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Discontinuous Three-component Self-assembly: A Leap from Simple Polymers to 3D Networks of Spherical Host-Guest Assemblies

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In the artificial self-assembling systems based on metal atoms and spacing ligands small variations of reagents, stoichiometry, solvents or concentration may cause drastic changes in the structure of the resulting supramolecular architectures [1,2]. Methodologically based rational supramolecular design requires the systematic study of the effects of variation of one of the parameters when other controllable synthetic conditions are kept as close as possible.

Having experience in using pentaphosphaferrocenes [CpRFe(η 5-P5)] (CpR = η 5-C5R5, R = Me, CH2Ph) as building blocks to construct coordination polymers and giant supramolecules via coordination of the cyclo-P5 ligand to coinage metal cations [3,4], we systematically investigated how the direction of one-pot self-assembly reaction of [Cp*Fe(η 5-P5)] (A) with AgSbF6 and flexible aliphatic dinitriles NC(CH2)xCN (DNx) [5] depends on the length of the aliphatic chains in a range $x = 1 - 10$. We found that this reaction can lead to two distinct types of the products, namely, 1D–3D simple coordination polymers (CPs), or 3D supramolecular coordination polymers (SCPs), where huge polycationic nano-sized supramolecules are linked by the DNx spacers into 3D networks (Fig.). The value of $x = 7$ marks the borderline: for $x < 7$ the self-assembly leads to various 1D–3D CPs, while at $x = 7$ the system discontinuously switches to 3D SCP (SbF6)⁻(A)₉Ag₁₁(DN₇)₆₁₀ with huge, supramolecules of \varnothing 2.21 nm in size as nodes. For $x = 8 - 10$ the self-assembly leads to 3D SCPs (A)₁₂(A)₁₂Ag₁₂(DN_x)₆₁₂ with spherical cationic supramolecules of 2.40–2.44 nm in size acting as nodes. The SCPs specifically encapsulate guests, SbF6⁻ anion or A, inside the nodes, while the voids between the nodes in the 3D network are filled with solvent molecules and SbF6⁻ counterions. All products are characterized by NMR spectroscopy, MS spectrometry and single-crystal X-ray diffraction at 10–90 K.

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