Supplementary information

Cascade and commutative self-assembles of nanoscale three-component systems controlled by the configuration of thiacalix[4]arene

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Table S1. Logarithms of the association constants (lgK_{ass}) and stoichiometry (n ("guest" / "host")) of complexes of silver ions, dicarboxylic and hydroxy acids with macrocycles **1-3**[a]

associates	n	lgK_{ass}
cone **1** + $AgNO_3$	1.2±0.1	4.56±0.50
partial cone **2** + $AgNO_3$	1.1±0.1	4.18±0.63
1,3-alternate **3** + $AgNO_3$	2.1±0.1	9.44±0.45
cone **1** + oxalic acid	0.9±0.1	3.96±0.27
partial cone **2** + oxalic acid	1.2±0.2	4.38±0.79
1,3-alternate **3** + oxalic acid	0.9±0.04	3.66±0.20
cone **1** + malonic acid	0.8±0.05	3.00±0.21
partial cone **2** + malonic acid	1.0±0.1	3.26±0.54
1,3-alternate **3** + malonic acid	0.6±0.04	1.66±0.19
cone **1** + succinic acid	0.5±0.1	0.84±0.26
partial cone **2** + succinic acid	0.9±0.2	2.69±0.75
1,3-alternate **3** + succinic acid	0.6±0.1	1.12±0.32
cone **1** + glycolic acid	0.3±0.02	0.48±0.09
partial cone **2** + glycolic acid	0.4±0.1	0.41±0.58
1,3-alternate **3** + glycolic acid	0.4±0.1	1.13±0.47
cone **1** + tartaric acid	0.5±0.1	1.66±0.31
partial cone **2** + tartaric acid	1.0±0.2	2.47±1.06
1,3-alternate **3** + tartaric acid	1.1±0.2	3.89±0.85
cone **1** + maleic acid	2.1±0.2	8.91±0.72
partial cone **2** + maleic acid	1.0±0.02	5.03±0.08
1,3-alternate **3** + maleic acid	0.9±0.1	3.64±0.24
cone **1** + fumaric acid	1.3±0.1	5.53±0.67
partial cone **2** + fumaric acid	1.0±0.1	4.06±0.50
1,3-alternate **3** + fumaric acid	1.1±0.1	3.64±0.55

a) $[L]_{init} = 10^{-5}$ M, $[acid]_{init.} = 10^{-3}$ M.

Table S2. Size of aggregates (average hydrodynamic diameters, d_1, d_2, d_3 (nm)), and peak area intensity, S_1, S_2, S_3 (%), for peaks 1, 2, 3, respectively, obtained with p-*tert*-butyl thiacalix[4]arene derivatives **1-3** and silver cations, dicarboxylic and hydroxy acids in CH_2Cl_2 (HPLC), and polydispersity index (PDI) measured at 3 and 78 h after solution preparation [a]

system	d_1, nm/S_1, %		d_2, nm/S_2, %		d_3, nm/S_3, %		PDI	
	3 h	78 h	3 h	78 h	3 h	78 h	3 h	78 h
cone **1**	-	-	223.5±46.4/ 75.2±30.6	69.2±21.3/ 49.8±23.1	5124.8±539.9/ 24.8±30.6	5303.5±374.0/ 50.2±23.1	0.41±0.23	0.95±0.15
cone **1** + $AgNO_3$	-	7.8±0.4/ 9.2±1.9	77.4±10.0/ 95.5±2.1	59.1±4.1/ 90.8±1.9	4197.6±721.7/ 4.5±2.1	-	0.23±0.07	0.33±0.06
cone **1** + oxalic acid	10.3±12.0/ 19.5±5.5	-	251.0±50.0/ 59.1±12.9	111.5±36.8/ 97.0±6.7	4784.0±1032.8/ 21.4±9.1	5283.0±288.2/ 3.0±6.7	0.63±0.37	0.23±0.11
cone **1** + malonic acid	-	-	240.0±54.2/ 90.8±4.0	186.4±42.5/ 91.8±7.3	4239.4±486.2/ 9.2±4.0	4354.3±247.6/ 8.2±7.3	0.29±0.10	0.29±0.12
cone **1** + succinic acid	-	-	120.2±10.8/100	119.4±8.2/100	-	-	0.11±0.04	0.11±0.03
cone **1** + glycolic acid	-	-	117.9±17.9/ 93.9±7.1	76.2±31.3/ 97.3±4.9	4232.0±675.4/ 6.1±7.1	5327.3±448.0/ 2.7±4.9	0.17±0.17	0.43±0.42
cone **1** + tartaric acid	-	-	303.3±176.6/ 68.7±23.9	-	3921.8±983.5/ 31.3±23.9	-	0.53±0.18	-

cone **1** + maleic acid	-	-	221.6±73.2/ 92.2±9.2	144.7±23.3/ 90.0±5.9	4186.1±451.2/ 7.8±9.2	4795.4±758.2/ 10.0±5.9	0.28±0.15	0.15±0.02
cone **1** + fumaric acid	-	9.1±3.7/ 26.9±15.0	43.4±71.4/ 55.7±27.2	377.8±61.3/ 73.1±15.0	1840.0±922.0/ 44.3±27.2	-	0.53±0.97	0.95±0.17
partial cone **2** + $AgNO_3$	-	-	61.0±7.0/ 90.4±9.5	63.0±10.9/ 96.1±1.7	2895.8±1715.5/ 9.6±9.5	4895.9±4895.9/ 3.9±1.7	0.29±0.16	0.20±0.16
partial cone **2** + oxalic acid	-	-	80.5±0.9/100	100.6±1.9/100	-	-	0.10±0.02	0.06±0.01
partial cone **2** + malonic acid	-	-	183.3±4.0/100	215.0±4.2/100	-	-	0.04±0.02	0.06±0.02
partial cone **2** + glycolic acid	-	-	240.3±32.8/100	185.2±30.5/ 92.5±8.1	-	5071.9±237.4/ 7.6±8.1	0.13±0.03	0.17±0.07
partial cone **2** + tartaric acid	-	-	-	152.8±54.9/ 87.2±9.5	-	4329.6±511.9/ 12.8±9.5	-	0.21±0.10
partial cone **2** + maleic acid	-	-	-	143.6±90.6/ 87.2±43.2	-	3811.0±406.0/ 12.8±43.2	-	0.34±0.11
partial cone **2** + fumaric acid	-	-	139.9±8.6/100	176.8±27.3/100	-	-	0.10±0.03	0.15±0.04
1,3-alternate **3** + $AgNO_3$	-	-	112.5±16.1/100	108.9±7.0/ 99.2±1.3	-	4339.4±259.7/ 0.8±1.3	0.21±0.02	0.18±0.05

1,3-alternate **3** + oxalic acid	-	-	81.6±2.1/100	96.7±5.1/100	-	-	0.17±0.01	0.11±0.0.1
1,3-alternate **3** + malonic acid	-	-	182.6±3.8/100	211.9±6.4/100	-	-	0.05±0.03	0.09±0.04
1,3-alternate **3** + succinic acid	-	-	86.6±8.0/100	114.0±34.1/100	-	-	0.13±0.03	0.12±0.09
1,3-alternate **3** + glycolic acid	-	-	148.0±12.1/100	158.1±7.2/100	-	-	0.15±0.05	0.15±0.03
1,3-alternate **3** + maleic acid	-	-	278.1±11.3/100	-	-	-	0.17±0.21	-
1,3-alternate **3** + fumaric acid		-	118.7±5.0/100	261.7±49.8/100	-	-	0.13±0.04	0.20±0.04

[a] ±, standard deviation; -, no aggregates are formed.

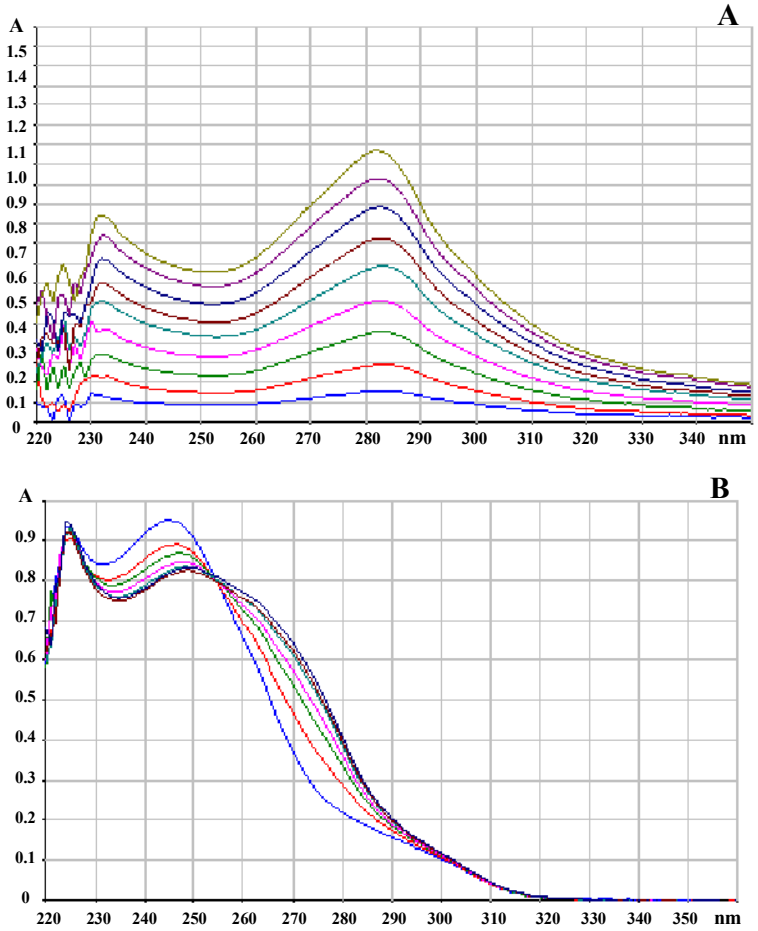

Figure S1. UV spectra (10^{-5} mol L^{-1}, 1 cm cell) of complexes based on (**A**) p-*tert*-butyl thiacalix[4]arene **3** and $AgNO_3$, (**B**) p-*tert*-butyl thiacalix[4]arene **1** and oxalic acid at different substrate concentrations ($2•10^{-5}$—$2•10^{-4}$ mol L^{-1}) in complex solvent dichloromethane/methanol.

Determination of the stability constant and stoichiometry of the complex by UV titration:

The system equilibrium is described by Eq. (1), where H, G, G_nH denote the ligands (receptor **1-3** or nanoparticles based on macrocycles **1-3** and substrates), substrates (silver nitrate and carboxylic acid (oxalic, malonic, succinic, glycolic, tartaric, maleic, fumaric acids)), complex with substrate, n – number of substrate interacting with one ligand.

$$nG + H \Leftrightarrow G_nH \qquad (1)$$

The association constant, K_{ass}, is defined by Eq. (2).

$$K_{ass} = [G_nH] / [G]^n [H] \qquad (2)$$

To determine the stoichiometry coefficient n of the complexes forming in the organic phase Eq. (2) was converted into Eq. (3).

$$\lg K_{ass} = \lg [G_nH] - n \lg [G] - \lg [H] \qquad (3)$$

The solution absorbance A, is a sum of those related to complex, ligand and substrate (A_{GnH}, A_H and A_G, respectevly) is equal to:

$$A = A_{GnH} + A_H + A_G \qquad (4)$$

Assuming that the Beer-lambert law is obeyed for all the components considered Eq. 5, the absorbance A is expressed as:

$$A_i = c_i \varepsilon_i l \qquad (5)$$

where c_i is a molar concentration of i-species, ε_i the molar absorptivity, and l the cel thickness. For complexation between the ligand and substrate the absorbance mesurement is commonly conducted at the wavelength of absorbance maximum in the charge-transfer region where A_G=0. This gives Eq. 6.

$$A = A_{GnH} + A_H \qquad (6)$$

Concentration of the complex $[G_nH]$ in the system is calculated according to equations (5) and (6).

The plot of lg $[G_nH]$- lg [H] versus lg [G] (Fig. 1) presents a straight line, slope of which equals to n. Assotiation constants K_{ass} are calculated using the intercept values (b).

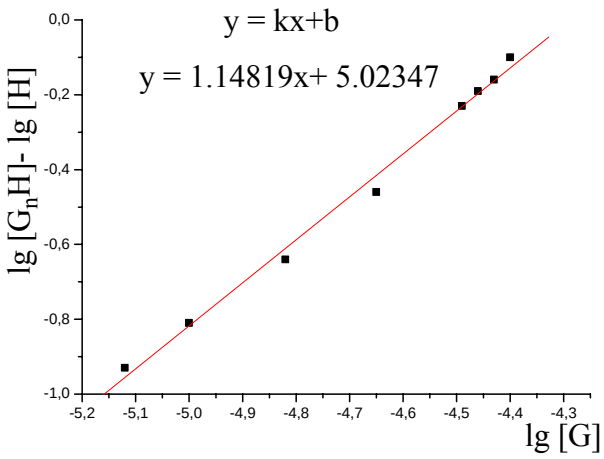

Figure 1. Plot of lg $[G_nH]$- lg [H] versus lg [G] for oxalic acid in methanol-dichloromehane solvent system by aggregates [p-*tert*-butyl thiacalix[4]arene **3**+$AgNO_3]_{agr.}$.

$b = \lg K_{acc}$ (7)

Origin 7.0 (Origin-Lab Corporation) was used for all the calculations.

Determination of the confidence interval:

The population standard deviation, denoted by **σ** is defined as follows:

$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2};$$

where $\{x_1, x_2, ..., x_N\}$ are the observed values of the sample items, $\bar{x}$ is the mean value of these observations and **n** is the sample size.

The sample standard deviation, denoted by **s** is defined as follows:

$$s = \sqrt{\frac{n}{n-1}\sigma^2} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2};$$

The arithmetic mean $\bar{X}$ is defined via the equation:

$$\bar{X} = \bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i = \frac{1}{n}(x_1 + \cdots - x_n) \ ;$$

The independent Student's **t-test** is defined via the equation(in testing the null hypothesis that the population mean is equal to a specified value μ, one uses the statistic):

$$t = Z = \frac{\bar{X} - \mu}{\sigma / \sqrt{n}} \ ;$$

dependent on the parameter **μ** to be estimated, but with a standard normal distribution independent of the parameter **μ**. Hence it is possible to find the values –z and z, independent of μ, between which Z lies with a probability of 1−α, a measure of how confident we want to be. Take 1−α = 0.95. We then have:

$$P(-z \leq Z \leq z) = 1 - \alpha = 0.95.$$

The number z follows from the cumulative distribution function, in this case the cumulative normal distribution function:

$$\Phi(z) = P(Z \leq z) = 1 - \tfrac{\alpha}{2} = 0.975,$$

$$z = \Phi^{-1}(\Phi(z)) = \Phi^{-1}(0.975) = 1.96,$$

and we get:

$$0.95 = 1 - \alpha = P(-z \leq Z \leq z) = P\left(-1.96 \leq \frac{\bar{X} - \mu}{\sigma/\sqrt{n}} \leq 1.96\right)$$

$$= P\left(\bar{X} - 1.96\frac{\sigma}{\sqrt{n}} \leq \mu \leq \bar{X} + 1.96\frac{\sigma}{\sqrt{n}}\right)$$

This may be interpreted as: with a probability of 0.95, there is a confidence interval within which the parameter μ will be found between the stochastic endpoints

$\bar{X} - 1.96\frac{\sigma}{\sqrt{n}}$ and $\bar{X} + 1.96\frac{\sigma}{\sqrt{n}}$.