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Supporting information

Inverted molecular cups: 1-D and 2-D Ag(I) coordination polymers from resorcinarene bis-thiacrowns

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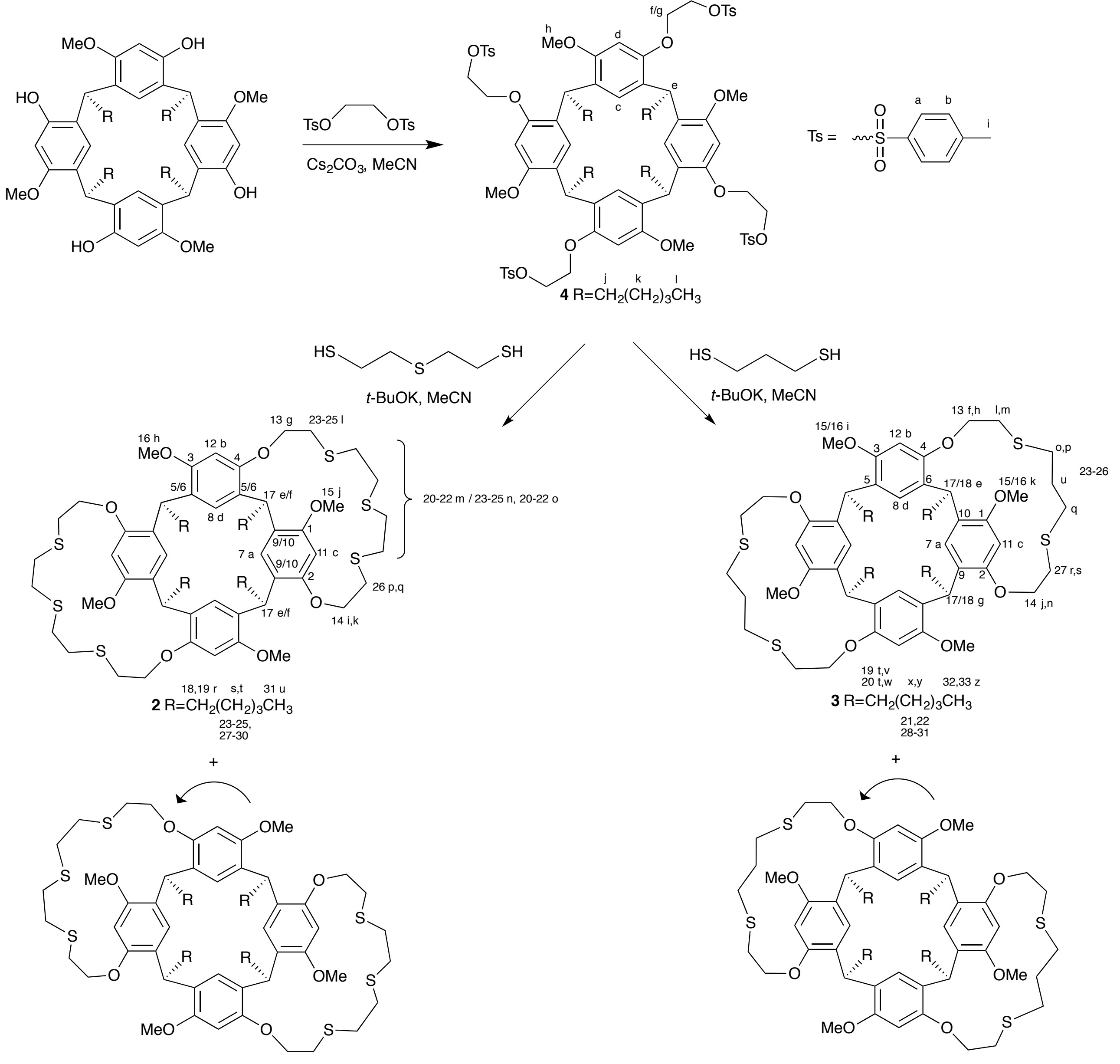
1. General

Solvents and reagents were purchased from commercial suppliers Sigma-Aldrich and VWR. Acetonitrile was dried with a MBraun solvent purification system. Cs_2CO_3 and the glassware used in the synthesis were dried at 120 °C prior to use and cooled in a desiccator. Flash chromatography was performed with a Combiflash Companion (Teledyne Isco) and Redisep Gold silica columns. NMR spectra were recorded with a Bruker Avance III 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) or a Bruker Avance III HD 300 (300 MHz for ^{1}H) spectrometer at 30 °C. The *J* values are given in Hz. The accurate mass measurements were performed with a Micromass LCT ESI-TOF or a ABSciex QSTAR Elite ESI-Q-TOF mass spectrometer. Melting points were measured with a Stuart Scientific SMP30 and are uncorrected.

2. Synthesis and characterization

The *C*-pentyl tetramethoxy resorcinarene,[1] tetratosylated resorcinarene **4** and resorcinarene bis-thiacrowns **2** and **3** were synthesized by applying the previously published procedures[2] according to Scheme S-1. The ethylene glycol ditosylate was prepared from ethylene glycol and tosyl chloride.



Scheme S-1. The synthesis of resorcinarene bis-thiacrowns **2** and **3**. The left-handed enantiomers are shown for **2** and **3**. The letters indicate NMR assignation for ^{1}H and numbers for ^{13}C signals.

2: *t*-BuOK (0.27 g, 2.41 mmol) was refluxed for 15 minutes in dry acetonitrile (50 ml) under nitrogen. Tosylated tetramethoxyresorcinarene **4** (0.48 g, 0.30 mmol) dissolved in dry acetonitrile (40 ml) was added dropwise to the mixture with vigorous stirring simultaneously with bis(2-mercaptoethyl)sulfide (87 µl, 0.67 mmol) in 20 ml of acetonitrile. The reaction mixture was refluxed for 41 hours. Resulting dark brown mixture was filtrated with suction through a pad of filter aid while still hot and the the residue was rinsed with hot acetonitrile. The combined filtrates were evaporated, and deionized water and dichloromethane were added to the residue. The water phase was discarded, and the organic phase was washed once with 1 M HCl and once with brine. The solution was dried with $MgSO_4$ and evaporated. Purification with flash chromatography on a silica column using hexane:ethyl acetate gradient (from 8:2 to 0:1) and subsequent recrystallization from dichloromethane-methanol gave white crystalline product (91 mg, 25 %). m.p. 173–175 ˚C.

^{1}H NMR (500 MHz, $CDCl_3$) 7.19 (s, 2H, a), 6.60 (s, 2H, b), 6.11 (s, 2H, c), 6.01 (s, 2H, d), 4.53–4.46 (m, 2H, e), 4.45–4.39 (m, 2H, f), 4.39–4.32 (m, 4H, g), 3.92 (s, 6H, h), 3.77–3.70 (m, 2H, i), 3.51 (s, 6H, j), 3.17–3.09 (m, 2H, k), 3.03 (t, J = 6.7, 4H, l), 2.98–2.82 (m, 8H, m), 2.70 (t, J = 7.2, 4H, n), 2.67–2.53 (m, 4H, o), 2.39–2.30 (m, 2H, p), 2.22–2.11 (m, 2H, q), 1.96–1.64 (m, 8H, r), 1.47–1.36 (m, 2H, s), 1.36–1.13 (m, 22H, t), 0.91–0.77 (m, 12H, u) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) 156.66 (1), 155.72 (2), 155.38 (3), 154.13 (4), 130.44 (5), 129.26 (6), 126.86 (7), 126.41 (8), 124.79 (9), 123.17 (10), 99.02 (11), 97.86 (12), 70.81 (13), 68.84 (14), 56.48 (15), 56.05 (16), 35.83 (17), 35.27 (18), 34.32 (19), 33.49 (20), 33.46 (21), 33.23 (22), 32.46 (23), 32.32 (24), 32.23 (25), 31.09 (26), 28.11 (27), 27.92 (28), 22.81 (29), 22.78 (30), 14.27 (31) ppm.

HR-MS (ESI-TOF): *m/z* calcd. for $C_{68}H_{100}O_8S_6Na^+$ 1259.5635 [M+Na$^+$]; found 1259.5659.

3: *t*-BuOK (0.24 g, 2.14 mmol) was refluxed for 15 minutes in dry acetonitrile (50 ml) under nitrogen. Tosylated tetramethoxyresorcinarene **4** (0.42 g, 0.26 mmol) dissolved in dry acetonitrile (20 ml) was added dropwise to the mixture dropwise with vigorous stirring simultaneously with 1,3-propanedithiol (58 µl, 0.58 mmol) in 20 ml of acetonitrile. The reaction mixture was refluxed for 42 hours. Resulting dark brown mixture was filtrated with suction through a pad of filter aid while still hot and the the residue was rinsed with hot acetonitrile. The combined filtrates were evaporated, and deionized water and dichloromethane were added to the residue. The water phase was discarded, and the organic phase was washed once with 1 M HCl and once with brine. The solution was dried with $MgSO_4$ and evaporated. Purification with flash chromatography on a silica column using hexane:ethyl acetate gradient (from 8:2 to 0:1) gave the product as a white solid (60 mg, 20 %). m.p. 199–201 ˚C.

^{1}H NMR (500 MHz, $CDCl_3$) 7.16 (s, 2H, a), 6.63 (s, 2H, b), 6.14 (s, 2H, c), 6.00 (s, 2H, d), 4.50–4.42 (m, 4H, overlapping e and f), 4.41–4.34 (m, 4H, overlapping g and h), 3.92 (s, 6H, i), 3.79–3.70 (m, 2H, j), 3.56 (s, 6H, k), 3.07–3.00 (m, 2H, l), 3.00–2.90 (m, 4H, overlapping m and n), 2.89–2.79 (m, 2H, o), 2.68–2.60 (m, 2H, p), 2.50–2.41 (m, 4H, q), 2.41–2.32 (m, 2H, r), 1.93–1.83 (m, 6H, overlapping s and t), 1.83–1.73 (m, 6H, overlapping u and v), 1.73–1.63 (m, 2H, w), 1.48–1.36 (m, 2H, x), 1.36–1.11 (m, 22H, y), 0.87–0.79 (m, 12H, z) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) 156.64 (1), 155.61 (2), 155.50(3), 153.98 (4), 130.67 (5), 128.84 (6), 127.26 (7), 126.43 (8), 125.05 (9), 122.04 (10), 98.64 (11), 98.04 (12), 71.06 (13), 68.38 (14), 56.19 (15), 56.16 (16), 36.05 (17), 35.98 (18), 35.19 (19), 33.98 (20), 32.35 (21), 32.08 (22), 31.30 (23), 31.28 (24), 31.15 (25), 31.03 (26), 29.61 (27), 28.15 (28), 27.92 (29), 22.83 (30), 22.75 (31), 14.30 (32), 14.26 (33) ppm.

HR-MS (ESI-TOF): *m/z* calcd. for $C_{66}H_{96}O_8S_4Na^+$ 1167.5880 [M+Na$^+$]; found 1167.5905.

4: *C*-pentyl tetramethoxy resorcinarene (1.37 g, 1.66 mmol) was refluxed with Cs_2CO_3 (4.90 g, 15.04 mmol) in dry acetonitrile (80 ml) under nitrogen athmosphere. Ethylene glycol ditosylate (2.60 g, 7.02 mmol) was added in 30 ml of acetonitrile. The white suspension was refluxed for 22 hours. The mixture was filtrated with suction while still hot through a pad of filter aid. The precipitate was washed with chloroform and filtrated. The combined filtrates were evaporated to dryness. The white residue was dissolved in dichloromethane and washed three times with water. The organic phase was dried with $MgSO_4$ and evaporated. The product was purified with flash chromatography using silica column and dichloromethane/acetone gradient (1–5 % acetone) resulting colourless glue (0.50 g, 19 %). ^{1}H NMR (300 MHz, $CDCl_3$) 7.62 (d, J = 8.2, 8H, a), 7.07 (d, J = 8.2, 8H, b), 6.78 (s, 4H, c), 6.03 (s, 4H, d), 4.43 (t, J = 7.5, 4H, e), 4.20 (t, J = 4.8, 8H, f), 4.02–3.87 (m, 4H, g), 3.74–3.57 (m, 4H, g), 3.49 (s, 12H, h), 2.22 (s, 12H, i), 1.88–1.68 (m, 8H, j), 1.32–1.12 (m, 24H, k), 0.90–0.76 (m, 12H, l) ppm. The product was used in the synthesis without further analysis.

2.1. NMR spectra for host 2

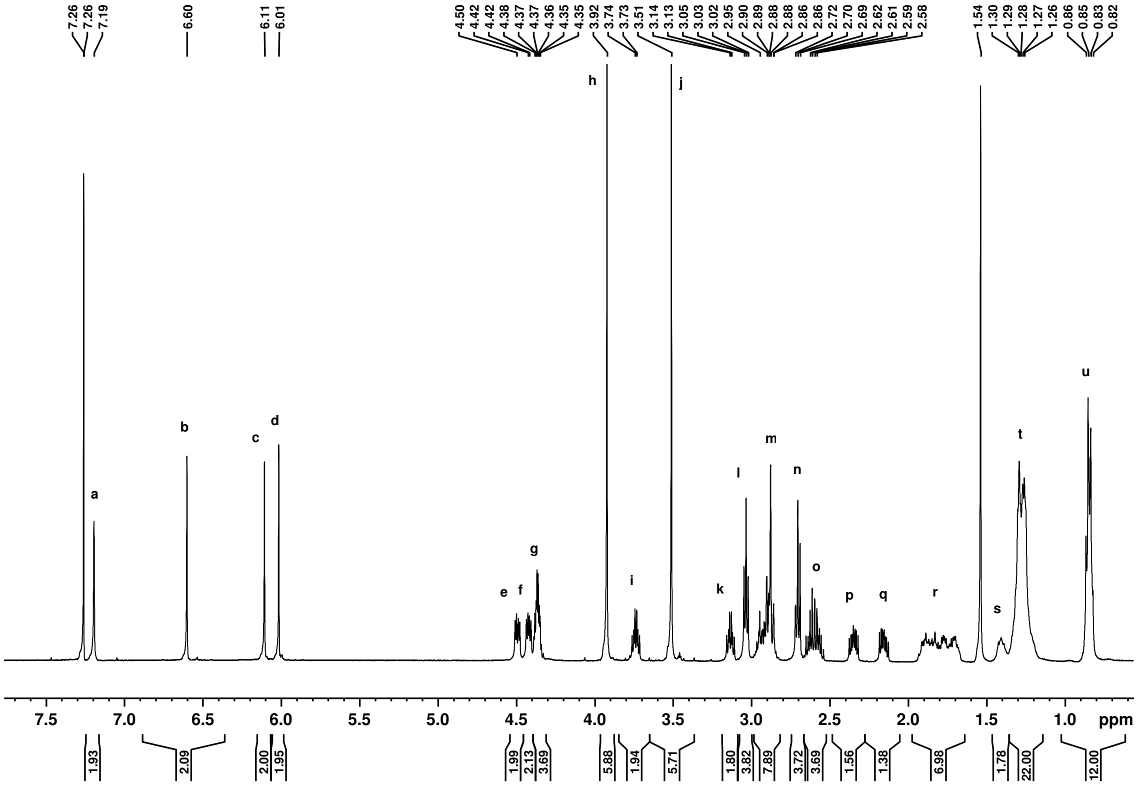


Fig. S-1 ^{1}H NMR spectra for host **2** in CDCl3.

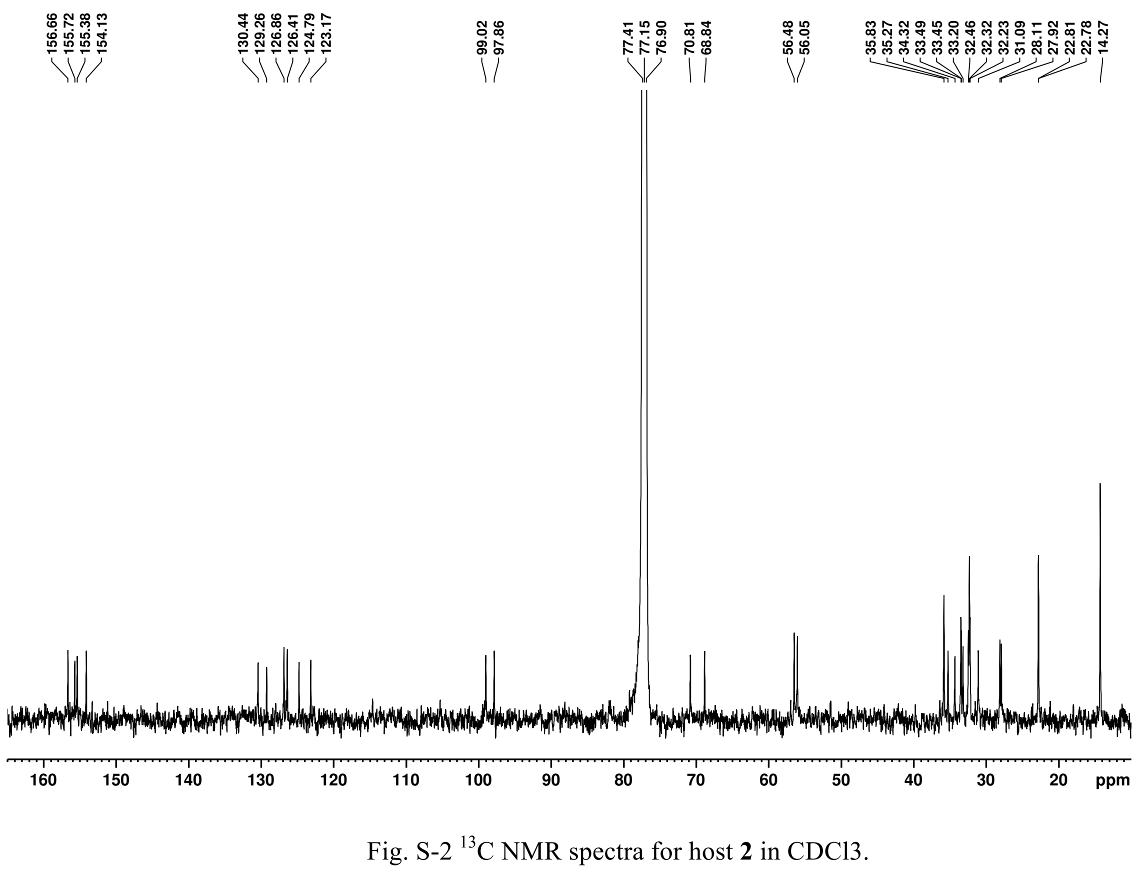


Fig. S-2 ^{13}C NMR spectra for host **2** in CDCl3.

2.2. NMR spectra for host 3

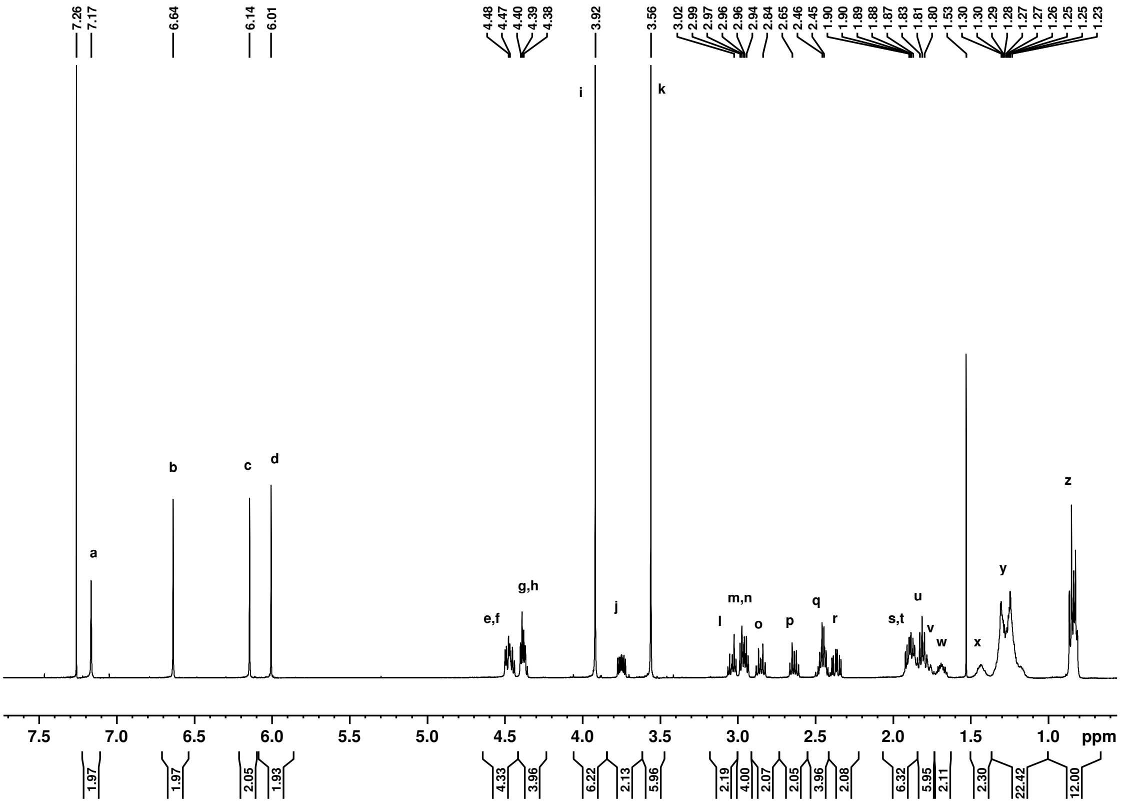


Fig. S-3 ^{1}H NMR spectra for host **3** in CDCl3.

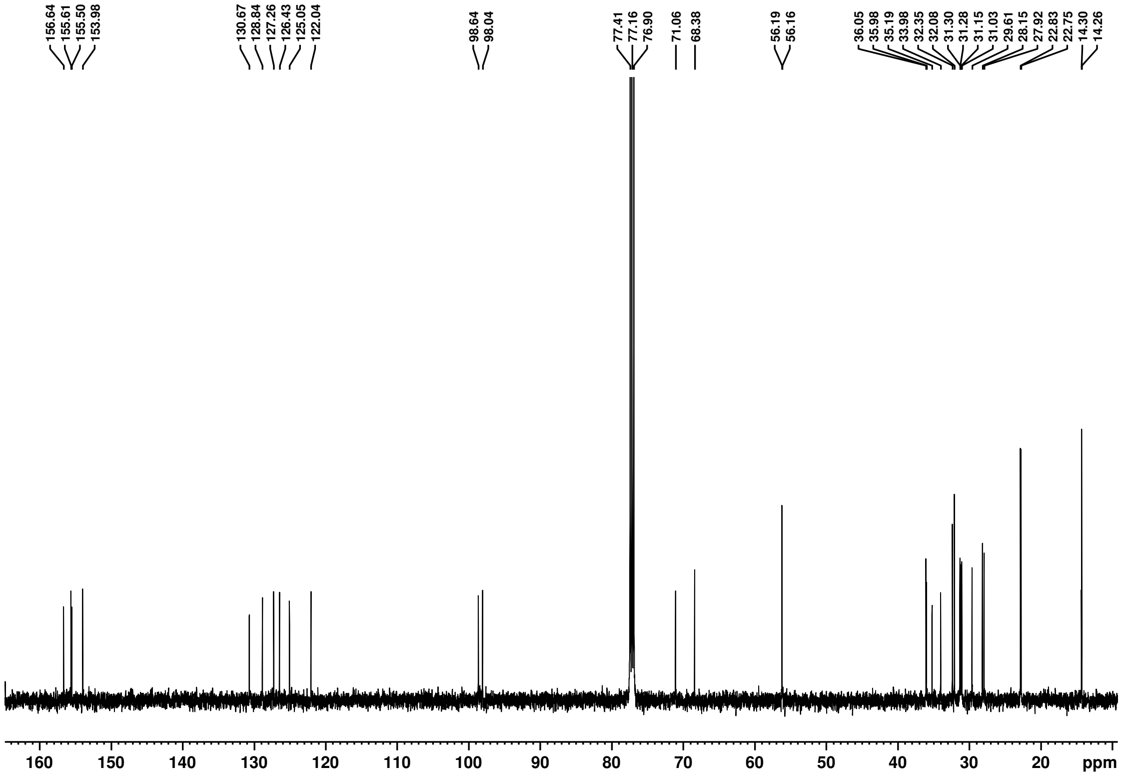


Fig. S-4 ^{13}C NMR spectra for host **3** in CDCl3.

3. Crystal structure refinement

1-B, $C_{120}H_{152}Ag_4F_{12}O_{24}S_{12}·(C_2H_6O)_6·(CH_2Cl_2)_3·(H_2O)_4$: Disordered S2A/S2B and Ag3/Ag3B were refined with site occupancies of 0.75:0.25. Disordered Ag2/Ag2B and Ag4/Ag4B were refined with site occupancies of 0.9:0.1. Disordered CF_3 groups were refined with site occupancies of 0.75:0.25 for F7–F9, and 0.6:0.4 for F10–F12. Disordered water O125/O12B was refined with site occupancies of 0.5:0.5. Structure contained residual electron density of a solvent, for which a reasonable disorder model could not be built, and which was removed from the final refinement using Mask-option in Olex2. Removed electron density per unit cell, 50 electrons, corresponds to approximately two ethanol molecules ($C_4H_{12}O_2$) which were added to the UNIT.

1-C, $C_{62}H_{76}Ag_3F_9O_{14}S_6·(C_2H_6O)_5·(H_2O)_{0.5}$: Disordered crown bridge C41/C41B-C42/C42B was refined with site occupancies of 0.58:0.42. Disordered CF_3COO anion C61/C61B, C62/C62B, O13/O13B, O14/O14B, F7/F7B, F8/F8B, F9/F9B was refined with site occupancies of 0.60:0.40. Disordered ethanol O109–C111/O112–C114 was refined with site occupancies of 0.60:0.40. Disordered water molecule O119 next to a special position was refined in PART -1 with site occupancy of 0.5.

2-A, $C_{77}H_{100}Ag_{4.5}F_{13.5}O_{17}S_6·(C_2H_6O)·(H_2O)_{2.5}$: Disordered crown bridge S1/S1B-C35/C35B was refined with site occupancies of 0.53:0.47. Disordered crown bridge S4/S4B-C43/C43B-C44/C44B-S5/S5B was refined with site occupancies of 0.5:0.5. Substitutional disorder of Ag5, C77, C78, O17, O18, F13–F15 inside the resorcinarene cavity was refined with a site occupancy of 0.5. The second position was filled by water molecules O107, O108, and O109 with site occupancies of 0.5. O109 was refined with an isotropic temperature factor. Disordered alkyl chains were refined with site occupancies of 0.65:0.35 for C50–C53, and 0.53:0.47 for C62/C62B-C63/C63B. Disordered CF_3 group F7–F9 was refined with site occupancies of 0.51:0.49. Disordered ethanol O100–C102/O103–C105 was refined with site occupancies of 0.5:0.5. Water molecules O106 and O110 were refined with site occupancies of 0.5.

3-A, $C_{142}H_{192}Ag_5F_{15}O_{26}S_8·(C_2H_6O)_{5.5}·H_2O$: Disordered crown bridge C33/C33B was refined with site occupancies of 0.76:0.24. Disordered alkyl chains were refined with site occupancies of 0.70:0.30 for C55A/C55B-C56A/C56B, 0.67:0.33 for C59/C59B-C60/C60B-C61/C61B, and 0.67:0.33 for C66A/C66B. Ethanol molecule O117-C116-C115 was refined with a site occupancy of 0.5. Water molecules O118 and O119 were refined with site occupancies of 0.5.

4. Crystallographic tables

4.1. Conformation analysis

The conformational properties of the resorcinarene bis-thiacrown ligands in coordination polymers **1**-B, **1**-C, **2**-A and **3**-A, and in silver complex **1**-A[2] are summarized in Table S-1. Twisting of the resorcinarene *boat* conformation is measured with tilt and twist angles (Fig. S-5). The resorcinarene macrocycle conformation and thiacrown bridge conformations of **1**-A and **1**-B is compared in Fig. S-6.

Table S-1. Conformational properties of the bis-thiacrowns.

Structure	**1-A**[2]	**1-B**[b]		**1-C**	**2-A**	**3-A**[b]	
		I	**II**			**I**	**II**
Conformation[a]	Twisted boat	Twisted boat	Boat	Boat	Twisted boat	Twisted boat	Twisted boat
Tilt /°	25.1	8.6	0.9	5.2	28.0	10.3	25.0
Twist /°	20.3	9.3	0.8	4.3	22.4	9.9	24.7
Distance / Å[c]	5.65 / 7.86	5.21 / 8.00	4.97 / 8.02	5.27 / 7.96	5.62 / 7.84	5.00 / 7.91	4.65 / 7.82
Dihedral angle between opposite rings /°	37.34 / N.D. [d]	11.4 / N.D.[d]	0.7 / 182.7	15.1 / 193.1	35.5 / N.D.[d]	-2.1 / N.D. [d]	-12.4 / N.D. [d]
Crown pocket diameter / Å[e]	5.60	5.27 / 5.40	5.33 / 5.11	5.38 / 5.18	5.62 / 5.54	5.20 / 5.23	5.17 / 5.26
Crown bridge orientation [f]	*g,g,g,g* / *g,g,a,g*	*g,g,a,g* / *a,g,g,g*	*g,g,g,g* / *g,g,g,g*	*g,g,a,g* / *g,g,a,g*	*g,g,g,g* / *g,g,g,g*	*g,g* / *a,g*	*a,g* / *a,g*
Avg $Ag^+\cdots O$ / Å	2.46	2.38	2.38	2.31	2.32	2.39	2.39
Avg $Ag^+\cdots S$ / Å	2.59	2.58	2.58	2.55	2.57	2.55	2.55
$Ag^+\cdots Ar$ / Å	-	-	-	-	2.88	-	-
$Ag^+\cdots Ag^+$ / Å [g]	5.22	4.78	4.78	4.03	2.93	3.38	3.38

[a] Twisted boat has twist/tilt angles > 5°, see Fig. S-1. [b] Two molecules in the asymmetric unit. [c] Centroid-centroid distance between opposite aromatic rings. [d] Dihedral angle between horizontal aryl rings cannot be determined due to twisting. [e] Average cavity diameter from O···O/S distances. [f] Torsion angles for O/S-C-C-O/S: *anti* (*a*) or *gauche* (*g*). [g] Shortest distance.

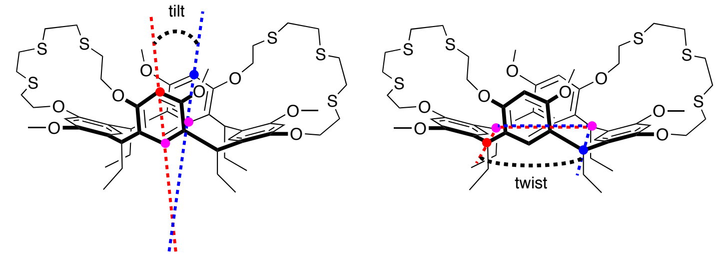


Fig. S-5 Definition of the tilt and twist angles.

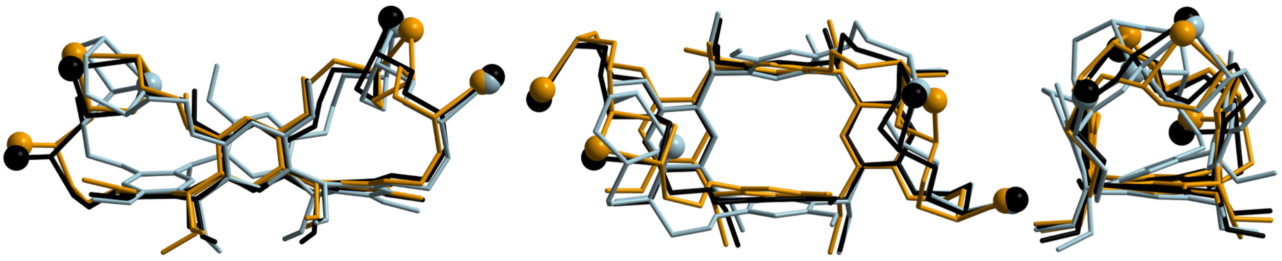


Fig. S-6 A structure overlay of **1**-A (in light blue), and two molecules of **1**-B (I in black, and II in orange) shows twisting of the resorcinarene *boat* conformation and differences in crown bridge conformations. Anions have been removed for clarity.

4.2. Thiacrown bridge torsion angles

The thiacrown bridge S/O-C-C-S/O torsion angles for **1**-B, **1**-C and **2**-A are compared in Table S-2. See also Table S-1 for classification of *anti* (~ 170–180°) and *gauche* (~ 60–70°) conformations. For structure **3**-A O/S-C-C-O/S torsions are given in Table S-3.

Table S-2. Thiacrown bridge torsion angles for **1**-B, **1**-C and **2**-A.

1-B[a]	°	**1-C**[b]	°	**2-A**[b]	°
O1 C33 C34 S1	72.3(12)	O1 C33 C34 S1	69.4(6)	O1 C33 C34 S1	91.6(10)
S1 C35 C36 S2	-65.4(9)	S1 C35 C36 S2	-61.6(7)	O1 C33 C34 S1B	49.5(12)
S2 C37 C38 S3	175.8(5)	S2 C37 C38 S3	172.5(5)	S1 C35 C36 S2	-26(2)
S3 C39 C40 O3	65.8(10)	S3 C39 C40 O3	67.4(8)	S2C36 C35B S1B	21(3)
O5 C41 C42 S4	-159.4(11)	O5 C41 C42 S4	80.1(11)	S2 C37 C38 S3	-66.5(8)
S4 C43 C44 S5	60.7(13)	O5 C41B C42B S4	-65.8(19)	S3 C39 C40 O3	71.5(9)
S5 C45 C46 S6	72.9(11)	S4 C43 C44 S5	-64.5(6)	O5 C41 C42 S4	54.9(10)
S6 C47 C48 O7	-81.1(10)	S5 C45 C46 S6	176.5(4)	O5 C41 C42 S4B	88.0(9)
O1A C33A C34A S1A	-71.0(14)	S6 C47 C48 O7	64.4(6)	S4 C43 C44 S5	45.8(16)
S1A C35A C36A S2A	79.5(9)			S4B C43B C44B S5B	58.5(17)
S2A C37A C38A S3A	-68.9(10)			S5 C45 C46 S6	-79.4(8)
S3A C39A C40A O3A	-66.8(10)			S5B C45 C46 S6	47.1(13)
O5A C41A C42A S4A	84.4(11)			S6 C47 C48 O7	72.3(7)
S4A C43A C44A S5A	-61.3(9)				
S5A C45A C46A S6A	-74.1(9)				
S6A C47A C48A O7A	78.1(9)				

[a] Two molecules in the asymmetric unit. [b] Disordered atoms labeled with B.

Table S-3. Thiacrown bridge torsion angles for 3-A.

3-A[a]	°
O1 C33 C34 S1	-45.7(9)
S1 C34 C33B O1	47(3)
S2 C38 C39 O3	55.1(7)
O5 C40 C41 S3	175.4(5)
S4 C45 C46 O7	51.5(7)
O1A C33A C34A S1A	-170.4(5)
S2A C38A C39A O3A	75.8(7)
O5A C40A C41A S3A	176.6(4)
S4A C45A C46A O7A	-63.3(7)

[a] Two molecules in the asymmetric unit, disordered atoms labeled with B.

4.3. Coordination bond lengths and angles

Table S-4. Selected coordination bond lengths and angles.

1-B[a]	Å / °	**1-C**[b]	Å / °	**2-A**[c]	Å / °	**3-A**[d]	Å / °
Ag1 S1	2.551(3)	Ag1 S1	2.570(2)	Ag1 Ag2	2.9341(9)	Ag1 S1	2.5655(17)
Ag1 S2	2.626(3)	Ag1 S2	2.5935(19)	Ag1 S1	2.463(4)	Ag1 O9	2.363(7)
Ag1 S3^{1}	2.559(2)	Ag1 S3^{1}	2.5117(18)	Ag1 S6^{1}	2.6654(19)	Ag1 O11	2.416(6)
Ag1 O9	2.421(8)	Ag1 O9	2.321(11)	Ag1 O9	2.248(7)	Ag1 S2A	2.4568(16)
Ag2 S6A	2.487(3)	Ag2 S3	2.5995(18)	Ag1 O11	2.384(9)	Ag2 S2	2.4986(19)
Ag2 S4	2.627(3)	Ag2 S4^{2}	2.450(2)	Ag2 S2	2.531(3)	Ag2 O12	2.275(7)
Ag2 S5	2.577(3)	Ag2 O11	2.287(6)	Ag2 S3	2.603(2)	Ag2 O18^{1}	2.527(5)
Ag2 O11	2.383(9)	Ag2 O100	2.358(10)	Ag2 O10	2.413(9)	Ag2 S1A	2.5431(18)
Ag3 S1A	2.624(4)	Ag3 S4^{3}	2.6198(19)	Ag2 O12	2.225(10)	Ag3 S3^{2}	2.5785(17)
Ag3 O13	2.369(11)	Ag3 S5^{3}	2.508(2)	Ag3 Ag4	2.9643(9)	Ag3 S4^{3}	2.4737(18)
Ag3 S2A	2.580(4)	Ag3 S6	2.5082(19)	Ag3 S3^{2}	2.6396(19)	Ag3 O13	2.422(6)
Ag3 S3A^{2}	2.512(3)	Ag3 O13	2.300(11)	Ag3 S4	2.427(4)	Ag3 O15	2.384(5)
Ag4 S4A	2.636(2)	S1 Ag1 S2	86.37(7)	Ag3 O13	2.252(9)	Ag4 S1	2.4552(18)
Ag4 S5A	2.599(3)	S3^{1} Ag1 S2	139.52(6)	Ag3 O15	2.314(8)	Ag4 O4	2.598(5)
Ag4 S6	2.537(3)	O100 Ag2 S4^{2}	93.88(29)	Ag4 S5	2.704(5)	Ag4 O14	2.352(6)
Ag4 O15	2.345(9)	O11 Ag2 S4^{2}	125.42(16)	Ag4 S6	2.6340(19)	Ag4 O16	2.257(5)
S3^{1} Ag1 S2	132.48(8)	O13 Ag3 S6	85.1(4)	Ag4 O14	2.403(11)	Ag5 O17	2.362(6)
S1 Ag1 S2	86.42(9)	S5^{3} Ag3 S6	138.40(7)	Ag4 O16	2.222(7)	Ag5 S3A	2.5301(15)
S6A Ag2 S5	131.98(11)			Ag5 S5	2.540(6)	Ag5 S4A^{4}	2.4875(17)
S5 Ag2 S4	84.84(10)			Ag5 O17	2.19(4)	Ag5 S2^{2}	3.0218(16)
S3A^{2} Ag3 S2A	127.12(12)			Ag5 C23	2.652(8)	S2A Ag1 S1	131.24(6)
S2A Ag3 S1A	84.59(12)			Ag5 C24	2.491(7)	O9 Ag1 O11	93.0(3)
S6 Ag4 S5A	124.32(12)			S1 Ag1 O9	132.6(3)	O12 Ag2 S2	123.55(18)
S5A Ag4 S4A	84.17(8)			S1 Ag1 O11	125.9(3)	O18^{1} Ag2 S1A	89.06(13)
				S2 Ag2 O10	87.4(3)	O13 Ag3 S4^{3}	127.06(14)
				S2 Ag2 O12	151.0(3)	O15 Ag3 O13	90.3(2)
				S4 Ag3 O13	133.1(4)	O16 Ag4 S1	75.54(18)
				S4 Ag3 O15	118.0(3)	O14 Ag4 O4	75.54(18)
				S5 Ag4 O14	110.3(4)	S4A^{4} Ag5 S3A	140.50(7)
				S5 Ag4 O16	141.2(3)	S4A^{4} Ag5 S2^{2}	89.06(5)

[a] Symmetry operations for **1**-B: ^{1}2-X,3-Y,-Z; ^{2}1-X,-Y,1-Z; maximum and minimum bond angles reported. [b] Symmetry operations for **1**-C: ^{1}1-X,1-Y,-Z; ^{2}1-X,2-Y,-Z; ^{3}-X,2-Y,1-Z; maximum and minimum bond angles reported. [c] Symmetry operations for **2**-A: ^{1}1/2-X,1/2+Y,1/2-Z; ^{2}3/2-X,-1/2+Y,1/2-Z; S-Ag-O bond angles reported. [d] Symmetry operations for **3**-A: ^{1}-1+X,+Y,+Z; ^{2}1+X,+Y,+Z; ^{3}-X,-Y,1-Z; ^{4}3-X,1-Y,2-Z; maximum and minimum bond angles reported.

4.4. Ag···Ag distances

The Ag···Ag distances in structures **1**-A, **1**-B, **1**-C, **2**-A and **3**-A were measured with Mercury CSD 3.5.1 (Table S-5).

Table S-5. Ag···Ag distances

1-A[2,a]	Å	**1-B**[b]	Å	**1-C**[c]	Å	**2-A**[d]	Å	**3-A**[e]	Å
Ag1 Ag1^{1}	5.220	Ag1 Ag1^{1}	6.235	Ag1 Ag1^{1}	6.051	Ag1 Ag2	2.934	Ag1 Ag2	4.925
Ag2 Ag2^{2}	6.185	Ag2 Ag4	4.781	Ag2 Ag1^{1}	4.030	Ag1 Ag4^{1}	4.779	Ag 1 Ag3	4.475
		Ag3 Ag3^{2}	5.318	Ag3 Ag3^{3}	5.969	Ag2 Ag3^{2}	4.739	Ag1 Ag4	4.263
				Ag2 Ag3^{4}	4.208	Ag3 Ag4	2.964	Ag3 Ag4	3.384
						Ag4 Ag5	4.816	Ag2 Ag5	4.090
								Ag3 Ag3^{1}	5.592
								Ag5 Ag5^{2}	4.805

[a] Symmetry operations for **1**-A: ^{1} 1-x,-y,1-z; ^{2} -x, -y, -z. [b] Symmetry operations for **1**-B: ^{1} 2-x,3-y,-z; ^{2} 1-x,-y,1-z. [c] Symmetry operations for **1**-C: ^{1} 1-x,1-y,-z; ^{2} 1-x,2-y,-z; ^{3} -x,2-y,1-z; ^{4} 1+x,+y,-1+z. [d] Symmetry operations for **2**-A: ^{1} 1/2-x, 1/2+y, 1/2-z; ^{2} 3/2-x,1/2+y,1/2-z. [e] Symmetry operations for **3**-A: ^{1} 1-x,-y,1-z; ^{2} 3-x,1-y,2-z.

4.5. Hydrogen bond parameters

Table S-6. Hydrogen Bonds for **1**-B (D···A < 3.2 Å, DHA > 120°).

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C35	H35A	O1	0.99	2.32	3.003(13)	125.3
C35A	H35D	O1A	0.99	2.40	3.050(12)	122.6
O123	H123	O12[1]	0.84	2.14	2.908(18)	152.3
O106	H106	O109[2]	0.84	1.93	2.728(13)	158.0
O100	H100	O16	0.84	1.96	2.785(13)	169.2
O103	H103	O100	0.84	1.95	2.788(17)	173.3
C104	H10L	F8B	0.99	2.37	3.14(5)	134.8
O109	H109	O9[1]	0.84	1.98	2.815(15)	170.2

[1] +X,-1+Y,1+Z; [2] +X,+Y,-1+Z

Table S-7. Hydrogen Bonds for **1**-C (D···A < 3.2 Å, DHA > 120°).

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C43	H43A	O5	0.97	2.33	2.979(8)	124.1
O109	H109	O14[1]	0.82	1.81	2.55(3)	149.1
O106	H106	O13	0.82	2.08	2.84(2)	154.4
O106	H106	O14B	0.82	2.18	2.85(3)	139.7
O100	H100	O106[2]	0.82	2.01	2.777(16)	156.2
O103	H103	O109	0.82	2.27	2.95(4)	140.7
O115	H115	O10[3]	0.82	1.91	2.508(19)	129.5

[1] -X,2-Y,1-Z; [2] 1+X,+Y,-1+Z; [3] 1-X,1-Y,-Z

Table S-8. Hydrogen Bonds for **2**-A (D···A < 3.2 Å, DHA > 120°).

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C34	H34C	O14[1]	0.97	2.28	3.148(14)	147.8
C38	H38B	O3	0.97	2.43	3.169(10)	132.3
C46	H46B	O7	0.97	2.45	3.166(11)	130.5
C51	H51B	O4	0.97	2.51	3.15(2)	122.6
C43B	H43D	O5	0.97	2.46	3.167(17)	129.7
O103	H13	F13	0.82	1.43	2.20(4)	153.8

[1] 1/2-X,1/2+Y,1/2-Z

Table S-9. Hydrogen Bonds for **3**-A (D···A < 3.2 Å, DHA > 120°).

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C36	H36A	O11	0.97	2.41	3.083(11)	126.4
C41	H41A	O13[1]	0.97	2.36	3.143(9)	137.9
C44	H44A	O7	0.97	2.48	3.086(10)	120.2
C34A	H34F	O18[1]	0.97	2.35	3.199(8)	145.3
C52A	H52D	O3A	0.97	2.34	2.948(9)	120.1
C62A	H62D	O7A	0.97	2.39	3.008(9)	121.0
O106	H106	O109	0.82	2.15	2.97(2)	175.4
O117	H117	O119[2]	0.82	1.81	2.45(7)	134.2
C116	H11D	O118	0.97	2.28	3.08(8)	140.1
O109	H109	O10[3]	0.82	2.27	2.847(12)	127.5
O112	H112	O9	0.82	2.10	2.849(15)	152.5
O100	H100	O106	0.82	1.86	2.67(2)	165.9
O103	H103	O100	0.82	2.02	2.79(3)	158.6

[1] -1+X,+Y,+Z; [2] 1-X,2-Y,1-Z; [3] 1-X,1-Y,1-Z

5. Crystallographic figures

5.1. 1-D coordination polymer 1-B

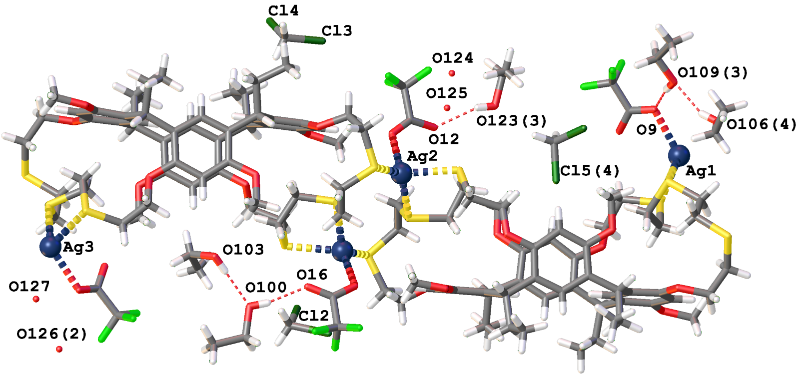


Fig. S-7 Structure **1**-B with solvents. Hydrogen bonds marked with dashed bonds. Disorder not shown for clarity.

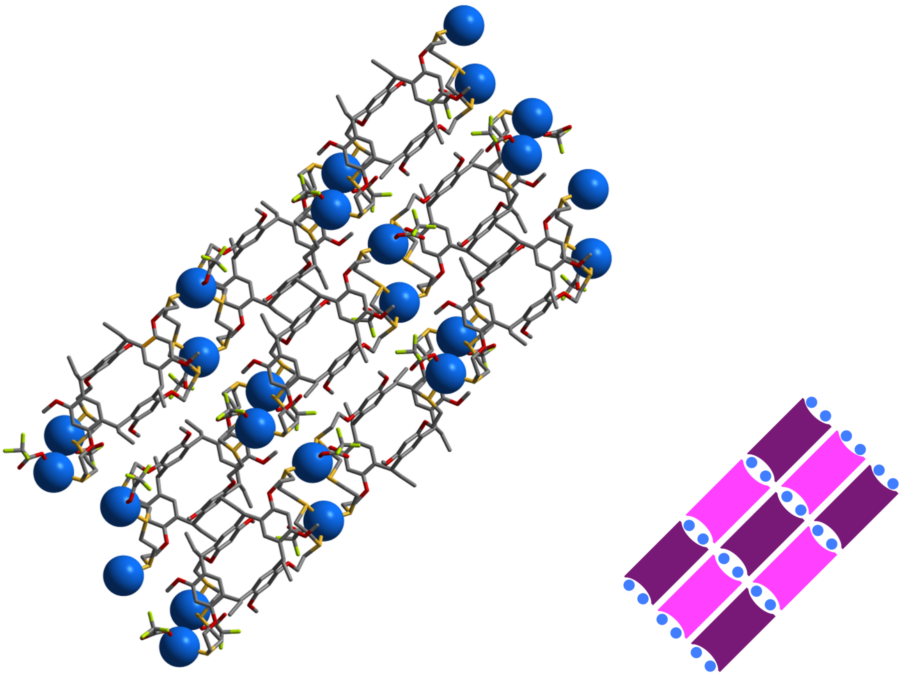


Fig. S-8 Crystal packing of **1**-B polymer chains.

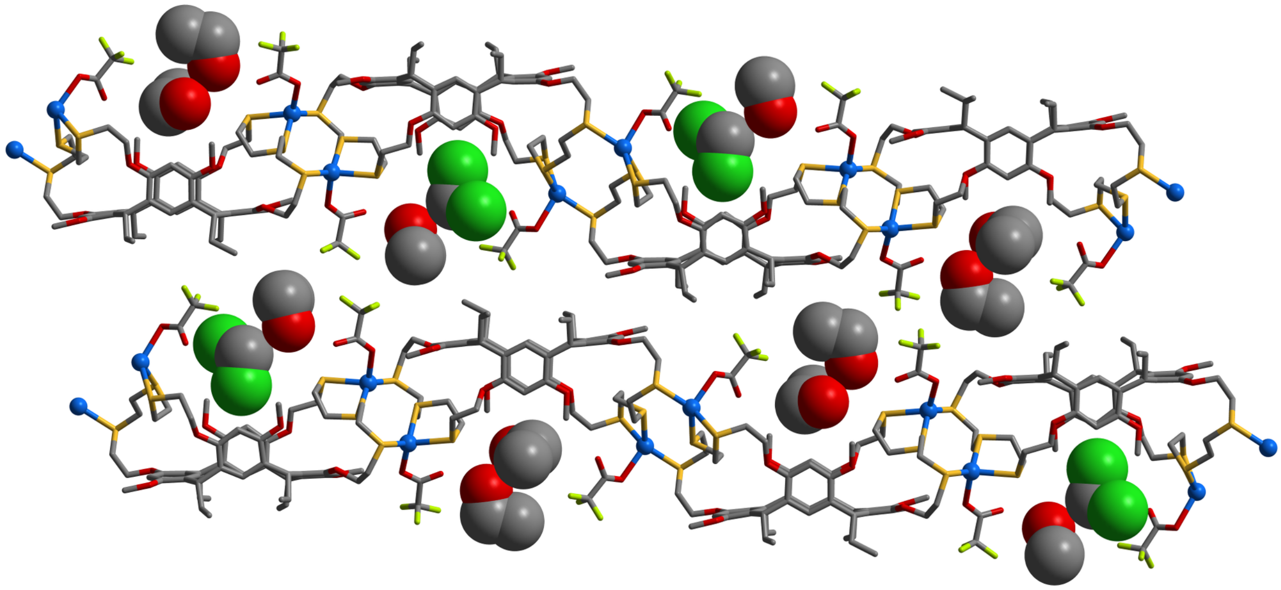


Fig. S-9 Crystal packing in **1**-B showing ethanol and dichloromethane solvents on top of resorcinarene cavity with a space fill presentation. Hydrogen atoms and disorder not shown for clarity.

5.2. 2-D coordination polymer 1-C

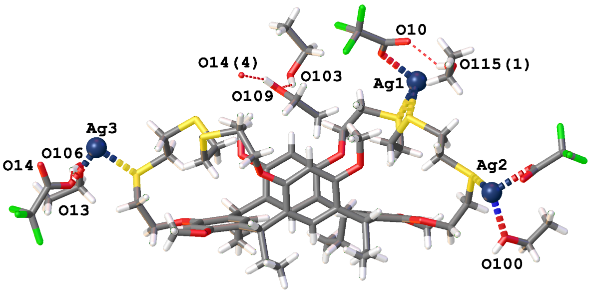


Fig. S-10 Structure **1**-C with solvents. Hydrogen bonds marked with dashed bonds. Disorder not shown for clarity.

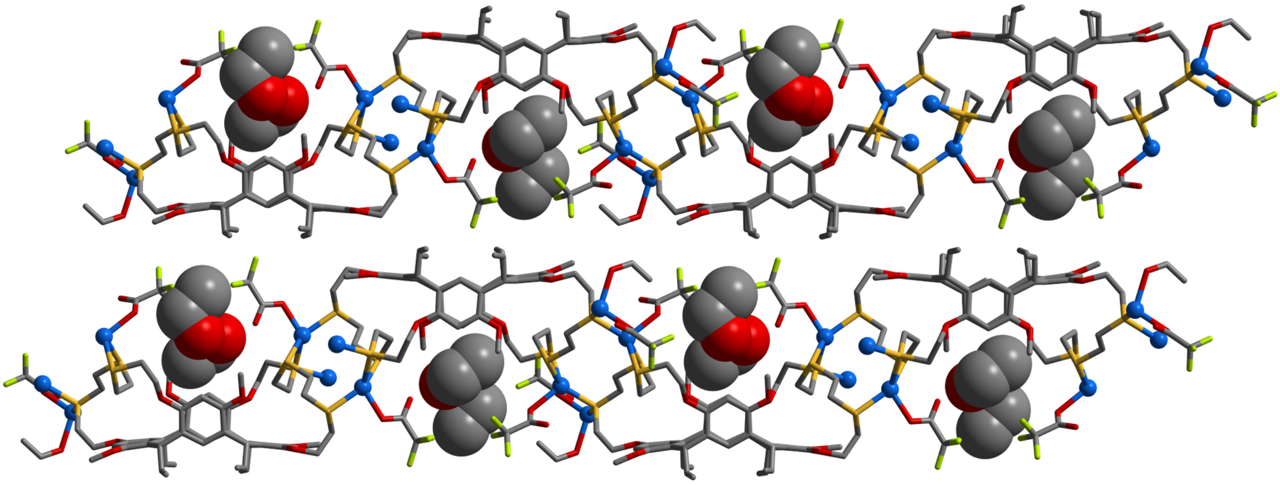


Fig. S-11 Crystal packing in **1**-C showing ethanol solvents on top of resorcinarene cavity with a space fill presentation. Hydrogen atoms and disorder not shown for clarity.

5.3. 2-D coordination polymers 2-A and 3-A

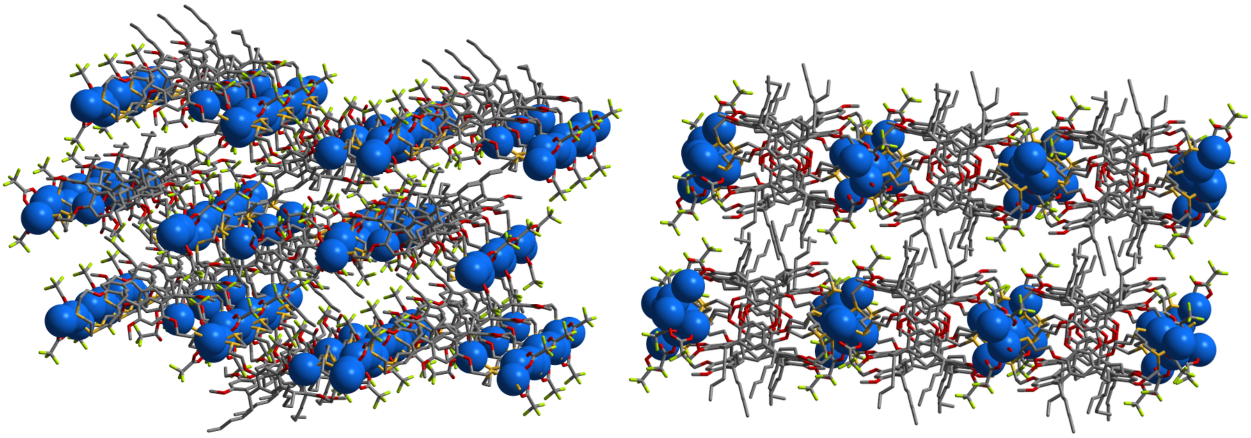


Fig. S-12 Packing of sheets in **2**-A (left) and **3**-A (right).

5.4. Void space

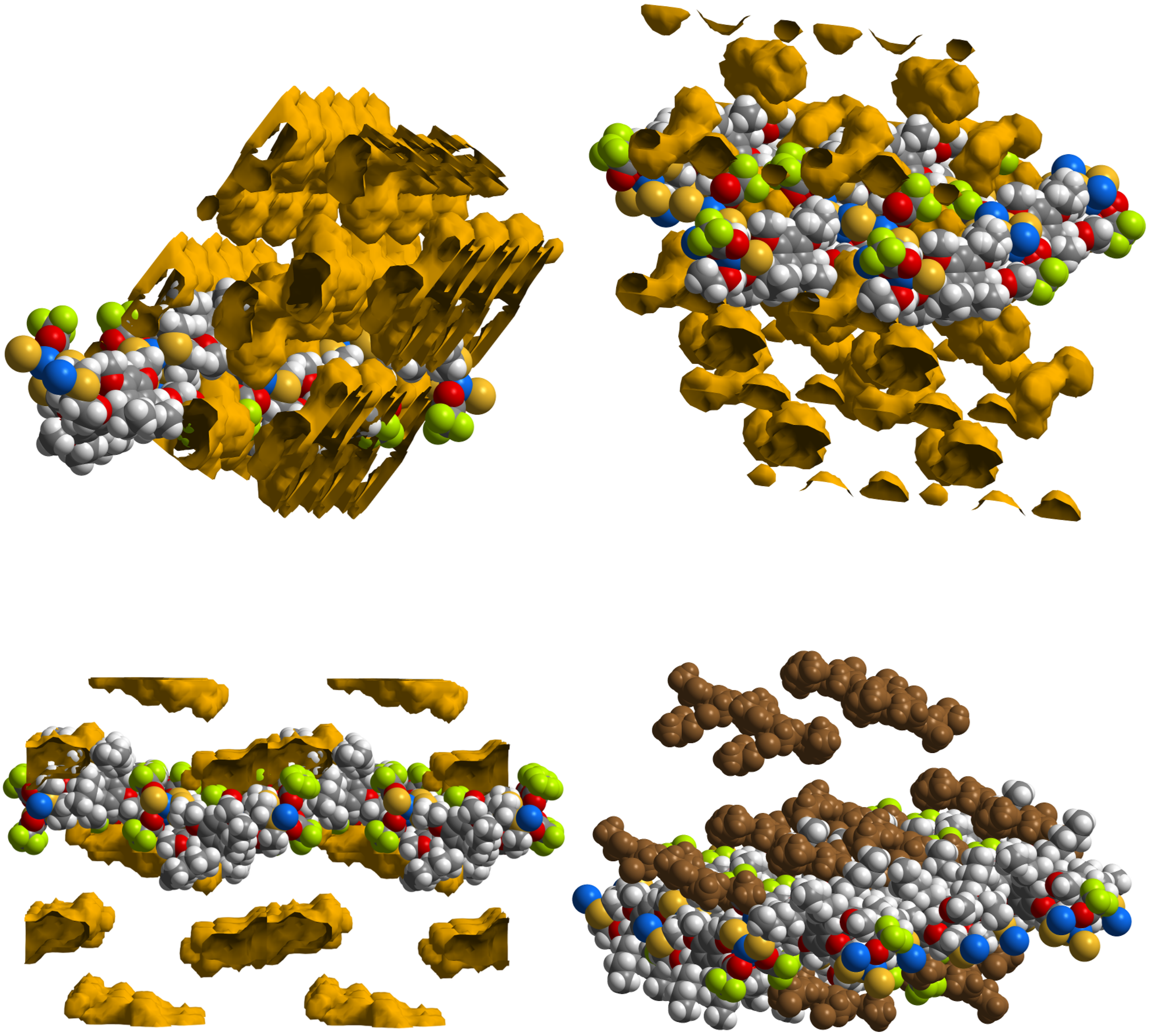


Fig. S-13 Solvent filled channels in **1**-B (top left), sheet of **1**-C (top right), solvent pockets between layers of **2**-A (bottom left), and solvates in layers of **3**-A (bottom right).

6. Cambridge Structural Database searches

The Cambridge Structural Database (CSD 5.36 November 2014 + one update) was searched using Ag···SCCS···Ag unit as a search string. From the 88 matching structures, only one $Ag_9L_6^{3-}$ cluster[3] had Ag···Ag contacts below 3 Å, and eight structures had contacts below 3.4 Å.[4] There were 44 macrocyclic thiacrown silver complexes including structure **1**-A, but no other calixarene or resorcinarene ligands were found. One macrocyclic structure contained a silver coordination polymer with Ag···Ag distance < 3.4 Å.[4e] A search with Ag···SCCCS···Ag string yielded 71 hits, from which seven coordination polymers with 1,3-dithiacyclohexane[5] and four other structures[6] had Ag···Ag contacts under 3.4 Å. Another search was conducted using Ag···OCO···Ag unit as a search string. The large number of matching structures, 1005, indicate that this is very typical coordination motif, in which short Ag···Ag contacts are frequently found (827 structures, <3.4 Å). However, the combination of carboxylate and sulfur containing ligands was found only from 29 structures. Trifluoroacetate ligand with Ag···Ag distance under 3.4 Å was found only from 11 structures.

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