

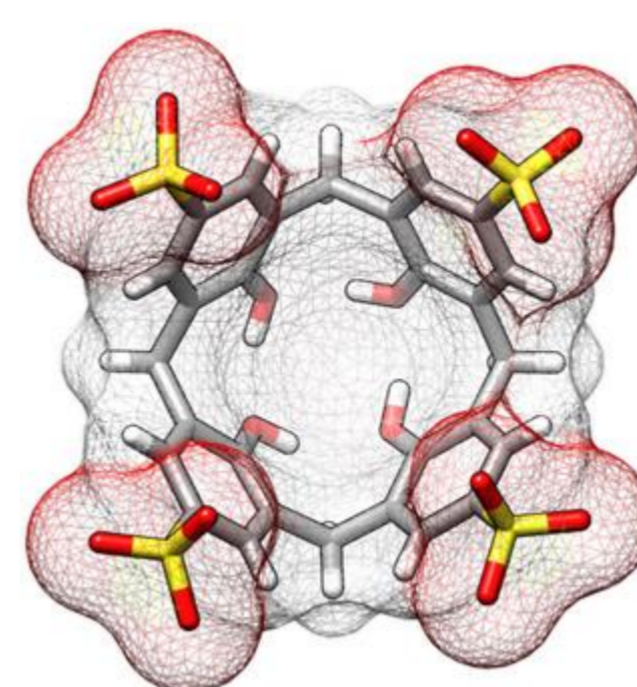


Electrostatic self-assembly of *p*-sulfonatocalix[4]arene and pillar[4]pyridiniums into organic crystals

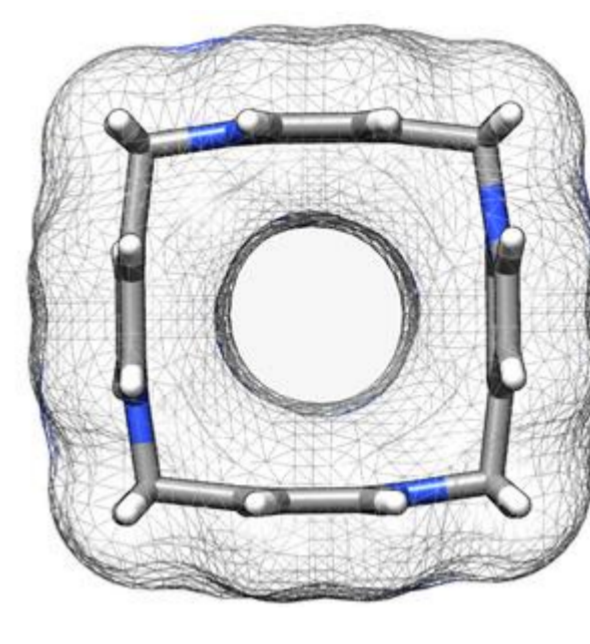
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Abstract

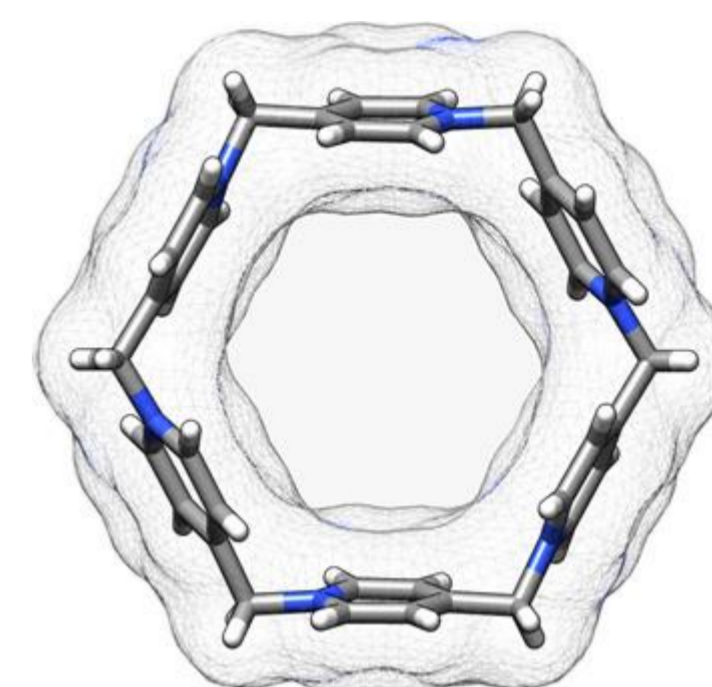
Macrocyclic host molecules are versatile building blocks in the supramolecular chemistry and crystal engineering. Depending on their structure and properties, macrocycles have found numerous applications in the host-guest systems, sensing, catalysis, design of porous materials, etc. We report here an aqueous self-assembly driven by complementarity in charge and shape between two families of oligocharged macrocyclic hosts - cationic pillar[4]pyridiniums and anionic *p*-sulfonatocalix[4]arene.



C4S



P4P



P6P

Conception

- Design of porous molecular crystals from cavity containing macrocycles
- Current approach — self-assembly of cationic and anionic macrocycles

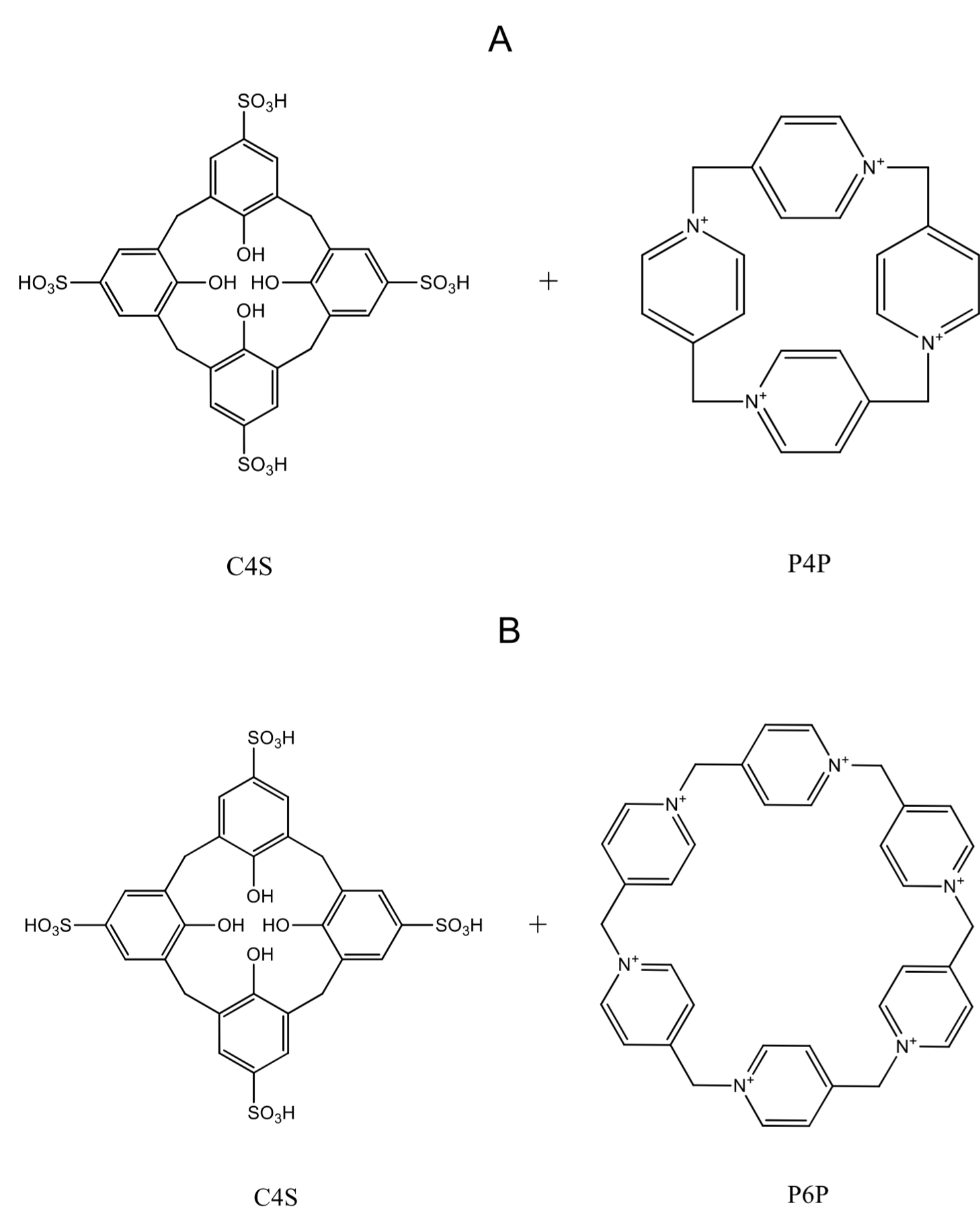
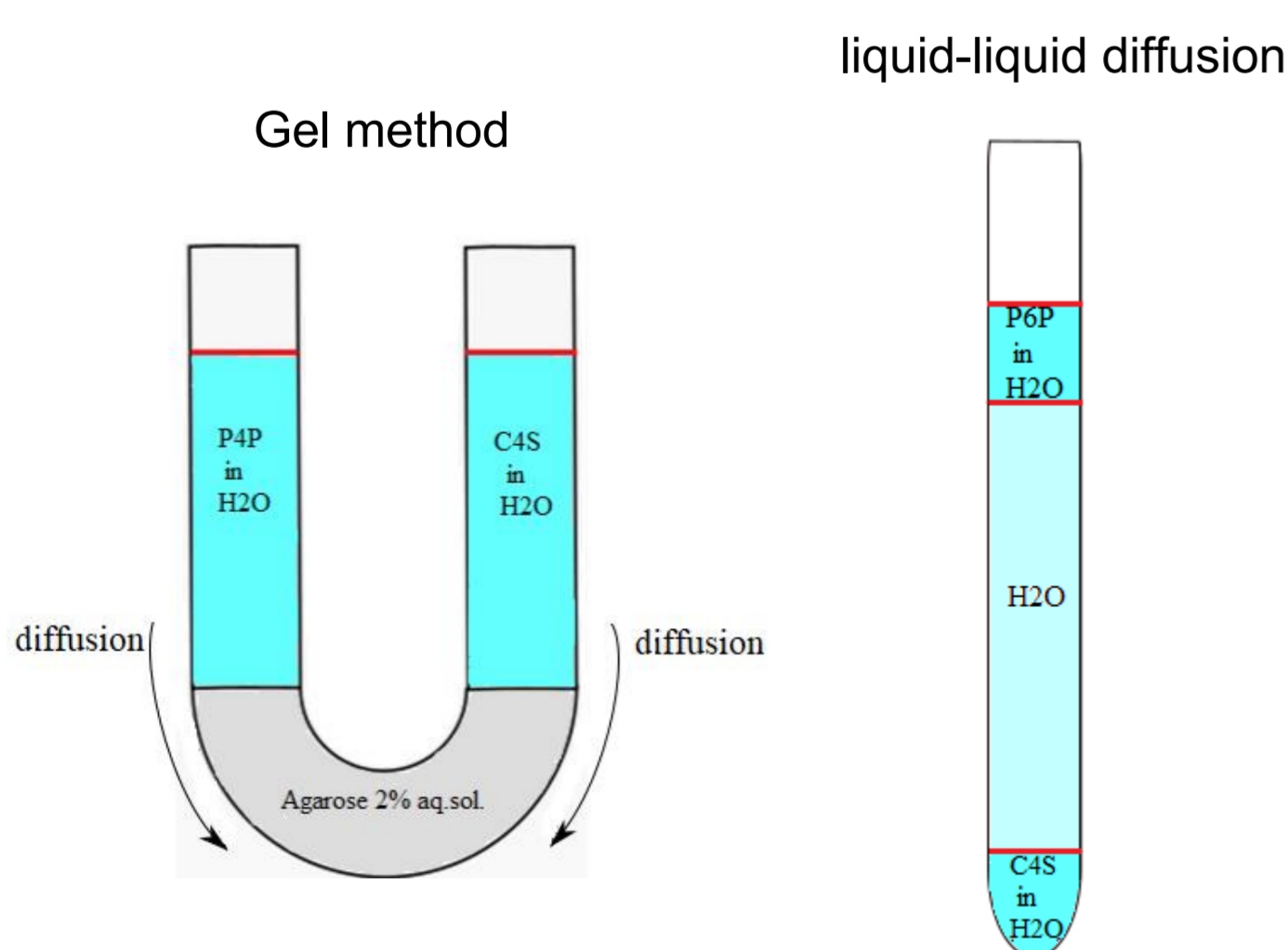


Fig.1 Schematic representation of interaction of *p*-sulfonatocalix[4]arene with pillar[4]pyridiniums (C4S+P4P) (A) and *p*-sulfonatocalix[4]arene with pillar[6]pyridiniums (C4S+P6P) (B).

Crystal growth



C4S+P4P



C4S+P6P



Results

C4S+P4P



C4S+P6P

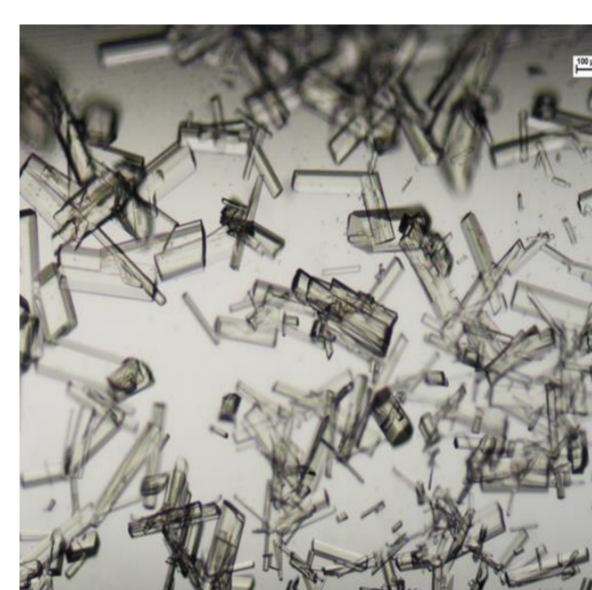
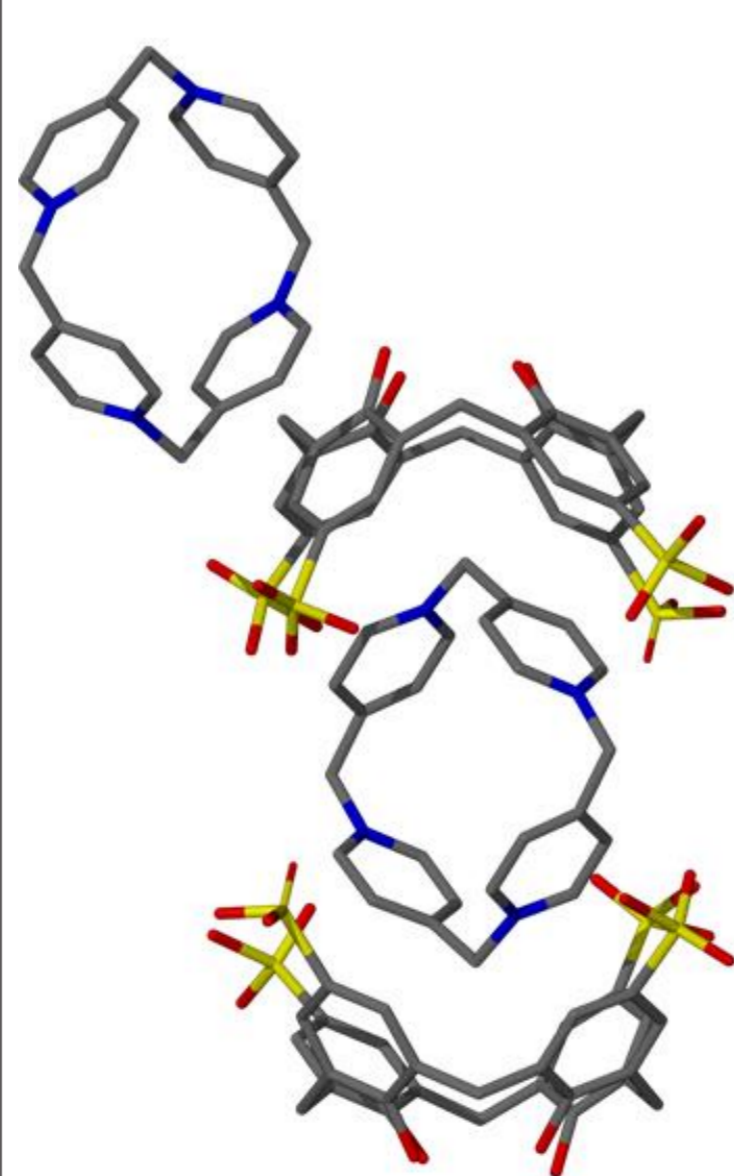


Fig.2 Crystals under an optical microscope.

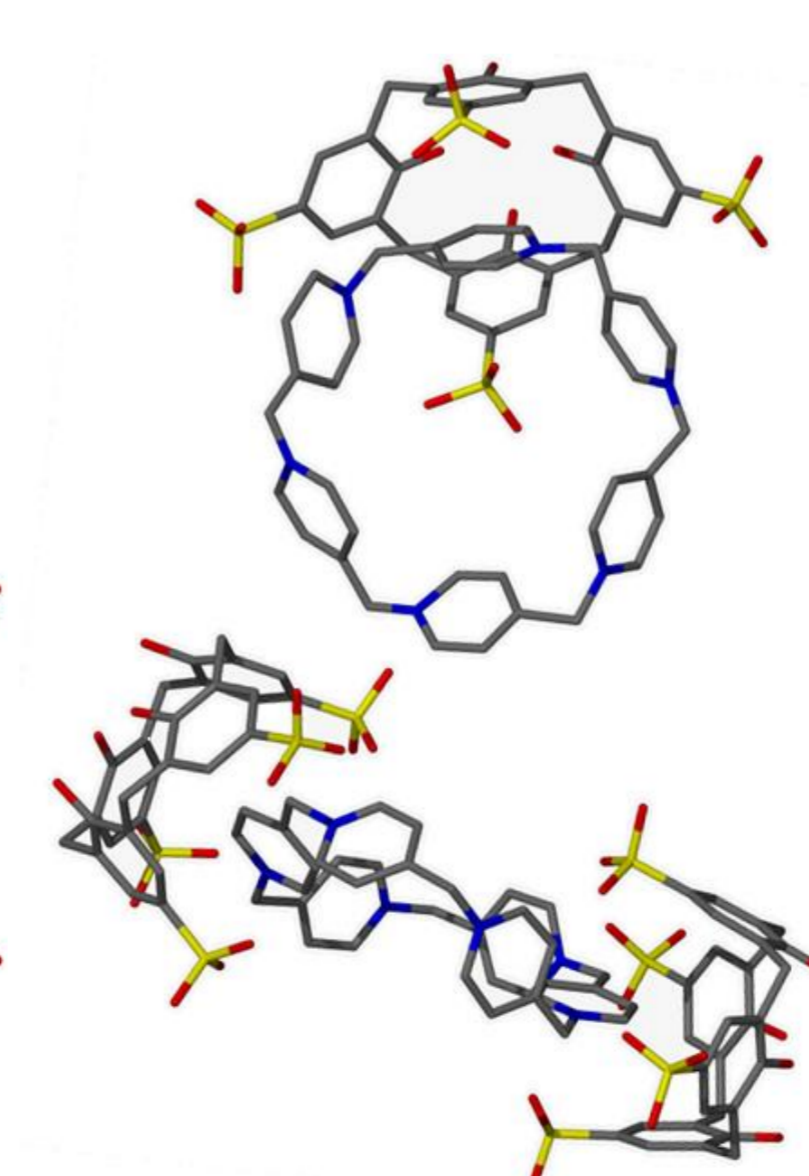
The main characteristics of two crystalline complexes

Complex	C4S:P4P	C4S:P6P
Formula	C ₂₀₈ H ₁₄₄ N ₁₆ O ₉₈ S ₁₆	C ₂₈₁ H ₂₂₈ N ₁₉ O ₁₇₅ S ₂₄
Formula weight	1224.8	1231.3
Crystal system	Tetragonal	Triclinic
Space group	<i>P</i> 43/ <i>m</i>	<i>P</i> -1
<i>a</i> /Å	18.397(1)	20.925(7)
<i>b</i> /Å	18.397(1)	21.550(5)
<i>c</i> /Å	20.660(2)	28.210(6)
α /°	90.000	102.793(2)
β /°	90.000	91.143(2)
γ /°	90.000	116.562(3)
Volume/Å ³	6992.81(1)	10992.44(214)

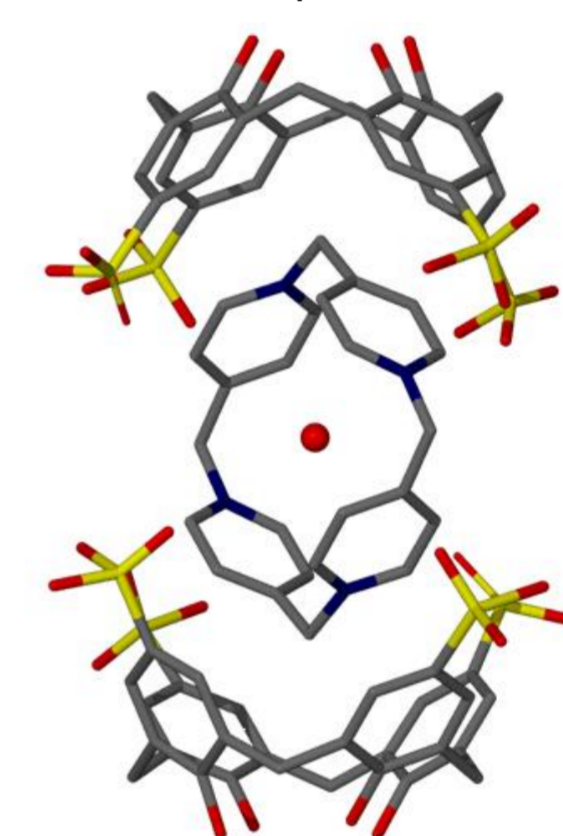
C4S+P4P



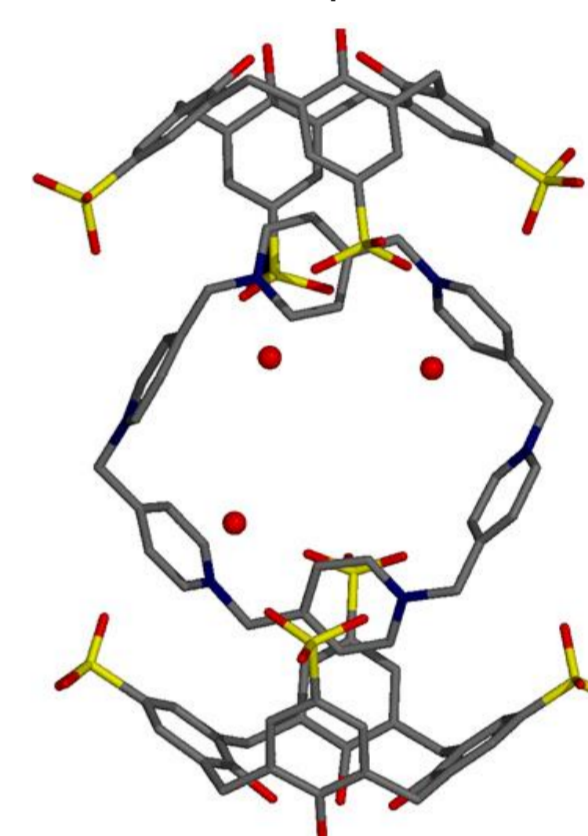
C4S+P6P



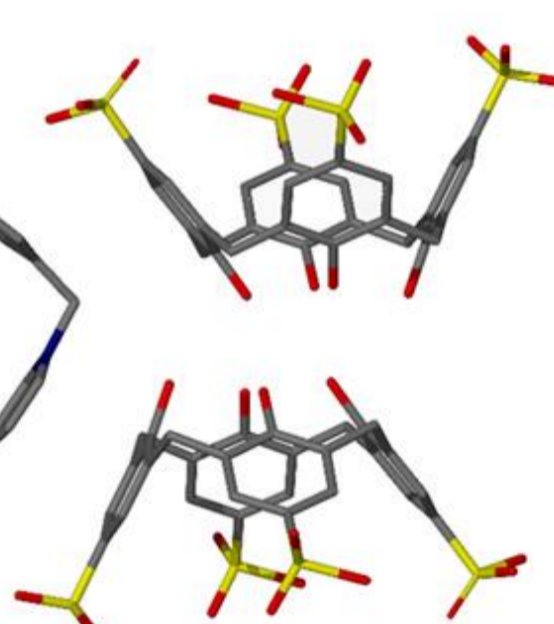
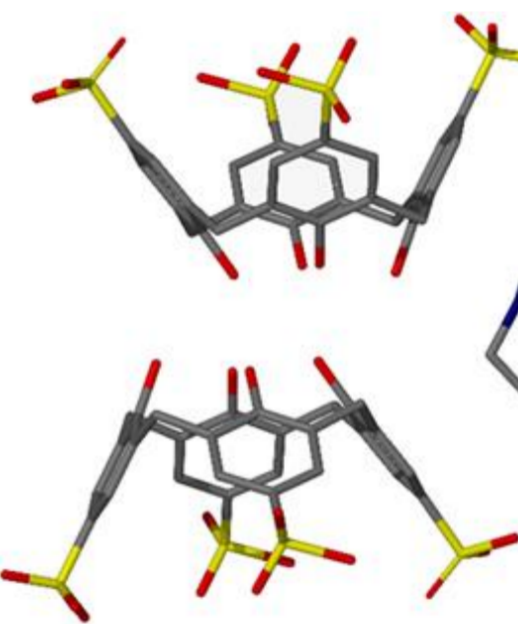
C4S+P4P capsule



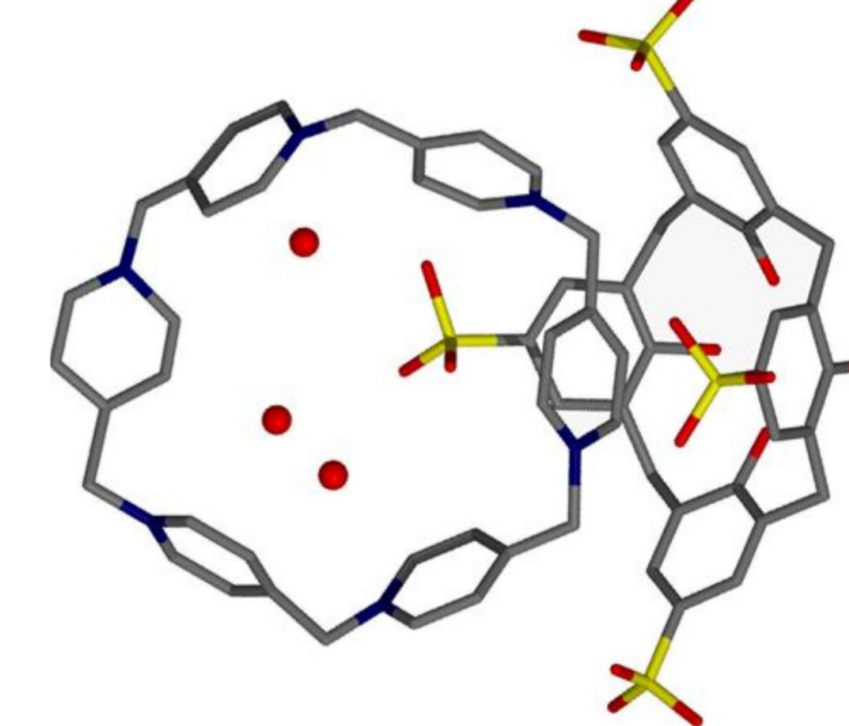
C4S+P6P capsule



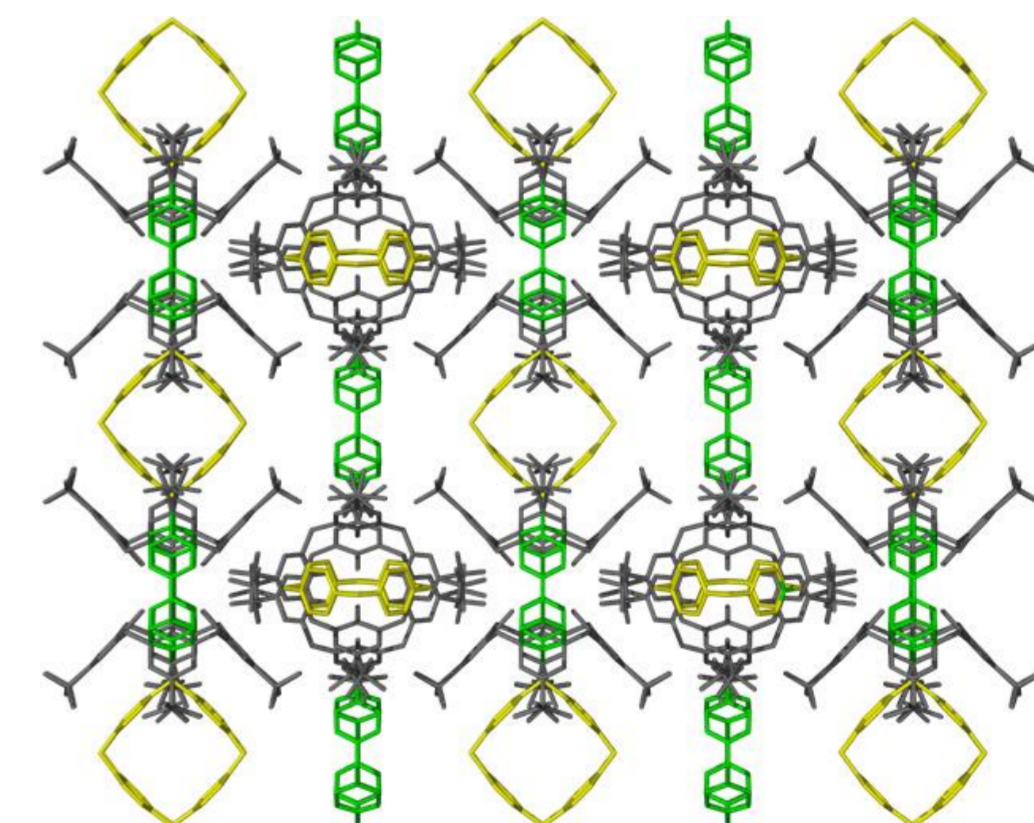
Cage of C4S+P4P



Open complex of C4S+P6P



Packing of C4S+P4P



Conclusions

- Self-assembly of cationic and anionic macrocycles leads to crystalline complexes.
- Different types of complexation: capsule, cage, open complex.

Literature Cited

- [1] Dalgarno S. J., Hardie M. J., Makha M., Raston C. L. Controlling the Conformation and Interplay of *p*-Sulfonatocalix[6]arene as Lanthanide Crown Ether Complexes. *J. Chem. Eur.*, 9, 2834 (2003)
- [2] Kosiorek S., Butkiewicz H., Danylyuk O., Sashuk V. Pillar[6]pyridinium: a hexagonally shaped molecular box that selectively recognizes multicharged anionic species. *J. Chem. Commun.*, 54, 6316 (2018)

Acknowledgments

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Further Information

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