Supporting Information

Synthesis and hydrogen-bond capabilities of an amino-pyridine functionalized cavitand

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Experimental:

All chemicals were purchased from Aldrich and used without further purification. The synthetic procedures along with the full characterization of compounds **1** and **2** have been carried out and reported.[1] Resorcinarene based cavitands **3** and **4** have also been synthesized and fully characterized.[2,3] 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 $CDCl_3$. Compounds were prepared for infrared spectroscopic (IR) analysis as a mixture in KBr. MALDI-TOF / TOF-MS was carried out on a Bruker Daltonics Ultraflex TOF/TOF.

C-pentyltetra(2-amino-5-ethynylpyridine)cavitand, **5**. C-pentyltetraiodocavitand **4** (250 mg, 0.189 mmol), 2-amino-5-ethynylpyridine **2** (217 mg, 1.89 mmol), *bis*(triphenylphosphine)palladium (II) dichloride (30 mg, 0.04 mmol), triphenylphosphine (10 mg, 0.04 mmol), copper(I) iodide (7 mg, 0.04 mmol) were added to a round bottom flask. Tetrahydrofuran (15 mL) and triethylamine (15 mL) were added and dinitrogen bubbled through the resultant mixture of 10 minutes. A condenser was attached and the mixture heated at 50 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 a yellow solid. The product **5** was then reprecipitated from dissolving in chloroform and adding to hexanes. Product **5** precipitated as a yellow solid (178 mg, 74 %). M.p. >285 ˚C; ^{1}H NMR (δ_H; 400 MHz, $CDCl_3$): 8.16 (d, J = 2 Hz, 4H), 7.47 (dd, J = 8.4 Hz, J = 2 Hz, 4H), 7.06 (s, 4 H), 6.45 (d, J = 8.8 Hz, 4H), 5.98 (d, J = 7.2 Hz, 4H), 4.84 (t, J = 8 Hz, 4H), 4.75 (s, 8H), 4.59 (d, 7.2 Hz, 4H), 2.28 – 2.21 (m, 8H), 1.44 – 1.36 (m, 24H), 0.98 – 0.90 (m, 12 H). ^{13}C NMR (δ_H; 200 MHz, $CDCl_3$): 157.64, 155.08, 151.53, 140.36, 138.38, 119.77, 113.32, 109.64, 107.94, 98.41, 95.32, 81.62, 36.52, 31.85, 29.52, 27.43, 22.67, 14.07. IR (KBr): 3380, 3196, 2930, 2853, 2203, 1608, 1445, 1086, 1020, 974, 697.

*C-pentyltetra(2-amino-5-ethynylpyridine)cavitand:3,5-dinitrobenzoic acid***,** **6**. C-pentyltetra(2-amino-5-ethynylpyridine)cavitand (10 mg, 0.05 mmol) and 3,5-dinitrobenzoic acid (105 mg, 0.50 mmol) were placed in a beaker containing a solution of acetonitrile, ethanol, p-xylenes and nitrobenzene (5:10:1:1 mL) and heated until a clear yellow homogeneous solution was obtained. After 1 day of slow evaporation, yellowish/orange prism-shaped crystals were obtained. mp 155-157 ºC; IR (KBr pellet) υ 3331 and 3198 cm^{-1} (NH_2, m), 2442 and 1912 cm^{-1} (O-H···N, br), 1635 cm^{-1} (C=O, m).

*C-pentyltetra(2-amino-5-ethynylpyridine)cavitand:glutaric acid***,** **7**. C-pentyltetra(2-amino-5-ethynylpyridine)cavitand (10 mg, 0.05 mmol) and glutaric acid (27 mg, 0.20 mmol) were placed in a beaker containing a solution of acetonitrile, ethanol, p-xylenes and nitrobenzene (5:10:1:1 mL) and heated until a clear yellow homogeneous solution

was obtained. After 1 day of slow evaporation, yellowish/orange prism-shaped crystals were obtained. mp 155-157 °C; IR (KBr pellet) υ 3331 and 3198 cm^{-1} (NH_2, m), 2442 and 1912 cm^{-1} (O-H···N, br), 1635 cm^{-1} (C=O, m).

Crystallographic experimental data:

Datasets for compound **6** were collected on a SMART 1000. Data for compound **7** were collected on a SMART APEX. All datasets were collected using MoKα radiation and were uncorrected for absorption.

Data were collected using SMART.[4] Initial cell constants were found by small widely separated "matrix" runs. An entire hemisphere of reciprocal space was collected. Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[5] using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied, and data were corrected for absorption.

Data were reduced with SHELXTL.[6] The structures were solved in all cases by direct methods without incident. Except as noted, hydrogens were assigned to idealized positions and were allowed to ride. With some exceptions, heavy atoms on the cavitand molecule were refined with anisotropic thermal parameters. Solvent atoms were refined with isotropic thermal parameters. Generally, occupancies of solvent molecules were allowed to refine until near convergence, then occupancies were fixed to allow for proper unit-cell-content calculation.

6 One of the four alkyl chains was disordered and was treated with two PARTs with anisotropic thermal parameters constrained with pairwise EADP commands. The occupancies, which were constrained to 100%, refined to an ~55% / 45% ratio. The set of solvent molecule consisted of one fully-occupied isotropic acetonitrile, two superimposed acetonitriles with a single isotropic temperature factor (occupancies ~80% / 20% constrained to 100%), and a superimposed isotropic methanol / acetonitrile pair, with occupancies for each molecule fixed for the final refinement.

7 The cavitand molecule has crystallographically imposed mirror symmetry, in which a mirror-plane bisects two pairs of the saturated carbon atoms (C41/C47 and C51/C57) in the cavitand cylinder. These four atoms and the alkyl chains attached to them were all given half occupancy due to their location on a special position. One of these two alkyl chains showed signs of disorder and was treated as two isotropic PARTs, with total occupancy constrained to 50%, with idealized geometries enforced by DFIX commands. The remaining (fully occupied) alkyl chain also showed signs of disorder and was treated as two anisotropic PARTs, with total occupancy constrained to 100%, with idealized geometries enforced by DFIX commands. The set of solvent molecules consisted of two *p*-xylene molecules. The first was given an overall isotropic thermal parameter (which was allowed to refine) and was constrained to 35% occupancy. The second was given a fixed overall thermal parameter of 0.15, and was constrained to 25% occupancy. Because of their location near special positions, the PART -1 command was used to suppress bond generation between unique and equivalent species. As a result of

this PART command, the standard AFIX 33 command for methyl hydrogen generation was unstable, and explicit bond length and angle constraints were imposed (using DFIX commands) to generate ideal methyl geometries. The latter *p*-xylene molecule was overlapped by two partially occupied isotropic acetonitrile molecules. Occupancy for these two molecules were constrained to 25%.

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[1] C. B. Aakeröy, N. Schultheiss,J. Desper, *Dalton Trans*., 2006, **13**, 1627.
[2] (a) Y. Aoyama, Y. Tanaka and S. Sugahara, *J. Am. Chem. Soc*., 1989, **111**, 5397. (b) J. A. Bryant, M. T. Blanda, M. Vincenti and D. J. Cram, *J. Am. Chem. Soc*., 1991, **113**, 2167. (c) C. B. Aakeröy, N. Schultheiss, J. Desper, *Org. Lett*. 2006, **8**, 2607.
[3] (a) E. S. Barrett, J. L. Irwin, P. Turner and M. S. Sherburn, *J. Org. Chem*., 2001, **66**, 8227. (b) T. Haino, M. Kobayashi, M. Chikaraishi and Y. Fukazawa, *Chem. Commun*., 2005, **18**, 2321. (c) C. B. Aakeröy, N. Schultheiss, J. Desper, *CrystEngComm*. 2006, **8**, 502.
[4] SMART v5.060, © 1997 - 1999, Bruker Analytical X-ray Systems, Madison, WI.
[5] SAINT v6.02, © 1997 - 1999, Bruker Analytical X-ray Systems, Madison, WI.
[6] SHELXTL v5.10, © 1997, Bruker Analytical X-ray Systems, Madison, WI.