Giant self-contained metallosupramolecular entities

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We present an approach to fabricate very large, soluble, self-contained metallosupramolecular entities employing a template-directed strategy based on charged nanoparticles: consecutive deposition of negatively charged macromolecules and positively charged metallosupramolecular coordination polyelectrolytes is exploited to assemble the metallosupramolecular components on the nanoparticles.

Self-assembly provides an efficient approach to create large supramolecular architectures through non-covalent interactions, bypassing problems associated with stepwise covalent synthetic methodologies.[1] In recent years, metal ion mediated self-assembly has been intensely investigated as a means to construct complex structures. Two dominant metallosupramolecular architectures can be identified. The first involves closed, self-contained (solution) architectures of well-defined shape and nanometer size with a small number of components, a representative example being the cage-type architectures of polytopic bipyridine ligands, 6-PhHat and $\mathrm{Cu^I}$ or $\mathrm{Ag^I}$ ions.[2] The other class consists of infinite solid-state architectures, as in crystals of 1,2-di(4-pyridyl)ethane and $\mathrm{Fe^{II}}$ ions.[3] Complementarity and metal ion–ligand interactions are the dominating assembly principles for the spatial organization of the components.

Metal ion containing assemblies are expected to exhibit novel physicochemical properties such as optical, magnetic, electrochemical and catalytic functions, similar to a variety of proteins bearing multi-metal active sites.[4] In order to integrate active functional units into operating molecular based materials and devices, existing assembly methodologies have to be improved and new methods need to be developed. To date, it has not been possible to construct metallosupramolecular assemblies that bridge the gap between closed cage-type structures (few components) and extended solid-state architectures (infinite number of components). Here, we present a template-directed strategy to fabricate metallosupramolecular entities that contain a very large, yet finite, number of components which remain in solution. To achieve this goal, two types of interaction that operate on two different length scales are utilized. At the molecular level, metal ion mediated interactions generate the supermolecules. Primarily electrostatic interactions effect self-assembly of single layers at the mesoscopic level. The concept of template-directed self-organization is analogous to biological processes; for instance, spontaneous assembly of protein segments along an RNA strand generates the tobacco mosaic virus.[5]

Terpyridine transition metal ion complexes were found to present an array of interesting electronic, photonic, magnetic and reactive properties.[6] Recently, Kurth *et al.* showed that metal ion mediated self-assembly of the ditopic ligand 1,4-bis(2,2′:6′,2″-terpyridin-4′-yl)benzene with transition metal ions results in the formation of metallosupramolecular coordination polyelectrolytes (MEPE).[7] Using the layer-by-layer technique, consecutive deposition of the positively charged MEPE and oppositely charged polyelectrolytes results in well-defined multilayers.[8] This facile method relies on electrostatic interactions of oppositely charged macromolecules. The resulting films present a periodic architecture of active supramolecular components. Thin films with functional components and a well-defined architecture provide an interesting class of advanced materials or devices with tailored properties.

Here, we extend this concept to produce self-contained, yet large metallosupramolecular entities by using nanometer-size templates, namely nanoparticles. In contrast to the previously mentioned methods, this approach offers the following advantages: (i) a large number of active components can be assembled in an easy and inexpensive way; (ii) different functional units can be easily combined within one layer or along the radial direction in order to tailor the properties of the final entity; (iii) the final entity remains in solution (in contrast to crystalline solids); and (iv) the total number of components is readily controlled through the size of the template and the number of layers deposited. A simplified scheme of our approach is shown in Fig. 1.

As templates we employed cetyltrimethylammonium-stabilized, positively charged polystyrene (PS) latices with an average diameter of 73 ± 14 nm (determined from light scattering).[9] Consecutive adsorption of sodium polystyrene-

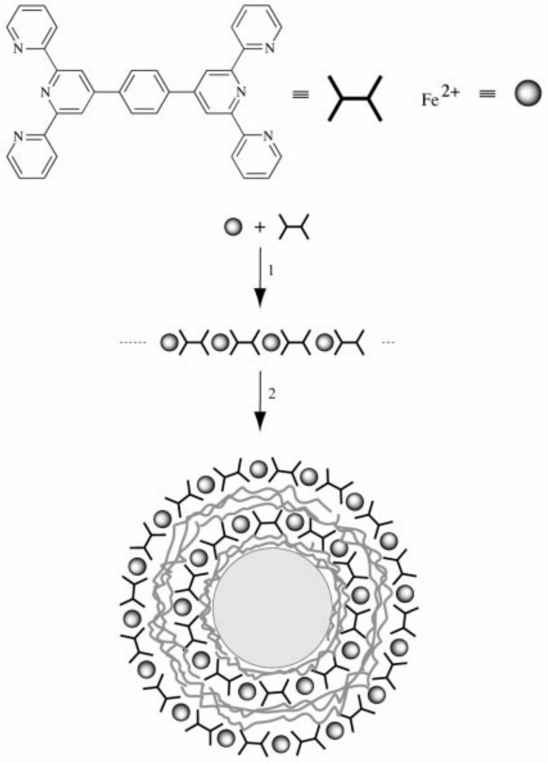

Fig. 1 Two different types of interactions at two different length scales are operative in generating giant, self-contained metallosupramolecular entities (bottom). Metal ion coordination is operative at the molecular level to produce the supermolecules (step 1). Electrostatic interactions are employed to assemble single layers of charged macromolecules on charged nanoparticles at the mesoscopic length scale (step 2). Using PS latices with a diameter of 73 nm, each layer contains approximately 7600 metal ions and ligands; multilayer sheaths with a total of 53 000 components per nanoparticle were created by consecutive deposition of PSS and $\mathrm{Fe^{II}}$–MEPE. The counterions are omitted for clarity; the configurations of the polymers are simplified and the molecules are not drawn to scale.

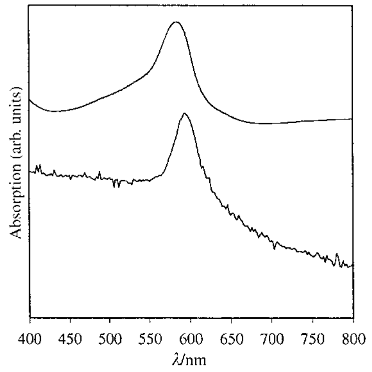

Fig. 2 UV/vis absorption (arbitrary units) spectrum of Fe^{II}–MEPE in aqueous solution (top) and of the coated Fe^{II}–MEPE nanoparticles (bottom). The UV/vis spectrum of the Fe^{II}–MEPE coated nanoparticles was corrected for particle background scattering.

sulfonate (PSS) and Fe^{II}–MEPE results in multilayers on the PS latices.[10] Repeated centrifugation and washing of the PS latices removes excess polyelectrolyte.

Evidence for the deposition of PSS/Fe^{II}–MEPE multilayers on the PS latices is obtained by visual inspection: upon deposition, the PS latices turn blue, the characteristic color of Fe^{II}–MEPE. A representative UV/vis absorption spectrum of the coated PS latices and of Fe^{II}–MEPE in aqueous solution is shown in Fig. 2. The band at 583 nm is characteristic of the Fe^{II}–terpyridine complex; it is associated with a metal-to-ligand charge transfer transition. In the case of the coated PS latices, this band is observed at 593 nm.The red shift is attributed to the different polarity within the multilayer polyelectrolyte film and is characteristic of PSS/Fe^{II}–MEPE layers.

Layer-by-layer growth is confirmed by successful recharging of the particle surface with each deposition cycle. The neat PS latices have a positive ζ-potential of +60 mV. Deposition of PSS reverses the sign of the ζ-potential (approximately −42 mV). Subsequent deposition of Fe^{II}–MEPE results in a positive ζ-potential (app. +18 mV).[11] The ζ-potential for deposition of 14 PSS/Fe^{II}–MEPE layers is summarized in Fig. 3. Alternating ζ-potentials are characteristic of regular multilayer growth on colloidal templates.[12]

Additional evidence for the adsorption of Fe^{II}–MEPE on the particles is provided by energy dispersive X-ray analysis measurements, which clearly show the presence of Fe^{II} on the Fe^{II}–MEPE/PSS-coated particles. Preliminary TEM experiments reveal that PS latices coated with PSS/Fe^{II}–MEPE multilayers have a rougher surface than the uncoated nanocolloids. This is attributed to the linear, rigid-rod type shape of Fe^{II}–MEPE.

A single metallosupramolecular component consisting of one ligand and one metal ion occupies roughly a surface area of 1.2 × 1.8 nm^2. Based on the surface area of *ca.* 17 000 nm^2 per nanoparticle, one particle can accommodate approximately 7600 metallosupramolecular components in one layer. Since up to 7 Fe^{II}–MEPE layers were assembled, a total of 53 000 metal ions and ligands are confined on a single particle. This number can be readily increased, simply by carrying out extra deposition cycles.

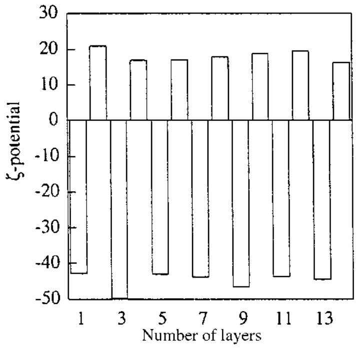

Fig. 3 ζ-potential of alternating layers of PSS (negative values) and Fe^{II}–MEPE (positive values) on PS latices. Alternating ζ-potential values confirm layer-by-layer growth of PSS/Fe^{II}–MEPE multilayers on colloidal templates.

Due to the non-covalent nature of the coordination bond, the metal ion–ligand union is labile and subject to exchange processes. Adding chelating agents, like phenanthroline or salicylic acid, to a solution of Fe^{II}–MEPE results in discoloration of the solution. This is due to disassembly of the Fe^{II}–terpyridine bond. In contrast to the solution species, PSS/Fe^{II}–MEPE multilayers show a much greater stability under these conditions: no color change was detected by UV/vis spectroscopy even after prolonged exposure to chelating agents. Apparently, the adsorption of the charged macromolecules at multiple contact points reduced the degrees of freedom of the Fe^{II}–MEPE to such an extent that removal of a single component becomes strongly hindered.

The template-directed approach based on nanoparticles presented here opens a novel entry to stable dispersed metallosupramolecular entities with a large number of active components. Ongoing research in our laboratories suggests that this approach is generally applicable to the construction of other 'giant', dispersed metallosupramolecular entities. Due to the facile and efficient layer-by-layer method, different active components can be assembled in each layer, thus opening avenues to construct complex functional materials and devices (*e.g.* with vectorial properties). The fact that these entities remain in solution makes them potential candidates for various technological applications. Stimulus-responsive ligands could trigger the release of the metal ions, similar to neuronal action.[13] After removal of the template, the remaining shell constitutes an internal, separated micro-compartment.[14] Motion of the shell may be induced by electrochemical switching of the metal ion coordination geometry. In addition, the permeability of the shell may be controlled with an electrochemical stimulus.

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