**Supporting Information for** 

# Solvent Driven Formation of Silver Embedded **Resorcinarene Nanorods**

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## **Experimental**

Tetramethoxy resorcinarene bis-crown-5 (1) was previously prepared by us.<sup>1</sup> Single crystals of the complexes were grown by slow evaporation of alcohol solutions (methanol, ethanol and *i*- or *n*-propanol) of 1 with excess of  $AgPF_6$  at room temperature.

#### **Crystal Structure Data and Details**

Data were recorded on a Nonius Kappa CCD diffractometer with Apex II detector using graphite monochromatized  $CuK_{\alpha}$  [ $\lambda(CuK_{\alpha}) = 1.54178$  Å] radiation at a temperature of 173.0 K. The data were processed with Denzo-SMN v0.97.638.<sup>2</sup> The structures were solved by direct methods (SHELXS-97<sup>3</sup>) and refinements based on  $F^2$  were made by full-matrix least-squares techniques (SHELXL-97<sup>4</sup>). The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. Hydroxyl hydrogens were located from the difference Fourier map when possible and the bond distances were fixed (DFIX 0.84) when necessary. Absorption correction<sup>5</sup> was made to all structures. CCDC numbers 813688 - 813691 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request.cif.

Crystal data for I:  $C_{56}H_{76}O_{14}$ ·AgPF<sub>6</sub>·4.5 CH<sub>3</sub>OH·1.5 H<sub>2</sub>O, M = 1369.21, colorless block,  $0.15 \times 0.10 \times 0.05$ mm, triclinic, space group P-1 (No. 2), a = 10.8013(3), b = 17.5560(5), c = 20.4806(5) Å, a = 69.649(2),  $\beta = 10.8013(3)$ , b = 17.5560(5), c = 20.4806(5) Å, a = 69.649(2),  $\beta = 10.8013(3)$ , b = 17.5560(5), c = 20.4806(5) Å, a = 69.649(2),  $\beta = 10.8013(3)$ , b = 10.8013(3), b =

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76.099(2),  $\gamma = 73.507(2)^\circ$ , V = 3447.9(2) Å<sup>3</sup>, Z = 2, 17974 reflections collected, 11823 unique ( $R_{int} = 0.0586$ ), 868 parameters, 2 restraints, *GOF* on  $F^2 = 1.065$ , final  $R_1 = 0.0949$ ,  $wR_2 = 0.1762$  (all data),  $R_1 = 0.0623$ ,  $wR_2 = 0.1548$  ( $I > 2\sigma I$ ). Hydroxyl hydrogens of solvent methanol could not be located from the difference Fourier map and were calculated to their idealized positions and refined as riding atoms. Hydrogen atoms for water molecules could not be constructed. Structure contains disordered solvent methanol and water molecules.



Fig S1. Ellipsoid plot at 50 % probability and a schematic of the capsules of structure I.

<u>Crystal data for II</u>: C<sub>56</sub>H<sub>76</sub>O<sub>14</sub>·2 AgPF<sub>6</sub>·2 C<sub>2</sub>H<sub>5</sub>OH, M = 1570.98, colorless block, 0.25 × 0.10 × 0.05 mm, triclinic, space group P-1 (No. 2), a = 21.3724(5), b = 24.3735(4), c = 24.5548(5) Å, a = 112.3624(8),  $\beta = 106.9775(9)$ ,  $\gamma = 105.9447(9)^{\circ}$ , V = 10180.3(4) Å<sup>3</sup>, Z = 6, 52671 reflections collected, 35304 unique ( $R_{int} = 0.0747$ ), 2524 parameters, 16 restraints, *GOF* on  $F^2 = 1.045$ , final  $R_1 = 0.1457$ ,  $wR_2 = 0.2758$  (all data),  $R_1 = 0.0996$ ,  $wR_2 = 0.2436$  ( $I > 2\sigma I$ ). Hydroxyl hydrogens of all solvent ethanol could not be located from the difference Fourier map and were calculated to their idealized positions and refined as riding atoms. One disordered solvent ethanol and crown bridge (-O57C-C58C-C59C-) over two positions with site occupancies of 0.76:0.24 and 0.71:0.29, respectively. Bonding distances were restrained to be equal (SADI).



Fig S2. Ellipsoid plot at 50 % probability for structure II.

<u>Crystal data for III</u>: C<sub>56</sub>H<sub>76</sub>O<sub>14</sub>·2 AgPF<sub>6</sub>·2 *i*-C<sub>3</sub>H<sub>7</sub>OH, M = 1599.04, colorless block,  $0.25 \times 0.25 \times 0.05$  mm, orthorhombic, space group Pbcn (No. 60), a = 15.1333(4), b = 19.3949(5), c = 23.3326(6) Å, V = 6848.3(3) Å<sup>3</sup>, Z = 4, 10941 reflections collected, 5882 unique ( $R_{int} = 0.0407$ ), 443 parameters, 8 restraints, *GOF* on  $F^2 = 1.036$ , final  $R_1 = 0.0904$ ,  $wR_2 = 0.1316$  (all data),  $R_1 = 0.0533$ ,  $wR_2 = 0.1145$  ( $I > 2\sigma I$ ). Disorder over two positions at crown bridge (-O46-**C47-C48**-O49-) with site occupancy of 0.32:0.68. Bonding distances were restrained to be equal (SADI).



Fig S3. Ellipsoid plot at 50 % probability for structure III.



Fig S4. Schematic of the sheets and their packing in structure III.

<u>Crystal data for IV (isostructural to III)</u>: C<sub>56</sub>H<sub>76</sub>O<sub>14</sub>·2 AgPF<sub>6</sub>·2 n-C<sub>3</sub>H<sub>7</sub>OH, M = 1599.04, colorless block, 0.25 × 0.15 × 0.05 mm, orthorhombic, space group Pbcn (No. 60), a = 14.8806(3), b = 19.7336(4), c = 23.4274(6) Å, V = 6879.4(3) Å<sup>3</sup>, Z = 4, 11001 reflections collected, 5923 unique ( $R_{int} = 0.0359$ ), 468 parameters, 16 restraints, *GOF* on  $F^2 = 1.020$ , final  $R_1 = 0.0899$ ,  $wR_2 = 0.1422$  (all data),  $R_1 = 0.0558$ ,  $wR_2 = 0.1231$  ( $I > 2\sigma I$ ). Disordered solvent propanol and crown bridge (-O46-C47-C48-O49-) over two positions with site occupancies of 0.43:0.57 and 0.44:0.56, respectively. Bonding distances were restrained to be equal (SADI).





Fig S5. Ellipsoid plot at 50 % probability for structure IV.

	Ι	$\mathbf{II}^{\mathrm{a}}$	III	Calc MeOH <sup>d</sup>	Calc EtOH <sup>d</sup>	Calc <i>i</i> - propanol <sup>d</sup>
Crystal packing arrangement	Capsule	nanorod	sheet	-	-	-
Conformation	Boat	twisted boat	twisted boat	boat	twisted boat	twisted boat
Dihedral angle /°	33.5 / 146.1	34.1 / 153.2	23.7 / 169.1	37.5 / 146.6	31.9 / 151.2	26.9 / 164.0
Distance /Å	5.74 / 7.89	5.63 / 7.89	5.46 / 7.99	5.87 / 7.92	5.62 / 7.92	5.58 / 7.97
Tilt /°	4.1	27.7	10.9	6.2	26.8	13.9
Twist /°	3.3	21.7	8.1	5.4	22.1	12.0
Crown pocket diameter /Å	5.63 / 6.29 <sup>b</sup>	6.51	6.11 <sup>c</sup>	5.73 / 6.48 <sup>b</sup>	6.48	6.18
Average Ag <sup>+</sup> … O /Å (crown)	2.60	2.56	2.48 <sup>c</sup>	2.64	2.68	2.62
Average Ag <sup>+</sup> … O /Å (solvent)	2.30	2.32	2.27	2.44	2.41	2.40
Average $Ag^+ \cdots$ Ar /Å ( $\eta^1$ )	$2.53 (\eta^2)$	2.40	$2.60 (\eta^2)$	2.30	2.37	2.36

**Table S1.** Conformational properties and bond distances of the  $AgPF_6$ .1 complexes and of the corresponding calculated structures.

<sup>a</sup> Average values of the three independent molecules in the asymmetric unit. <sup>b</sup> Only one crown pocket contains silver cation, the other one is occupied with water molecule, respectively. <sup>c</sup> Asymmetric unit contains half of the molecule, the coordination of both of the cations is identical due to symmetry. <sup>d</sup> Calculations with counterion.

# Descriptions and descriptive figures of the conformational and geometrical properties:

Dihedral angles are the angles between the upright aromatic rings and the aromatic rings in the horizontal plane, respectively. The distance is measured between the centroids of the upright aromatic rings and between the centroids of the aromatic rings in the horizontal plane, respectively. Crown pocket diameter is the average of the distances between the methoxy oxygen (O6) and crown ether oxygens (O18, O54, O57 and O60), see Fig S6.



Fig S6. a) Tilt and b) twist angles of resorcinarene bis-crown-5 (shown for structure II). Hydrogen atoms have been omitted for clarity.



**Fig S7**. Geometrical properties of a one resorcinarene bis-crown-5 molecule within the disc unit of the nanorod assembly (structure **II**): The torsion angle between the neighbouring molecules is measured through the axis formed by the silver cations (> ABCD) and the inclination from the disc plane (grey line; plane BCE) with respect to the molecule shown in blue.

## **Computational methods**

All energy calculations were performed using the density functional theory (DFT) real space grid-based code GPAW.<sup>6,7</sup> GPAW makes use of the all-electron projector augmented wave (PAW) method by Blöchl and the frozen core approximation.<sup>8,9</sup> The outermost 11, 6, and 4 electrons as valence for Au, O, and C, were used, respectively. All GPAW setups include scalar-relativistic effects. Exchange and correlation effects were included through the Perdew, Burke, and Ernzerhof (PBE) energy functional.<sup>10</sup> The Kohn-Sham wave functions were expanded directly on a real space grid with grid spacing of 0.2 Å. Optimisations of the considered structures have been performed until the maximal force is below 0.01 eV/ Å on any atom.

All complex systems are composed of a resorcinarene host, silver cations and solvents with an overall positive charge. Bader analysis was used to check that the charge depleting  $PF_6$  molecule, close to the host, takes almost exactly the same charge (0.98 e per  $PF_6$ ). The relaxation has been performed in a non periodic cell, starting from the crystal coordinates.

The HOMO-LUMO gap of all systems varies from 2.01-3.10 eV depending on the solvent (Table S2). The HOMO level is constituted by the orbitals localized in the resorcinarene and the LUMO is localized in the silver cation (Figure S1). Using a Projected Local Density of States (PLDOS) analysis the LUMO can be

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characterized as the empty *s* orbital of the silver. The transfer of charge from the silver cation to the complex is lower than the one expected from the PLDOS. According to Bader charge analysis each silver cation has a high positive charge of 0.6 e. This implies that the resorcinarene-solvent system also has a charge of positive 0.4 e per cation. We have checked that the charge distribution remains the same when using the  $PF_6$  molecule close to the host instead of modifying the overall charge of the system.

Table S2. Comparation of the energetics of the systems when the solvent is varied.

	Methanol	Ethanol	iPropanol
Complex energy of formation in kJ/mol (1)	480.8	756.7	736.5
Cation binding energy in kJ/mol (2)	429.8	352.9	354.8
HOMO-LUMO gap in eV	2.01	2.81	3.10

The complex corresponds to the system composed of the resorcinarene host, silver and solvent with an overall positive charge.

- (1) The quantity energy of formation per solvent corresponds to:
- (2)  $E(host) + x E(Ag^+) + x E(solvent) E(complex)$
- (2) The cation binding energy is calculated from: ( E(host-solvent) + x E(cation) E(complex) ) / x

x is 1 for the system with methanol as solvent, and x is 2 for ethanol and *i*-propanol.



**Fig S8.** PLDOS of the complex resorcinarene, silver and *i*-propanol solvent. The highest occupied molecular orbital (HOMO) lies at -8.81933 eV and it is composed of the states localized in the resorcinarene (middle panels). There is no weight at that energy in the solvent or the cation (top and bottom). The lowest unoccupied molecular orbital (LUMO) is completely localized in the cation (top panel). The orbital lies at - 5.71966 eV and can simply be described as the empty *s* state of the cation.