Supporting Information

Electron Paramagnetic Resonance Structure Investigation of Copper Complexation in a Hemicarcerand

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Spectroscopy

NMR Spectroscopy: Commercially available solvents and reagents were purified according to literature procedures.[1] 2-Methylresorcinol and hexanal were distilled prior to use. NBS was recrystallized and carefully dried. DMA was dried over molecular sieve. CH_2BrCl was used as received. NaOAc p.a. was dried (120°C, 0.1 Torr) prior to use. Column chromatography was done on silica MN60 (63-200 m), tlc on Merck plates coated with silica gel 60, F254.

Spectra were recorded at 300 K with a Bruker Avance 500 (^{1}H-NMR 500 MHz, ^{13}C-NMR 125 MHz), Bruker AC 300 (^{1}H NMR 200 MHz, ^{13}C NMR 75 MHz) or a Bruker AC 200 (^{1}H NMR, 200 MHz). ^{1}H NMR were referenced to residual ^{1}H-impurities in the solvent and ^{13}C NMR to the solvent signals: CDCl3 (7.26 ppm, 77.0 ppm).

Mass Spectra: ESI-MS, APCI-MS and FD-MS were recorded on a Bruker-Franzen Esquire-LC.

IR-Spectra: Impact 400, Nicolet Analytical Instruments. UV/VIS-Spectra: Zeiss Speccord S10.

Molecular Modelling

Structure models for the hemicarcerand **23** including all *n*-pentyl side-chains (Figure 1) were build from analogous single cavitand geometries ob-

tained from the Cambridge Structural Database (CSD)[2] and fully energy optimized at the semiempirical PM3 level[3] using HyperChem 5.1 Pro.[4] Generation of the Connolly-type surfaces[5] was achieved using the *MolArch+* program[6] and a probe sphere of 1.4 Å radius (approx. size of a water molecule); surface quality mapping (molecular electrostatic potentials and lipophilicity profiles[7] was carried out using *MOLCAD*.[8]

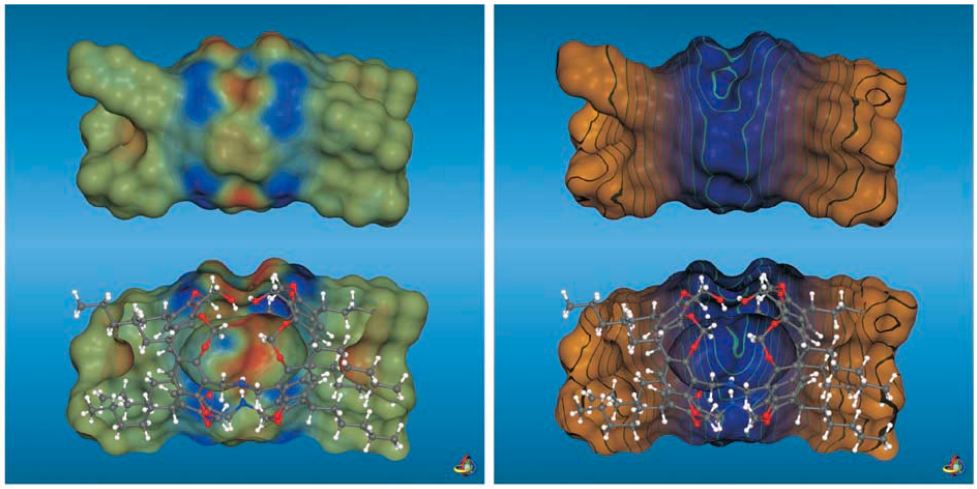


Figure 1. Molecular electrostatic potential (MEP, left) and molecular lipophilicity patterns (MLP, right) mapped onto the Connolly-type surface of the hemicarcerand **23** in color-coded form (MEP: colors range from red over green to blue for electropositive to electronegative potentials; MLP: yellow-brown to blue colors designating most hydrophobic to most hydrophilic surface regions). Both "ends" of the ligand are characterized by the apolar *n*-pentyl side-chains, whereas the circular arrangement of oxygen atoms (hydroxyl groups and acetal oxygens) and nitrogens dominate the polar central cavity.

The geometry of **23** was used as a starting point for the structural analysis of the hemicarcerand metal complexes ($M^{2+} = Ni^{2+}$, Cu^{2+}) by DFT methods. To minimize computational efforts, all *n*-pentyl side-chains were replaced by hydrogen atoms in the complexes. Initial models were generated by directing the four benzylic hydroxyl groups inwards (i.e. pointing towards the molecular center), minimizing the O$\cdots$O distances between the hydroxyl ligands, and removing the OH-protons. Ni^{2+} was placed at the center of the four alkoxide ligands and the two nitrogen linkers were protonated to yield a neutral structure of the M^{2+}[A,B-$(CH_2O^-)_2$-Cav]-$(CH_2NH_2^+CH_2)_2$-[A,B-$(CH_2O^-)_2$-Cav] type.

To maximize computational efficiency in the first step, we found that various initial geometries of low symmetry (C_1) tended to converge towards conformations of higher symmetry, and therefore, the corresponding Ni^{2+} low-spin species was fully pre-optimized in C_{2v} symmetry at the B3LYP[9]/6-31G level using Gaussian03.[10] The analogous Cu^{2+}-hemicarcerand complex (d^9, spin = 2) was generated by replacing Ni^{2+} with Cu^{2+}, followed by full energy optimization at the UB3LYP/6-31G level (Gaussian03, symmetry C_{2v}). Symmetry properties were verified by displacing two oxygen atoms bound to the central metal cation by 0.1 Å (reduction of symmetry from C_{2v} to C_2 only), and re-optimization; convergence tended to restore full symmetry.

In the final step, the Ni^{II}-complex was protonated at two alkoxide units (reduction of symmetry from C_{2v} to C_2), and both this cationic Ni^{2+} species as well as the neutral Cu^{2+} complex (as described above) were refined by

full energy-optimization (B3LYP and UB3LYP, resp.) using a 6-31G* basis set for the ligand, augmented by additional polarization and diffuse functions (6-311+G** basis) for the polar $M^{2+}[(^{-}OCH_2)_n(HOCH_2)_{4-n}]$ core regions of the complexes, as well as for the two -CH_2-NH_2^+-CH_2- linkers. In these calculations, the central transition metal ions were represented by a LACV3P+** type effective core potential (ECP)[11] including metal diffuse d-functions; these optimizations were carried out using the Jaguar[12] program. The complex analysis yielded the following structural parameters:

Ni^{2+}-complex : $[C_{72}H_{62}O_{20}N_2Ni]^{2+}$, Ni^{2+}[A-(CH_2O^-)-B-(CH_2OH)-Cav]-($CH_2NH_2^+CH_2$)$_2$-[A-(CH_2OH)-B-(CH_2O^-)-Cav], charge = +2, multiplicity = 1, framework group $C_2[C_2(Ni), X(C_{72}H_{62}N_2O_{20})]$, E = -4563.823950 h, d_{Ni-O} = 1.907 and d_{Ni-OH} = 2.063 Å, d_{O-O} = 2.386 and 3.123 Å, Ni^{2+} out-of-plane deviation 0.292 Å.

Cu^{2+}-complex : $[C_{72}H_{60}O_{20}N_2Cu]^0$, Cu^{2+}[A,B-(CH_2O^-)$_2$-Cav]-($CH_2NH_2^+CH_2$)$_2$-[A,B-(CH_2O^-)$_2$-Cav], charge = 0, multiplicity = 2, framework group $C_{2v}[C_2(Cu), \sigma_v(C_8H_{16}), \sigma_{v'}(H_4N_2), X(C_{64}H_{40}O_{20})]$, E = -4589.794393 h, d_{Cu-O} = 1.995 Å, d_{O-O} = 2.779 and 2.802 Å, Cu^{2+} out-of-plane deviation 0.294 Å.

Although the rather large basis set employed above was successfully used in previous studies on Cu^{II}-complexes of amino acids[13] and redox-active enzymes[14] (as well as the recommended use of ECPs on the metal ions), we have observed little significant geometry changes as compared to the corresponding DFT/6-31G geometries which were obtained with significantly cheaper computational effort (bond lengths for the 6-31G optimized com-

plexes: $d_{\mathrm{Ni-O}} = 1.905$, $d_{\mathrm{Ni-OH}} = 2.003$ Å, and $d_{\mathrm{Cu-O}} = 1.960$ Å). Although changes in this order of magnitude may be meaningful when comparing transition state geometries and energies of metal catalyzed reaction of complexes of this type, they add little improvement on the discussion of the principal structures described in this paper.

However, calculations on small model Ni^{II}-complexes of the $[Ni^{2+}(^{-}OCH_3)_n(HOCH_3)_{4-n}]$ type using ECP (LACV3P++**)[11] as well as non-ECP basis sets (TZV(f)*)[15] yielded no indication on the involvement of high-spin states in these complexes; all complexes turned out to represent low-spin compounds in accordance with the experimental findings. As described above, geometries of low symmetry tended to optimize towards higher symmetry conformations.

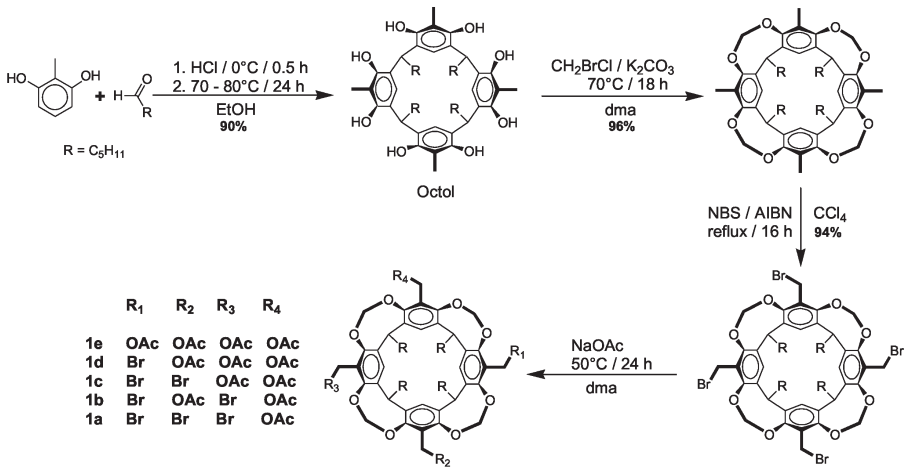
Structural analysis and generation of all molecular graphics was performed using the *MolArch*$^+$ program.[6]

Synthesis

Synthesis of the Octol.

Under a protective nitrogen atmosphere 2-methylresorcinol (100 g, 0.81 mol) and hexanal (96.7 mL, 0.81 mol, ρ 0.834 gcm^{-3}) dissolved in ethanol (800 mL) are cooled to 0°C in an ice bath. HCl (37%, 133 mL) was added dropwise during 30 min, whereupon a white precipitate is formed. The reaction mixture is heated to 75°C for 18h. After cooling to room temperature the

precipitate is filtered off, washed with hot water several times and the product dried under vacuum (Figure 1). Yield: 150.2 g (90%). Physical data as described by Cram et al.[16] The reaction can be further scaled up and was once performed in a 4 l flask using 200 g of 2-methylresorcinol to produce 300 g of product.



Scheme 1. Synthesis of the $(CH_2Br)_n(CH_2OAc)_{4-n}$-cavitands.

Synthesis of the $(CH_3)_4$-Cavitand

Into a three-necked flask equipped with a mechanical stirrer and reflux condenser were filled degassed dma (600 mL), the octol (66 g, 0.08 mol), K_2CO_3 (221.1 g, 1.6 mol) and CH_2BrCl (107.5 mL, ρ 1.93 gcm^{-3}, 1.6 mol) and the

reaction mixture stirred at 70°C overnight (14 h). The cooled suspension was filtered and the solids washed with dma several times. Most of the dma solvent in the combined filtrates can be evaporated on a rotavap. The slushy residue is taken up in $CHCl_3$ (400 mL) and the remaining dma extracted two times with 2 N aq. HCl (ca. 400 mL). The first filtrate (mostly potassium salts + some product) is washed again with $CHCl_3$ (500 mL), which is also extracted two times with 2 N aq. HCl (ca. 400 mL). The combined yellow to brown $CHCl_3$ solutions are separated from the aq. phase, dried over $MgSO_4$, filtered and reduced in volume to ca. 200 mL. This solution is filtered over a column filled with 1000 g of silica to remove the dark brown impurities, which are absorbed on the silica. The product was eluted from the column, the solution evaporated to dryness and the pure, white product dried in vacuo over night (Figure 1). Yield: 67 g (96%). Physical data as described by Cram et al..[16] The reaction can be scaled up easily and was once performed in a 4 l flask using 250 g of the octol to produce 240 g of the $(CH_3)_4$-cavitand.

Synthesis of $(CH_2Br)_4$-Cavitand

N-Bromosuccinimide (41.5 g, 0.23 mol), $(CH_3)_4$-cavitand (39.4 g, 0.045 mol) and AIBN (ca. 4 g) were dissolved in CCl_4 and heated under reflux for overnight (14 h). A tlc control was necessary afterwards to ensure completion of the reaction, otherwise more AIBN (1 g) was added and reflux continued until tlc indicated the absence of $(CH_3)_4$-cavitand. The cold reaction mixture was filtered and the solid washed carefully with CCl_4. The

filtrate was evaporated to dryness, dissolved in $CHCl_3$ and washed two times with a 1 M aq. solution of $Na_2S_2O_3$/NaOH = 1/1. The organic layer was separated, dried over $MgSO_4$, filtered and reduced in volume to ca. 200 mL. This solution was filtered over a column filled with 1000 g of silica to remove the dark brown impurities, which are absorbed on the silica. The product was eluted from the column, the solution evaporated to dryness and the pure, white product dried in vacuo over night (Figure 1). Yield: 50.1 g (94%). Physical data as described by Reinhoudt et al.[17] The reaction can be scaled up easily and was once performed in a 4 l flask using 100 g of the octol to produce 124 g of the $(CH_2Br)_4$-cavitand.

Synthesis of $(CH_2Br)_3(CH_2OAc)_1$-Cavitand, A,B-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand, A,C-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand and $(CH_2Br)_1(CH_2OAc)_3$-Cavitand

$(CH_2Br)_4$-cavitand (**1**) (47.6 g, 40 mmol) and NaOAc (7.22 g, 88.8 mmol, 2.2 equivalents) were added to dimethyl-acetamide (500 mL) and the reaction mixture stirred at 50°C. After 12 h most of the solvent was removed in vacuo and water (500 mL) added to the residue and stirred for 2 h to completely extract the remaining solvent. The suspension was filtered, washed with water and air-dried. The remaining solid was dissolved in $CHCl_3$ and the solution dried over $MgSO_4$ and filtered. The volatiles were evaporated to obtain 42 g of the crude acetate mixture.

The residue was dissolved in CH_2Cl_2 and ca. 50 g of silica added to absorb

the products, followed by careful evaporation of the volatiles. The product mixture and the silica was applied to a column with silica (ca. 1000 g of silica per 15 g of acetate mixture) and cyclohexane/ethyl acetate = 10:1 used for the separation. The different products were chromatographed with cyclohexane/ethyl acetate gradient mixtures. The polarity of the eluents was changed after elution of the respective product. For $(CH_2Br)_4$-cavitand and $(CH_2Br)_3(CH_2OAc)_1$-cavitand a 10:1 -mixture, for $(CH_2Br)_2(CH_2OAc)_2$-cavitand a 4:1 -mixture, for $(CH_2Br)_1(CH_2OAc)_3$-cavitand a 3:1 -mixture and for $(CH_2OAc)_4$-cavitand a 1:1 -mixture of cyclohexane-ethyl acetate was used. The overall yield of isolated products corresponds to a total yield of 95% (Figure 1). A typical product distribution is $(CH_2Br)_4$-cavitand= 11.5 %, $(CH_2Br)_3(CH_2OAc)_1$-cavitand= 21%, $(CH_2Br)_2(\ CH_2OAc)_2$-cavitand = 25% as the combined yield of A,B- and A,C-isomers, $(CH_2Br)_1(CH_2OAc)_3$-cavitand= 22% and $(CH_2OAc)_4$-cavitand= 15%. The separation of the isomeric diacetates by chromatography is possible, but impractical.

Separation of the isomeric mixture of A,B-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand and A,C-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand. 10 g of the isomeric mixture are stirred in 100 mL of diethylether for 24 h. The suspension is carefully filtered over a silica plug. The silica plug is washed with 10 mL of diethylether. The filtrate contains a solution of the almost pure A,B-diacetate, which is isolated after evaporation of the solvent. The silica plug is washed with CH_2Cl_2 to obtain the A,C-diacetate after evaporation of the new filtrate (Figure 1). Typical yields of the A,B-diacetate are 8.2 g (purity

> 95%) and of the A,C-diacetate 1.5 g (purity > 99%).

$(CH_2Br)_3(CH_2OAc)_1$-Cavitand (2):

^{1}H-NMR ($CDCl_3$): δ 7.15, 7.20 (ArH, s, 1+3 H), 6.03 (OC<u>H</u>HO, d, 2 H,0 7.0 Hz), 5.95 (OC<u>H</u>HO outer, d, 2 H, 7.0 Hz), 4.93 ($ArCH_2OAc$, s, 2 H), 4.82 (ArCHAr, t, 2 H, J= 8.1 Hz), 4.81 (ArCHAr, t, 2 H, J= 8.2 Hz), 4.57 (OCH<u>H</u>O inner, d, 2 H, J= 7.0 Hz), 4.49 (OCH<u>H</u>O, d, 2 H, J= 7.4 Hz), 4.47 (CH_2Br, s, 4 H), 4.39 (CH_2Br, s, 2 H), 2.14 -2.29 ($CHCH_2$, m, 8 H), 1.95 ($OOCCH_3$, s, 3 H), 1.3- 1.5 ($CH_2CH_2CH_3$, m, 24 H), 0.91 (CH_3, t, J= 6.4 Hz, 12 H). ^{13}C-NMR ($CDCl_3$): δ 170.8, 154.4, 153.7, 153.6, 138.3, 138.2, 138.1, 124.6, 121.9, 121.2, 121.0, 99.5, 99.2, 57.0, 37.0, 32.1, 30.2, 27.7, 23.2, 22.8, 21.0, 14.3.

A,B-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand (3):

^{1}H-NMR ($CDCl_3$): δ 7.21 (ArH, s, 2 H), 7.13 (ArH, s, 2 H), 6.03 (OC<u>H</u>HO, d, 1 H, J= 7.4 Hz), 5.91 (OC<u>H</u>HO outer, d, 2 H, J= 7.4 Hz), 5.87 (OC<u>H</u>HO, d, 1 H, J= 7.0 Hz), 4.98 ($ArCH_2OAc$, s, 4 H), 4.76 - 4.87 (ArCHAr, m, 4 H), 4.58 (OCH<u>H</u>O, d, 1 H, J= 7.4 Hz), 4.50 (OCH<u>H</u>O, d, 2 H, J= 7.4 Hz), 4.42 (OCH<u>H</u>O inner, d, 1 H, J= 7.0 Hz), 4.45 (CH_2Br, s, 4 H), 2.15 - 2.28 ($CHCH_2$, m, 8 H), 2.01 ($OOCCH_3$, s, 6 H), 1.3- 1.5 ($CH_2CH_2CH_3$, m, 24 H), 0.91 (CH_3, t, J= 6.4 Hz, 12 H). ^{13}C-NMR ($CDCl_3$): δ 170.7, 154.4, 153.7, 153.6, 138.3, 138.2, 138.1, 124.7, 121.8, 121.3, 121.0, 99.8, 99.4, 99.2, 57.1, 36.5, 32.2, 32.1, 30.2, 27.7, 23.2, 21.1, 20.9, 14.2.

A,C-$(CH_2Br)_2(CH_2OAc)_2$-Cavitand (4):

^{1}H-NMR ($CDCl_3$): δ 7.18 (ArH, s, 2 H), 7.14 (ArH, s, 2 H), 5.92 (OC<u>H</u>HO

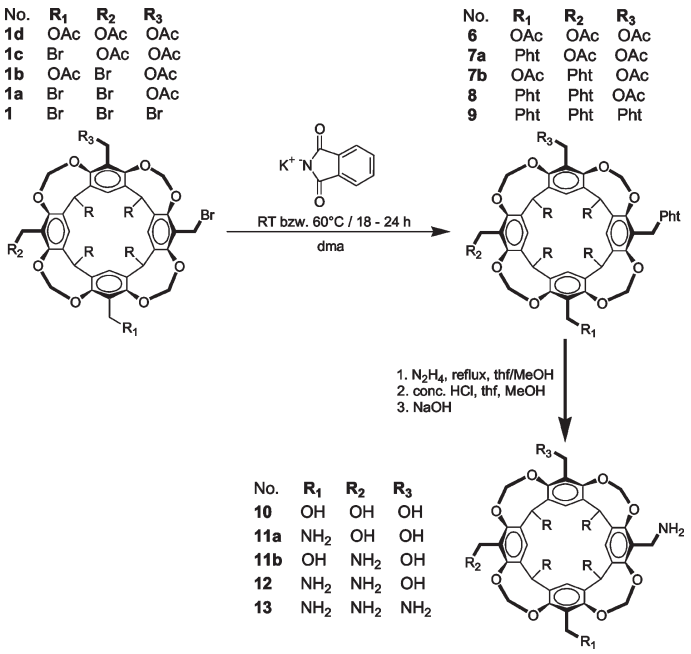
outer, d, 4 H, J= 7.0 Hz), 4.92 ($ArCH_2OAc$, s, 4 H), 4.81 (ArCHAr, t, 4 H, J= 8.1 Hz), 4.53 (OCH<u>H</u>O inner, d, 4 H, J= 7.0 Hz), 4.52 (CH_2Br, s, 4 H), 2.14 - 2.28 ($CHCH_2$, m, 8 H), 2.03 ($OOCCH_3$, s, 6 H), 1.3- 1.5 ($CH_2CH_2CH_3$, m, 24 H), 0.91 (CH_3, t, J= 6.4 Hz, 12 H). ^{13}C-NMR ($CDCl_3$): δ 170.9, 154.3, 153.9, 138.2, 124.7, 121.9, 121.3, 121.2, 99.5, 57.0, 37.0, 32.2, 32.1, 27.7, 23.2, 21.1, 20.9, 14.2.

$(CH_2Br)_1(CH_2OAc)_3$-Cavitand (5):

^{1}H-NMR ($CDCl_3$): δ 7.21 (ArH, s, 1 H), 7.19 (ArH, s, 2 H), 7.13 (ArH, s, 1 H), 5.91 (OC<u>H</u>HO outer, d, 2 H, J= 7.4 Hz), 5.86 (OC<u>H</u>HO inner, d, 2 H, J= 7.0 Hz), 5.05 ($ArCH_2OAc$, s, 2 H), 4.94 ($ArCH_2OAc$, s, 4 H), 4.84 (ArCHAr, t, 2 H, J= 8.1 Hz), 4.81 (ArCHAr, t, 2 H, J= 8.5 Hz), 4.53 (OCH<u>H</u>O, d, 2 H, J= 7.4 Hz), 4.38 (OCH<u>H</u>O, d, 2 H, J= 7.0 Hz), 4.51 (CH_2Br, s, 2 H), 2.14 - 2.29 ($CHCH_2$, m, 8 H), 2.00 ($OOCCH_3$, s, 9 H), 1.3- 1.5 ($CH_2CH_2CH_3$, m, 24 H), 0.91 (CH_3, t, J= 6.4 Hz, 12 H). ^{13}C-NMR ($CDCl_3$): δ 170.8, 170.5, 154.6, 154.4, 153.9, 138.5, 138.4, 138.2, 124.9, 121.8, 121.6, 121.3, 121.2, 99.9, 99.5, 57.3, 57.1, 37.1, 32.2, 30.3, 27.7, 22.8, 21.2, 21.1, 14.2.

General Procedure for the Synthesis of $(CH_2Pht.)_n(CH_2OAc)_{4-n}$-Cavitand: A mixture of $(CH_2Br)_n$ $(CH_2OAc)_{4-n}$-Cavitand **(2-5)** (1 mmol) and n equivalents K-Pht. (n mmol) in dma (20 mL) was stirred overnight at 60°C. The solution was reduced in volume to ca. 10 mL, water (20 mL) added to the stirred reaction mixture and the precipitate filtered off. The solid was dried in vacuo, dissolved in $CHCl_3$ extracted with aq. NaOH (2

M). The organic layer was separated, dried over $MgSO_4$. After evaporation of the solvent in vacuo, the residue was purified by chromatography (cyclohexane/ethyl acetate 1:1) (Figure 2).



Scheme 2. Synthesis of the $(CH_2NH_2)_n(CH_2OH)_{4-n}$-cavitands.

$(CH_2Pht)(CH_2OAc)_3$-Cavitand (6):

$(CH_2Br)(CH_2OAc)_3$-Cavitand **(2)**: 2.01 g / 1.82 mmol, K-Pht.: 0.47 g / 2.72 mmol, Yield: 1.29 g / 1.08 mmol / 60 % / white powder.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78 - 7.62 (4 H, m, Pht.), 7.10 (3H, s, H-Ar-CH_2OAc), 7.05 (1 H, s, H-Ar-CH_2NPht), 5.79 (4 H, t, OCHHO, J = 7,5 Hz), 4.95 (4 H, s, Ar-CH_2OAc beside Ar-CH_2NPht), 4.85 (2 H, s, Ar-CH_2OAc be-

tween Ar-C$\underline{H}_2$OAc), 4.68 (4 H, m, Ar-C$\underline{H}$-Ar), 4.57 (2 H, s, Ar-C$\underline{H}_2$NPht), 4.29 (4 H, t, OCH$\underline{H}$O, J = 7,5 Hz), 2.15 (8 H, m, C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 2.00 (9 H, s, OOCCH$_3$), 1.28 (24 H, m, CH$_2$(C$\underline{H}_2$)$_3$CH$_3$), 0.88 (12 H, m, CH$_2$(CH$_2$)$_3$C$\underline{H}_3$). ^{13}C-NMR (75 MHz, CDCl$_3$): δ 170.87, 170.44, 168.03, 154.66, 154.34, 154.22, 153.78, 138.40, 138.22, 138.15, 134.10, 132.14, 123.41, 121.95- 121.35, 120.30, 99.79, 57.43, 57.02, 36.98, 32.78- 22.77, 21.20, 14.21. IR: ν 1720 cm-1 (O=C-N-C=O), 1260 cm-1 (O=C-O). Formula: $C_{70}H_{81}O_{16}N$ (1192.40 g/mol).

A,B-(CH$_2$Pht)$_2$(CH$_2$OAc)$_2$-Cavitand (7a):

(2) A,B-(CH$_2$Br)$_2$ (CH$_2$OAc)$_2$-Cavitand **(3a)**: 2.0 g / 1.78 mmol, K-Pht.: 0.968 g / 5.32 mmol. Yield: 1.57 g / 1.227 mmol / 69 % / white powder. ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.82 - 7.62 (8 H, m, Pht.), 7.26 (2 H, s, $\underline{H}$-Ar-CH$_2$OAc), 7.07 (2 H, s, $\underline{H}$-Ar-CH$_2$NPht), 5.84 - 5.77 (4 H, d, OC$\underline{H}$HO, J = 7,3 Hz), 4.97 (4 H, s, Ar-C$\underline{H}_2$ OAc) , 4.72 (4 H, s, Ar-CH$_2$NPht), 4.61 (4 H, s, Ar-C$\underline{H}$-Ar), 4.33 (4 H, d, OCH$\underline{H}$O, J = 7,1 Hz), 2.21 (8 H, m, C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 2.01 (6 H, s, OOCCH$_3$), 1.27 (24 H, m, CH$_2$(C$\underline{H}_2$)$_3$CH$_3$), 0.88 (12 H, m, CH$_2$(CH$_2$)$_3$C$\underline{H}_3$). ^{13}C-NMR (75 MHz, CDCl$_3$): δ 170.70, 168.04, 154.58, 154.09, 153.96, 138.25, 138.19, 134.13, 132.10, 126.21, 121.59 - 121.33, 120.22, 99.87, 99.64, 57.37, 36.97, 32.78 - 22.77, 14.21. IR: ν 1776 cm-1 (C=O), 1720 cm-1 (O=C-N-C=O), 1250 cm-1 (O=C-O). ESI-MS (positive ions) m/z (%): 1301.7 (100) [M + Na$^+$], Formula: $C_{76}H_{82}O_{16}N_2$ (1279.48 g/mol).

A,C-(CH$_2$Pht)$_2$(CH$_2$OAc)$_2$-Cavitand (7b):

A,C-(CH$_2$Br)(CH$_2$OAc)$_3$-Cavitand **(3b)**: 0.25 g / 0.218 mmol, K-Pht. :

0.121 g / 0.754 mmol. Yield: 0.05 g / 0.039 mmol / 20 % / white powder. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.82 - 7.68 (8 H, m, Pht.), 7.14 (2 H, s, H-Ar-CH_2OAc), 7.06 (2 H, s, H-Ar-CH_2NPht), 5.88 - 5.83 (4 H, dd, OCHHO), 5.05 - 4.97 (4 H, s, Ar-CH_2 OAc) , 4.75 - 4.72 (4 H, s, Ar-CH-Ar), 4.62 (4 H, s, Ar-CH_2NPht), 4.33 (4 H, b, OCHHO,), 2.2 (8 H, m, CH_2(CH_2)$_3$$CH_3$), 1.99 (6 H, s, OOC$CH_3$), 1.39 - 1.27 (24 H, m, CH_2(CH_2)$_3$$CH_3$), 0.88 (12 H, m, CH_2(CH_2)$_3$CH_3). Formula: $C_{76}H_{82}O_{16}N_2$ (1279.48 g/mol).

(CH_2Pht)$_3$(CH_2OAc)-Cavitand (8):

(CH_2Br)$_3$(CH_2OAc)-Cavitand **(4)**: 1.00 g / 0.856 mmol, K-Pht. : 0.735 g / 3.968 mmol. Yield: 660 mg / 0.48 mmol / 56 % / white powder. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77- 7.62 (12 H, m, Pht.), 7.19 (1 H, s, H-Ar-CH_2OAc), 7.05 (3 H, s, H-Ar-CH_2NPht), 5.79 - 5.70 (4 H, 2·d, OCHHO, J = 7.1 Hz), 4.95 (2 H, s, Ar-CH_2OAc), 4.66 (6 H, s, Ar-CH_2NPht), 4.55 (4 H, m, Ar-CH-Ar), 4.29 (4 H, 2·d, OCHHO, J = 7.1 Hz), 2.15 (8 H, m, CH_2(CH_2)$_3$$CH_3$), 2.00 (3 H, s, OOC$CH_3$), 1.24 (24 H, m, CH_2(CH_2)$_3$$CH_3$), 0.82 (12 H, m, CH_2(CH_2)$_3$$CH_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 170.60, 168.06, 167.98, 154.52, 154.12, 153.96, 153.78, 38.22, 138.07, 137.95, 134.07, 132.14, 123.4, 121.95 - 121.35, 120.22, 99.79, 60.50, 57.67, 51.27, 36.97, 32.78 - 22.77, 14.21. IR: ν 1776, 1720 cm-1 (C=O), 1260 cm-1 (O=C-O). Formula: $C_{82}H_{83}O_{16}N_3$ (1366.56 g/mol).

(CH_2Pht)$_4$-Cavitand (9): (CH_2Br)$_4$-Cavitand **(5)**: 1.00 g / 0.841 mmol, K-Pht. : 0.935 g / 5.047 mmol. Yield: 740 mg / 0.509 mmol / 60 % / white powder. Physical data as given by Reinhoudt.[17]

General Procedure for the Synthesis of $(CH_2NH_2)_n(CH_2OH)_{4-n}$-Cavitands

The $(CH_2Pht.)_n(CH_2OAc)_{4-n}$-Cavitands **6-9** (0.4 mmol) were dissolved in thf/methanol (9:1 v/v) (30 mL) and treated with a 50-fold excess of hydrazine monohydrate (0.95 mL, 20 mmol) and heated under reflux over night. To the hot solution was added an equimolar amount of HCl (37%, 1.75 mL, 20 mmol) and reflux continued for 2 h. After cooling aq. NaOH (2 M, 10 mL, 20 mmol) and water were added. The pale-yellow precipitate was filtered off, washed with dilute aq. NaOH and water and finally dried in vacuo. The solid was dissolved in $CHCl_3$, dried over $MgSO_4$, filtered and the volatiles evaporated in vacuo (Figure 2).

$(CH_2NH_2)(CH_2OH)_3$-Cavitand (10):

$(CH_2NPht)(CH_2OAc)_3$-Cavitand **(6)**: 1.5 g/ 1.258 mmol, $N_2H_4 \cdot H_2O$: 3.06 ml / 62.9 mmol, HCl (37 %): 6.12 ml / 63 mmol, aq. NaOH (2 M): 31.5 ml / 63 mmol. Yield: 1.1 g / 1.175 mmol / 93 % / pale-yellow powder.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.08 (4 H, s, H-Ar), 5.90 (4 H, d, OCHHO, J = 7,1 Hz), 4.76 (4 H, m, Ar-CH-Ar),4.54 (4 H, s, Ar-CH_2OH next to Ar-CH_2NH_2), 4.47 (2 H, s, Ar-CH_2OH between Ar-CH_2OH), 4.20 (4 H, s, OCHHO), 3.51 (2 H, s, Ar-CH_2NH_2), 2.17 (8 H, m, $CH_2(CH_2)_3CH_3$), 1.30 (24 H, m, CH_2 $(CH_2)_3CH_3$), 0.89 (12 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.71, 153.61, 153.07, 138.43, 138.22, 138.04, 126.96, 126.63, 120.10, 99.67, 55.34, 54.61, 36.98, 32.78 - 22.77, 14.21. ESI-MS (positive ions) m/z (%): 936.5 (50) [M + H^+], 958.6 (60) [M + Na^+]. ESI-MS

(negative ions) m/z (%): 970.4 (100)[M - H + Cl^-]. Formula: $C_{56}H_{73}O_{11}N$ (936.19 g/mol).

A,B-$(CH_2NH_2)_2(CH_2OH)_2$-Cavitand (11a):

A,B-$(CH_2NPht)_2(CH_2OAc)_2$-Cavitand (**7a**): 1.4 g / 1.094 mmol, $N_2H_4 \cdot H_2O$: 2.66 ml / 55 mmol, HCl (37 %): 5.33 ml / 55 mmol, NaOH (2 M): 22.5 ml / 55 mmol. Yield: 0.75 g / 0.791 mmol / 72 % / pale-yellow powder.

^{1}H-NMR (300 MHz, $CDCl_3$ + dmso): δ 7.17 & 7.11 (each 2 H, s, H-Ar), 5.89 (4 H, dd, OCHHO, J = 7.8 Hz), 4.86 (4 H, t, Ar-CH-Ar), 4.70 - 4.50 (4 H, m, Ar-CH_2OH & 4 H, m, OCHHO), 3.68 (4 H, s, Ar-CH_2NH_2), 2.19 (8 H, m, $CH_2(CH_2)_3CH_3$), 1.30 (24 H, m, $CH_2(CH_2)_3CH_3$), 0.86 (12 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (75 MHz, $CDCl_3$ + dmso): δ 148.09, 147.90, 147.46, 132.95, 132.90, 132.59, 132.32, 122.25, 120.19, 115.07, 114.87, 94.73, 94.38, 93.75, 33.84, 31.40 - 22.06, 8.51. FD-MS (negative ions) m/z (%): 969.5 (100) [M - H + Cl^-] / 934 (100) [M - H]. ESI-MS (positive ions) m/z (%): 918.8 (60) [M - H_2O], 935.7 (35) [M + H^+]. Formula: $C_{56}H_{74}O_{10}N_2$ (935.20 g/mol).

$(CH_2NH_2)_3(CH_2OH)$-Cavitand (12):

$(CH_2NPht)_3(CH_2OAc)$-Cavitand **(8)**: 0.550 g / 0.402 mmol, $N_2H_4 \cdot H_2O$ 0.947 ml / 20.18 mmol, HCl (37 %): 1.75 ml / 20.2 mmol, NaOH(2 M): 10.1 ml / 20.2 mmol. Yield: 220 mg / 0.235 mmol / 60 % / white powder.

^{1}H-NMR (300 MHz, $CDCl_3$ + dmso): δ 7.08 (1 H, s, H-Ar-CH_2OH), 7.03 (3 H, s, H-Ar-CH_2OH), 5.90 (4 H, dd, OCHHO, J= 7,9 Hz),4.70 (4 H, m, Ar-CH-Ar),4.48 (2 H, s, Ar-CH_2OH), 4.30 (4 H, dd, OCHHO, J = 7,9 Hz), 3.62

(2 H, s, Ar-C$\underline{H}_2NH_2$ next to ArC$\underline{H}_2$NH), 3.45 (4H, s, Ar-C$\underline{H}_2NH_2$ between Ar-C$\underline{H}_2$OH), 2.12 (8 H, bs, C$\underline{H}_2(CH_2)_3CH_3$), 1.30 (24 H, m, $CH_2(C\underline{H}_2)_3CH_3$), 0.89 (12 H, m, $CH_2(CH_2)_3C\underline{H}_3$). ^{13}C-NMR (75 MHz, $CDCl_3$ + dmso): δ 53.65, 153.24, 152.94, 138.37, 138.23, 138.15, 129.96 - 127.26, 120.10 -118.85, 99.67, 55.34, 53.32, 37.07, 36.83 - 22.73, 14.23. ESI-MS (negative ions) m/z (%): 969.5 (100) [M - H + Cl^-]. ESI-MS (positive ions) m/z (%): 957.6 (20) [M + Na^+], 974.7 (100) [M + K^+]. Formula: $C_{56}H_{75}O_9N_3$ (934.22 g/mol).

$(CH_2NH_2)_4$-Cavitand (13): $(CH_2NPht)_4$-Cavitand **(9)**: 0.325 g / 0.224 mmol, $N_2H_4 \cdot H_2O$: 0.543 ml / 11.18 mmol, HCl (37 %): 0.95 ml / 11.2 mmol, NaOH (2 M) : 5.6 ml / 11.2 mmol. Yield: 120 mg / 0.128 mmol / 57 % / white powder.

^{1}H-NMR (300 MHz, $CDCl_3$ + dmso): δ 7.48 (4 H, s, $\underline{H}$-Ar), 5.90 (4 H, d, OC$\underline{H}$HO, J = 7,1 Hz), 4.61 (4 H, t, Ar-C$\underline{H}$-Ar, J = 6,8 Hz), 4.35 (4 H, d, OCH$\underline{H}$O, J = 7,9 Hz), 3.57 (8 H, s, Ar-C$\underline{H}_2NH_2$), 2.30 (8 H, bs, C$\underline{H}_2(CH_2)_3CH_3$), 1.32 (24 H, m, $CH_2(C\underline{H}_2)_3CH_3$), 0.89 (12 H, m, $CH_2(CH_2)_3\underline{H}H_3$). ^{13}C-NMR (75 MHz, $CDCl_3$ + dmso): δ 153.14, 152.58, 137.90, 137.05, 128.77, 119.55, 99.24 (O$\underline{C}H_2$O), 36.52, 35.53 - 22.25, 14.23. ESI-MS (negative ions) m/z (%): 968.5 (100) [M - H + Cl^-]. ESI-MS (positive ions) m/z (%): 957.5 [M + Na^+], 974.7 [M + K^+]. Formula: $C_{56}H_{76}O_8N_4$ (933.24 g/mol).

General Procedure for the Synthesis of Hemicarcerands

The $(CH_2NH_2)_n(CH_2OH)_{4-n}$-cavitands **10-13** (0.5 mmol), 50 equiv. of the templating molecule 1,4-dioxane (2.2 mL, 25 mmol) and 5 equiv. of Na_2CO_3 (265 mg, 2.5 mmol) were added to dma (15 - 25 mL) and heated to 60°C.

A solution of the $(CH_2Br)_n$-cavitands **2-5** (0.5 mmol) in dma (15-25 mL) was added dropwise into the reaction mixture, which was stirred for 18-48 h. Finally most of the solvent was removed in vacuo and water added to the slushy residue. The suspension was stirred for 1 h and the pale-yellow solid filtered off, washed with water and dried in vacuo. The crude product was dissolved in $CHCl_3$/MeOH = 9:1 (for the mono-bridged hemicarcerands) or in $CHCl_3$/MeOH = 5:1 (for the double-bridged hemicarcerands) and purified by chromatography on silica neutralized with Et_3N, yielding the pure hemicarcerands **14, 16, 18, 20, 22, 24, 26, 28, 30**.

For the cleavage of the acetates the hemicarcerands **14, 16, 18, 20, 22, 24, 26** (0.5 mmol) were dissolved in THF (20 mL) and treated with methanolic KOH (5 mmol per acetate group) at 60°C over night (thf/methanol= 9/1 v/v). The volatiles were evaporated in vacuo and the yellow solid dissolved in $CHCl_3$ and extracted three times with NaOH (2 M) to remove NaOAc. The organic layer was dried over $MgSO_4$, filtered and the volatiles removed in vacuo to obtain the hemicarcerands **15, 17, 19, 21, 23, 25, 27** in virtually quantitative yields.

Mono-bridged Hemicarcerands

[$(CH_2OAc)_3$-Cav]-(CH_2NHCH_2)-[$(CH_2OH)_3$-Cav] (14)

$(CH_2Br)(CH_2OAc)_3$-Cavitand **(2)**: 600 mg / 0.534 mmol, $(CH_2NH_2)(CH_2OH)_3$-Cavitand **(10)**: 500 mg / 0.534 mmol, Na_2CO_3: 283 mg / 2.67 mmol, 1,4-dioxane : 2.35 mL / 26.7 mmol. Yield: 800 mg / 0.408 mmol / 76 % / pale yellow powder. R_f-data ($CHCl_3$ / methanol / triethylamine = 10/0.5/0.5):

0.9 reactant **(2)** / 0.51 product / 0 reactant **(10)**. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.18 - 7.04 (8H, m, H-Ar), 5.79 (8 H, m, OCHHO), 5.10 (6 H, b, Ar-CH_2OAc), 4.75 (8 H, m, Ar-CH-Ar), 4.47 (6 H, b s, Ar-CH_2OH), 4.26 (8 H, m, OCHHO), 4.04 (4 H, b, CH_2NHC H_2), 2.15 (16 H, m, $CH_2(CH_2)_3CH_3$), 2.00 (9 H, s, $OOCCH_3$), 1.28 (48 H, m, $CH_2(CH_2)_3CH_3$), 0.88 (24 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.81, 170.27, 160.11, 154.27, 154.04, 153.62, 138.72, 138.22, 137.68, 126.90, 123.29 - 116.51, 99.79 - 97.57, 56.91, 54.87, 38.43, 36.96, 32.09 - 22.74, 20.99, 14.21. APCI-MS (positive ions) m/z (%): 1981.7 (100) $[M + H]^+$. Formula: $C_{118}H_{149}O_{25}N$ (1981.46 g/mol).

[$(CH_2OH)_3$-Cav]-(CH_2NHCH_2)-[$(CH_2OH)_3$-Cav] (15)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.10 - 7.04 (8H, m, H-Ar), 5.83 (8 H, dd, OCHHO), 4.71 (8 H, m, Ar-CH-Ar), 4.45 (16 H, b m, Ar-CH_2OH & CH_2NHCH_2), 4.31 (8 H, m, OCHHO), 2.14 (16 H, m, $CH_2(CH_2)_3CH_3$), 1.33 (48 H, m, $CH_2(CH_2)_3CH_3$), 0.89 (24 H, m, $CH_2(CH_2)_3C$ H_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.5, 137.2, 126.5, 118.5, 98.86, 54.75, 35.90, 31.03 - 21.62, 13.05. APCI-MS (positive ions) m/z (%) 1856.3 (100) $[M + H]^+$, 1838.8 (95) $[M - H_2O + H]^+$. Formula: $C_{112}H_{143}O_{22}N$ (1855.35 g/mol).

[$(CH_2OAc)_3$-Cav]-(CH_2NHCH_2)-[A,B-$(CH_2OH)_2(CH_2NH_2)$-Cav] (16)

$(CH_2Br)(CH_2OAc)_3$-Cavitand **(2)**: 240 mg/ 0.214 mmol, $(CH_2NH_2)_2(CH_2OH)_2$-Cavitand **(11a)**: 200 mg / 0.214 mmol,Na_2CO_3: 113 mg / 1.07 mmol, 1,4-dioxane: 0.943 mL / 10.7 mmol, Yield: 360 mg / 0.182 mmol / 85 % / pale yellow powder. R_f-data (CHCl3 / methanol = 10/1): 0.9 reactant **(2)** / 0.57

product / 0 reactant **(11a)**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.18 - 7.09 (8H, m, $\underline{H}$-Ar), 5.77 (8 H, m, OC$\underline{H}$HO), 4.93 (6 H, b, Ar-C$\underline{H}_2$OAc), 4.70 (8 H, m, Ar-C$\underline{H}$-Ar), 4.42 (4 H, bs, Ar-C$\underline{H}_2$OH), 4.25 (8 H, m, OCH$\underline{H}$O), 4.05 - 3.90 (6 H, b, C$\underline{H}_2$NHC$\underline{H}_2$ & C$\underline{H}_2$NH$_2$), 2.13 (16 H, m, C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 2.00 (9 H, s, OOCCH$_3$), 1.28 (48 - 52 H, m, CH$_2$(C$\underline{H}_2$)$_3$CH$_3$), 0.84 (24 - 26 H, m, CH$_2$(CH$_2$)$_3$C$\underline{H}_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.62, 153.32, 152.67, 137.17, 120.88, 117.85, 99.55 - 97.47, 56.17, 55.87, 36.96, 31.00 - 21.65, 20.99, 13.06. APCI-MS (positive ions) m/z (%): 2107.4 (100) [M + Na + DMA+ H$_2$O]$^+$, 2066.4 (85) [M + DMA]$^+$. Formula: $C_{118}H_{150}O_{24}N_2$ (1980.47 g/mol).

[(CH$_2$OH)$_3$-Cav]-(CH$_2$NHCH$_2$)-[A,B-(CH$_2$OH)$_2$(CH$_2$NH$_2$)-Cav] (17)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.07 (8H, m, $\underline{H}$-Ar), 5.83 (8 H, bd, OC$\underline{H}$HO), 4.71 (8 H, b, Ar-C$\underline{H}$-Ar), 4.45 - 4.25 (18 H, b , Ar-C$\underline{H}_2$OH & OCH$\underline{H}$O), 3.80 - 3.60 (6 H, Ar-CH$_2$N), 2.14 (16 H, m, C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 1.33 (48 H, m, CH$_2$(C$\underline{H}_2$)$_3$CH$_3$), 0.89 (24 H, m, CH$_2$(CH$_2$)$_3$C$\underline{H}_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.3, 137.4, 127.5, 119.5, 98.83, 55.75, 35.80, 30.03 - 21.62, 14.05. APCI-MS (positive ions) m/z (%): 1837 (100) [M - OH + H]$^+$, 1853 (65) [M]$^+$. Formula: $C_{112}H_{144}O_{21}N_2$ (1854.32 g/mol).

[(CH$_2$OAc)$_3$-Cav]-(CH$_2$NHCH$_2$)-[(CH$_2$OH)(CH$_2$NH$_2$)$_2$-Cav] (18)

(CH$_2$Br)(CH$_2$OAc)$_3$-Cavitand **(2)**: 241 mg / 0.214 mmol, (CH$_2$NH$_2$)$_3$(CH$_2$OH)-Cavitand **(12)**: 200 mg / 0.214 mmol, Na_2CO_3 : 113 mg / 1.07 mmol, 1,4-dioxane : 0.943 mL / 10.7 mmol, Yield: 320 mg / 0.161 mmol / 75 % / yellow powder. R_f-data ($CHCl_3$ / methanol = 10/1): 0.9 reactant **(2)** / 0.55 product / 0 reactant **(12)**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.19 - 7.01 (8H,

m, H-Ar), 5.77 (8 H, m, OCHHO), 5.03 (6 H, b, Ar-CH$_2$OAc), 4.75 (8 H, m, Ar-CH-Ar), 4.65 (6 H, bs, Ar-CH$_2$OH), 4.19 (8 H, m, OCHHO), 4.04 (8 H, b, Ar-CH$_2$N), 2.09 (16 H, m, CH$_2$(CH$_2$)$_3$CH$_3$), 1.96 (9 H, s, OOCCH$_3$), 1.32 (48 H, m, CH$_2$(CH$_2$)$_3$CH$_3$), 0.84 (24 H, m, CH$_2$(CH$_2$)$_3$CH$_3$). ^{13}C-NMR (125 MHz, CDCl$_3$): δ 170.83, 170.30, 160.17, 154.27, 153.77, 139.03, 138.28, 127.96, 122.35 - 116.64, 100.44, 99.90, 56.92, 46.17, 36.96, 32.09 - 22.74, 21.03, 14.61. APCI-MS (positive ions) m/z (%): 1978.7 (75) $[M]^+$, 2108.3 [M + DMA + H2O + Na]$^+$. Formula: $C_{118}H_{151}O_{23}N_3$ (1979.49 g/mol).

[(CH$_2$OH)$_3$-Cav]-(CH$_2$NHCH$_2$)-[(CH$_2$OH)(CH$_2$NH$_2$)$_2$-Cav] (19)

^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.18 - 6.97 (8H, m, H-Ar), 5.81 (8 H, m, OCHHO), 4.75 (8 H, m, Ar-CH-Ar), 4.47 (6 H, bs, Ar-CH$_2$OH), 4.33 (8 H, m, OCHHO), 4.11 & 3.70 - 3.40 (8 H, b, Ar-CH$_2$N), 2.09 (16 H, m, CH$_2$(CH$_2$)$_3$CH$_3$), 1.32 - 1.23 (48 H, m, CH$_2$(CH$_2$)$_3$CH$_3$), 0.88 (24 H, m, CH$_2$(CH$_2$)$_3$CH$_3$). ^{13}C-NMR (125 MHz, CDCl$_3$): δ 159.63, 152.55, 137.94, 137.27, 125.70, 118.86 - 114.61, 98.86, 52.3, 35.90, 31.03 - 21.62, 13.05. APCI-MS (positive ions) m/z (%): 1853.7 (75) $[M + H]^+$. Formula: $C_{112}H_{145}O_{20}N_3$ (1853.38 g/mol).

[(CH$_2$OAc)$_3$-Cav]-(CH$_2$NHCH$_2$)-[(CH$_2$NH$_2$)$_3$-Cav] (20)

(CH$_2$Br)(CH$_2$OAc)$_3$-Cavitand **(2)**: 241 mg / 0.214 mmol, (CH$_2$NH$_2$)$_4$-Cavitand **(13)**: 200 mg / 0.214 mmol, Na$_2$CO$_3$: 113 mg / 1.07 mmol, 1,4-dioxane : 0.943 mL / 10.7 mmol, Yield: 240 mg / 0.161 mmol / 56 % / pale yellow powder. R$_f$-data (CHCl$_3$ / methanol = 10/1): 0.9 reactant **(2)** / 0.53 product / 0 reactant **(13)**. ^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.19 - 7.01 (8H, m, H-Ar),

5.77 (8 H, m, OC<u>H</u>HO), 4.96 (6 H, b, Ar-C<u>H</u>$_2$OAc), 4.71 (8 H, bs, Ar-C<u>H</u>-Ar), 4.27 (8 H, m, OCH<u>H</u>O), 4.14 - 3.90 (10 H, b, Ar-C<u>H</u>$_2$N), 2.09 (16 H, m, <u>H</u>H$_2$(CH$_2$)$_3$CH$_3$), 1.96 (9 H, s, OOCCH$_3$), 1.33 (48 H, m, CH$_2$(C<u>H</u>$_2$)$_3$CH$_3$), 0.83 (24 H, m, CH$_2$(CH$_2$)$_3$<u>H</u>H$_3$). ^{13}C-NMR (125 MHz, CDCl$_3$): δ 170.83, 170.35, 153.32, 152.77, 138.04 - 136.40, 120.67 - 118.20, 99.85, 55.9, 36.97, 32.09 - 22.74, 21.03, 14.61. APCI-MS (positive ions) m/z (%): 1014.8 (45) [M + DMSO + H$_2$O + Na]$^{2+}$, 2047.3 (20) [M + DMA - H$_2$O]$^+$, 2064.4 (10) [M + DMA]$^+$, 2107.3 (100) [M + DMA + H$_2$O + Na]$^+$. Formula: C$_{118}$H$_{152}$O$_{22}$N$_4$ (1978.50 g/mol).

[(CH$_2$OH)$_3$-Cav]-(CH$_2$NHCH$_2$)-[(CH$_2$NH$_2$)$_3$-Cav] (21)

^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.06 & 6.97 (8H, s, <u>H</u>-Ar), 5.85 (8 H, bd, OC<u>H</u>HO,), 4.74 (8 H, m, Ar-C<u>H</u>-Ar), 4.46 (6 H, bs, Ar-C<u>H</u>$_2$OH), 4.33 (8 H, bd, OCH<u>H</u>O), 4.11 & 3.70 - 3.40 (10 H, b, Ar-C<u>H</u>$_2$N), 2.14 (16 H, m, <u>H</u>H$_2$(CH$_2$)$_3$CH$_3$), 1.32 - 1.23 (48 H, m, CH$_2$(C<u>H</u>$_2$)$_3$CH$_3$), 0.88 (24 H, m, CH$_2$(CH$_2$)$_3$C<u>H</u>$_3$). ^{13}C-NMR (125 MHz, CDCl$_3$): δ 152.60, 137.26, 121.32 - 116.19, 98.87, 35.90, 31.03 - 21.66, 13.05. APCI-MS (positive ions) m/z (%): 1852.2 (95) [M + H]$^+$, 1850.2 (100) [M - 2 H]$^+$. Formula: C$_{112}$H$_{146}$O$_{19}$N$_4$ (1852.39 g/mol).

Double-bridged Hemicarcerands

[A,B-(CH$_2$OAc)$_2$-Cav]-(CH$_2$NHCH$_2$)$_2$-[A,B-(CH$_2$OH)$_2$-Cav] (22)

A,B-(CH$_2$Br)$_2$(CH$_2$OAc)$_2$-Cavitand **(3a)**: 614 mg / 0.534 mmol, A,B-(CH$_2$NH$_2$)$_2$(CH$_2$OH)$_2$-Cavitand **(11a)**: 500 mg / 0.534 mmol, Na$_2$CO$_3$: 284 mg / 2.67 mmol, 1,4-dioxane : 2.29 mL / 26.7 mmol, Yield: 980 mg

/ 0.510 mmol / 95 % / pale yellow powder. R_f-data ($CHCl_3$ / methanol / triethylamine = 10/0.5/0.5): 0.9 reactant **(3a)** / 0.53 product/ 0 reactant **(11a)**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.19 - 7.06 (8H, m, H-Ar), 5.91 (8 H, bm, OCHHO), 4.85 (8 H, b, Ar-CH_2O), 4.69 (8 H, bs, Ar-CH-Ar), 4.44 (8 H, b, Ar-CH_2N), 4.26 (8 H, bm, OCHHO), 2.09 (16 H, m, CH_2(CH_2)$_3$$CH_3$), 1.99 (6 - 7 H, s, OOC$CH_3$), 1.33 (48 - 50 H, m, CH_2(CH_2)$_3$$CH_3$), 0.83 (24 H, m, CH_2(CH_2)$_3$CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.83, 153.32, 152.77, 138.99 - 136.40, 120.67 - 118.20, 98.74, 55.96, 35.90, 31.09 - 20.06, 19.99, 13.06. APCI-MS (positive ions) m/z (%) 1920.3 (100) $[M + H]^+$. APCI-MS (negative ions) m/z (%) 1918.2 (100) $[M - H]^-$. APCI-MS, negative ions) m/z (%): 975.5 (100) $[M + MeOH]_{2-}$, 1954.5 (30) $[M + MeOH]^-$. Formula: $C_{116}H_{146}O_{22}N_2$ (1920.46 g/mol).

[A,B-(CH_2OH)$_2$-Cav]-(CH_2NHCH_2)$_2$-[A,B-(CH_2OH)$_2$-Cav] (23)

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.06 (8H, bs, H-Ar), 5.86 (8 H, b, OCHHO,), 4.73 (8 H, m, Ar-CH-Ar), 4.48 (8 H, b, Ar-CH_2OH), 4.33 - 4.11 (16 H, b, OCHHO + Ar-CH_2N), 2.14 (16 H, m, CH_2(CH_2)$_3$$CH_3$), 1.35 - 1.23 (48 -52 H, m, CH_2(CH_2)$_3$$CH_3$), 0.88 (24 H, m, CH_2(CH_2)$_3$CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.6, 137.2, 120.3, 98.8, 57.1, 35.9, 31.03 - 21.66, 13.05. APCI-MS (positive ions) m/z (%): 1835.2 (100) $[M]^+$, 1837.2 (95) $[M + 2 H]^+$. Formula: $C_{112}H_{142}$ $O_{20}N_2$ (1836.38 g/mol).

[A,B-(CH_2OAc)$_2$-Cav]-(CH_2NHCH_2)$_2$-[A,B-(CH_2OH)(CH_2NH_2)-Cav] (24)

(CH_2Br)$_3$(CH_2OAc)-Cavitand **(3a)**: 240 mg / 0.214 mmol, (CH_2NH_2)$_3$(CH_2OH)-

Cavitand **(12)**: 200 mg / 0.214 mmol, Na_2CO_3 : 113 mg / 1.07 mmol, 1,4-dioxane : 0.943 mL / 10.7 mmol. Yield: 380 mg / 0.198 mmol / 92 % / pale yellow powder. R_f-data ($CHCl_3$ / methanol = 10/1) : 0.9 reactant (3a) / 0.53 product/ 0.0 reactant **(12)**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.15 - 7.03 (8H, m, H-Ar), 5.77 (6 - 8 H, m, OCHHO), 4.93 (6 H, b, Ar-CH_2OAc), 4.72 (8 + 2 H, b, Ar-CH-Ar & Ar-CH_2OH), 4.30 (8 H, b, OCHHO), 4.04 & 3.61 (10 H, b, Ar-CH_2N), 2.14 (16 H, m, $CH_2(CH_2)_3CH_3$), 1.99 6 H, s, $OOCCH_3$), 1.32 (48 - 52 H, m, $CH_2(CH_2)_3CH_3$), 0.88 (24 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.88, 159.87, 152.90, 136.93, 121.57- 113.60, 99.39, 98.42, 45.04, 35.85, 30.95- 21.64, 19.8, 13.04. APCI-MS (positive ions) m/z (%): 1919.3 (90) $[M + H]^+$. Formula: $C_{116}H_{147}O_{21}N_3$ (1919.47 g/mol).

[A,B-$(CH_2OH)_2$-Cav]-$(CH_2NHCH_2)_2$-[A,B-$(CH_2OH)(CH_2NH_2)$-Cav] (25) ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.12 - 7.00 (8H, m, H-Ar), 5.86 (8 H, m, OCHHO), 4.75 (8 H, m, Ar-CH-Ar), 4.52 (6 H, b, Ar-CH_2OH), 4.33 (8 H, b, OCHHO), 4.11 & 3.70 (8 H, b, Ar-CH_2N), 2.09 (16 H, m, $CH_2(CH_2)_3CH_3$), 1.32 - 1.23 (48 - 52 H, m, $CH_2(CH_2)_3CH_3$), 0.88 (24 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 159.63, 152.58, 136.00, 122.18, 115.86, 98.00, 56.2, 35.94, 30.92- 21.61, 13.05. APCI-MS (positive ions): m/z (%) 1834.2 (100) $[M]^+$. Formula: $C_{112}H_{143}O_{19}N_2$ (1835.40 g/mol).

[A,B-$(CH_2OAc)_2$-Cav]-$(CH_2NHCH_2)_2$-[A,B-$(CH_2OH)(CH_2NH_2)$-Cav] (26)

$(CH_2Br)(CH_2OAc)_3$-Cavitand **(3a)**: 240 mg / 0.214 mmol, $(CH_2NH_2)_4$-Cavitand **(13)**: 200 mg / 0.214 mmol, Na_2CO_3 : 113 mg / 1.07 mmol,

1,4-dioxane : 0.943 mL / 10.7 mmol. Yield: 370 mg / 0.193 mmol / 90 % / pale yellow powder. R_f-data ($CHCl_3$/methanol = 10/1) : 0.9 reactant **(3a)** / 0.55 product/ 0 reactant **(13)**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.10 - 7.01 (8H, m, H-Ar), 5.80 (6 - 8 H, b, OCHHO), 4.97 (4 H, b, Ar-CH_2OAc), 4.72 (8 H, b, Ar-CH-Ar), 4.24 (8 H, b, OCHHO), 3.80 - 3.61 (9 (12) H, b, Ar-CH_2N), 2.14 (16 H, m, $CH_2(CH_2)_3CH_3$), 1.99 (9 (6) H, s, $OOCCH_3$), 1.34 (48 H, m, $CH_2(CH_2)_3CH_3$), 0.88 (24 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 169.88, 159.87, 153.56, 135.52, 122.23, 116.10, 98.72, 55.6, 35.85, 32.76 - 21.62, 22.35, 13.04. APCI-MS (positive ions) m/z (%): 1900.2 (100) $[M - H_2O + H]^+$, 1917.2 $[M + H]^+$. Formula: $C_{116}H_{148}O_{20}N_4$ (1918.49 g/mol).

[A,B-(CH_2OH)$_2$-Cav]-(CH_2NHCH_2)$_2$-[A,B-(CH_2OH)(CH_2NH_2)-Cav] (27) ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.12 - 7.00 (8H, m, H-Ar), 5.87 (8 H, m, OCHHO), 4.72 (8 H, m, Ar-CH-Ar), 4.50 (4 H, b, Ar-CH_2OH), 4.33 (8 H, b, OCHHO), 3.80 - 3.60 (10 H, b, Ar-CH_2N), 2.14 (16 H, m, $CH_2(CH_2)_3CH_3$), 1.34 - 1.23 (48 - 56 H, m, $CH_2(CH_2)_3CH_3$), 0.88 (24 H, m, $CH_2(CH_2)_3CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): only poorly resolved spectra with broad peaks could be obtained. APCI-MS (positive ions) m/z (%): 1817.2 (100) $[M - H_2O + H]^+$. Formula: $C_{112}H_{144}O_{18}N_4$ (1834.41 g/mol).

Metal Complexes of Hemicarcerand 23

Equimolar amounts of the respective metal salts [$Mn(SO_3CF_3)_2$, $Co(SO_3CF_3)_2$, $Ni(SO_3CF_3)_2$, $Cu(SO_3CF_3)_2$] and the hemicarcerand **23** in the solution were combined and heated to 55°C for 24 h. The complexes were recrystallized by allowing diethyl ether to slowly diffuse onto the solution, producing the

respective metal complexes as powdery materials in quantitative yields.

23·$Cu(CF_3SO_3)_2$ $C_{114}H_{142}CuF_6N_2O_{26}S_2$ (2198.1 g/mol) : C 62.2% (found 63.5%), H 6.5% (found 6.9%), N 1.3% (found 1.6%).

23·$Ni(ClO_4)$·5 THF: $C_{116}H_{150}Cl_2N_2NiO_{33}$ (2230.0 g/mol): C 62.5% (found 63.6%), H 6.8% (found 6.75), N 1.3% (found 1.2%).

^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.35-7.05 (br, 8H, Ar<u>H</u>), 6.05-5.70 (br, 8H, OC<u>H</u>HO-2), 4.82-3.45 (br, 32H, OCH<u>H</u>O,ArC<u>H</u>Ar, Ar$C\underline{H_2}$N, $ArCH_2O$), 2.34-1.73 (br, 16H, $C\underline{H_2}CH_2CH_3$), 1.58-1.32 (br, 16H, $CH_2C\underline{H_2}CH_3$), 1.16-0.85 (br, 24H, $CH_2CH_2C\underline{H_3}$).

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