Supplementary Material (ESI) for Chemical Communications

Binding Properties of Cavitands in Aqueous Solution – Influence of the Upper Rim Charge

Supporting Information

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General Considerations. Deuterated solvents were used as purchased from Cambridge Isotope Laboratories. All other chemicals were obtained from Sigma-Aldrich or Acros chemicals and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectral data were recorded on a Bruker 600-DRX spectrophotometer. Chemical shifts are expressed as parts per million (δ) relative to $SiMe_4$ (TMS, $\delta = 0$), and referenced internally with respect to the protio solvent impurity. Electrospray ionization time-of-flight reflectron (ESI-TOF) spectra were determined on an Agilent ESI-TOF mass spectrometer. Molecular modeling (molecular mechanics calculations) was carried out using out using the AMBER force field with the solvation (dielectric) setting for water as implemented by Macromodel or Maestro (Schroedinger, Inc.) on a Silicon Graphics Octane workstation.

Cavitand tetra-CBZ-amine 6. The octanitro cavitand **3** (870mg, 692µmol, 1.0eq.) and $SnCl_2 \cdot 2H_2O$ (4.13g, 18.3mmol, 26.0eq.) were suspended in EtOH (70mL). HCl (20mL, 36%) was added and the mixture was stirred at 70°C for 14h. After cooling to room temperature the pH was adjusted to 12 with 2N NaOH. The precipitate was centrifuged and washed with water, CH_2Cl_2 and hexane. The residue was dried *in vacuo*. The obtained amine **4** (700mg, 688µmol, 1.0eq.) and the imidate **5** (1,50g, 5.50mmol, 8.0eq.) were suspended in dry EtOH under nitrogen and stirred at 70°C for 20h. The solvent was evaporated and the residue was taken up in acetone and filtered. The filtrate was evaporated and the residue was taken up in CH_2Cl_2. The precipitate was filtered off and washed with water and diethyl ether to give a pale yellow solid (823mg, 481µmol, 70%). ^{1}H-NMR (300 MHz, DMSO-d_6): δ= 0.93 (*t*, 12H, *J* = 6.4), 2.39 (*s*, 8H), 3.97 (*d*, 4H, *J* = 5.8), 4.31 (*s*, 8H), 5.05 (*s*, 8H), 7.20-8.11 (*m*, 46H); ESI-TOF [MH$^+$] calcd for $C_{100}H_{84}N_{12}O_{16}$ 1709.6201, found 1709.6208.

Cavitand tetra-ammonium hydrobromide salt 2. Tetra-CBZ-amine cavitand **6** (50mg, 29.2µmol) was suspended in HBr in acetic acid (33%) (3mL) and stirred for 4h at room temperature. The excess HBr was evaporated and diethylether (20mL) was added. The precipitate was filtered off and dried *in vacuo* to give a light brownish solid (43.3mg, 28.9µmol, 99%). ^{1}H-NMR (600 MHz, D_2O/THF-d_8 1:1): δ= 1.10 (*t*, 12H, *J* = 7.1), 2,46 (*t*, 8H, *J* = 7.4), 4.23 (*s*, 4H), 4.56 (*s*, 8H), 5.77 (*t*, 4H, *J* = 8.3), 7.54 (*s*, 4H), 7.79 (*s*, 4H), 8.01 (*s*, 8H); MALDI-TOF [MH$^+$] calcd for $C_{68}H_{60}N_{12}O_8$ 1173, found 1173.