Encapsulation of secondary and tertiary ammonium salts by resorcinarenes and pyrogallarenes: The effect of size and charge concentration

Ngong Kodiah Beyeh,*[a] Fanfang Pan,[a] Arto Valkonen[a,b] and Kari Rissanen*[a]

[a] *Department of Chemistry, University of Jyväskylä, P. O. Box 35, 40014 Jyväskylä, Finland.*
[b] *Department of Chemistry and Bioengineering, Tampere University of Technology, P. O. Box 541, 33101 Tampere, Finland.*

Supporting Information

Table of Contents

I General Information

The resorcinarene and pyrogallarene hosts **1**-**3**, were synthesized according to reported procedures.[1] The ammonium salts **4a**, **4b** **5a** and **5b** were commercially available. The ammonium salts **4c** and **5c** were obtained from the corresponding piperazine and 1,4-dimethylpiperazine through simple protonation with HCl. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) and a Bruker Avance DRX 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometers. The mass spectrometric studies were performed with a QSTAR Elite ESI-Q-TOF mass spectrometer equipped with an API 200 TurboIonSpray ESI source from AB Sciex (former MDS Sciex) in Concord, Ontario (Canada). All experiments were performed on positive polarization. The parameters of the ion source, ion optics and quadrupole were optimized to get maximum abundance of the ions under study.

II. X-Ray Crystallographic Analyses

Single crystals X-ray diffractions for **2MeOH**@**2**$_2$, **5a**@**2**$_2$, **5b**@**3**$_2$ and **4a**@**2** were collected at 173 K on an Agilent Super-Nova diffractometer using mirror-monochromatized Mo-*K*α (λ = 0.71073 Å) radiation. The single crystal data for **5b**@**2**$_2$ and **5c**@**1** were collected at 123K using an Agilent SuperNova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Cu-*K*α (λ = 1.54184 Å) radiation. All the data collection and reduction were performed using the program *CrysAlisPro*[2]. The intensities were corrected for absorption using multi-scan method implemented in SCALE3 ABSPACK scaling algorithm[2] for **2MeOH**@**2**$_2$, **5a**@**2**$_2$, **4a**@**2** and **5c**@**1**, and analytical face index absorption correction method[3] for **5b**@**2**$_2$ and **5b**@**3**$_2$. The structures were solved by direct methods with *SHELXS*[4] and refined by full-matrix least-squares methods using the *OLEX2*[5], which utilizes the *SHELXL-97* module[4].

For **4a**@**2**, despite the guest ammonium salt molecule fully located, some weak electron densities were observed around the cation. They might be accounted for by disordered solvent molecules, however, they were too weak to be assigned (the maximum density is 1.02 e/Å^3). SQUEEZE[6] was used to remove these unassigned electrons. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were treated with the riding model.

For **5a**@**2**$_2$, the resorcinarene molecule was well ordered. Due to the hydrogen bonds, some of the O-H hydrogens were located at two positions. All these hydrogens can be found from difference Fourier maps and refined either with the riding model or with fixed positions. The guest molecules including the cationic trimethyl ammonium, the chloride anion, water molecules and methanol molecules were severely disordered. Based on the experience from other similar host-guest systems, the trimethyl ammonium cation was assigned in the cavity of the **2**$_2$ capsule with partial Cl^- in the middle of the lower rim of the four ethyl chains and partial Cl^- beside the

upper rim of the bowl of the resorcinarene molecule. All the atoms in the trimethyl ammonium were kept isotropic refinement with the carbon atoms having the same thermal displacement parameters, and geometry constraints were applied to the cation.

The resorcinarene molecule was also ordered in the structure of **5b**@$\mathbf{2}_2$. Similar with those in **5a**@$\mathbf{2}_2$, some of the O-H hydrogens were positioned at two places as well. They were located from difference Fourier maps and their positions were also refined with O-H distances (0.84 Å) constraint. All the other hydrogen atoms were refined with the riding model. For the cationic guest, due to the symmetry of the lattice, it was disordered. Distances constraints were applied with C-N of 1.45 Å and C-C of 1.54 Å. Additionally, the anisotropic parameters for some of the carbon atoms in the cation were constrained with "ISOR" or "SIMU". The hydrogen atoms bonded to C atoms in the guest were refined with the riding model, while the N-H hydrogen was obtained by the hydrogen bonding with the O and the position was fixed without refinement with U_{eq}(H) = 1.5U_{eq}(N) .

For **5b**@$\mathbf{3}_2$, all the atoms in the pyrogallarene molecule were well ordered including the O-H hydrogens, which were found from difference Fourier maps. They were refined either with the riding model or with fixed positions. All the hydrogens bonded to C atoms were refined with the riding model. Because of crystallized in different space group with that in **5b**@$\mathbf{2}_2$, the distribution of the triethylammonium cation was also different with that in **5b**@$\mathbf{2}_2$, although, distances constraints had to be applied for the cation with C-N of 1.45 Å and C-C of 1.54 Å. The hydrogen atoms bonded to C atoms in the guest were refined with the riding model, while the position of the N-H hydrogen was calculated from the ideal geometry with the N-H distance of 0.88 Å and U_{eq}(H) of 1.5U_{eq}(N) without position refinement. Because of disorder, the guest water molecules were not added with hydrogen when no suitable hydrogen bonds found. For the water with hydrogen atoms, the positions were also calculated from the geometries of the H_2O molecule and the hydrogen bonds without refinement. The U_{eq} of the hydrogen was constrained to 1.5 U_{eq}(O).

The crystals of **5c**@**1** suffered from twinning problem. Two twinning domains were detected from the diffraction. They were separated with the program CrysAlisPro and processed individually. The structure was solved with the reflections in the main domain and finalized with the hkl5-format data containing both twinning domains. Not only twinning, disorder also happened to the guests in the structure. All the hydrogen atoms were refined using riding models with U_{eq}(H) of 1.5U_{eq}(parent) for terminal groups and 1.2 U_{eq}(parent) for non-terminal groups.

In the structure of **2MeOH**@$\mathbf{2}_2$, all non-hydrogen atoms were refined with anisotropic thermal parameters without any constraint or restraint. Hydrogen atoms except O-H in MeOH molecules and H1, H4 atoms in the resorcinarene were introduced in proper positions with isotropic thermal parameters using riding models. The O-H hydrogen atoms in methanol molecules and H1, H4 were found from difference Fourier maps. Both of their positions and isotropic displacement parameters were freely refined.

Crystal data, information concerning data collection and reduction, and convergence results are documented in Table S1. The classical hydrogen bonds in all the structures are listed in Table S2.

Table S1. Crystallographic details for structures of **MeOH@2**$_2$, **5a@2**$_2$, **5b@2**$_2$, **5b@3**$_2$, **4a@2** and **5c@1**.

	MeOH@2$_2$	**5a@2**$_2$	**5b@2**$_2$	**5b@3**$_2$	**4a@2**	**5c@1**
Crystal data						
Chemical formula	$C_{40}H_{48}O_8 \cdot 2(CH_4O)$	$2(C_{40}H_{48}O_8) \cdot 2(CH_4O) \cdot 4(H_2O) \cdot C_3H_{10}N \cdot Cl$	$2(C_{40}H_{48}O_8) \cdot 4(CH_4O) \cdot 6(H_2O) \cdot C_6H_{16}N \cdot Cl$	$C_{36}H_{40}O_{12} \cdot 6(H_2O) \cdot (C_6H_{16}N) \cdot Cl$	$C_{40}H_{48}O_8 \cdot C_2H_8N \cdot Cl$	$C_{36}H_{40}O_8 \cdot 3(CH_4O) \cdot 2(H_2O) \cdot C_6H_{16}N_2 \cdot 2(Cl)$
M_r	720.86	1545.28	1687.47	1683.23	738.32	919.97
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, *Pnnn*	Orthorhombic, *Pnnn*	Triclinic, $P\bar{1}$	Orthorhombic, $Pna2_1$	Triclinic, $P\bar{1}$
Temperature (K)	173	173	123	173	173	123
a, *b*, *c* (Å)	12.1523 (17), 12.5597 (19), 14.3332 (14)	12.6722 (4), 15.1699 (5), 22.9465 (11)	12.6356 (2), 15.1060 (2), 23.0509 (3)	11.4812 (2), 11.7421 (2), 17.0131 (3)	22.4355 (13), 12.3522 (6), 15.3459 (7)	11.5090 (3), 11.5275 (2), 18.1749 (4)
α, β, γ (°)	104.789 (11), 102.134 (10), 107.641 (13)	90, 90, 90	90, 90, 90	102.6693 (14), 92.3148 (13), 102.5625 (14)	90, 90, 90	94.3636 (17), 101.9147 (18), 97.3470 (18)
V (Å^3)	1915.0 (5)	4411.2 (3)	4399.81 (9)	2174.82 (6)	4252.8 (4)	2326.86 (9)
Z	2	2	2	2	4	2
Radiation type	Mo *K*α	Mo *K*α	Cu *K*α	Mo *K*α	Mo *K*α	Cu *K*α
μ (mm^{-1})	0.09	0.11	1.02	0.13	0.14	1.79
Crystal size (mm)	0.21 × 0.11 × 0.08	0.35 × 0.27 × 0.18	0.4 × 0.29 × 0.22	0.19 × 0.11 × 0.07	0.11 × 0.1 × 0.06	0.21 × 0.16 × 0.10
Data collection						
T_{min}, T_{max}	0.819, 1.000	0.943, 1.000	0.715, 0.822	0.940, 0.972	0.445, 1.000	0.886, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10958, 6909, 4682	12721, 4003, 3009	13394, 4163, 3752	42658, 9085, 8267	52560, 7694, 5414	24223, 24223, 20623
R_{int}	0.046	0.027	0.020	0.022	0.135	0.0317
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.600	0.600	0.609	0.631	0.600	0.596
Refinement						
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.177, 1.08	0.063, 0.205, 1.05	0.068, 0.192, 1.04	0.085, 0.262, 1.08	0.079, 0.165, 1.02	0.056, 0.164, 1.02
No. of parameters	501	322	383	9085	7694	24223
No. of restraints	0	26	105	655	495	686
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.24, -0.26	0.48, -0.30	0.88, -0.55	109	7	49
Flack parameter	-	-	-	-	-0.05 (8)	-

Table S2. Intra- and intermolecular hydrogen bonds in the structures of 2MeOH@**2**$_2$, **5a**@**2**$_2$, **5b**@**2**$_2$, **5b**@**3**$_2$, **4a@2**, **5c**@**1**.

Donor-H···Acceptor	D-H	H···A	D···A	D-H···A
2MeOH@2$_2$				
Intramolecular				
O2-H2···O3	0.84	1.86	2.695(3)	171.2
O5-H5···O4	0.84	1.91	2.736(3)	167.3
O7-H7···O6	0.84	1.96	2.796(3)	175.1
O8-H8···Cl1A	0.84	1.98	2.821(3)	173.9
O10-H10···O5	0.97(4)	1.81(4)	2.775(3)	170(3)
Intermolecular				
O1-H1···O10^a	0.83(4)	2.03(4)	2.779(3)	151(3)
O3-H3···O9^b	0.84	1.80	2.640(3)	174.3
O4-H4O10^c	0.84	1.91	2.791(3)	148(3)
O6-H6O2^d	0.84	1.92	2.715(2)	158.7
4a@2				
Intramolecular				
O1-H1···O8	0.84	1.94	2.713(6)	153.0
O3-H3···O2	0.84	2.02	2.855(7)	174.5
O5-H5···O4	0.84	1.96	2.790(7)	170.5
O7-H7···O6	0.84	1.93	2.728(7)	159.3
N1A-H1AA···Cl1	0.99	2.14	3.1239	171.8
N1B-H1BB···Cl1	0.99	2.18	3.160(15)	172.4
O2-H2···Cl1	0.84	2.38	3.163(5)	155.7
Intermolecular				
O4-H4···Cl1^a	0.84	2.41	3.171(5)	150.9
O6-H6···O2^b	0.84	2.10	2.840(6)	146.8
O8-H8···Cl1^c	0.84	2.38	3.139(5)	150.0
5a@2$_2$				
Intramolecular				
O3-H3B···O2	0.84	1.93	2.765(2)	176.4
O2-H2B···O3	0.84	1.93	2.765(2)	172.9
Intermolecular				
O4-H4A···O1^a	0.84	1.87	2.697(3)	168.7
O4-H4B···O6^b	0.87	1.82	2.654	158.9
O4-H4B···Cl1^b	0.87	1.84	2.67(2)	158.6
O2-H2A···O7^c	0.88	1.84	2.697(8)	161.8
O6-H6A···O4^b	0.84	1.84	2.654(8)	162.2
O1-H1B···O4^a	0.84	1.86	2.697(3)	174.0
O1- H1A···O5^d	0.84	1.99	2.78(2)	155.3
5b@2$_2$				
Intramolecular				
O3- H3···O2	0.855(17)	1.870(18)	2.723(3)	175(4)
O6- H6A···Cl1B	0.84	1.97	2.774(14)	158.5
O6B- H6B···Cl1	0.84	2.08	2.851(14)	153.0
O7- H7A···O3	0.81(2)	2.12(5)	2.829(2)	146(9)
O9B- H9BA···O6B	0.87	1.94	2.731(12)	151.0
N1- H1···O10	0.85	1.91	2.758(8)	180.0
Intermolecular				
O1- H1B···O4^a	0.84(2)	1.94(2)	2.781(2)	172(7)
O1- H1A···O1^b	0.85(2)	1.91(2)	2.767(3)	177(7)
O2- H2···O6^c	0.843(19)	1.80(2)	2.614(4)	161(4)
O2- H2···O6B^c	0.843(19)	2.05(3)	2.805(12)	149(3)

O4- H4B···O1[a]	0.85(2)	1.94(2)	2.781(2)	174(7)
O4- H4A···O9B[d]	0.86(2)	1.81(2)	2.664(4)	172(7)
O4- H4A···Cl1B[d]	0.86(2)	2.17(4)	2.940(13)	148(6)
O7- H7B···O7[e]	0.82(2)	2.17(6)	2.780(6)	131(6)
5b@3$_2$				
Intramolecular				
O2- H2···O16A	0.84	2.14	2.791(5)	134.6
O2- H2···O16B	0.84	1.98	2.760(9)	154.4
O3- H3···O12	0.84	1.90	2.715(3)	164.0
O5- H5···O2	0.84	1.98	2.779(3)	160.0
O6- H6···O8	0.84	2.11	2.880(3)	153.3
O11- H11···Cl2A	0.84	2.08	2.90(2)	163.6
O11- H11···O18	0.84	1.80	2.621(7)	164.8
O12- H12···Cl1B	0.84	2.27	3.018(11)	148.7
O12- H12···O19	0.84	1.81	2.635(6)	168.5
O13A- H13A···O1	0.87	2.18	2.854(4)	133.9
O13A- H13B···O14A	0.87	2.21	2.749(6)	120.3
O14A- H14A···O13A	0.8401(10)	1.98(2)	2.749(6)	151(5)
O14B- H14D···O13B	0.87	1.95	2.709(12)	145.4
O15- H15A···O1	0.85	2.801(4)	2.801(4)	151.7
O15- H15B···O13B	0.85	2.696(9)	2.696(9)	152.7
O17- H17D···O3	0.87	2.35	3.022(11)	134.4
Intermolecular				
O4- H4···O13A[a]	0.84	2.11	2.810(5)	141.2
O6- H6···O3[a]	0.84	2.33	2.889(3)	124.2
O8- H8···O14[b]	0.84	2.02	2.817(4)	157.6
O10- H10···O13A[c]	0.84	1.96	2.712(5)	148.6
O13A- H13A···O18[d]	0.87	2.10	2.678(11)	123.1
O14A- H14B···O7[b]	0.8401(10)	1.933(6)	2.772(5)	175(5)
O16A- H16B···O7[b]	0.84	2.18	2.769(5)	127.0
4a@2				
Intramolecular				
O1-H1···O8	0.84	1.94	2.713(6)	153.0
O3-H3···O2	0.84	2.02	2.855(7)	174.5
O5-H5···O4	0.84	1.96	2.790(7)	170.5
O7-H7···O6	0.84	1.93	2.728(7)	159.3
N1A-H1AA···Cl1A	0.99	2.14	3.1239	171.8
N1B-H1AB···Cl1B	0.99	2.18	3.160(15)	172.4
O2-H2···Cl1A	0.84	2.38	3.163(5)	155.7
Intermolecular				
O4-H4···Cl1A[a]	0.84	2.41	3.171(5)	150.9
O6-H6···O2[b]	0.84	2.10	2.840(6)	146.8
O8-H8···Cl1A[c]	0.84	2.38	3.139(5)	150.0
5c@1				
Intramolecular				
O5- H5···Cl1	0.84	2.23	3.0622(19)	171.7
O8- H8···O1	0.84	2.15	2.885(3)	146.6
O4- H4···O5	0.84	2.35	3.078(3)	145.9
O12A- H12B···O7	0.87	1.89	2.588(8)	136.2
N1- H1A···O10	1.00	1.91	2.826(4)	151.5
N2- H2A···O12A	1.00	1.78	2.747(14)	161.2
O10- H10···Cl1	0.84	2.24	3.076(3)	170.8
Intermolecular				
O2- H2···O12B[a]	0.84	1.76	2.585(7)	165.4
O2- H2···O12C[a]	0.84	2.01	2.80(3)	154.7

O2- H2···O12G[a]	0.84	2.13	2.92(2)	157.2
O1- H1···O12D[b]	0.84	1.92	2.73(2)	161.6
O1- H1···O12E[b]	0.84	1.82	2.653(5)	169.1
O4- H4···O1[c]	0.84	2.48	3.014(3)	122.5
O3- H3···O11[a]	0.84	1.83	2.664(3)	173.4
O7- H7A···O9B[d]	0.84	1.81	2.638(3)	170.8
O7- H7A···O9A[d]	0.84	1.81	2.638(3)	170.8
O11- H11···O8[c]	0.84	1.97	2.760(3)	155.7
O9A- H9AA···O4[e]	0.84	1.95	2.663(3)	142.5
O12A- H12A···Cl3A[b]	0.87	2.02	2.74(2)	139.8
O12A- H12A···Cl3B[b]	0.87	2.18	3.033(10)	164.8
O12A- H12A···Cl3C[b]	0.87	1.77	2.564(13)	150.5
O12A- H12A···Cl3D[b]	0.87	2.14	2.95(4)	155.6
O6- Cl1···Cl1[f]	0.80(4)	2.36(4)	3.149(2)	167(4)

Note: symmetry operation, in 2MeOH@$\mathbf{2}_2$, *a*: *x*-1, *y*-1, *z*; *b*: -*x*, -*y*, 1-*z*; *c*: 1-*x*, 1-*y*, 1-*z*; *d*: *x*, 1+*y*, *z*; **5a**@$\mathbf{2}_2$, *a*: 1.5-*x*, 0.5-*y*, z; *b*: 1-*x*, *y*, 1-*z*; *c*: 1-*x*, 1-*y*, 1-*z*; *d*: 1.5-*x*, 1.5-*y*, *z*; **5b**@$\mathbf{2}_2$, *a*: 0.5-*x*, 0.5-*y*, *z*; *b*: 1.5-*x*, 0.5-*y*, *z*; *c*: 1-*z*, 1-*y*, -*z*; *d*: -*x*, 1-*y*, -*z*; *e*: *x*, 1.5-*y*, 0.5-*z*; **5b**@$\mathbf{3}_2$, *a*: *x*+1, *y*, *z*; *b*: 2-*x*, 1-*y*, 2-*z*; *c*: *x*, *y*-1, *z*; *d*: *x*, *y*+1, *z*; **4a@2**, *a*: 1-*x*, 2-*y*, *z*-0.5; *b*: *x*,*y*-1,*z*; *c*: 1-*z*, 2-*y*, *z*+0.5; **5c@1**, *a*: *x*, *y*+1, *z*; *b*: -*x*-1, 1-*y*, 1-*z*; *c*: 1+*x*, *y*, *z*; *d*: *x*, *y*-1, *z*; *e*: *x*-1, *y*, *z*.

III NMR Spectroscopic Analyses

The Job Plots

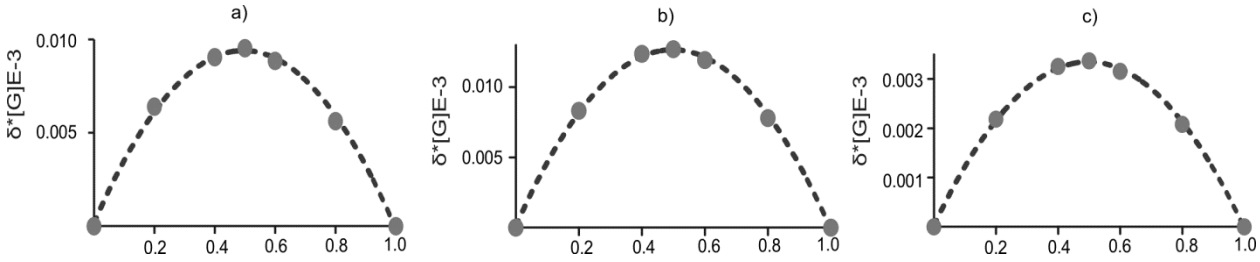

Figure S1. Job plot from **4a**+**1** (a), **4a**+**2** (b) and **4a**+**3** (c) in CD_3OD at 303 K depicting a 1:1 binding stoichiometry.

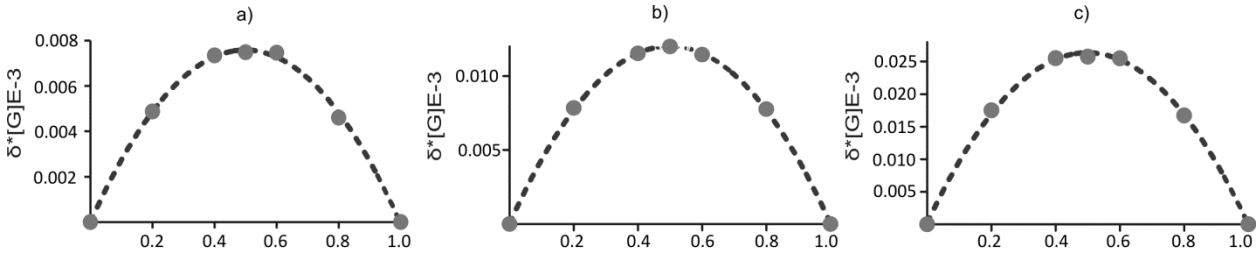

Figure S2. Job plot from **4b**+**1** (a), **4b**+**2** (b) and **4b**+**3** (c) in CD_3OD at 303 K depicting a 1:1 binding stoichiometry.

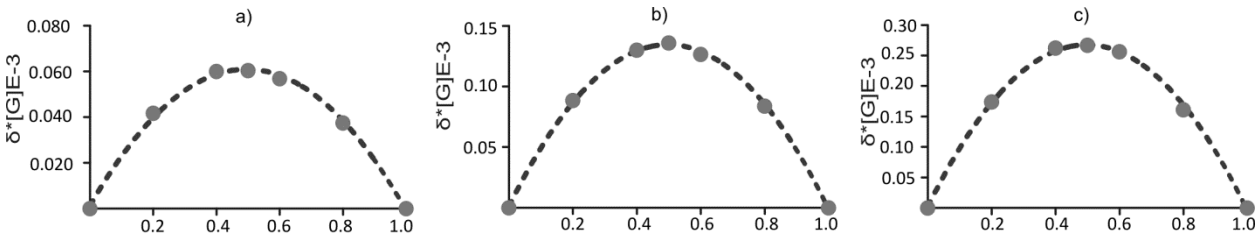

Figure S3. Job plot from **5a**+**1** (a), **5a**+**2** (b) and **5a**+**3** (c) in CD_3OD at 303 K depicting a 1:1 binding stoichiometry.

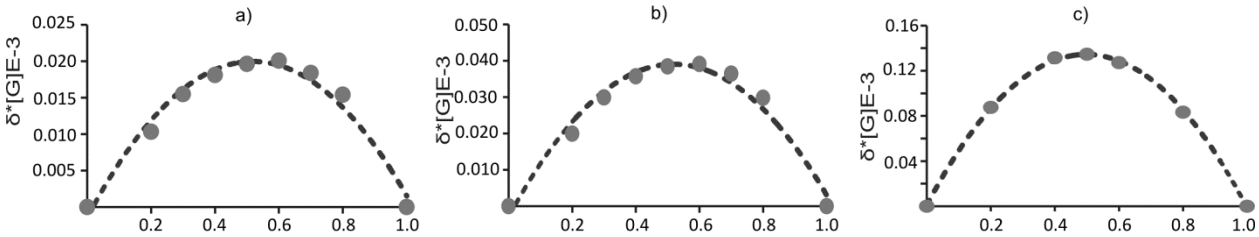

Figure S4. Job plot from **5b**+**1** (a), **5b**+**2** (b) and **5b**+**3** (c) in CD_3OD at 303 K depicting a 1:1 binding stoichiometry.

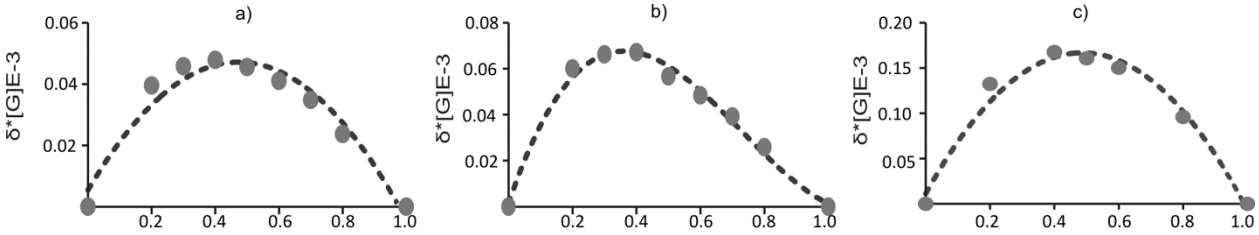

Figure S5. Job plot from **5c**+**1** (a), **5c**+**2** (b) and **5c**+**3** (c) in CD_3OD at 303 K depicting a dynamic mixture of 1:1 and 2:1 species.

The titration experiment

In the titration experiment, at each step, 0.2 equivalent of a 50 mM solution of the guests (**4-5**) was added to a 5 mM solution of the hosts (**1-3**). After reaching 2 equivalents, the increments were increased to 1 or 2 equivalents reaching a total of 3 or 6 equivalents in some cases. The CH_3 signals were followed in all cases and the binding constants were obtained by non-linear least square titration curve fit of the respective titration data based on a 1:1 and 2:1 (for **5c**) host-guest binding mode using the winEQNMR2 computer program.[7]

The Spectra Changes

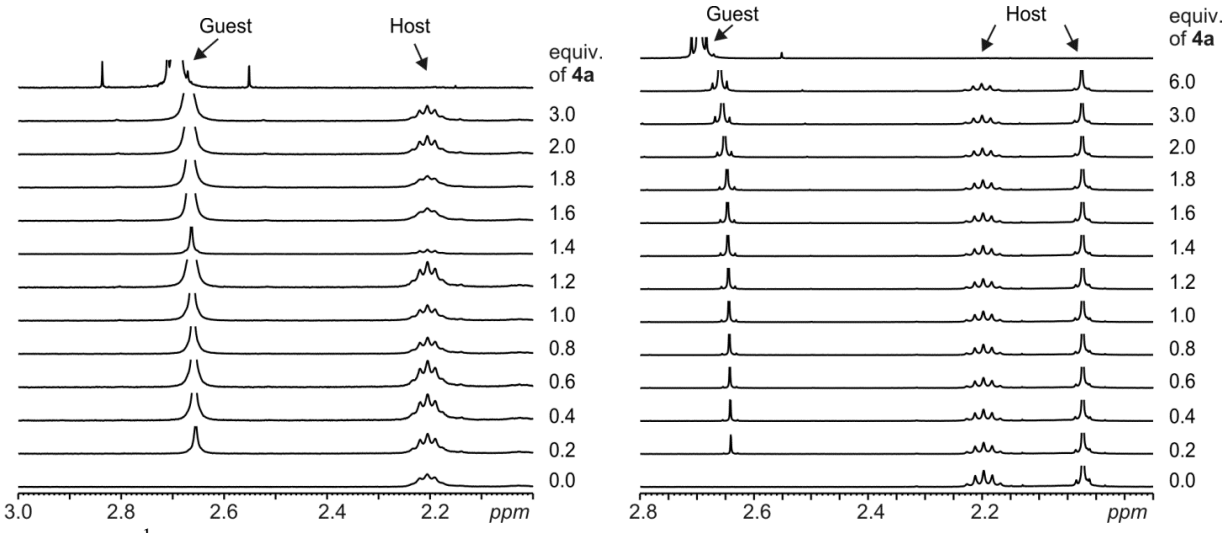

Figure S6. ^{1}H NMR spectral changes observed upon the addition of **4a** to resorcinarene **1** (left) and **2** (right) in CD_3OD at 303 K.

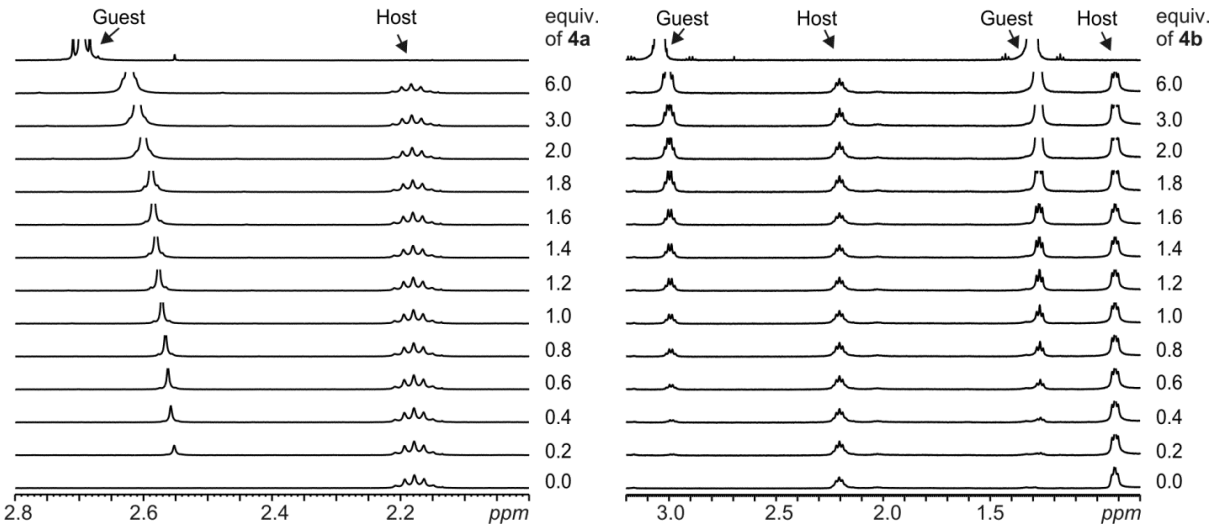

Figure S7. ^{1}H NMR spectral changes observed upon the addition of **4a** to pyrogallarene **3** (left) and **4b** to resorcinarene **1** (right) in CD_3OD at 303 K.

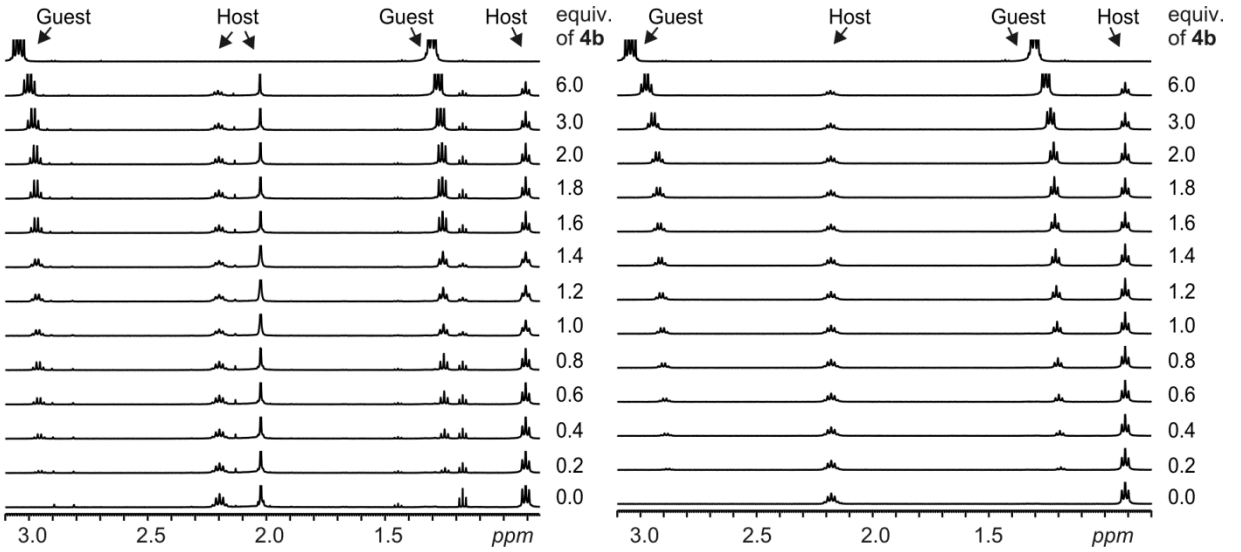

Figure S8. ^{1}H NMR spectral changes observed upon the addition of **4b** to resorcinarene **2** (left) and pyrogallarene **3** (right) in CD_3OD at 303 K.

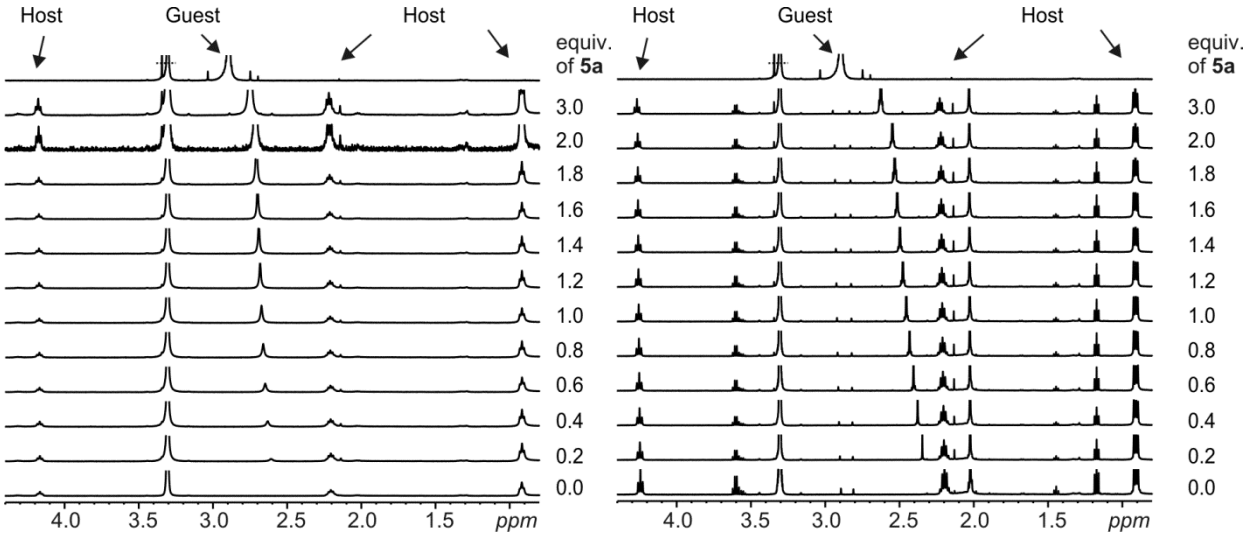

Figure S9. ^{1}H NMR spectral changes observed upon the addition of **5a** to resorcinarene **1** (left) and **2** (right) in CD_3OD at 303 K.

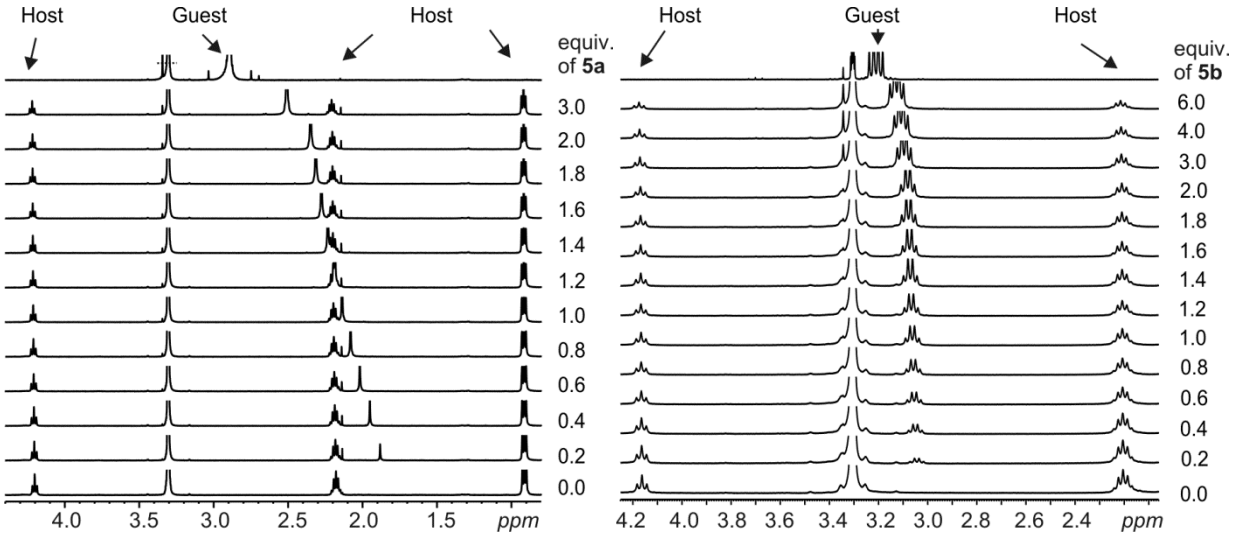

Figure S10. ^{1}H NMR spectral changes observed upon the addition of **5a** to pyrogallarene **3** (left) and **5b** to resorcinarene **1** (right) in CD_3OD at 303 K.

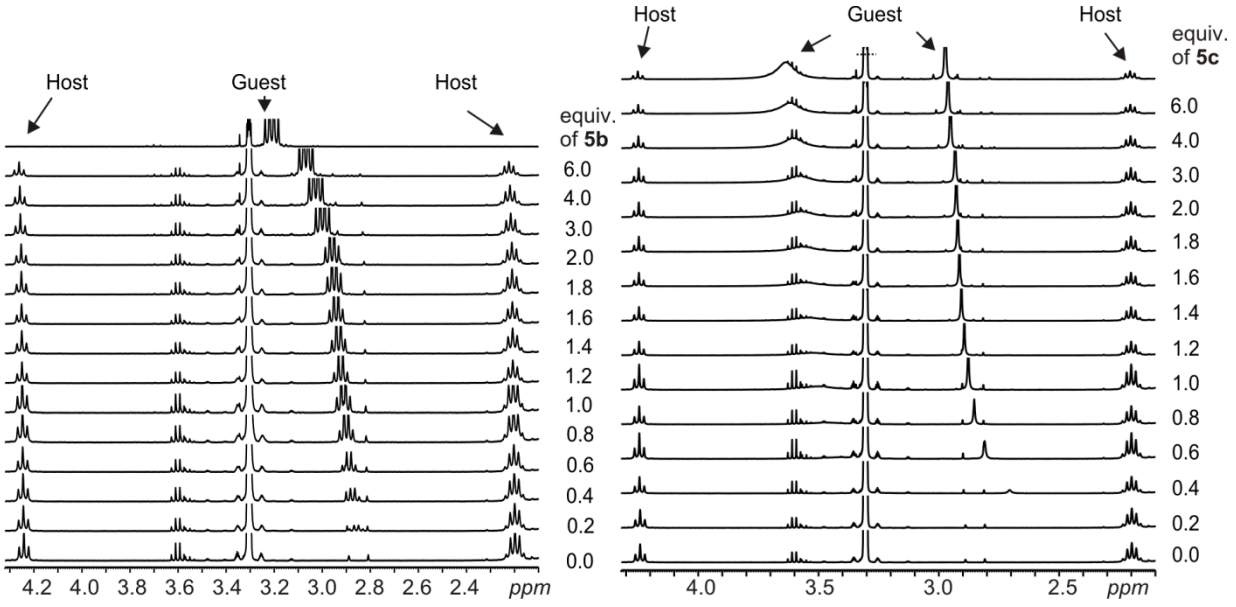

Figure S11. ^{1}H NMR spectral changes observed upon the addition of **5b** to resorcinarene **2** (left) and **5c** to resorcinarene **2** (right) in CD_3OD at 303 K.

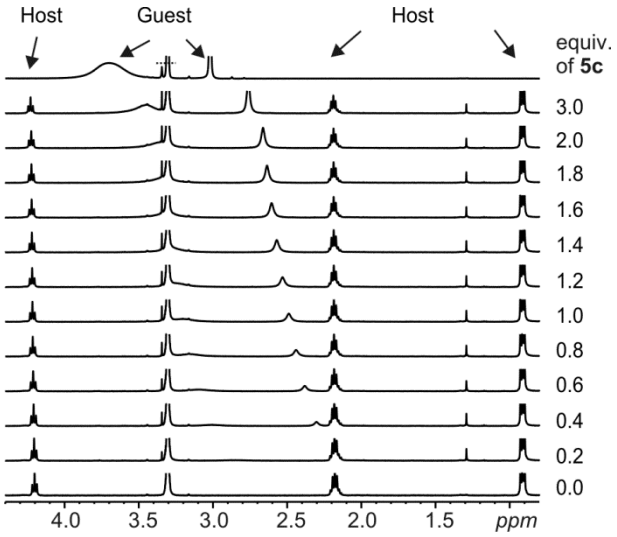

Figure S12. ^{1}H NMR spectral changes observed upon the addition of **5c** to pyrogallarene **3** in CD_3OD at 303 K.

Spectral Fits

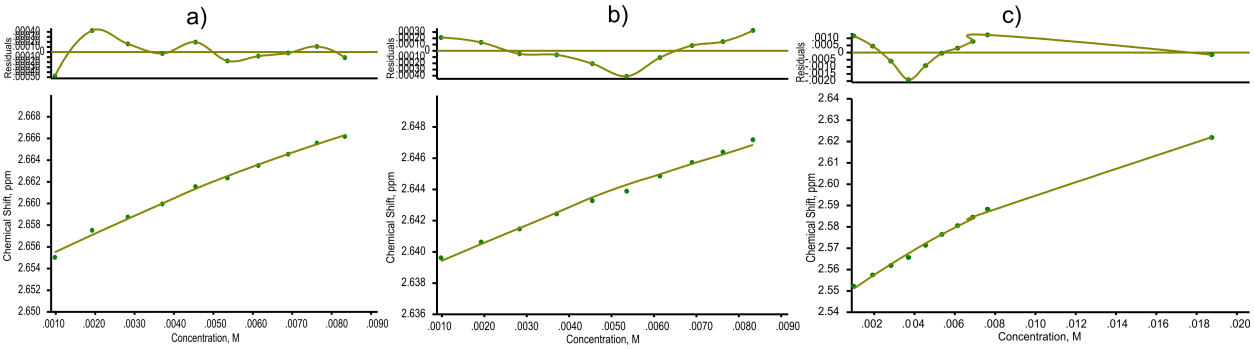

Figure S13. ^{1}H NMR fittings of –CH_3 signals of **4a** (1:1 binding model) upon the addition of **4a** to host **1** (a), host **2** (b) and host **3** (c) in CD_3OD at 303 K.

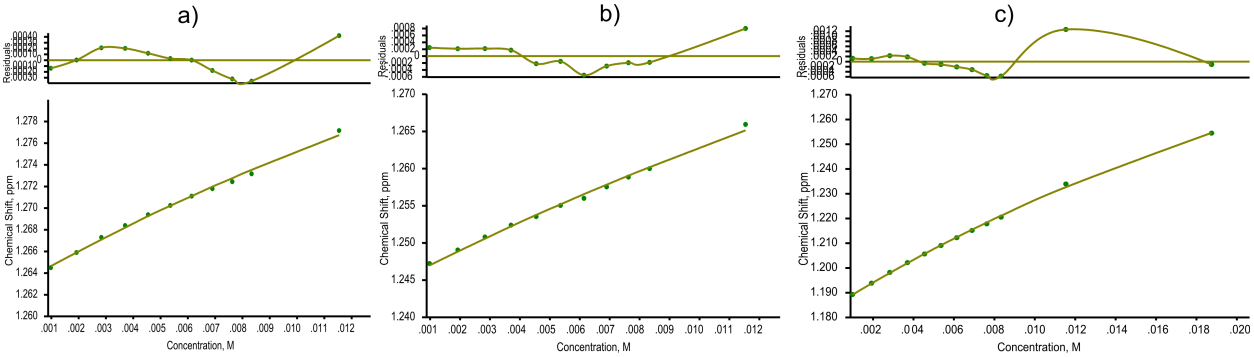

Figure S14. ^{1}H NMR fittings of –CH_3 signals of **4b** (1:1 binding model) upon the addition of **4b** to host **1** (a), host **2** (b) and host **3** (c) in CD_3OD at 303 K.

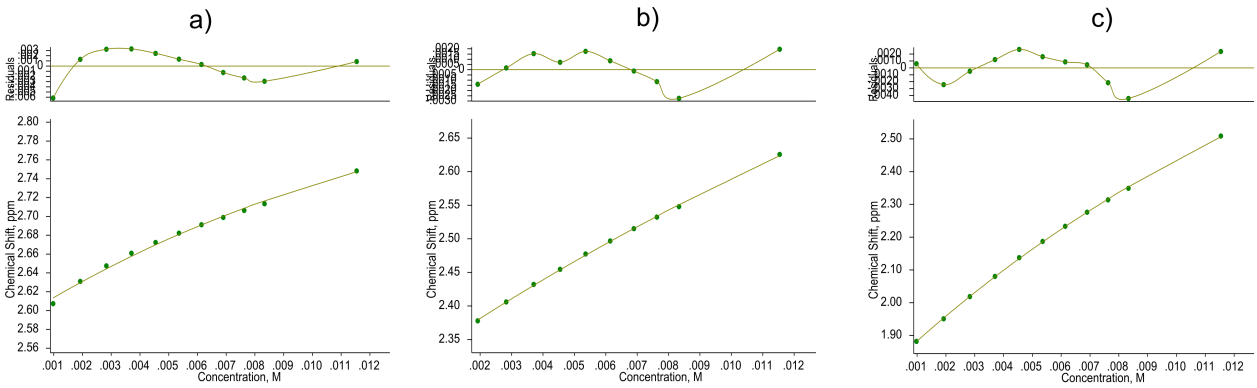

Figure S15. ^{1}H NMR fittings of –CH_3 signals of **5a** (1:1 binding model) upon the addition of **5a** to host **1** (a), host **2** (b) and host **3** (c) in CD_3OD at 303 K.

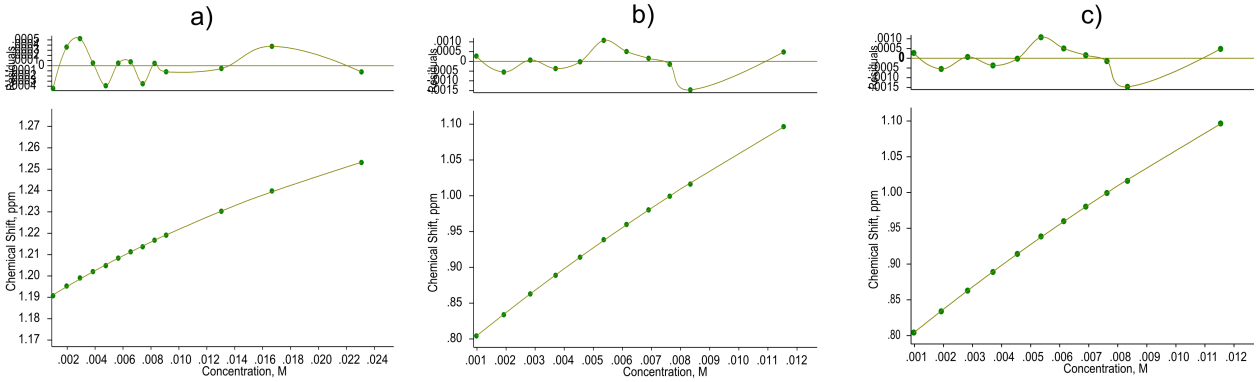

Figure S16. ^{1}H NMR fittings of –CH_3 signals of **5b** (1:1 binding model) upon the addition of **5b** to host **1** (a), host **2** (b) and host **3** (c) in CD_3OD at 303 K.

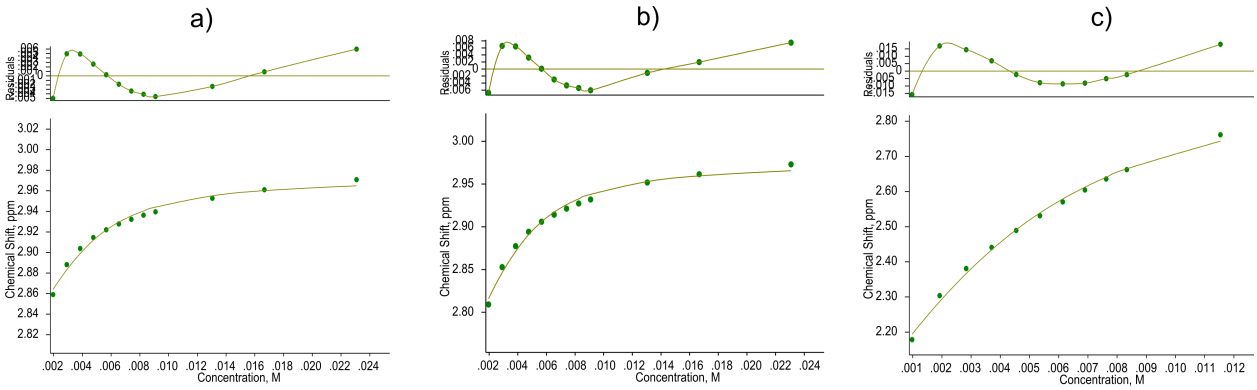

Figure S17. ^{1}H NMR fittings of –CH_3 signals of **5c** (2:1 binding model) upon the addition of **5c** to host **1** (a), host **2** (b) and host **3** (c) in CD_3OD at 303 K.

IV Mass Spectrometric Figures

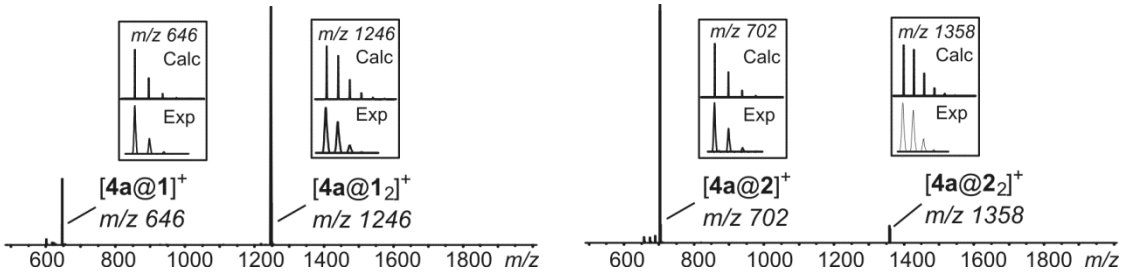

Figure S18. ESI mass spectra of a mixture of host **1** and guest **4a** (left) and of host **2** and guest **4a** (right) showing the monomeric and dimeric assemblies.

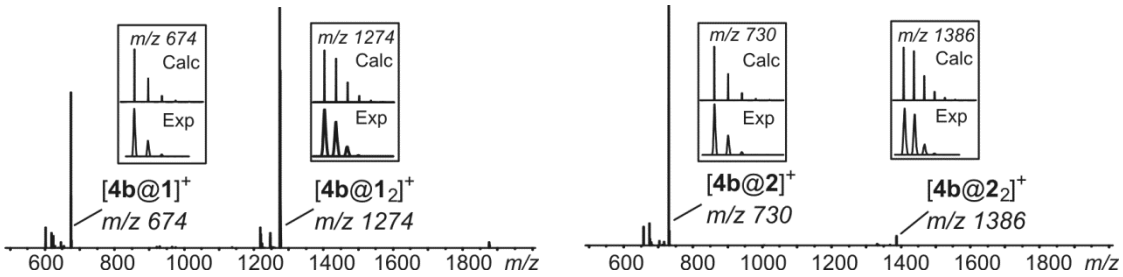

Figure S19. ESI mass spectra of a mixture of host **1** and guest **4b** (left) and of host **2** and guest **4b** (right) showing the monomeric and dimeric assemblies.

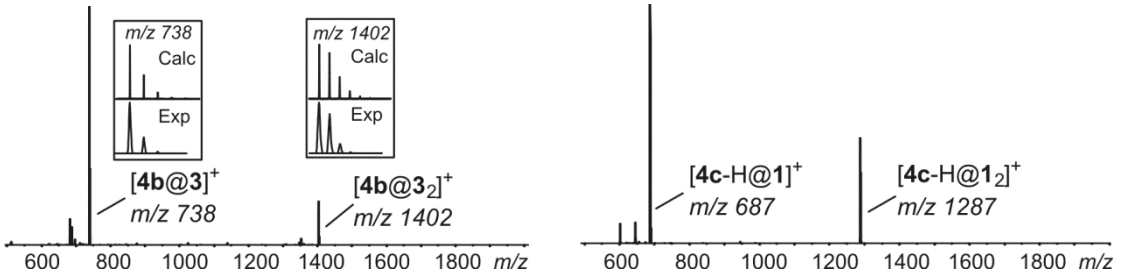

Figure S20. ESI mass spectra of a mixture of host **3** and guest **4b** (left) and of host **1** and guest **4c** (right) showing the monomeric and dimeric assemblies.

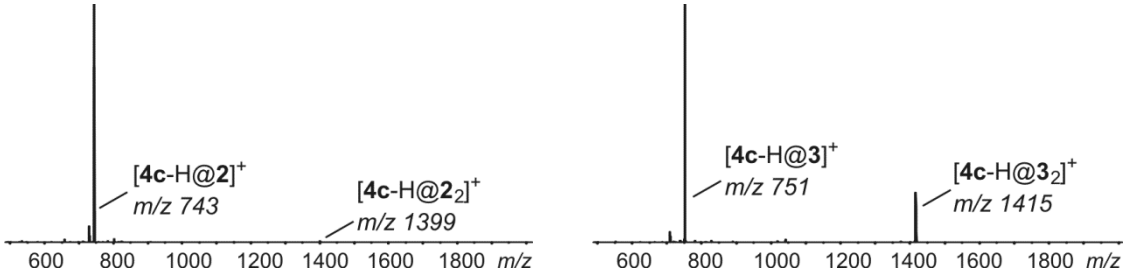

Figure S21. ESI mass spectra of a mixture of host **2** and guest **4c** (left) and of host **3** and guest **4c** (right) showing the monomeric and dimeric assemblies.

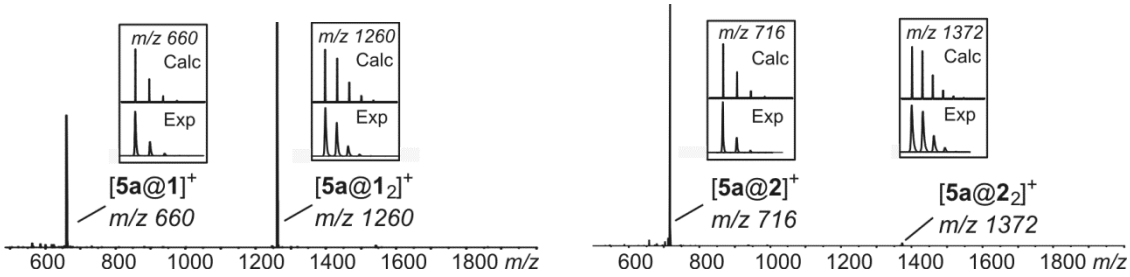

Figure S22. ESI mass spectra of a mixture of host **1** and guest **5a** (left) and of host **2** and guest **5a** (right) showing the monomeric and dimeric assemblies.

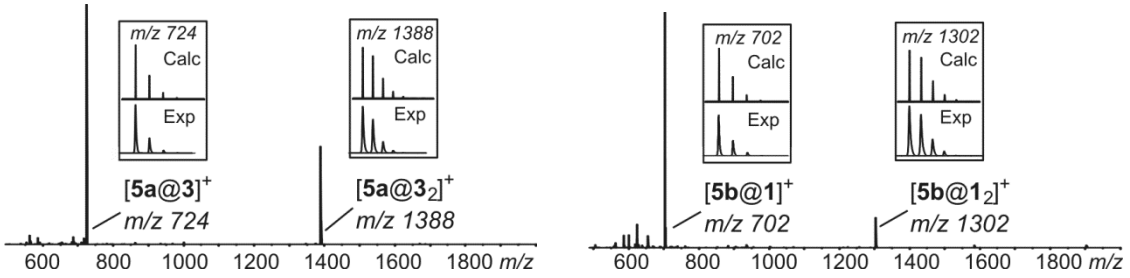

Figure S23. ESI mass spectra of a mixture of host **3** and guest **5a** (left) and of host **1** and guest **5b** (right) showing the monomeric and dimeric assemblies.

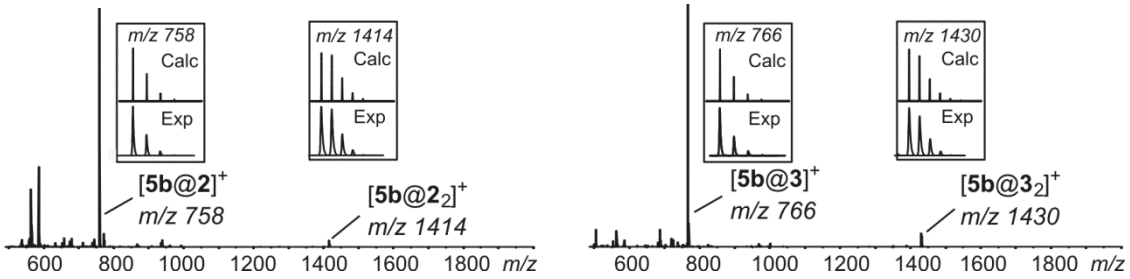

Figure S24. ESI mass spectra of a mixture of host **2** and guest **5b** (left) and of host **3** and guest **5b** (right) showing the monomeric and dimeric assemblies.

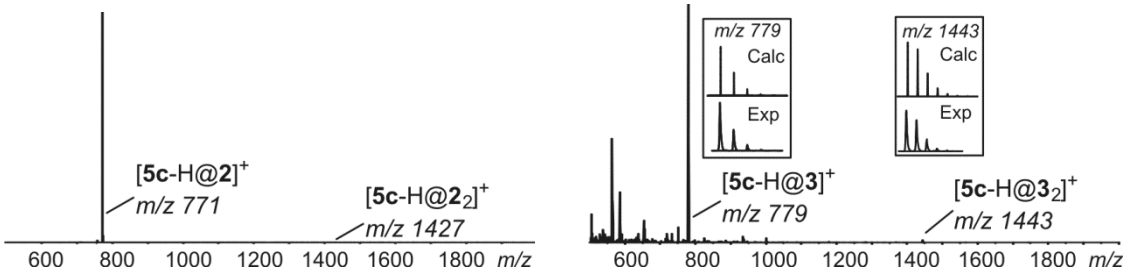

Figure S25. ESI mass spectra of a mixture of host **2** and guest **5c** (left) and of host **3** and guest **5c** (right) showing the monomeric and dimeric assemblies.

V References

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