

Electronic Supplementary Information

Electrostatic co-assembly of pillar[n]pyridiniums and calix[4]arene in aqueous media

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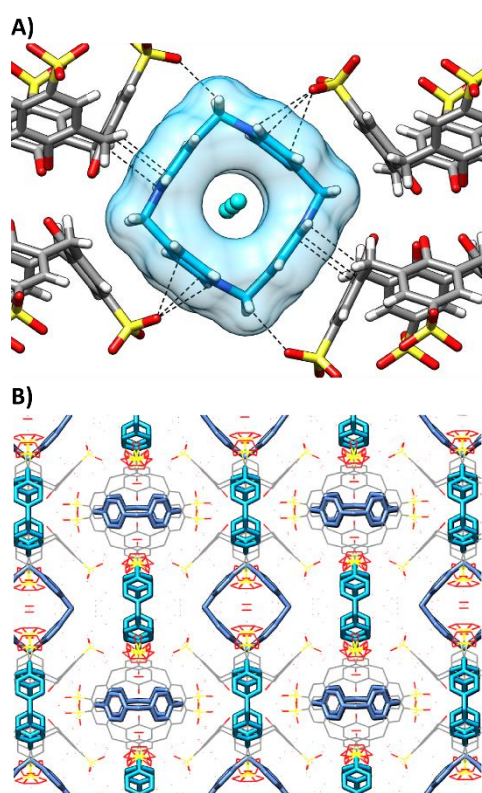


Fig. ESI-1(a) exo-type complexation of second **P4P** (colored in sky blue) in the cage formed by four skeletons of **C4S**, note anion $\cdots\pi^+$, $\pi\cdots\pi^+$ and (C-H) $^+\cdots$ O interaction between external walls of macrocycles, **P4P** is spanned by 3 water molecules in the linear arrangement; (b) crystal packing viewed from **b** direction, **P4P** in cornflower blue are complexed in the capsule mode, **P4P** in sky blue are complexed outside in the crystal lattice.

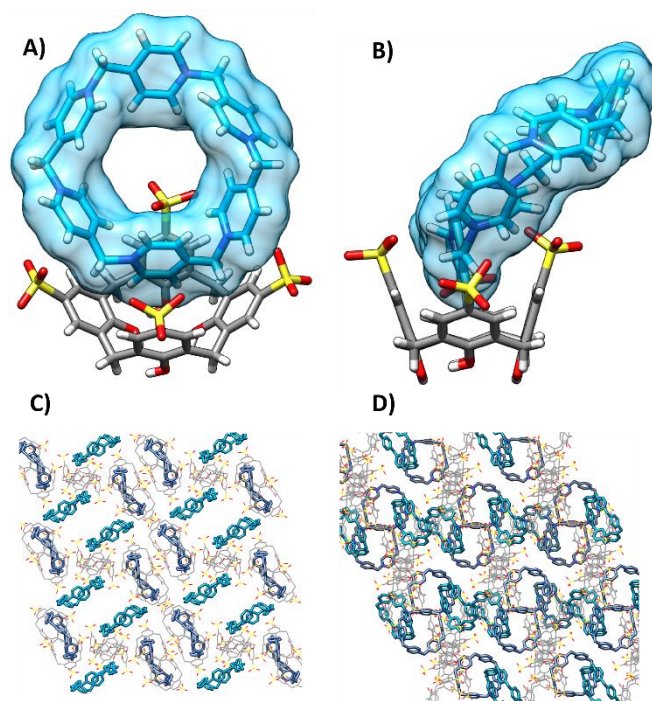


Fig. ESI-2 A) 1:1 open **P6P-C4S** complex, the aromatic rings of **P6P** are alternatively twisted in and out from the macrocycle plane, B) slant-wise inclusion of **P6P** into **C4S**. Water molecules inside **P6P** and surrounding the ensemble are disordered and not shown. C) and D) crystal packing of **P6P-C4S** complex.

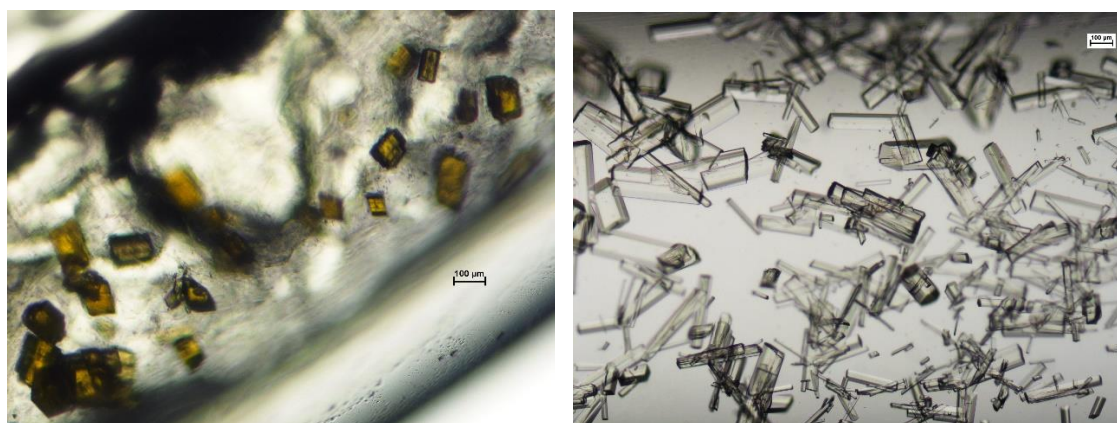


Fig. ESI-3 Optical microscopy images of the crystals of **P4P-C4S** co-assembly grown in agarose gel in U-tube (left) and **P6P-C4S** co-assembly (right) grown by slow liquid-liquid diffusion in NMR tube.

General information

p-Sulfonatocalix[4]arene **C4S** was purchased from TCI company and used without further purification. Pillar[4]pyridinium **P4P** and pillar[6]pyridinium **P6P** were synthesized according to a literature procedure.¹ Experiments were performed at room temperature unless otherwise noted. Deionized water (18.3 MΩ·cm) was obtained from Milli-Q station. NMR spectra were recorded on an Agilent 400 MHz spectrometer. NMR data were analyzed using MestReNova software. UV-Vis spectra were recorded on Evolution 220 UV-Visible Spectrophotometer.

Stability in solution

UV-Vis measurements

0.8 M Tris solutions (pH=11.2) of P[n]Ps or P[n]Ps with C4S were transferred in 3 ml quartz cuvettes and spectra were recorded.

NMR measurements

0.8 M Tris solutions (pH=11.2, 500 μ l) of P[n]Ps or P[n]Ps with C4S were transferred in NMR tubes and spectra were recorded.

Stability in the solid state

Crystalline powders of P[n]Ps and their complexes with C4S (2 mg each) were placed on weighting papers and 50 μ l of triethylamine was added. Note that powder complexes were prepared by mixing equimolar aqueous solutions of P[n]Ps and C4S followed by the evaporation of water.

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 CuK α radiation ($\lambda = 1.54184$ Å). Since the crystals have been found to be solvent dependent, several unit cells have been determined 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

Crystal data for **P4P-C4S**: (C₂₈H₂₀O₁₆S₄)·(C₂₅H₂₄N₄)·14(H₂O), *Mr* = 1361.4, yellow prisms, tetragonal, space group *P4*₂/*m*, *a* = 18.3974(1), *c* = 20.6604(2) Å, *V* = 6992.8(1) Å³, *Z* = 4, $\rho_{calc} = 1.29$ g·cm⁻³, $\mu(\text{CuK}\alpha) = 1.97$ mm⁻¹, $\theta_{max} = 68.2^\circ$, 41529 reflections measured, 6549 unique, 557 parameters, *R* = 0.089, *wR* = 0.262 (*R* = 0.099, *wR* = 0.278 for all data). GooF = 1.03. CCDC 2127199.

Crystal data for **P6P-C4S**: 3(C₂₈H₂₀O₁₆S₄)·2(C₃₆H₃₆N₆)·57(H₂O), *Mr* = 4354.4, colourless prisms, triclinic, space group *P*-1, *a* = 20.9250(7), *b* = 21.5501(5), *c* = 28.2109(6) Å, $\alpha = 102.793(2)$, $\beta = 91.143(2)$, $\gamma = 116.562(3)^\circ$, *V* = 10992.4(6) Å³, *Z* = 2, $\rho_{calc} = 1.32$ g·cm⁻³, $\mu(\text{CuK}\alpha) = 1.96$ mm⁻¹, $\theta_{max} = 65.1^\circ$, 84106 reflections measured, 37424 unique, 2973 parameters, *R* = 0.115, *wR* = 0.307 (*R* = 0.179, *wR* = 0.376 for all data). GooF = 1.15. CCDC 2127200.

Refinement details

P4P-C4S: The nitrogen atoms of the pyridinium rings of P4P molecules cannot be reliably distinguished from the carbon atoms, therefore, the substitutional disorder has been introduced into model. This disorder implies that the same site may be occupied by different atoms (carbon or nitrogen) in the different unit cells. As neither position has clear advantage over another, it is equally possible that nitrogen atoms might be found in the clockwise or anti clockwise directions around the macrocycle. The disorder model was built using PART instructions, the positions of nitrogen and carbon atoms sharing the same site have been refined using EXYZ (same position) and EADP (same thermal parameter) constraints. The

sulfonate groups of C4S have been found to be disordered. The SADI restraints on the S-O distances have been applied.

P6P-C4S: One of P6P molecules have been refined as disordered over 2 positions using PART instructions. The SAME, SIMU and DELU restraints have been applied. The sulfonate groups of one of the C4S molecules have been found to be disordered and were refined using SADI restraints on the S-O distances.

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