 (106.0 mg, 767.0 μmol), KI (39.0 mg, 235.0 μmol) and NFP (9 mL) were added to a single neck round bottom flask and stirred at 70 °C for at least 1 h 2,4,6-tris(bromomethyl)-mesitylene (5.2 mg, 13.0 μmol) was then added in NFP (1 mL) and the reaction was allowed to stir overnight. The solvent was then rotary evaporated *in vacuo* and the yellow-orange residue was resuspended in 2 M HCl (10 mL) and extracted with $CHCl_3$ (3 × 10 mL). The $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Carceplex **5**•NFP was then purified by flash chromatography on silica gel (10-40 μm, "TLC grade") eluting with $CHCl_3$:hexanes (2:1) and then precipitated from $CHCl_3$/hexanes to give a white solid. Carceplex **5**•NFP was isolated as an inseparable mixture that also contained ~15 % **5**•$(NFP)_2$.

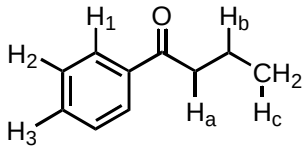
^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300K) δ 7.32-7.14 (m, 60H, ArH (feet)), 6.97 (s, 6H, H_{p1}), 6.78 (s, 6H, H_{p2}), 6.23 (s, 1H, H_f), 6.00 (d, 12H, H_o), 5.79 (s, 6H, H_{ac}), 5.13 (s, 12H, H_x), 4.92 (t, 12H, H_m), 4.10 (d, 12H, H_i), 2.80 (s, 18H, C*H*$_3$ (cap)), 2.71 (m, 24H, $CH_2CH_2C_6H_5$), 2.63-2.39 (m, 24H, $CH_2CH_2C_6H_5$), 1.68 (m, 2H, H_d or H_e), 1.46 (m, 2H, H_d or H_e), -0.11 (m, 2H, H_b or H_c), -0.23 (m, 2H, H_b or H_c), -0.30 (m, 2H, H_a). 2D COSY spectra were also recorded.

MS (MALDI) *m/z* (rel intensity) 3537 (($M \bullet C_{225}H_{203}O_{37}N + Na^+)^+$; 100), calcd for $C_{225}H_{203}O_{37}N \bullet Na^+$ = 3536.



5•11. Procedure B. Hexa-hydroxyl trimer **4** (50.4mg, 16.3 μmol), KI (251.6 mg, 1.52 mmol), and K_2CO_3 (289.5 mg, 2.09 mmol) were allowed to stir in 40 mL or **11** at 85-95 °C under a N_2 atmosphere for 1h, after which 2,4,6-tris(bromomethyl)mesitylene was added (21.4 mg, 52.6 μmol) in 1 mL **11**. After 4 d, the solvent was then rotary evaporated *in vacuo* and the yellow-orange residue was resuspended in 2 M HCl (10 mL) and extracted with $CHCl_3$ (3 × 10 mL). The $CHCl_3$ extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. Carceplex **5•11** was then purified by flash chromatography on silica gel (10-40 μm, "TLC grade") eluting with $CHCl_3$:hexanes (2:1) and then precipitated from $CHCl_3$/methanol and then $CHCl_3$/hexanes to give a white solid (13.2 mg, 23 %).

^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K). δ 7.27-7.15 (m, 24H, ArH (pendant groups) and residual $CHCl_3$), 7.00 (s, 3H, H_{p1}), 6.78 (s, 3H, H_{p2}), 6.32 (d, 2H, H_1), 5.90 (d, 12H, H_o), 5.71 (s, 12H, H_{ac}), 5.20 (s, 12H, H_x), 5.15 (t, 2H, H_2), 4.91 (brt, 12H, H_m), 4.77 (t, 1H, H_3), 4.03 (d, 12H, H_i), 2.83 (s, 18H, C*H*$_3$ (cap)), 2.68 (t, 24H, $CH_2CH_2C_6H_5$), 2.49 (t, 24H, $CH_2CH_2C_6H_5$), 0.94 (m, 2H, H_a), -0.02 (m, 2H, H_b), -2.28 (t, 3H, H_c). 2D COSY spectra were also recorded.



11

MS (MALDI) *m/z* (rel intensity) 3655 (($M \bullet C_{219}H_{192}O_{36} + Ag^+)^+$; 100), calcd for $C_{219}H_{192}O_{36} \bullet Ag^+$ = 3656.

13•11. Procedure B, except 1,3,5-tris(bromomethyl)benzene[3] (5.4 mg, 15.1 μmol, ~5 equiv.) was used instead of 2,4,6-tris(bromomethyl)mesitylene, with hexa-hydroxyl trimer **4** (9.5 mg, 3.08 μmol), K_2CO_3 (24.6 mg, 178 μmol, 57 equiv.), KI (11.7 mg, 70.5 μmol, 2.4 equiv.) and **11** (10 mL). Carceplex **13•11** was isolated as a white solid (2.4 mg, 22 %).

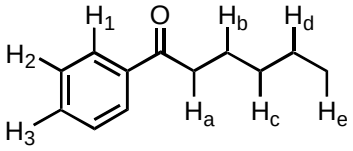
^{1}H NMR (500 MHz, $CDCl_3$, 300 K). δ 7.44 (s, 6H, ArH (cap)), (m, 24H, ArH (pendant groups) and residual $CHCl_3$), 6.97 (s, 3H, H_{p1}), 6.78 (s, 3H, H_{p2}), 6.28 (d, 2H, H_1), 5.93 (d, 12H, H_o), 5.82 (s, 12H, H_{ac}), 5.22 (t, 2H, H_2), 4.98 (s, 12H, H_x), 4.89 (brt, 12H, H_m), 4.07 (d, 12H, H_i), 2.69 (brm, 24H, $CH_2CH_2C_6H_5$), 2.51 (brm, 24H, $CH_2CH_2C_6H_5$), 0.97 (m, 2H, H_a), -0.14 (m, 2H, H_b), -2.33 (t, 3H, H_c). H_3 is hidden.

MS (MALDI) *m/z* (rel intensity) 3503 ($(M•C_{223}H_{192}O_{37} + K^+)^+$; 100), calcd for $C_{223}H_{192}O_{37}•K^+$ = 3503.

5•12. Procedure A. Hexa-hydroxyl trimer **4** (10.2 mg, 3.30 μmol), K_2CO_3 (106.0 mg, 767.0 μmol), KI (39.0 mg, 235.0 μmol), NFP (6.5 mL), **12** (3.5 mL), 2,4,6-tris(bromomethyl)mesitylene (5.0 mg, 12.5 μmol). Precipitation from $CHCl_3$/hexanes gave **5•12** as a white solid (2.6 mg, 22 %). **5•12** was isolated as a mixture with 13 % **5**•NFP.

^{1}H NMR (500 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.30-7.14 (m, 60H, ArH (feet)), 7.20 (s, 3H, H_p), 6.80 (s, 3H, H_p), 6.40 (d, 2H, H_1), 5.87 (d, 12H, H_o), 5.74 6.01 (s, 6H, H_{ac}), 5.19 (s, 12H, H_x), 5.00 (t, 2H, H_2), 4.91 (t, 12H, H_m), 4.36 (t, 1H, H_3), 4.12 (d, 12H, H_i), 2.81 (s, 18H, CH_3 (cap)), 2.71 (m, 12H, $CH_2CH_2C_6H_5$ (feet)), 2.52 (m, 12H, $CH_2CH_2C_6H_5$ (feet)), 1.06 (m, 2H, H_a), 0.05 (m, 2H, H_b), -0.60 (m, 2H, H_c), -0.97 (m, 2H, H_d), -2.58 (t, 2H, H_e). 2D COSY spectra were also recorded.

^{1}H NMR (500 MHz, nitrobenzene-d_5, 400 K) δ 7.68 (s, 3H, H_p), 7.52 (s, 3H, H_p), 7.32 (d, 24H, H_{ortho} (feet)), 7.21 (t, 24H, H_{meta} (feet)), 7.14 (t, 12H, H_{para} (feet)), 6.60 (d, 2H, H_1), 6.04 (d, 12H, H_o), 6.01 (s, 6H, H_{ac}), 5.40 (t, 2H, H_2), 5.34 (s, 12H, H_x), 5.27 (brt, 12H, H_m), 4.68 (t, 1H, H_3), 4.46 (d, 12H, H_i), 2.91 (brm, 66H, CH_3 (cap) and $CH_2CH_2C_6H_5$ (feet) and $CH_2CH_2C_6H_5$ (feet)), 1.32 (m, 2H, H_a), -0.38 (m, 2H, H_b), -0.26 (m, 2H, H_c), -0.60 (m, 2H, H_d), -2.08 (t, 2H, H_e).



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MS (MALDI) *m/z* (rel intensity) 3601 ((M•$C_{221}H_{208}O_{37}$ + Na^+)$^+$; 100), calcd for $C_{221}H_{208}O_{37}$•Na^+ = 3599.

5•8. Similar to procedure A. Hexa-hydroxyl trimer **4** (11.5 mg, 3.73 μmol), K_2CO_3 (51.3 mg, 372 μmol), KI (38.7 mg, 233 μmol), NFP (10 mL), **8** (884.6 mg, 5.26 mmol), 2,4,6-tris(bromomethyl)-mesitylene (9.8 mg, 24.6 μmol). Precipitation with $CHCl_3$/hexanes gave **5•8** as a white solid (2.8 mg, 19 %).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.30-7.14 (m, 60H, ArH (feet)), 7.00 (s, 6H, H_{p1}), 6.81 (s, 6H, H_{p2}), 6.00 (d, 12H, H_o), 5.87 (s, 6H, H_{ac}), 5.05 (s, 12H, C*H*$_2$ (cap)), 4.95 (t, 12H, H_m), 4.34 (s, 3H, ArH (guest)), 4.31 (d, 12H, H_i), 2.72 (m, 24H, $CH_2CH_2C_6H_5$), 2.67 (s, 18H, C*H*$_3$ (cap)), 2.53 (m, 24H, $CH_2CH_2C_6H_5$), 0.53 (s, 9H, OC*H*$_3$ (guest)).

MS (MALDI) *m/z* (rel intensity) 3592 ((M•$C_{231}H_{204}O_{39}$ + Na^+)$^+$; 100), calcd for $C_{221}H_{204}O_{39}$•Na^+ = 3591.

5•9. Similar to procedure A. Hexa-hydroxyl trimer **4** (11.2 mg, 3.63 μmol), K_2CO_3 (63.0 mg, 457 μmol), KI (58.9 mg, 355 μmol), NFP (8 mL), **9** (2 mL, μmol), 2,4,6-tris(bromomethyl)mesitylene (5.0 mg, 12.5 μmol). Precipitation with $CHCl_3$/hexanes gave **5•9** as a white solid (7.3 mg, 56 %).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.29-7.15 (m, 60H, Ar*H* (feet)), 7.00 (s, 6H, H_{p1}), 6.80 (s, 6H, H_{p2}), 5.98 (d, 12H, H_o), 5.86 (s, 6H, H_{ac}), 5.12 (s, 3H, Ar*H* (guest)), 5.11 (s, 12H, H_x), 4.94 (t, 12H, H_m), 4.28 (d, 12H, H_i), 2.78-2.63 (m, 24H, $CH_2CH_2C_6H_5$), 2.70 (s, 18H, C*H*$_3$ (cap)), 2.63-2.41 (m, 24H, $CH_2CH_2C_6H_5$), 0.77 (q, 6H, C*H*$_2$CH$_3$ (guest)), -2.03 (s, 9H, CH_2CH_3 (guest)).

MS (MALDI) *m/z* (rel intensity) 3585 (($C_{231}H_{210}O_{36}$ + Na^+)$^+$; 100), calcd for $C_{231}H_{210}O_{36}$•Na^+ = 3585.

5•7. Similar to procedure A. Hexa-hydroxyl trimer **4** (10.1 mg, 3.27 μmol), K_2CO_3 (50.7 mg, 367 μmol, 112 equiv.), KI (38.4 mg, 231 μmol, 71 equiv.), NFP (10 mL), 1,3,5-trimethylbenzenecarboxylate (962.9 mg, 3.82 mmol), 2,4,6-tris(bromomethyl)mesitylene (6.0 mg, 15.0 μmol, ~4.5 equiv.). Precipitation with $CHCl_3$/hexanes gave **5•7** as a white solid (1.9 mg, 16 %).

^{1}H NMR (nitrobenzene-d_5, 500 MHz, 400 K) δ 7.62 (s, 6H, H_{p1} or H_{p2}), 7.57 (s, 3H, ArH (guest)), 7.34 (d, 24H, H_{ortho} (feet)), 7.22 (t, 24H, H_{meta} (feet)), 7.15 (t, 12H, H_{para} (feet)), 6.25 (s, 6H, H_{ac}), 6.00 (d, 12H, H_o), 5.36 (t, 12H, H_m), 5.08 (s, 12H, H_x), 4.79 (d, 12H, H_i), 3.03-2.86 (m, 66H, $CH_2CH_2C_6H_5$ and CH_3 (cap) and $CH_2CH_2C_6H_5$), -0.10 (s, 9H, $COOCH_3$ (guest)). Note, signal(s) for the other six H_p protons are hidden under nitrobenzene-d_5 residual proton signals.

^{1}H NMR ($CDCl_3$, 500 MHz, 250 K) δ 7.29-7.14 (brm, 63H, Ar*H* (feet) and Ar*H* (guest) and H_1 and H_2 and H_3), 6.90 (s, 12H, H_{p1}), 6.85 (s, 6H, H_{p2}' or H_{p2}"), 6.66 (s, 6H, H_{p2}' or H_{p2}"), 6.06 (brd, 6H, H_o or H_o'), 6.98 (s, 6H, H_{ac}), 5.85 (brd, 6H, H_o or H_o'),4.98 (t, 6H, H_m or H_m'), 4.94 (t, 6H, H_m or H_m'), 4.92 (d, 6H, H_x' or H_x"), 4.83 (d, 6H, H_x' or H_x"), 4.58 (d, 6H, H_i or H_i'), 4.30 (d, 6H, H_i or H_i'), 2.72 (brm, 24H, $CH_2CH_2C_6H_5$), 2.53 (s, 18H, CH_3 (cap)), 2.53 (brm, 24H, $CH_2CH_2C_6H_5$), -0.66 (s, 9H, H_a). See Chart 1 for guest proton labels.

MS (MALDI) *m/z* (rel intensity) 3677 (($C_{227}H_{204}O_{42}$ + Na^+)$^+$; 85), calcd for $C_{227}H_{204}O_{42}$•Na^+ = 3675.

5•6. Procedure C. Procedure A, except at room temperature. Hexa-hydroxyl trimer **4** (28.6 mg, 9.26 μmol), K_2CO_3 (167.9 mg, 1.22 mmol), KI (167.5 mg, 1.01 mmol), NFP (10 mL), 1,3,5-tris(ethynyl)benzene[4] (51.4 mg, 325 μmol), 2,4,6-tris(bromomethyl)mesitylene (15.6 mg, 39.1 μmol). Precipitation with $CHCl_3$/hexanes gave **5•6** as a white solid (12.4 mg, 40 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.29-7.16 (m, 60H, Ar*H* (feet)), 6.98 (s, 3H, H_{p1}), 6.80 (s, 3H, H_{p2}), 5.99 (d, 12H, H_o), 5.91 (s, 3H, H_b (guest)), 5.87 (s, 6H, H_{ac}), 5.06 (s, 12H, H_x), 4.94 (t,

12H, H_m), 4.37 (d, 12H, H_i), 2.72 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.67 (s, 18H, CH_3 (cap)), 2.53 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), -1.24 (s, 3H, H_a). See Chart 1 for guest proton labels.

MS (MALDI) *m/z* (rel intensity) 3574 (($C_{231}H_{198}O_{36} + Na^+$)$^+$; 100), calcd for $C_{231}H_{198}O_{36}\bullet Na^+$ = 3573.

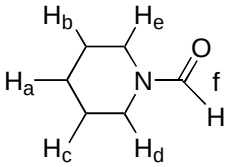
13•6. Procedure C, except that 1,3,5-tris(bromomethyl)benzene[3] (14.0 mg, 39.3 μmol, 4.0 equiv.) was used instead of 2,4,6-tris(bromomethyl)mesitylene. Hexa-hydroxyl trimer **4** (31.0 mg, 0.010 mmol), K_2CO_3 (152.01 mg, 1.10 mmol), KI (124.7 mg, 0.75 mmol, 75 equiv.), NFP (30 mL), 1,3,5- tris(ethynyl)benzene[4] (58.0 mg, 0.384 mmol). Carceplex **13•6** was isolated as a white solid (21.0 mg, 60 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.27-7.08 (m, 66H, ArH (cap) and ArH (feet)), 6.94 (s, 3H, H_{p1}), 6.80 (s, 3H, H_{p2}), 6.00 (d, 12H, H_o), 5.99 (s, 6H, H_{ac}), 5.87 (s, 3H, H_b), 4.91 (t, 12H, H_m), 4.79 (s, 12H, H_x), 4.33 (d, 12H, H_i), 2.71 (brm, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.52 (brm, 24H, $CH_2CH_2C_6H_5$ (feet)), -1.18 (s, 3H, H_a). See Chart 1 for guest proton labels.

MS (MALDI) *m/z* (rel intensity) 3491 (($C_{225}H_{186}O_{36} + Na^+$)$^+$; 100), calcd for $C_{225}H_{186}O_{36}\bullet Na^+$ = 3489.

5•(NFP)$_2$. Procedure C was used with hexa-hydroxyl trimer **4** (15.6 mg, 5.05 μmol), K_2CO_3 (41.2 mg, 299 μmol), KI (52.0 mg, 313 μmol), 2,4,6-tris(bromomethyl)mesitylene (12.9 mg, 32.3 μmol), and NFP (10 mL). Carceplex **5**•$(NFP)_2$ was isolated as a white solid (6.1 mg, 26 %). Note that **5**•$(NFP)_2$ was isolated as a mixture with **5**•NFP (~2:1 **5**•$(NFP)_2$:**5**•NFP).

^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.28-7.16 (m, 60H, ArH (feet)), 6.99 (s, 3H, H_{p1}), 6.77 (s, 3H, H_{p2}), 5.99 (d, 12H, H_o), 5.84 (s, 6H, H_{ac}), 5.19 (s, 12H, H_x), 4.93 (t, 12H, H_m), 4.30 (d, 12H, H_i), 2.84 (s, 18H, CH_3 (cap)), 2.72 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.52 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 1.70 (m, 4H, H_d or H_e), 1.51 (m, 4H, H_d or H_e), 0.13 (m, 4H, H_b or H_c), -0.01 (m, 4H, H_b or H_c), -0.32 (m, 4H, H_a). 2D COSY spectra were also recorded. C*H*O is hidden under H_o for **5**•$(NFP)_2$ at 6.00 ppm. This is based on the observation that the C*H*O shifts downfield from the H_i protons in spectra in nitrobenzene-d_5 at temperatures above 350 K.



MS (MALDI) *m/z* (rel intensity) 3650 (($C_{231}H_{214}O_{38}N_2 + Na^+)^+$; 100), calcd for $C_{227}H_{210}O_{38}N_2 \bullet Na^+$ = 3649.

5•(DMA)$_2$. Procedure C was used with hexa-hydroxyl trimer **4** (22.9 mg, 7.40 μmol), K_2CO_3 (53.3 mg, 384 μmol), KI (57.4 mg, 346 μmol), DMA (10 mL), and 2,4,6-tris(bromomethyl)mesitylene (9.9 mg, 39.1 μmol). Carceplex **5•**$(DMA)_2$ was obtained as a white solid (8.8 mg, 33 %).

^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.27-7.15 (m, 60H, Ar*H* (feet)), 6.99 (s, 3H, H_{p1}), 6.78 (s, 3H, H_{p2}), 5.96 (d, 12H, H_o), 5.83 (s, 6H, H_{ac}), 5.13 (s, 12H, H_x), 4.93 (t, 12H, H_m), 4.31 (d, 12H, H_i), 2.78 (s, 18H, C*H*$_3$ (cap)), 2.71 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.54 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 1.44 (s, 6H, NC*H*$_3$), 0.56 (s, 6H, NC*H*$_3$), -0.97 (s, 6H, COC*H*$_3$). 2D COSY spectra were also recorded.

MS (MALDI) *m/z* (rel intensity) 3596 (($C_{227}H_{210}O_{38}N_2 + Na^+)^+$; 100), calcd for $C_{227}H_{210}O_{38}N_2 \bullet Na^+$ = 3597.

13•(DMA)$_2$. Procedure C, except 1,3,5-tris(bromomethyl)-benzene[3] (4.9 mg, 13.7 μmol) was used instead of 2,4,6-tris(bromomethyl)mesitylene with hexa-hydroxyl trimer **4** (10.8 mg, 3.50 μmol), K_2CO_3 (51.0 mg, 370 μmol), KI (37.4 mg, 225 μmol), DMA (10 mL). Carceplex **13•**$(DMA)_2$ was obtained as a white solid (9.9 mg, 81 %).

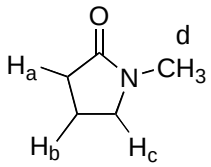
^{1}H NMR (400 MHz, $CDCl_3$ 300 K) δ 7.44 (s, 6H, Ar*H* (cap)), 7.27-7.15 (m, 60H, Ar*H* (feet)), 6.97 (s, 3H, H_{p1}), 6.75 (s, 3H, H_{p2}), 5.97 (d, 12H, H_o), 5.91 (s, 6H, H_{ac})), 4.95 (s, 12H, H_x), 4.91 (t, 12H, H_m), 4.30 (d, 12H, H_i), 2.71 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.51 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 1.41 (s, 6H, NC*H*$_3$), 0.44 (s, 6H, NC*H*$_3$), -0.94 (s, 6H, COC*H*$_3$).

MS (MALDI) *m/z* (rel intensity) 3514 (($C_{227}H_{210}O_{38}N_2 + Na^+)^+$; 100), calcd for $C_{227}H_{210}O_{38}N_2 \bullet Na^+$ = 3513.

5•(NMP)$_2$. Procedure C was used with hexa-hydroxyl trimer **4** (14.9 mg, 4.83 μmol), K_2CO_3 (28.6 mg, 172 μmol), KI (34.4 mg, 249 μmol), NMP (13 mL), 2,4,6-tris(bromomethyl)-mesitylene (7.3 mg, 183 μmol). Carceplex **5•**$(NMP)_2$ was obtained as a white solid (8.8 mg, 33 %).

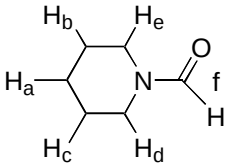
^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.30-7.10 (m, 60H, Ar*H* (feet)), 6.99 (s, 3H, H_{p1}), 6.77 (s, 3H, H_{p2}), 5.96 (d, 12H, H_o), 5.82 (s, 6H, H_{ac}), 5.14 (s, 12H, H_x), 4.93 (t, 12H, H_m), 4.31 (d, 12H, H_i), 2.79 (s, 18H, C*H*$_3$ (cap)), 2.70 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.49 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 1.87 (m, 4H, H_a), 0.16 (m, 4H, H_b), 0.06 (m, 4H, H_c), -0.53 (s, 6H, H_d). 2D COSY spectra were also recorded.

MS (MALDI) *m/z* (rel intensity) 3620 (($C_{229}H_{210}O_{38}N_2 + Na^+)^+$; 100), calcd for $C_{229}H_{210}O_{38}N_2 \bullet Na^+$ = 3621.



5•(NFP•DMSO). Procedure A was used with hexa-hydroxyl trimer **4** (10.8 mg, 3.50 μmol), K_2CO_3 (42.1 mg, 305 μmol), KI (32.3 mg, 195 μmol), NFP (10 mL), DMSO (60 μL), 2,4,6-tris(bromo- methyl)mesitylene (10.3 mg, 25.8 μmol). Carceplex **5•**(NFP•DMSO) was obtained as a white solid (4.7 mg, 37 %). Note that **5•**(NFP•DMSO) was isolated with ~7 % **5•**NFP.

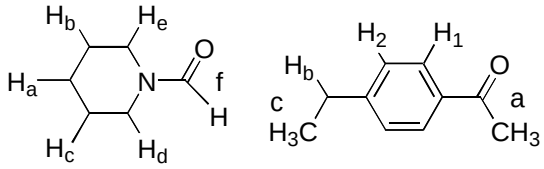
^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.30-7.13 (m, 60H, Ar*H* (feet)), 6.98 (s, 3H, H_{p1}), 6.77 (s, 3H, H_{p2}), 6.43 (s, 1H, H_f), 5.97 (d, 12H, H_o), 5.80 (s, 6H, H_{ac}), 5.16 (s, 12H, H_x), 4.93 (t, 12H, H_m), 4.29 (d, 12H, H_i), 2.81 (s, 18H, C*H*$_3$ (cap)), 2.71 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 2.51 (m, 24H, $CH_2CH_2C_6H_5$ (feet)), 1.73 (brm, 2H, H_d or H_e), 1.36 (brm, 2H, H_d or H_e), -0.13 (brm, 2H, H_b or H_c), -0.02 (brm, 2H, H_b or H_c), -0.40 (brs, 6H, $(CH_3)_2SO$), -0.59 (brm, 2H, H_a). 2D COSY spectra were also recorded.



MS (MALDI) *m/z* (rel intensity) 3615 (($C_{227}H_{198}O_{38}NS + Na^+)^+$; 100), calcd for $C_{227}H_{198}O_{38}NS \bullet Na^+$ = 3614.

5•(NFP•4'-ethylacetophenone). Procedure A was used with hexa-hydroxyl trimer **4** (10.1 mg, 3.27 μmol), K_2CO_3 (42.5 mg, 308 μmol), KI (42.8 mg, 258 μmol), NFP (10 mL), 4'-ethylacetophenone (1 mL), 2,4,6-tris(bromomethyl)mesitylene (9.4 mg, 23.6 μmol). Carceplex **5•**(NFP•4'-ethylacetophenone) was obtained as a white solid (1.2 mg, 10 %).

^{1}H NMR (500 MHz, nitrobenzene-d_5, 400 K) δ 7.72 (s, H_p), 7.68 (s, H_p), 7.58 (s, H_p), 7.55 (s, H_p), 7.35-7.12 (brm, 60H, Ar*H* (feet)), 6.63 (brd, 2H, H_1), 6.33 (brd, 2H, H_o), 6.20 (brs, 2H, H_{ac}), 6.15 (brm, 4H, H_{ac} and H_o), 6.11 (brd, 2H, H_o), 6.08 (brs, 2H, H_{ac}), 6.03 (brd, 2H, H_o), 6.00 (brd, 2H, H_o), 5.93 (brd, 2H, H_2), 5.91 (brd, 2H, H_o), 5.40-5.25 (brm, 20H, H_xs and H_ms), 5.20 (brd, 2H, H_x), 5.10 (brd, 2H, H_x), 5.06 (brd, 2H, H_i), 4.76 (brd, 2H, H_i), 4.67 (brd, 2H, H_i), 4.63 (brd, 2H, H_i), 4.57 (brd, 2H, H_i), 4.54 (brd, 2H, H_i), 4.42 (brd, 2H, H_i), 2.97 (brm, 66H, $CH_2CH_2C_6H_5$ and $CH_2CH_2C_6H_5$ and CH_3 (cap)), 1.66 (brm, 2H, H_d or H_e), 1.47 (brm, 2H, H_d or H_e), 1.09 (q, 2H, CH_2CH_3), -0.02 (brm, 2H, H_b or H_c), -0.41 (brm, 2H, H_b or H_c), (s, 3H, C(CO)CH_3), -1.15 (brm, 2H, H_a), -1.89 (t, 3H, CH_2CH_3). 2 D COSY spectra were also recorded.

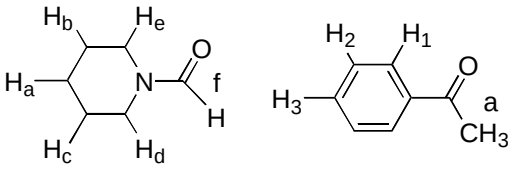


MS (MALDI) *m/z* (rel intensity) 3684 (($C_{235}H_{215}O_{38}N + Na^+)^+$; 100), calcd for $C_{235}H_{215}O_{38}N \bullet Na^+$ = 3684.

5•(NFP•acetophenone). Procedure A was used with hexa-hydroxyl trimer **4** (12.5 mg, 4.05 μmol), K_2CO_3 (41.2 mg, 299 μmol), KI (31.9 mg, 192 μmol), NFP (10 mL), acetophenone (100

μL), 2,4,6-tris(bromomethyl)mesitylene (9.8 mg, 24.6 μmol). Carceplex **5**•(NFP•acetophenone) was obtained as a white solid (2.2 mg, 10 %). Note that **5**•(NFP•acetophenone) was isolated as a mixture containing 52 % **5**•NFP.

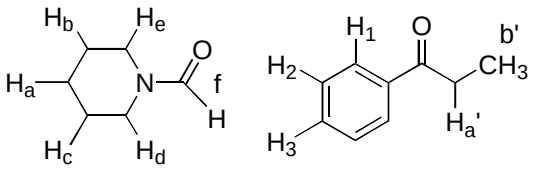
^{1}H NMR (500 MHz, nitrobenzene-d_5, 400 K) δ 7.69 (s, 6H, H_{p1} or H_{p2}), 7.53 (s, 6H, H_{p1} or H_{p2}), 7.32 (brd, 24H, H_{ortho} (feet)), 7.21 (brt, 24H, H_{meta} (feet)), 7.14 (brt, 12H, H_{para} (feet)), 6.73 (d, 2H, H_1), 6.12 (s, 6H, H_{ac}), 6.11 (d, 12H, H_o), 5.89 (t, 2H, H_2), 5.69 (t, 2H, H_3), 5.53 (s, 1H, C*H*O (NFP guest)), 5.29 (s, 12H, H_x), 5.27 (t, 12H, H_m), 4.66 (d, 12H, H_o), 3.00-2.85 (brm, 66H, $CH_2CH_2C_6H_5$ and $CH_2CH_2C_6H_5$ and CH_3 (cap)), 1.67 (brm, 2H, H_d or H_e), -0.33 (brm, 2H, H_b or H_c), -0.46 (brm, 2H, H_b or H_c), -0.60 (s, 3H, $COCH_3$), -0.80 (brm, 2H, H_a). Note that either H_d or H_e is hidden under the H_2O signal at ~1.85ppm, as indicated in the COSY spectrum.



MS (MALDI) *m/z* (rel intensity) 3664 (($C_{233}H_{211}O_{38}N + Na^+$)$^+$; 100), calcd for $C_{233}H_{211}O_{38}N$•Na^+ = 3665.

5•(NFP•propiophenone). Procedure A was used with hexa-hydroxyl trimer **4** (10.9 mg, 3.53 μmol), K_2CO_3 (46.0 mg, 333 μmol), KI (32.0 mg, 193 μmol), NFP (10 mL), propiophenone (60 μL), 2,4,6-tris(bromomethyl)mesitylene (13.1 mg, 32.9 μmol). Carceplex **5**•(NFP•propiophenone) was isolated as a white solid (1.9 mg, 15 %). Note that carceplex **5**•(NFP•propiophenone) was isolated as a mixture containing 65 % **5**•NFP and **5**•$(NFP)_2$).

^{1}H NMR (500 MHz, nitrobenzene-d_5, 400K) δ 7.69 (s, 6H, H_{p1} or H_{p2}), 7.67 (s, 6H, H_{p1} or H_{p2}), 7.33 (brd, 24H, H_{ortho} (feet)), 7.21(brt, 24H, H_{meta} (feet)), 7.14 (brt, 12H, H_{para} (feet)), 6.90 (d, 2H, H_1), 6.14 (d, 12H, H_o), 6.07 (s, 6H, H_a), 5.50 (t, 2H, H_2), 5.34 (s, 12H, H_x), 5.27 (t, 12H, H_m), 5.14 (s, 1H, H_f), 5.04 (t, 1H, H_3), 4.64 (d, 12H, H_o), 2.93 (brm, 66H, $CH_2CH_2C_6H_5$ and $CH_2CH_2C_6H_5$ and CH_3 (cap)), 1.71 (m, 2H, H_d or H_e), 1.33 (m, 2H, H_d or H_e), 0.19 (q, 2H, H_a'), -0.24 (brm, 2H, H_b or H_c), -0.36 (brm, 2H, H_b or H_c), -1.01 (brm, 2H, H_a), -2.24 (t, 3H, H_b'). 2D COSY spectra were also recorded.



MS (MALDI) *m/z* (rel intensity) 3669 (($C_{234}H_{213}O_{38}N + Na^+)^+$; 100), calcd for $C_{234}H_{213}O_{38}N•Na^+$ = 3670.

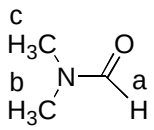
5•(DMSO)$_3$. Procedure C was used with hexa-hydroxyl trimer **4** (11.0 mg, 3.56 μmol), K_2CO_3 (61.4 mg, 445 μmol), KI (52.3 mg, 315 μmol), NFP (8 mL), DMSO (2 mL), 2,4,6-tris(bromomethyl)mesitylene (4.9 mg, 12.3 μmol). Carceplex **5**•$(DMSO)_3$ was obtained as a white solid (3.1 mg, 13 %).

^{1}H NMR (400 MHz, sieve-dried $CDCl_3$, 300 K) δ 7.30-7.15 (m, 60H, ArH (feet)), 7.00 (s, 3H, H_{p1}), 6.74 (s, 3H, H_{p2}), 5.91 (d, 12H, H_o), 5.78 (s, 6H, H_{ac}), 5.19 (s, 12H, H_x), 4.94 (t, 12H, H_m), 4.50 (d, 12H, H_i), 2.73 (s, 18H, C*H*$_3$ (cap)), 2.72 (m, 24H, C*H*$_2$CH$_2$C$_6$H$_5$ (feet)), 2.51 (m, 24H, C*H*$_2$CH$_2$C$_6$H$_5$ (feet)) -0.06 (brs, 18H, (C*H*$_3$)$_2$SO).

MS (MALDI) *m/z* (rel intensity) 3659 (($C_{225}H_{210}O_{37}S_3 + Na^+)^+$; 100), calcd for $C_{225}H_{210}O_{37}S_3•Na^+$ = 3657.

13•(DMF)$_3$. Procedure C was used, except 1,3,5-tris(bromomethyl)benzene[3] (2.2 mg, 6.18 μmol) was used instead of 2,4,6-tris(bromomethyl)-mesitylene with A,C-trimer **4** (5.0 mg, 1.62 μmol), K_2CO_3 (20.3 mg, 0.147 mmol, 24 equiv.), KI (4.7 mg, 0.028 mmol, 4.5 equiv.), DMF (5 mL). Carceplex **13**•$(DMF)_3$ was obtained as a white solid (2.3 mg, 40 %).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.42 (s, 6H, ArH (cap)), 7.30-7.10 (m, 60H, ArH (feet)), 6.96 (s, 3H, H_{p1}), 6.75 (s, 3H, H_{p2}), 5.94 (d, 12H, H_o), 5.90 (s, 3H, H_a), 5.88 (s, 6H, H_{ac}), 4.96 (s, 12H, H_x), 4.92 (t, 12H, H_m), 4.47 (d, 12H, H_i), 2.70 (m, 24H, CH$_2$C*H*$_2$C$_6$H$_5$ (feet)), 2.50 (m, 24H, C*H*$_2$CH$_2$C$_6$H$_5$ (feet)), 0.97 (s, 9H, H_c), -0.17 (s, 9H, H_b).



MS (MALDI) *m/z* (rel intensity) 3560 (($C_{222}H_{201}O_{39}N_3 + Na^+)^+$; 100), calcd for $C_{225}H_{210}O_{37}S_3 \bullet Na^+$ = 3558.

NMR Spectroscopy. NMR spectra were recorded on Bruker Avance 400 or AMX 500 spectrometers equipped with inverse-gradient probes. Prior to beginning experiments at different temperatures and at different solvents, the probe was tuned. Before starting all 2D (NOESY, ROESY, COSY, HMQC) experiments and 1D EXSY experiments, the 90° pulse width was optimized. Chemical shifts are reported relative to the residual proton signals in the deuterated solvent used (i.e., $CDCl_3$, CD_2Cl_2, $(CDCl_2)_2$, C_6D_6, toluene-d_8, pyridine-d_5 and nitrobenzene-d_5). All deuterated solvents used were purchased from Cambridge Isotopes Inc.

Temperature calibrations[5] were performed for all kinetic runs (1D EXSY experiments and coalescence temperature measurements). Calibration standards (4 % methanol in methanol-d_4 (T < 300 K) or 80 % ethylene glycol in DMSO-d_6 (T > 300)) provided by Bruker were equilibrated in the probe of the spectrometer for at least 10 min before recording a ^{1}H NMR spectrum. The temperature dependent Δδ values between the hydroxyl protons and the methylene (ethylene glycol) or methyl protons (methanol), respectively, were measured and the actual probe temperature was interpolated from a calibration graph provided by Bruker. The temperatures reported were the temperatures that were measured and should not differ from the actual temperature by more than 1-2 °C.

Activation energies ($\Delta G_c^{\ddagger}$) in kcal/mole for the two-site exchange processes in **5•7** and **5**•(NFP•DMSO) were calculated using equation S1,

$$\Delta G_c^{\ddagger} = RT_c[\ln(k_B/\pi h) + \ln(T_c/\Delta\nu)] \qquad \text{equation S1}$$

where R (universal gas constant) = 1.9872 cal K^{-1} mole^{-1}; k_B (Boltzman constant) = 3.2995×10^{-24} cal K^{-1}; h (Planck's constant) = 1.5836×10^{-34} cal s; T_c is the coalescence temperature in K; and $\Delta\nu$ is the chemical shift difference, in Hz.[6] This equation only applies to exchange between two equally populated noncoupled spin systems.

The activation energy ($\Delta G^{\ddagger}$) for the exchange process observed in complex **17•6** was calculated using the method reported by Shanan-Atidi and Bar-Eli.[7] This method provides a quick and convenient way of determining the activation energies from the coalescence temperature for two unequally populated noncoupled spin systems that are in exchange. X ($X = 2\pi\Delta\nu\tau$), where τ is the average lifetime of the two spin states and $\Delta\nu$ is the frequency difference in Hz) is first is calculated from the population difference ΔP, with the equation S2:

$$\Delta P = P_A - P_B = \left(\frac{X^2 - 2}{3}\right)^{3/2} \frac{1}{X} \qquad \text{equation S2}$$

For **17•6**, $\Delta P = 2 - 1 = 1$, and therefore, $X = 2.83$. The free energies of exchange between both spin systems are then calculated using equations S3 and S4,

$$\Delta G_A^{\ddagger} = RT_c \ln\left[\frac{k}{h\pi}\left(\frac{T_c}{\Delta\nu}\right)\left(\frac{X}{1-\Delta P}\right)\right] \qquad \text{equation S3}$$

$$\Delta G_B^{\ddagger} = RT_c \ln\left[\frac{k}{h\pi}\left(\frac{T_c}{\Delta\nu}\right)\left(\frac{X}{1+\Delta P}\right)\right] \qquad \text{equation S4}$$

$\Delta G_A^{\ddagger}$ is undefined, but $\Delta G_B^{\ddagger}$ can be solved by inserting $\Delta\nu = 39.0$ Hz, $T_c = 330$ K, and $X = 2.83$.

1D EXSY Experiments. All 1D EXSY (NOESY) experiments were performed on a Bruker Avance 400 MHz spectrometer. The pulse sequence used was selnogp.2 (Avance-version- 00/02/07), which is a 1D NOESY that uses selective refocusing with a shaped pulse. Dipolar coupling may be due to NOE or chemical exchange. NOE was discounted for carceplex **5•7** and complexes **3•6** and **15•6** from the broadening and coalescence of exchanging signals observed by variable temperature ^{1}H NMR spectroscopy.

For each specific set of experiments, a relaxation delay (d1) of 5 T_1s of the exchanging nuclei was used. T_1s were measured by the inversion-recovery method using the Bruker pulse program called invgs (avance- version- 00/02/07). A total of ten experiments were performed at different relaxation delays of 0.001 s, 0.003 s, 0.010 s, 0.030 s, 0.100 s, 0.300 s, 1.00 s, 3.00 s, 10.0 s, 30.0 s. Peak heights were measured using the Bruker xwinnmr software and T_1s were calculated using the simfit command from the equation:

$$\mathrm{I}_t = \mathrm{I}_0 + \mathrm{P}e^{-t/\mathrm{T}_1}$$

where I_t is the peak height at time t (s), I_0 is the initial peak height, P is a constant and T_1 is the longitudinal relaxation time constant (in s).

Each set of EXSY experiments involved the selective irradiation of the signals for each exchanging nucleus at a series of at least five mixing times (t_m). The choice of t_ms depended on the observed rate of exchange, which could be adjusted by changing the temperature. Temperatures were set so that integration of the irradiated (I_{irr}) and response (I_r) signals in each EXSY spectrum gave ratios (I_{irr}:I_r) between 10:1 and 1:1 at t_ms below 400 ms. Relative peak areas were obtained from the integration values of both irradiated and response signals in each 1D ^{1}H-^{1}H EXSY spectrum obtained using Bruker Win NMR 1D software (ver. 6.0). The equilibrium magnetization ($\mathbf{M_0}$) was measured from the integration of the signals of interest in the 1D ^{1}H spectrum. Rate constants were calculated using matrix analysis[8] from the equation:

$$\mathbf{M}\,\mathbf{M_0^{-1}} = e^{-\mathbf{R}/t_m} \qquad \text{equation S5}$$

where the variables in bold are $n \times n$ (n = 1, 2, 3…) square matrices: **M** is the matrix of integration intensities at a particular mixing time (t_m, in s), $\mathbf{M_0}$ is the matrix of equilibrium magnetization values and **R** is the matrix containing the site-to-site rate constants. The matrix **R** was calculated from the linearized form of equation S5:

$$\mathbf{R}t_m = -\ln[\mathbf{M}\mathbf{M_0^{-1}}] = -\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X^{-1}} \qquad \text{equation S6}$$

where **X** is the square matrix that diagonalizes $\mathbf{MM_0^{-1}}$ to $\mathbf{\Lambda}$, so that ln $\mathbf{\Lambda}$ is a diagonal matrix whose elements are the logarithms of the eigenvalues of $\mathbf{MM_0^{-1}}$. All matrix operations were performed using Maple 5.0 software. The individual first order site-to-site rate constants (in s^{-1}) that make up the matrix **R**, were obtained graphically by plotting each element of the matrix-$\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X^{-1}}$ versus t_m (see Figures S1-S3).[9] Note that for two-site exchange,

$$\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X^{-1}} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$$

Additional EXSY Data for Complexes 3•6 and 15•6. The kinetics of guest exchange for complexes **3•6** and **15•6** were examined by 1D NOESY (EXSY) spectroscopy at 330 K in nitrobenzene-d_5 (see Tables S1 and S2, and Figures S1 and S2). A sample calculation is shown for complex **3•6** from the EXSY data for t_m = 0.250 s.

Table S1 Additional 1D EXSY data for complex **3•6** (nitrobenzene-d_5, 330 K).

t_m (s)	I_{11} (G_{free})	I_{12} (G_{bound})	I_{21} (G_{free})	I_{22} (G_{bound})	a_{12}	a_{21}
0.050	7.90	1.00	1.00	6.79	0.14	0.14
0.100	4.08	1.00	1.00	3.37	0.27	0.28
0.150	2.82	1.00	1.00	2.34	0.41	0.41
0.200	2.18	1.00	1.00	1.78	0.55	0.56
0.250	1.90	1.00	1.00	1.47	0.68	0.69
0.300	1.71	1.00	1.00	1.28	0.81	0.83
0.350	1.56	1.00	1.00	1.17	0.94	0.96
0.400	1.49	1.00	1.00	1.08	1.05	1.07

I_{ij} ($i = j$) = Integration intensities of selectively irradiated signal. I_{ij} ($i = j$) = Integration intensities response signals. $a_{ij} = \mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements. G_{free} = free guest. G_{bound} = bound guest. Integration of ^{1}H NMR spectrum gave the ratio 1.02:1 for the signals at G_{free}:G_{bound}.

Sample calculation. From the integration in the 1D ^{1}H NMR spectrum, the ratio of free:bound (I_f:I_g) guest **6** was measured to be 1.02:1.00. Therefore,

$$\mathbf{M_o} = \begin{bmatrix} I_f & 0 \\ 0 & I_b \end{bmatrix} = \begin{bmatrix} 1.02 & 0.00 \\ 0.00 & 1.00 \end{bmatrix} \text{ and } \mathbf{M_o^{-1}} = \begin{bmatrix} 1/I_f & 0 \\ 0 & 1/I_b \end{bmatrix} = \begin{bmatrix} 1/1.02 & 0.00 \\ 0.00 & 1.00 \end{bmatrix}$$

At t_m = 0.250 s,

$$\mathbf{M} = \begin{bmatrix} I_{11} & I_{12} \\ I_{21} & I_{22} \end{bmatrix} = \begin{bmatrix} 1.90 & 1.00 \\ 1.00 & 1.47 \end{bmatrix}$$

Therefore,

$$\mathbf{MM_o^{-1}} = \begin{bmatrix} 1.87 & 0.98 \\ 1.00 & 1.47 \end{bmatrix}$$

Using Maple 5.0 the eigenvalues of $\mathbf{MM_0^{-1}}$ were calculated to be 0.47 and 2.49 and the eigenvectors of $\mathbf{MM_0^{-1}}$ were calculated to be

$$\begin{bmatrix} -0.63 \\ -0.78 \end{bmatrix} \text{ and } \begin{bmatrix} 0.77 \\ 0.64 \end{bmatrix}$$

Therefore,

$$\mathbf{X} = \begin{bmatrix} -0.63 & 0.77 \\ 0.78 & 0.64 \end{bmatrix} \text{ and } \mathbf{\Lambda} = \begin{bmatrix} 0.47 & 0.00 \\ 0.00 & 2.49 \end{bmatrix}$$

Using Maple 5.0, $\mathbf{X}^{-1}$, $\ln\mathbf{\Lambda}$, and then $\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ were calculated,

$$\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} 0.42 & 0.68 \\ 0.69 & 0.15 \end{bmatrix}$$

where $a_{12} = 0.68$ and $a_{21} = 0.69$ (Table 3.18). Note that

$$\mathbf{R} = \begin{bmatrix} k_{11} & k_{12} \\ k_{21} & k_{22} \end{bmatrix}$$

where the elements k_{ij} ($i, j = 1, 2$) are the rate constants for exchange from site i to j, which can be calculated from the average of slopes of the two plots of a_{12} and a_{21} vs t_m (equation S6, Figure S1). k_{ij} can also be determined from single point calculations at each t_m:

$$\mathbf{R} = \mathbf{R} = \frac{\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}}{t_m} = \begin{bmatrix} 0.42/0.25 & 0.68/0.25 \\ 0.69/0.25 & 0.15/0.25 \end{bmatrix} = \begin{bmatrix} 1.68 & 2.72 \\ 2.76 & 0.60 \end{bmatrix}$$

where $k_{12} = 2.7\ s^{-1}$ and $k_{21} = 2.8\ s^{-1}$.

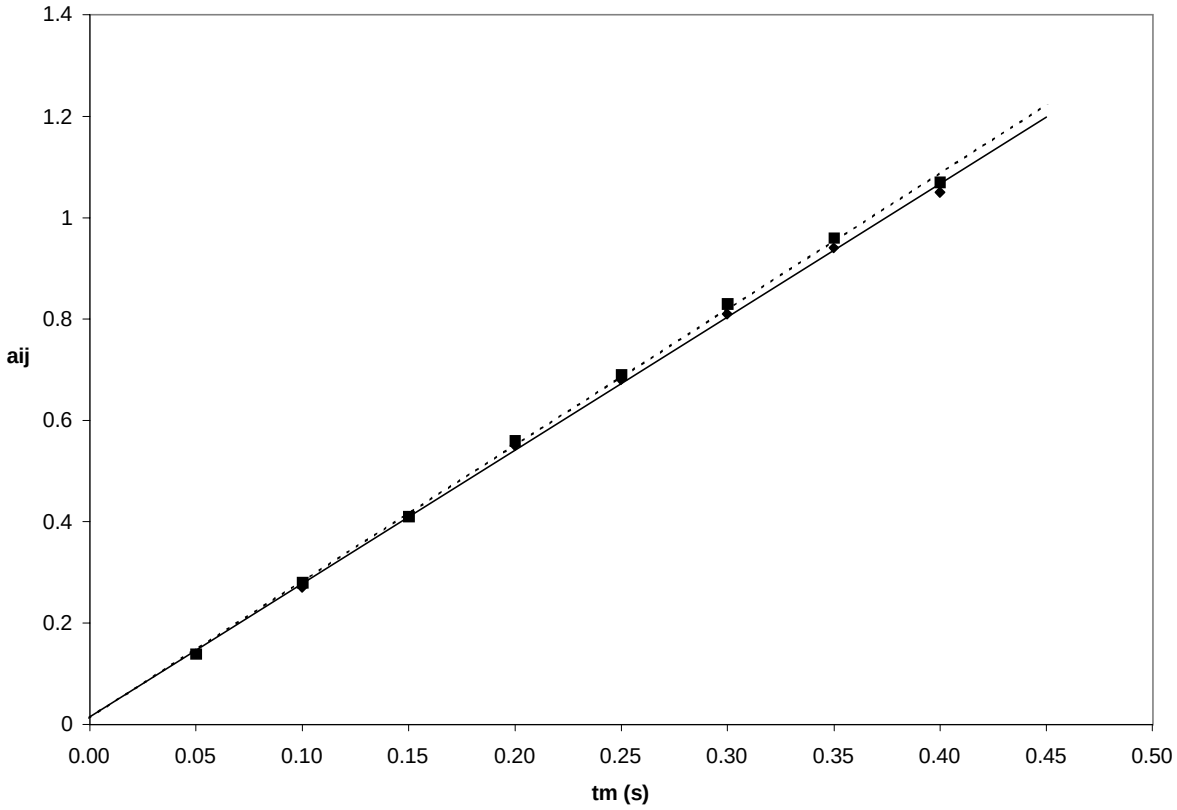


Figure S1 Plot of $\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements (a_{12} and a_{21}) versus mixing time (t_m) for complex **3•6** (nitrobenzene-d_5, 330 K). [**3**] = 6.37 mM, [**6**] = 12.4 mM and [**7**] = 318 mM. = a_{12} (slope (k_{12}) = (2.63 ± 0.8) s^{-1}, *y*-intercept = 0.0143, r^2 = 0.999). = a_{21} (slope (k_{21}) = (2.69 ± 0.8) s^{-1}, *y*-intercept = 0.0121, r^2 = 0.999). Errors in k_{ij}s were based on 95 % confidence limits from regression analysis.

Table 3.19 Additional 1D EXSY data for complex **15•6** (nitrobenzene-d_5, 330 K).

t_m (s)	$\mathbf{I_{11}}$ (G_{free})	$\mathbf{I_{12}}$ (G_{bound})	$\mathbf{I_{21}}$ (G_{free})	$\mathbf{I_{22}}$ (G_{bound})	a_{12}	a_{21}
0.050	10.12	1.00	9.83	1.00	0.11	0.09
0.100	4.27	1.00	5.03	1.00	0.22	0.20
0.150	3.16	1.00	3.13	1.00	0.35	0.30
0.200	2.41	1.00	2.40	1.00	0.46	0.41
0.250	2.05	1.00	1.99	1.00	0.61	0.53
0.300	1.71	1.00	1.74	1.00	0.71	0.63
0.350	1.60	1.00	1.61	1.00	0.80	0.71
0.400	1.44	1.00	1.44	1.00	0.93	0.82

I_{ij} ($i = j$) = Integration intensities of selectively irradiated signal. I_{ij} ($i = j$) = Integration intensities response signals. $a_{ij} = \mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements. G_{free} = free guest. G_{bound} = bound guest. Integration of ^{1}H NMR spectrum gave the ratio 1:1.14 for the signals at G_{free}:G_{bound}.

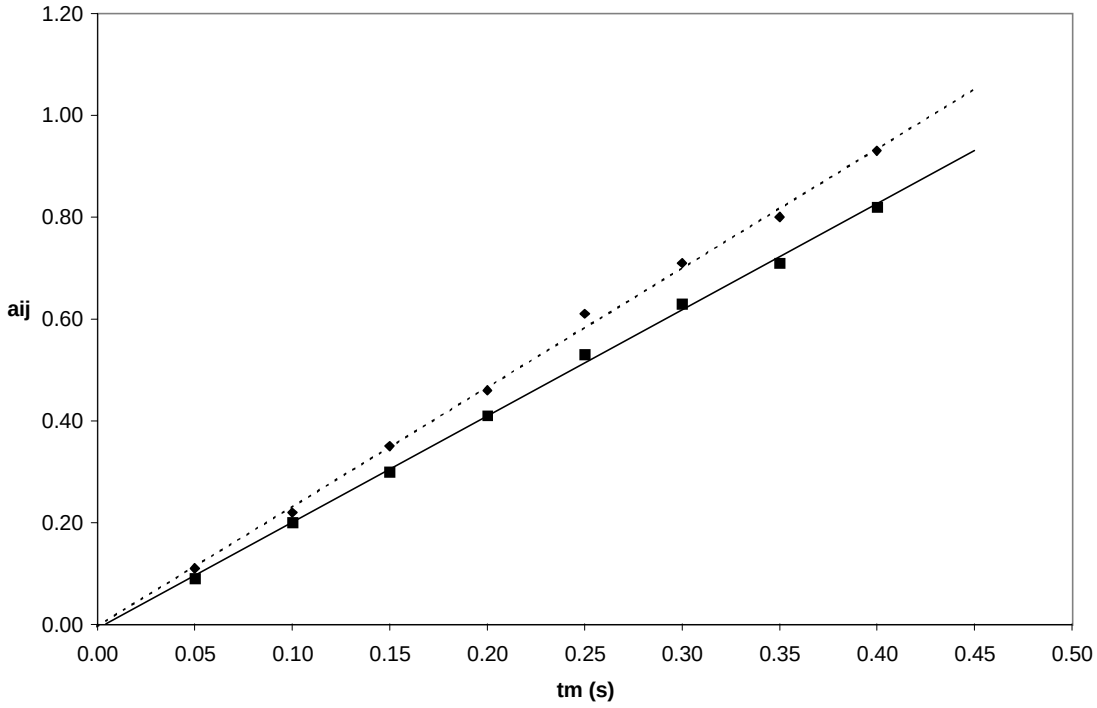


Figure S2 Plot of $\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements (a_{12} and a_{21}) vs. mixing time for complex **15•6** (nitrobenzene-d_5, 330 K). [**15**] = 5.67 mM and [**6**] = 8.22 mM. = a_{12} (slope (k_{12}) = 2.35 ± 0.11) s^{-1}, *y*-intercept = 0.005, r^2 = 0.998). = a_{21} (slope (k_{21}) = (2.09 ± 0.08) s^{-1}, *y*-intercept = 0.009, r^2 = 0.999). Errors in k_{ij}s were based on 95 % confidence limits from regression analysis.

Additional 1D EXSY Data for Trimer Carceplex 5•7. The individual elements a_{ij}, (i, j = 1, 2) of the matrix $\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ were calculated at various randomized mixing times at 267 K in $CDCl_2$ for **5•7** are shown in Table S3. The rate constants were obtained from the linear plots shown in Figure S3.

Table S3 Additional 1D EXSY data for trimer carceplex **5•7** (CD_2Cl_2, 267 K).

t_m (s)	$\mathbf{I_{11}}$ (4.87 ppm)	$\mathbf{I_{12}}$ (4.69 ppm)	$\mathbf{I_{21}}$ (4.87 ppm)	$\mathbf{I_{22}}$ (4.69 ppm)	a_{12}	a_{21}
0.005	13.10	1.00	1.00	13.64	0.08	0.07
0.015	4.44	1.00	1.00	4.86	0.22	0.21
0.030	2.35	1.00	1.00	2.36	0.44	0.48
0.045	1.81	1.00	1.00	1.89	0.64	0.59
0.060	1.48	1.00	1.00	1.44	0.83	0.88
0.075	1.28	1.00	1.00	1.45	0.96	0.93
0.100	1.14	1.00	1.00	1.15	1.31	1.37

I_{ij} ($i = j$) = Integration intensities of selectively irradiated signal. I_{ij} ($i = j$) = Integration intensities response signals. $a_{ij} = \mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements. Integration of ^{1}H NMR spectrum gave the ratio 1:1 for the signals at 4.87 ppm:4.69 ppm.

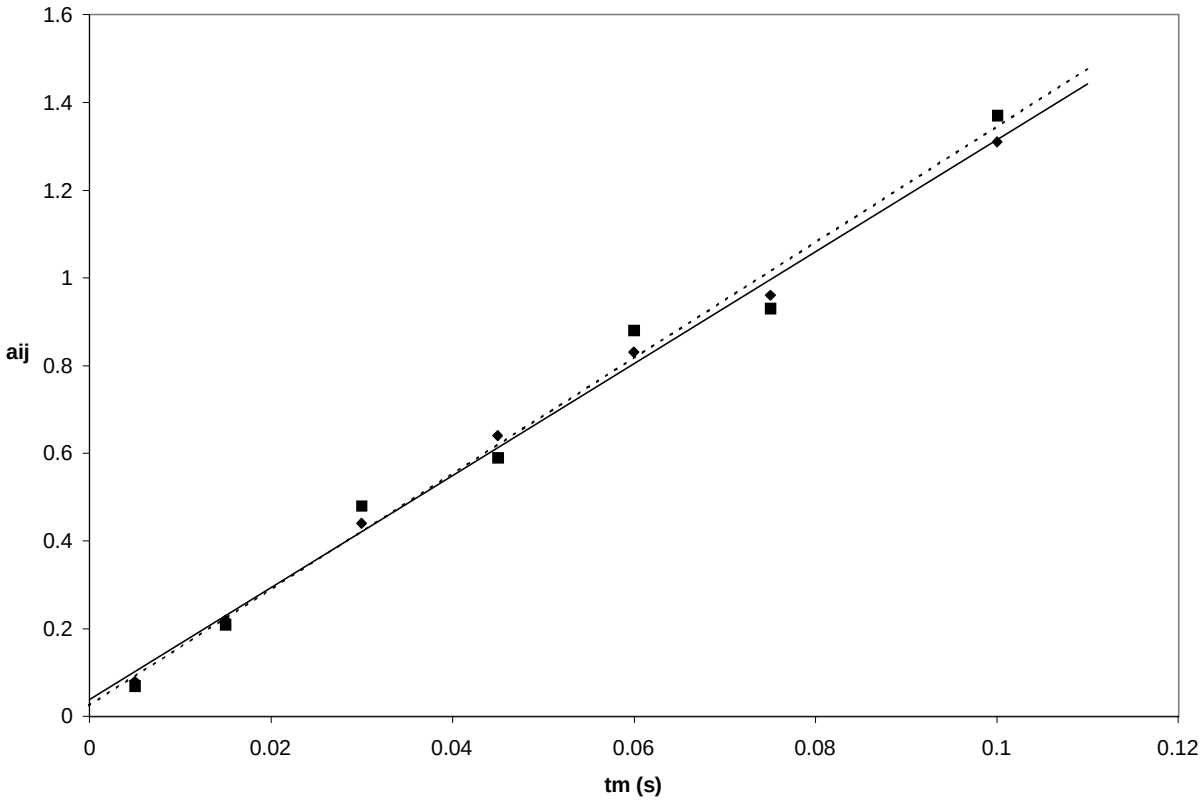


Figure S3 Plot of $\mathbf{X}(\ln\mathbf{\Lambda})\mathbf{X}^{-1}$ matrix elements (a_{12} and a_{21}) versus mixing time for **5•7** (CD_2Cl_2, 267 K). = a_{12} (slope (k_{12}) = (12.8 ± 1.8) s^{-1}, y-intercept = 0.0386, r^2 = 0.997). = a_{21} (slope (k_{21}) = (13.2 ± 1.8) s^{-1}, y-intercept = 0.0241, r^2 = 0.986). Errors in k_{ij}s were based on 95 % confidence limits from regression analysis.

Free energies of activation ($\Delta G^{\ddagger}$, in kcal/mol) were calculated from k (in s^{-1}) using the equation:

$$\Delta G^{\ddagger} = -RT\ln(kh/k_B T)$$

Template Ratios

Competition Experiments. Competition experiments were conducted using a procedure similar to procedure A, except that the competing guests, guest 1 (G_1) and guest 2 (G_2), were added at concentrations ranging from 0.1 to 5.0 mole % of the solvent, NFP. Separate reactions were conducted both at ambient conditions (298 K) and at 70 °C. The results of all competition experiments at room temperature and 70 °C are listed in Table S4 in Table S5, respectively.

Table S4 Single-guest competition experiments at room temperature.

G_1	G_2	*TR* (G_1)	*TR* (G_2)
6	**9**	50.1	1.00
6	**7**	2.25	1.00
6	**8**	38.9	1.00
7	**8**	4.46	1.00
8	**9**	1.08	1.00
8	**12**	4.70	1:00
8	**11**	24.6	1.00

Table S5 Single-guest competition experiments at 70 °C.

G_1	G_2	*TR* (G_1)	*TR* (G_2)
6	7	38.8	1.00
6	**8**	42.4	1.00
7	**8**	1.09	1.00
7	NFP	264	1.00
8	NFP	256	1.00
8	**12**	5.70	1.00
8	**11**	24.1	1.00
12	**11**	10.9	1.00
12	NFP	47.0	1.00

Competitions between NFP•guest1 versus NFP•guest2 (Table S6), and NFP•guest versus single-molecule guests (Table S7) were also conducted using procedure A.

Table S6 Competition results for **5**•(NFP•guest) at 70 °C.

G_1	G_2	TR_{22} (G_1)	TR_{22} (G_2)
4'-ethylacetophenone	propiophenone	15.5	1.00
4'-ethylacetophenone	acetophenone	6.3	1.00
acetophenone	propiophenone	2.3	1.00

Table S7 Single- versus two-molecule template competition results at 70 °C.[a]

G_B	G	*PR* (G/NFP•G_B)	TR_{12} (G/NFP•G_B)
4'-ethylacetophenone (0.0130)	NFP (8.70)	0.73	0.00952 M
4'-ethylacetophenone (0.0133)	NFP (8.96)	0.60	0.00781 M
4'-ethylacetophenone (0.0132)	NFP (8.87)	0.62	0.00847 M
4'-ethylacetophenone (0.0132)	NFP (8.85)	0.62	0.00813 M
4'-ethylacetophenone (0.00669)	NFP (8.92)	1.36	0.00909 M
4'-ethylacetophenone (0.0267)	NFP (8.89)	0.33	0.00893 M
4'-ethylacetophenone (0.0132)	**8** (0.0618)	1.28	2.81 M
4'-ethylacetophenone (0.0132)	**8** (0.0802)	0.96	1.91 M
4'-ethylacetophenone (0.00669)	**8** (0.0551)	2.07	2.26 M
4'-ethylacetophenone (0.0267)	**8** (0.0549)	0.63	2.76 M
4'-ethylacetophenone (0.0132)	**12** (0.058)	0.23	0.32 M
acetophenone (0.0254)	NFP (8.92)	2.64	0.0671 M
acetophenone (0.0256)	NFP (8.96)	1.98	0.0513 M
propiophenone (0.0521)	NFP (8.92)	2.92	0.155 M
propiophenone (0.233)	NFP (8.70)	0.63	0.147 M

[a]Bracketed values in the first two columns correspond to [G_B] and [G], respectively, in M. *PR* = product ratio.

Temperature Dependence of the Template Ratios TR_{13}, TR_{12}, and TR_{23}. Procedure A was used for competitions between tris-acetylene **6**, NFP•DMSO, and $(DMSO)_3$, except

different temperatures were used. Reactions were heated at constant temperatures using thermostated silicon oil baths. Template ratios determined from each experiment at each temperature were the average of two runs.

Enthalpic ($\Delta\Delta H°+\Delta\Delta H^{‡}$) and entropic ($\Delta\Delta S°+\Delta\Delta S^{‡}$) values were obtained from the slopes and *y*-intercepts, respectively, of plots of R$\ln(TR_{mn})$ versus $1/T$. Note that:

$$R\ln(TR_{mn}) = -(\Delta\Delta H°+\Delta\Delta H^{‡})/T-(\Delta\Delta S°+\Delta\Delta S^{‡})$$

where m = 1,2, n = 2,3. The plots are shown below as Figures S4-S6. Refer to Table S6 for the template ratio data.

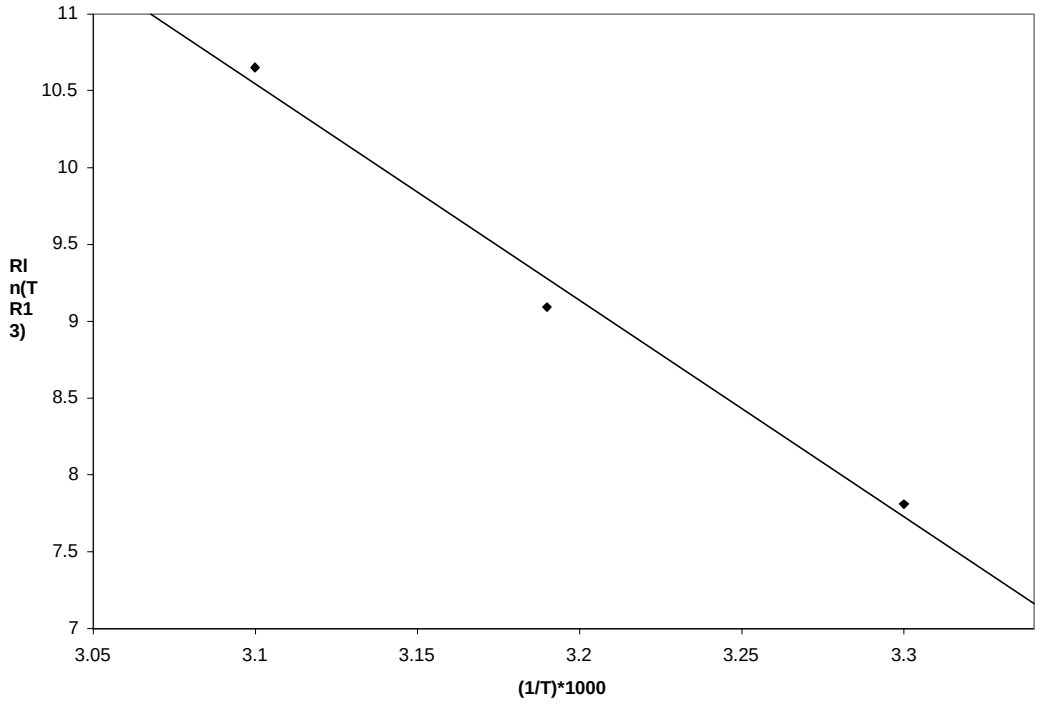


Figure S4 Plot of $\ln(TR_{13})$ versus $1/T$ for **6**/$(DMSO)_3$ competitions.
Slope = $\Delta\Delta H°+\Delta\Delta H^{‡}$ = -(14.1 ± 1.6) kcal/mol, *y*-intercept = $\Delta\Delta S°+\Delta\Delta S^{‡}$ = (54.3 ± 5.2) cal mol^{-1} K^{-1}, r^2 = 0.987. Errors are the standard errors of one standard deviation.

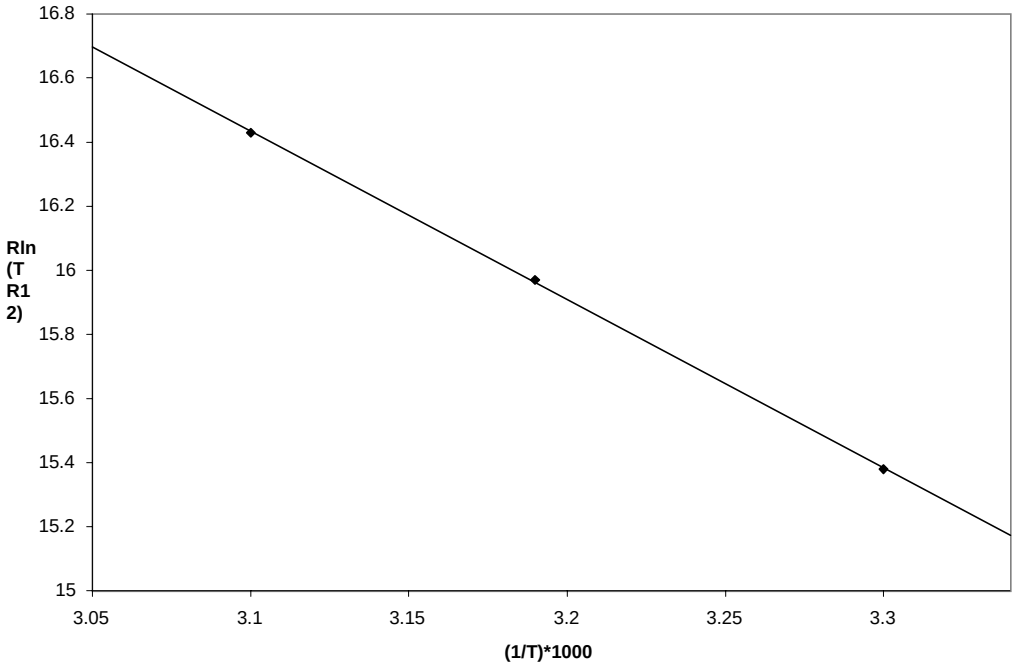


Figure S5 Plot of ln(TR_{12}) versus 1/T for **6**/(NFP•DMSO) competitions. Slope = $\Delta\Delta H°+\Delta\Delta H^{‡}$ = -(5.25 ± 0.07) kcal/mol, y-intercept = $\Delta\Delta S°+\Delta\Delta S^{‡}$ = (32.7 ± 0.2) cal mol^{-1} K^{-1}, r^2 = 1.000. Errors are the standard errors of one standard deviation.

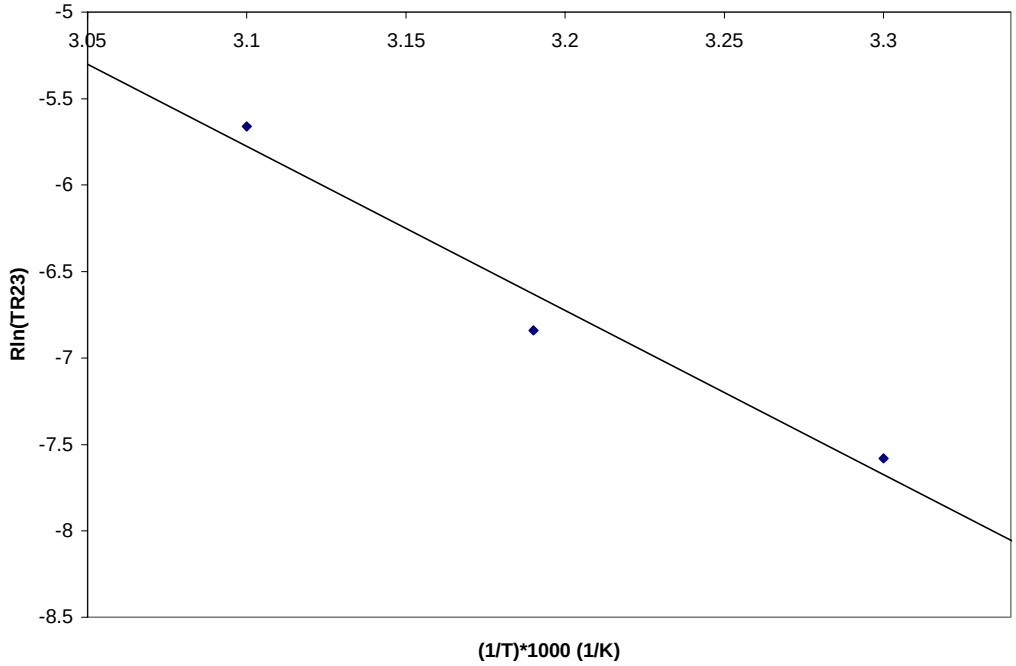


Figure S6 Plot of ln(TR_{23}) versus 1/T for (NFP•DMSO)/(DMSO)$_3$ competitions. Slope = $\Delta\Delta H°+\Delta\Delta H^{‡}$ = -(9.49 ± 1.82) kcal/mol, y-intercept = $\Delta\Delta S°+\Delta\Delta S^{‡}$ = (23.7 ± 5.8) cal mol^{-1} K^{-1}, r^2 = 0.965. Errors are the standard errors of one standard deviation.

Host–Guest Complexes with Trimer Derivatives

General Complexation Experiments. ^{1}H NMR complexation experiments were conducted as follows. Separate stock solutions of host and guest were prepared separately in each solvent. Aliquots of each host and guest stocks were added to an NMR tube. The tube was shaken to mix the two solutions and then a ^{1}H NMR spectrum was recorded immediately. Samples were equilibrated within minutes, as no further changes in the relative intensities of the signals after longer periods of time (except for *meta*-xylyl **17** with tris-acetylene **6**). Association constants, K_ss, were calculated from the relative integration of the free and bound host and guest signals measured in the ^{1}H NMR spectra, using the equation:

$$H + G \quad H{\bullet}G$$

$$K_s = \frac{[H \bullet G]}{[H][G]}$$

H is the host, G is the guest and H•G is the host-guest complex**.**

A,C-Trimers 3 and 4

Table S8 ^{1}H NMR chemical shifts (ppm) for selected protons of **3•6** in various deuterated solvents at 300 K.[a]

Solvent	H_o	H_{ac}	H_x	H_m	H_i	Guest
$CDCl_3$[b]	5.82	5.75	4.63	4.83	4.29	6.62, -0.84
CD_2Cl_2[b]	5.84	5.73	4.70	4.81	4.29	6.67, -0.82
C_6D_6[b]	6.17	5.90	4.77	5.22	4.44	-0.47
toluene-d_8[b]	6.12	5.87	4.74	5.16	4.67	-0.52
nitrobenzene-d_5[d]	6.20	6.15	4.95	5.19	4.76	-0.32

[a]The aryl protons and the methylene protons of the feet (R) of the host are not listed because either they are hidden under solvent or other host signals, or do not change in chemical shift significantly from that of the free host in the respective solvents. [b]400 MHz. [c]H_b of guest **6** is hidden. [d]500 MHz.

Table S9 ^{1}H NMR chemical shifts (ppm) of complex **4•6** in various deuterated solvents at 300 K.

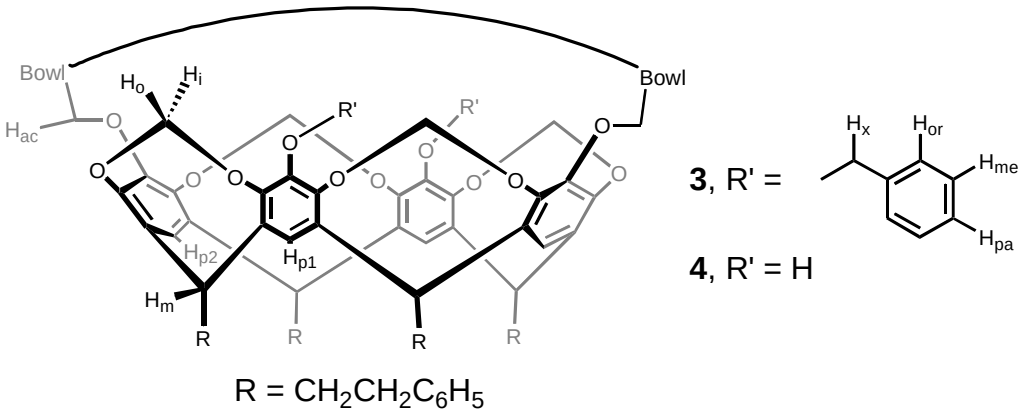
Solvent	ArH (feet)	H_p	H_o	H_{ac}	H_m	H_i	CH_2s (feet)	H_b, H_a (6)
$CDCl_3$[a]	7.22-7.07	6.86, 6.67	5.91	5.84	4.82	4.25	2.64, 2.45	6.44, -0.86
nitrobenzene-d_5	7.24, 7.10	h	6.42	6.25	5.19	4.88	2.82, 2.49	h, -0.13

[a]5% (v/v) CD_3OD added. h = hidden.

Table S10 ^{1}H NMR chemical shifts of selected protons of complexes **3**•guest (nitrobenzene-d_5, 300 K).[a]

Guest	H_o	H_{ac}	H_x	H_m	H_i	Guest
6	6.20	6.15	4.95	5.19	4.76	-0.32
18[a]	6.16	6.20	5.22	5.19	4.73	8.02, 7.98, h, 0.55
7[b]	6.27	6.27	5.26	4.90	4.83	7.99, 0.45
9[c]	6.28	6.12	5.01	5.15	4.64	6.15, 1.64, -1.24
8[d]	6.18	5.94	5.16	5.09	4.68	5.50, 1.48

[a]Additional signals: δ 4.56 (d, ArH (feet)), 7.64 (s, H_{p1} or H_{p2}), 7.52 (s, H_{p1} or H_{p2}), 7.41 (t, ArH (feet)), 7.24 (t, ArH (feet)), 7.21 (d, ArHs (feet)), 7.14 (t, ArHs (feet)), 7.12 (t, ArHs (feet)), 2.80 (brm, C*H*$_2$s (feet)). [b]Additional signals: δ 7.65 (s, H_{p1} or H_{p2}), 7.64 (s, H_{p1} or H_{p2}), 7.33-7.02 (m, ArHs (feet and benzyls)), 2.83 (m, C*H*$_2$s (feet)). [c]Additional signals: δ 7.64 (s, H_{p1} or H_{p2}), 2.77 (brm, C*H*$_2$s (feet)). Note that the other H_{p1} or H_{p2} is hidden under another signal. [d]Additional signals: δ 7.70 (s, H_{p1} or H_{p2}), 7.53-7.06 (m, ArHs (feet and benzyls)): 2.77 (brm, C*H*$_2$s (feet)). Note that the other H_{p1} or H_{p2} is hidden under another signal. h = hidden.



Trimer Cavitand Complexes

Table S11 ^{1}H NMR chemical shifts (ppm) of trimer cavitand **15** and complex **15•6** in (nitrobenzene-d_5, 500 MHz, 300 K).

Proton	15	15•6
ArH (feet and benzyl)	h (d), 7.45 (t), 7.29 (d), 7.35-7.05	h (d), 7.37-7.06 (m)
H_p	7.81, 7.71, h	7.72, 7.65, h
H_o	6.07, 6.07	6.19, 6.08
H_{ac}	5.81, 5.02	6.17, 6.05
H_b	5.37	4.88
H_m	5.25, 5.08	5.28, 5.14
H_b'	5.37	5.13
H_i	4.62, 4.37	4.69, 4.56
CH_3 (cap)	3.07	2.88
CH_2s (phenyl ethyl feet)	2.99-2.67	3.00-2.70 (m)
guest	-	6.67 (s), -0.54 (s)

h = hidden (either under other host signals or residual protio solvent signals).

Table S12 ^{1}H NMR chemical shifts (ppm) of trimer cavitand **16** and complex **16•6** in nitrobenzene-d_5 (500 MHz)

Proton	16	16•6
H_1	h	7.39 (d)
H_2	7.76 (d)	7.45 (d)
ArH (feet and benzyl)	7.28 (d), 7.18 (m), 7.09 (m)	7.25-7.04 (m)
H_p	7.81 (s), h, h	7.72 (s), h, h
H_o	6.19 (d), 6.08 (d)	6.18 (d), 6.18 (d)
H_{ac}	5.85 (d), 5.09 (d)	6.18 (d), 6.10 (d)
H_b	5.42 (s)	5.09 (s)
H_m	5.38 (t), 5.25 (t)	5.13 (t), 5.13 (t)
H_b'	5.09 (s)	5.29 (s)
H_i	4.66 (d), 4.37 (d)	4.68 (d), 4.64 (d)
CH_3 (cap)	3.06 (s)	2.91 (s)
CH_2s (phenyl ethyl feet)	2.88 (m), 2.82 (m), 2.76 (m)	2.91 (m), 2.81 (m)
guest	-	6.79 (s), -0.56 (s)

h = hidden (either under other host signals or residual protio solvent signals).

Table S13 ^{1}H NMR chemical shifts (ppm) of trimer cavitand **14** and complex **14•6** in nitrobenzene-d_5 (400 MHz).

Proton	14	14•6
OH	6.61 (s)	6.78 (s)
ArH (feet and benzyl)	7.39-7.01 (m)	7.39-7.01 (m)
H_p	7.79 (s), 7.69 (s), 7.47 (s)	7.42 (s), h, h
H_o	6.21 (d), 6.08 (d)	6.22 (d), 6.22 (d)
H_{ac}	6.02 (d), 5.94 (d)	6.22 (d), 6.15 (d)
H_m	5.22 (t), 5.15 (t)	5.22 (t), 5.15 (t)
H_b'	5.28 (s)	5.28 (s)
H_i	4.66 (d), 4.43 (d)	4.74 (d), 4.43 (d)
CH_3 (cap)	2.95 (s)	2.92 (s)
CH_2s (phenyl ethyl feet)	3.05-2.73 (m)	2.92 (m), 2.81 (m)
guest	-	6.88 (s), -0.53 (s)

h = hidden (either under other host signals or residual protio solvent signals).

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