Supporting Information for

Self-Organised Heteroditopic Macrocyclic Superstructures

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Experimental Procedure and full characterization for compound 1

4-phenylurea-benzo-15-crown-5, 1 was prepared by refluxing phenylisocyanate and 4'-aminobenzo-15-crown-5 (1.5/1 mol/mol) in $CHCl_3$ (5 h). After removal of the solvent, the residue was recrystallized in CH_3CN to afford 1 (90 % yield). 1, (yield =93%). ^{1}H NMR ($CDCl_3$) δ = 4.01 (m,12H), 6.27 (m, 1H), 6.56 (d, *J*= 3.81 Hz, 1H); 6.95 (m, 2H); 7.21 (m, 6H), 8.17 (s, 1H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$) δ= 68.54, 69.74, 70.45, 71.21, 108.61, 114.40, 115.34, 120.14, 123.19, 129.34, 133.00, 139.38, 145.45, 149.58, 154.68; ES-MS: m/z (%): 403 (100) MH^+. $C_{21}H_{26}N_2O_6$ (402.4 g/mol):calcd C 62.67, H 6.51, N, 6.96; found C 62.49, H 6.33, N 7.10.

Cooperative association model for calculation of dimerization (K_2) and association (K_a) constants of 1

The association dynamic equilibria of **1** were treated with a cooperative association model as previously described in references 9. Namely, one assumes that all oligomerization constants K_a are the same and the first dimerization constant K_2 is different.

$$\mathbf{1} + \mathbf{1} \overset{K_2}{\rightleftharpoons} \mathbf{1}_2$$

$$\mathbf{1} + \mathbf{1}_{i-1} \overset{K_i=K_a}{\rightleftharpoons} \mathbf{1}_i$$

with $K_2 \neq K_3 = K_4 = \cdots\cdots\cdots K_i = K_a$

The concentration dependency of the chemical shifts presented in Figure 1, can now be described with Equation (1)[8a] and gives the association constants K_2 and K_a.

$$\frac{(1-P_f)^{1/2}}{(2P_f - 1)\, c^{1/2}} = K_2^{1/2} + K_a \frac{P_f\,[(1-P_f)\, c]^{1/2}}{2P_f - 1} \qquad (1)$$

$$\text{with} \quad P_f = \frac{\delta_a - \delta_{obs}}{\delta_a - \delta_m}$$

where P_f : the population fraction of free N-H protons;

c: molar concentration of **1**;

δ_a: the limiting chemical shift for the fully H-bond state, determined by extrapolation from $\delta = f(1/X_1)$dependency, X_1=molar ratio of **1**;

δ_m: the limiting chemical shift for the non H-bond state, determined by extrapolation from $\delta = f(X_1)$ dependency, X_1=molar ratio of **1**;

δ_{obs}: observed chemical shift;

Measurements were performed in $CDCl_3$ using an Bruker AC250 spectrometer. The assignments were made on the base of the COSY and ROESY spectra. Equilibration between hydrogen-bonded and non-hydrogen bonded states for a given N-H proton is almost always fast on the NMR time scale and observed proton chemical shifts are weighted averages of the chemical shifts of contributing states. Variable temperature NH proton experiment were performed for the compound **1**in the range of 253-298 K.

Experimental Procedure and ^{1}H NMR spectra for 1-NaX complexes (X= F^-, Cl^-, NO_3^-, $CF_3SO_3^-$)

A solution of 2.5 M of **1** in $CDCl_3$ and solid salts were briefly ultrasonicated at room temperature, then filtered by gravity. The resulting solutions were studied by ^{1}H NMR (Figure S1) and ESI mass spectrometry.

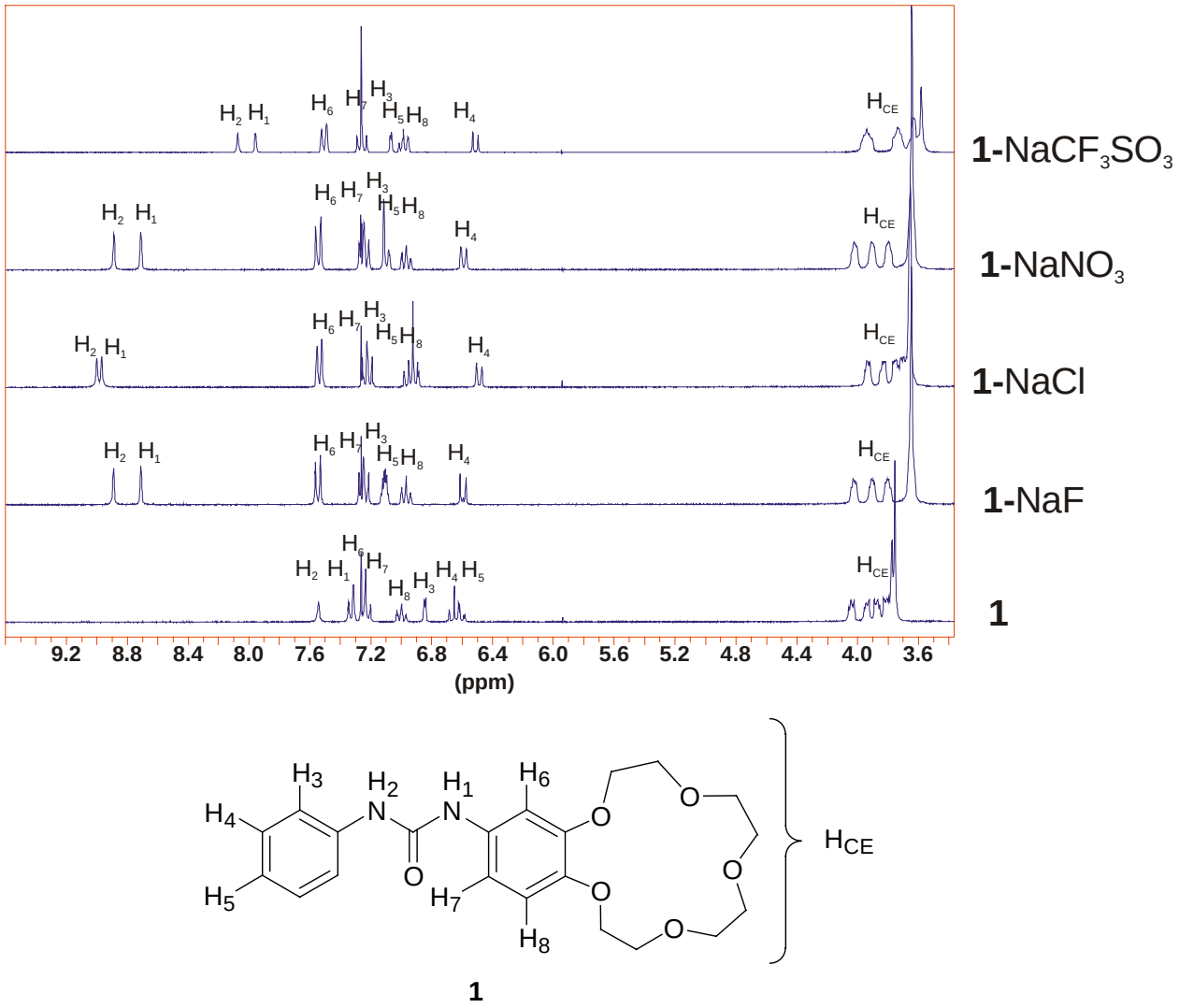

Figure S1 ^{1}H NMR spectra of receptor **1** and of **1**-NaX (X= F^-, Cl^-, NO_3^-, $CF_3SO_3^-$) salts into $CDCl_3$ at room temperature

Crystallographic data for 1, 1·NaCl and 1·$NaNO_3$

X-ray diffraction data for **1**, **1**·NaCl and **1**·$NaNO_3$ crystals, grown by slow diffusion of in *i*-propylether in an acetonitrile solution at room temperature. They were collected at beamline ID11 at the European Synchrotron Facility (ESRF), Grenoble. A wavelength of 0.50606 Å was selected using a double crystal Si (111) monochromator and data were collected with a Bruker "Smart" CDD camera system at fixed 2θ (*T*=120 K). The solutions were solved using direct methods and refined-based on F^2 using independent data $I>2\sigma(I)$- by full matrix least squares methods.

Crystal data for **1**: $C_{21}H_{26}N_2O_6$, M=402.45, colorless plates, 0.50 x 0.15 x 0.15 mm, monoclinic, space group $P2_1/n$, D_c=1.210 g cm^{-3}, a=19.333(3) Å, b=4.8301(7) Å, c=24.713(4) Å, α=90°, β=106.876(7)°, γ=90°, V= 2208.3(6) $Å^3$, Z=4, μ= 0.089 mm^{-1}. 23046 measured reflections, 6560 unique, 3930 with $I>2\sigma(I)$. Final *R* factors are R_1=0.0751 and wR_2=0.2061; 340 parameters, maximal residual electron density is 0.540 $eÅ^{-3}$. CCDC reference number 195270

Crystal data for **1**·NaCl: $C_{42}H_{52}ClN_4NaO_{12}$, M=863.34, colorless plates, 0.35 x 0.25 x 0.15 mm, monoclinic, space group $P2_1/c$, D_c=1.181 gcm^{-3}, a=11.390(2) Å, b=36.076(5) Å, c=12.420(2) Å, α=90°, β=107.900(7)°, γ=90°, V= 4856.4(6) $Å^3$, Z=4, μ= 0.146 mm^{-1}. 31050 measured reflections, 13367 unique, 9062 with $I>2\sigma(I)$. Final *R* factors are R_1=0.0879 and wR_2=0.0637; 542 parameters, maximal residual electron density is 1.710 $eÅ^{-3}$. CCDC reference number 195271

Crystal data for **1**·$NaNO_3$, $C_{23}H_{25}N_4NaO_9$, M=524.46, colorless plates, 0.40 x 0.15 x 0.10 mm triclinic, space group *P*-1, D_c=1.201 gcm^{-3}, a=8.7388(5) Å, b=11.2448(5) Å, c=15.318(1) Å, α=101.248(4)°, β=95.301(3)°, γ=98.076(3)°, V= 1450.5(2) $Å^3$, Z=2, μ= 0.106mm^{-1}. 17603 measured reflections, 7546 unique, 5925 with $I>2\sigma(I)$. Final *R* factors are R_1=0.0728 and wR_2=0.0696; 335 parameters, maximal residual electron density is 0.780 $eÅ^{-3}$. CCDC reference number 195272.

Membrane transport procedure

Membrane transport experiments were performed with magnetic stirring in a conventional U-tube glass cell at room temperature. The feed phase was a 25 ml of 1M NaX salt; the membrane phase consisted of $5*10^{-2}$ M $CHCl_3$ solution (25 ml) of **1-3** in chloroform and the strip phase consisted of 25 ml of distilled water. Aliquots (0.01 ml) of both aqueous solution were withdrawn at appropriate intervals. The diffusion coefficient of NaCl has been determined using the initial fluxes method by plotting initial flux value J_0 against $C_{receptor}$