Giant Pentaphosphaferrocene-Based Supramolecules as Molecular Containers

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An inorganic analogue of ferrocene, pentaphosphaferrocene, \([\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)]\) \((\text{Cp}^R = \eta^5\text{-C}_5\text{R}_5\), \(R = \text{Me (Cp*), CH}_2\text{Ph (CpBn), PhC}_4\text{H}_9\) \((\text{CpBIG})\), is able to coordinate \(\text{Cu}^+\) and \(\text{Ag}^+\) cations resulting in either coordination polymers or in giant supramolecules [1-7]. The self-assembled supramolecules of 2.1 – 4.6 nm in diameter can be isolated in high yields using special crystallization technique. A tetrahedral coordination of \(\text{Cu}^+\) together with the predetermined five-fold symmetry of the cyclo-P\(_5\) ligand favors the formation of giant cages with fullerene [1,2] or fullerene-like [3, 4] topologies.

Pentaphosphaferrocene-based supramolecules can play a role of molecular containers (Figure 1). The central cavities can include metalloocene and cage molecules, fullerene \(\text{C}_{60}\) molecules of metastable compounds such as white phosphorous and yellow arsenic [6]. The ability of \(\text{CuX}\) to aggregation allows adapting supramolecule to encapsulate cationic guest molecules like \(\text{Cp}_2\text{Co}^+\). Even more sophisticated supramolecules with multi-layered inorganic core built up with hundreds of metal, halogen and P atoms [5, 6] can be obtained, where external and internal cores are formed via \(\sigma\)- and \(\pi\)-coordination of the planar P\(_5\)-ring to copper, respectively.

Alternative way to influence the structure of the supramolecule is to use salts of copper(I) and silver(I) with larger anions. First results show that single-layered quasi-spherical supramolecules with large central cavity can be obtained by using of \(\text{RSO}_3^-\) anions that can coordinate three metal atoms with donor oxygen atoms. The resulting inorganic M-anion-Cp\(^*\)Fe(\(\eta^5\text{-P}_5\)) core resembles an icosidodecahedron, which is however essentially vacant in metal cation positions. The Cp\(^*\)-based supramolecules encapsulate Cp\(^*\)Fe(\(\eta^5\text{-P}_5\)) molecules. Host-guest intermolecular interactions are discussed.

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**Figure 1.** Ligands used for abtaining coordination polymers of Cu(II) and Zn(II). L\(_1\) = anthracene-9,10-diylbis(methylene) dinicotinate; L\(_2\) = anthracene-9,10-diylbis(methylene) dinicotinate.

**Keywords:** Coordination polymers, antimicrobial properties, luminescence
Figure 1. (left to right) Copper haide-based supramolecules encapsulating molecules of ferrocene, P$_5$S$_3$, and As$_4$. Inorganic core of a supramolecule based on copper triflate.

**Keywords:** giant supramolecule, pentaphosphaferrocene, inclusion compound, host-guest interaction, intermolecular interaction, single-crystal X-ray diffraction

**Small Angle Neutron Diffraction on the Vortex Lattice of Type II Superconductors**

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In type II superconductors in magnetic fields $H_{c1} < H < H_{c2}$, the flux form a Vortex Lattice VL, whose geometry represents a delicate balance of the electronic Fermi surface features and pinning. This provides a very sensitive probe of some microscopic electronic properties which can be measured using small angle neutron scattering technique SANS. Below we describe selected results.

i) YBa$_2$Cu$_3$O$_{7-\delta}$ with $\delta=0, 0.15$ at 2 K and for fields of up to 16 T applied parallel to the crystal c-axis, we observe in the SANS data (see Fig. 1) a sequence of field-driven and first-order transitions between different VL structures. By rotating the field away from the c-axis, we observe each structure transition to shift to either higher or lower field dependent on whether the field is rotated towards the [100] or [010] direction. We argue that these transitions are determined by the Fermi Surface Morphology [1].

(ii) KFe$_2$As$_2$, and related materials. We find an intrinsic anisotropy of the superconducting state in this material. With the SANS technique we monitor the vortex and find a field dependent anisotropy, indicating multiband superconductivity. These results support that KFe$_2$As$_2$ is Pauli limited for field applied in the basal plane.

iii) The flux-line lattice in CaAlSi has been studied by small-angle neutron scattering. A well-defined hexagonal flux-line lattice is seen just above $H_{c1}$ in an applied field of only 54 Oe. A 30° reorientation of this vortex lattice has been observed in a very low field of 200 Oe. This reorientation transition is first-order and reflect nonlocal effects [3].