

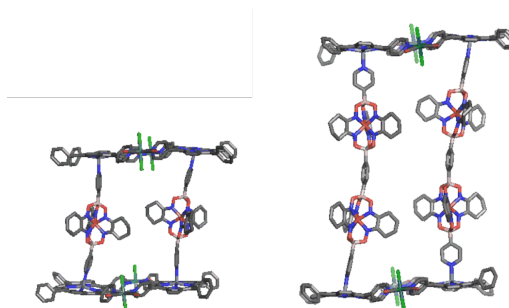
Heterotrimetallic assemblies based on Zn(II)-porphyrin metallacycles and dipyridyl-capped Fe(II)-clathrochelate complexes.

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In supramolecular coordination chemistry, metalloporphyrins and dipyridyl-capped clathrochelates are suitable and versatile building blocks for the construction of a variety of increasingly complex 2D and 3D metallosupramolecular architectures.^{1,2} Over the past few years, a modular strategy has been developed for the synthesis of multiporphyrinic discrete systems and coordination cages of different size and geometry based on pyridyl-capped clathrochelates.^{3,4}

New multiporphyrinic discrete systems were obtained by self-assembly of Ru(II)-based metallacycles of Zn(II)-porphyrins, [*trans*, *cis*, *cis*-RuCl₂(CO)₂(Zn•4'-*cis*DPyP)]₂, and dipyridyl Fe(II)-clathrochelates of tunable length up to 3.2 nm. These heterotrimetallic assemblies, bearing two bridging mono- and dinuclear clathrochelate ligands axially connected to the Zn(II)-metallacycles, were fully characterized by 1D and 2D NMR spectroscopy, including ¹H DOSY analysis, and by X-ray crystallography. A preliminary investigation on the self-sorting behaviour of mixtures of different type of Fe(II)-clathrochelate ligands and Zn(II)-porphyrin metallacycle was performed by ¹H NMR spectroscopy. A library of new 3D heterotrimetallic supramolecular systems with extended dimensions spanning 2.0 nm to 3.0 nm and increased number of metallic cores was assembled by separate combination of Zn(II)-metallacycles and dipyridyl Fe(II)-clathrochelate complexes. Introduction of these new discrete supramolecular assemblies looks promising for future potential application, due to their stability and the presence of metal-active centres and peripheral antenna units.



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