Electronic Supplementary Information

Incorporation of carboxylated pillar[5]arene and strontium (II) into supramolecular coordination complexes of different nuclearity

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Crystallization

Carboxylic acid substituted pillar[5]arene (**CPA5**) was synthesized according to a literature procedure.[1] Strontium chloride hexahydrate and 1,10-phenanthroline were purchased from Sigma Aldrich.

Complex **1**

2 mg of **CPA5** were dissolved in 1 ml of 1:1 water-ethanol mixture under gentle heating. The solution of 1.4 mg of strontium chloride hexahydrate in 1 ml of 1:1 water-ethanol mixture was slowly added to the solution of **CPA5**. The diffraction quality crystals grew after 1 week.

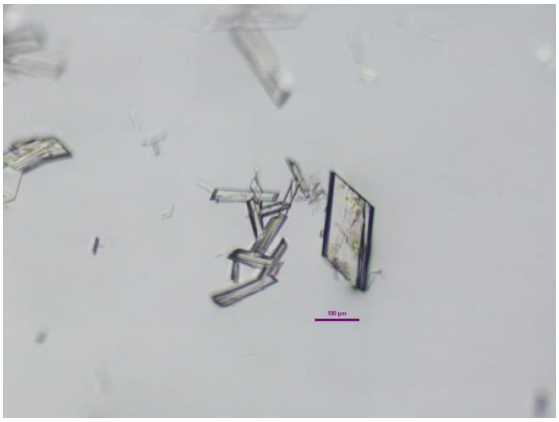

*Fig. ESI-1 Optical microscopy image of the crystals of complex **1** of **CPA5** with Sr(II) cation.*

Complex **2**

2 mg of **CPA5** were dissolved in 1 ml of 1:1 water-ethanol mixture under gentle heating. The solution of 1.2 mg 1,10-phenanthroline in 1 ml of 1:1 water-ethanol mixture was slowly added to the solution of **CPA5**. The diffraction quality crystals grew after 2 days.

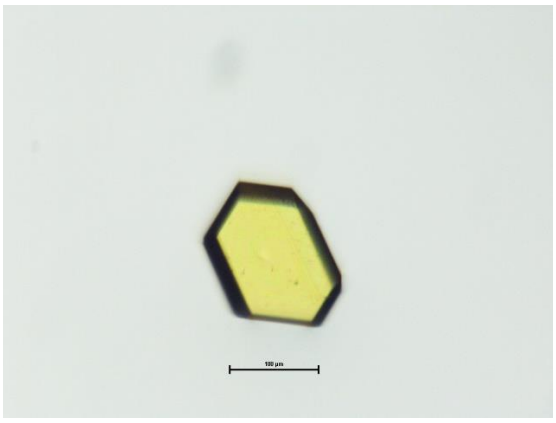

*Fig. ESI-2 Optical microscopy image of the crystal of complex **2** of **CPA5** with 1,10-phenanthroline.*

Complex **3**.

1 mg of **CPA5** was dissolved in 1 ml of 1:1 water-ethanol mixture under gentle heating. The solution of 0.6 mg of 1,10-phenanthroline and 0.7 mg of strontium chloride hexahydrate in 1 ml of 1:1 water-ethanol mixture was slowly added to the solution of **CPA5**. The initially turbid solution became clear after few minutes. The diffraction quality crystals grew after 2 weeks.

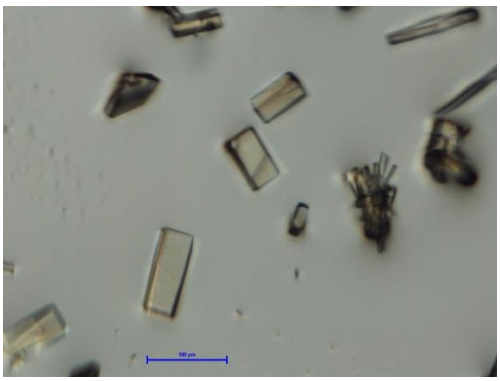

*Fig. ESI-3 Optical microscopy image of the crystals of complex **3** of **CPA5** with Sr(II) cations and 1,10-phenanthroline.*

Single crystal X-ray diffraction

The crystals were embedded in the inert perfluoropolyalkylether (viscosity 1800cSt; ABCR GmbH) and mounted using Hampton Research Cryoloops. The crystals were flash cooled to 100.0(1) K in a nitrogen gas stream and kept at this temperature during the experiments. The X-ray data were collected on a SuperNova Agilent diffractometer using CuKα radiation (λ = 1.54184 Å). Since the crystals have been found to be solvent dependent, several unit cells have been determined for all three complexes to confirm sample homogeneity. The data were processed with *CrysAlisPro*.[2] Structures were solved by direct methods and refined using *SHELXL*[3] under *WinGX*.[4] The figures were prepared using *Chimera*.[5]

Refinement details

Complex **1**. Two carboxylic substituents of the pillar[5]arene and solvent molecules (ethanol and water) inside the macrocyclic cavity and near the rims were modelled as disordered.

Complex **2**. One of the two crystallographically independent phenanthroline molecules was found to be disordered and was modelled as a two-component disorder labelled as Y and Z using PART instructions. The 'soft' restraints on the thermal displacement parameters (SIMU and DELU) were applied during refinement of the disordered phenanthroline molecule. Additionally several carboxylic substituents of pillar[5]arene were found to be disordered and were refined with the help of DFIX and DANG commands.

Complex **3**. Many of the carboxylic substituents of both pillar[5]arene molecules and even the macrocyclic core of one of the pillar[5]arene were modelled as disordered, also one of the Sr(II) centers was found to be disordered over 2 sites (Sr4 and Sr4a), as well as solvent molecules filling the cavities and interstitial space in the crystal lattice were treated as disordered. DFIX and DANG restraints were applied to treat heavy disorder of pillar[5]arene substituents and solvent molecules inside the macrocyclic cavities and near the pillar[5]arene rims. The 'soft' restraints on the thermal displacement parameters SIMU and DELU were applied during refinement of the disorder of the macrocyclic core of one of the pillar[5]arene molecules. The site occupancy factors of many disordered water and ethanol molecules, as well as of some of the disordered carboxylic substituents of both pillar[5]arene molecules were fixed to 0.5, 0.333 or 0.25 due to heavy disorder.

Crystal data for **1**: $[Sr(C_{55}H_{48}O_{30})\cdot(C_2H_6O)_2\cdot(H_2O)_4]\cdot 2.5(H_2O)$, *Mr* = 1531.9, colourless prisms, triclinic, space group *P*-1, *a* = 12.8565(4), *b* = 13.5028(5), *c* = 20.6644(6) Å, *α* = 72.641(3), *β* = 75.515(2)°, *γ* = 84.414(2)°, *V* = 3314.1(2) Å^3, *Z* = 2, ρ_{calc} = 1.54 g·cm^{-3}, μ(CuKα) = 2.05 mm^{-1}, θ_{max} = 65.08°, 20341 reflections measured, 11239 unique, 989 parameters, *R* = 0.081, *wR* = 0.192 (*R* = 0.095, *wR* = 0.199 for all data). GooF = 1.07. CCDC 2068743.

Crystal data for **2**: $(C_{55}H_{48}O_{30})\cdot 2(C_{12}H_9N_2)\cdot 2(C_2H_6O)\cdot 4.3(H_2O)$, *Mr* = 1714.3, yellow prisms, triclinic, space group *P*-1, *a* = 13.9854(6), *b* = 14.3768(5), *c* = 23.0984(9) Å, *α* = 73.904(3), *β* = 72.539(4), *γ* = 64.366(4)°, *V* = 3935.1(3) Å^3, *Z* = 2, ρ_{calc} = 1.45 g·cm^{-3}, μ(CuKα) = 0.98 mm^{-1}, θ_{max} = 63.69°, 23524 reflections measured, 12940 unique, 1274 parameters, *R* = 0.091, *wR* = 0.268 (*R* = 0.100, *wR* = 0.278 for all data). GooF = 1.04. CCDC 2068745.

Crystal data for **3**: $[Sr_4(C_{55}H_{46}O_{30})_2\cdot(C_{12}H_8N_2)\cdot(C_2H_6O)\cdot 14(H_2O)]\cdot 3.5(H_2O)$, *Mr* = 3244.8, colourless prisms, monoclinic, space group $P2_1/c$, *a* = 22.5830(11), *b* = 23.6561(6), *c* = 26.7360(11) Å, *β* = 95.186(5)°, *V* = 14224.6(10) Å^3, *Z* = 4, ρ_{calc} = 1.51 g·cm^{-3}, μ(CuKα) = 2.84 mm^{-1}, θ_{max} = 65.09°, 48739 reflections measured, 24152 unique, 12059 parameters, *R* = 0.115, *wR* = 0.289 (*R* = 0.195, *wR* = 0.369 for all data). GooF = 0.99 CCDC 2068744.

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[3] G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3.
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[5] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng and T. E. Ferrin, *J. Comput. Chem*., 2004, **25**(13), 1605.