Supramolecular Chemistry

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Coordination Polymer Nanostructures

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The greatest challenge in designing molecular-based materials is to predict and control the synthesis of precise assemblies that have well-defined (nano)structures and functions.[1] The properties of nanoscopically defined systems are determined by their size, shape, morphology, and composition, which determine their potential applications in optics,[1b] electronics,[1c] catalysis,[1d] sensors,[1e–g] and medical diagnostics.[1h] To this end, the use of geometrically demanding metal–ligand networks has been a successful strategy to fabricate structurally defined functional materials.[2] Coordination chemistry has traditionally focused on metal–ligand interactions of soluble metal complexes and/or of small clusters.[3] This field has undergone tremendous progress with the development of larger multicomplex assemblies, both in solution and in solid state, and the introduction of dynamic metal-organic and metal-ion templated structures.[4] Coordination building blocks are generally constructed from metal ions as connectors and ligands as linkers.[5] Depending on the metal type, its oxidation states, and coordination number, various geometries can be obtained and the linker nature (e.g., neutral vs. anionic) leads to different linking sites with tuned binding strength, length, and directionality.

Among the nanostructured materials, numerous reports have described the synthesis and properties of carbon, inorganic, and non-fullerene-based nanotubes.[6] Their preparation methods include chemical vapor deposition,[7] self-assembly,[8] sol–gel coating,[9] and template assembly,[10] to cite just a few. Recently, metal-mediated coordination building blocks have been developed to assemble inorganic–organic coordination nanotubes.[11] Coordination polymers are an intriguing class of materials that combine classical and modern metal-coordination chemistry with the often complex formation of large supramolecular structures.[12] These polymers may exhibit redox, optical, catalytic, and magnetic functions derived from their metallic elements. Although their primary structure is enforced by metal–ligand coordination chemistry, their secondary structure often involves other parameters such as intermolecular interactions and solvent effects. These types of polymers can be synthesized through direct metal–ligand coordination or chain polymerization of metal-containing monomers. Depending on the polymerization techniques and reagents, the resulting polymers can be realized in the form of insoluble networks, processible chain structures, gels, or colloids. Research into this increasingly popular multidisciplinary subject has benefited from recent progress in several related areas such as supramolecular chemistry and colloidal chemistry.[13] Despite numerous reports, coordination polymer nanotubes (CPNTs) are relatively rare and the mechanism underlying their formation remains unclear. In contrast, several other noncovalent nanotubes are known and seminal examples with a significant molecular component include hydrogen-bonded helical structures from the group of Sanders (Figure 1)[14] and heterocyclic peptide nanotubes from the group of Ghadiri.[15]

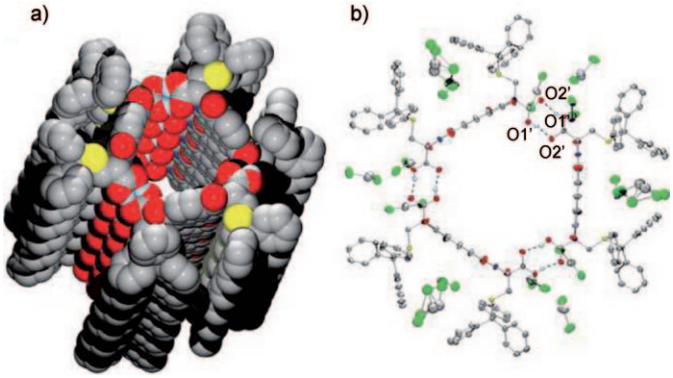

Figure 1. Side and top views of an example of a hydrogen-bonded nanotubular structure. Thermal ellipsoids are scaled at the 50% probability level.[14]

In a series of publications, van der Boom and co-workers have shown how the molecular structures of azine ligands control the formation and properties of coordination-based nanostructures, thin films,[16] and gold nanoparticle aggregates.[17] For instance, by systematically modifying the ligand structure, the corresponding films exhibited linear versus exponential growth[16b] and are composed of surface-bound 3D metal–ligand arrays.[16c] More recently, their elegant molecular approach resulted in coordination polymer nanostructures varying from interconnected spheres, rods, and sheets to nanotubes.[18] Both high-resolution TEM and SEM were used to elucidate structural information and mechanistic

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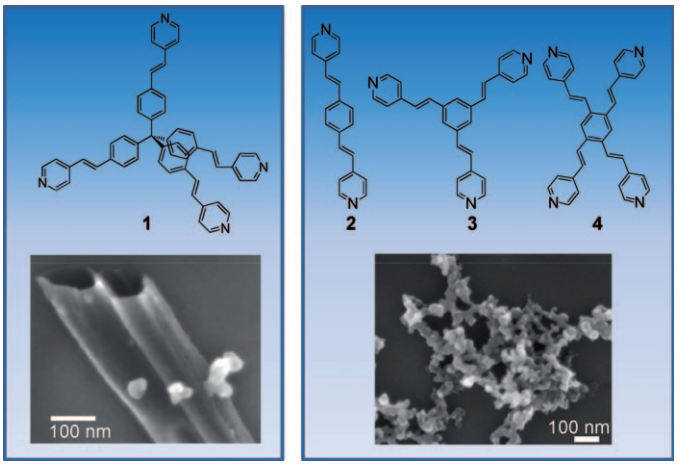

Figure 2. Representative SEM micrographs of assemblies formed by reacting $[PdCl_2(PhCN)_2]$ with ligand **1** (left) and ligands **2**–**4** (right) for three days in toluene at 95 °C under N_2.[18]

details. More specifically, multidentate ligands of type **1**–**4** reacted at room temperature with bisbenzonitrile palladium-dichloride, a common palladium salt, to give the coordination-based structures (i.e., interconnected spheres, rods) depicted in Figure 2. Vinylpyridine ligands are known to coordinate Pd^{II} with concurrent displacement of the weakly bound PhCN ligands. Interestingly, CPNTs formed when the palladium salt was reacted with ligand **1** at elevated temperatures. Thus, these apparently thermodynamically favorable CPNT structures were probably obtained from the spheres and rods since the Pd–N bonds can dissociate. Remarkably, heating the networks of interconnected spheres obtained with ligands **2**–**4** at room temperature resulted only in minor structural changes.

The palladium-to-nitrogen content of the CPNTs reflects the ideal value of a fully coordinated network (i.e., each metal center is bound to two vinylpyridyl moieties). The CPNTs are up to several micrometers long and have a diameter that ranges from 70 to 150 nm and a uniform wall thickness of approximately 25 nm. These dimensions are somewhat similar to the ones reported for multicomponent CPNTs by Qian and co-workers.[19] Their systems were obtained at the interface of an aqueous $HgCl_2$ solution and a chloroform solution that contained both tetrapyridineporphine and tris(4-pyridyl)-1,3,5-triazine ligands (Figure 3a). Surprisingly, the use of a single ligand did not result in the formation of tubular structures. Another interesting example of coordination polymer gels that consist of nanotubular structures was reported by You and co-workers[20] (Figure 3b). The 3D fibrillar network was synthesized from Ag^+ ions and imidazole-based derivatives. It is noteworthy that Tang and co-workers used a metallogel composed of Ag^+ ions and an organic ligand as a template to achieve polyacrylamide-based nanotubes.[21] This latter method is more commonly employed to synthesize inorganic nanotubes.[22]

The CPNT generation based on coordination chemistry of a pyridine derivative is highly versatile with respect to the nature of the metal center. It is remarkable that the geometry of the ligands used by van der Boom is the dominant factor that governs the molecular self-assembly of the CPNTs, whereas the number of metal-coordination sites seems to be less important. Presently, the reason underlying the geometry-driven selectivity of the ligand is not obvious. However, the authors have presented interesting experimental data that shed light on the mechanism underlying nanotube formation. Microscopic images show the presence of several sheets that have the dimensions necessary, upon rollup, to form the observed nanotubes; such a mechanism also operates for

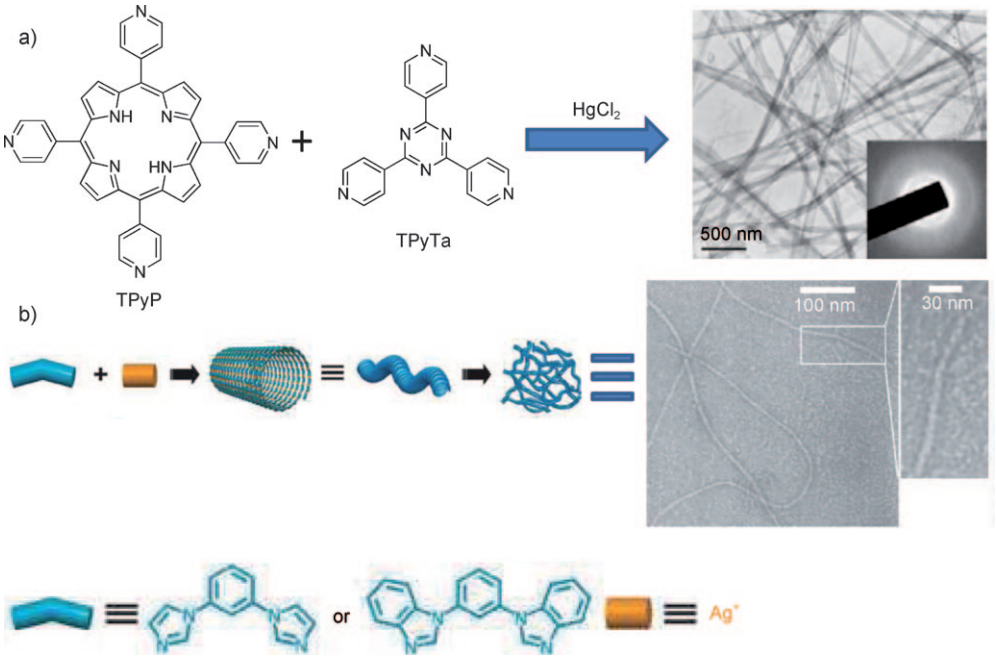

Figure 3. a) Synthesis and TEM image of CPNTs of TPyP, TPyTa, and $HgCl_2$. Inset: electron diffraction pattern.[19] b) Schematic representation of the self-assembly processes of the coordination polymer gels.[20]

carbon nanotubes.[23] For future works, it would be interesting to determine whether the CPNT dimensions can be controlled by systematically varying the reactivity of the metal salt. Another open question to be addressed is how the yields of the CPNT synthesis can be optimized. The fact that the CPNTs are thermally robust indicates that these structures can probably be synthesized and isolated in large quantities. Furthermore, for technology-driven applications, the formation and alignment of coordination-based nanotubes that have a narrow size distribution is of prime importance. Finally, the authors have also observed the formation of end-capped CPNTs, which might lead to encapsulation of other materials, as demonstrated previously.[24] These end-capped CPNTs could be used as microreactors.[24c] In conclusion, CPNTs are a versatile class of materials. These noncovalent hybrid structures are definitely a welcome addition to the numerous well-explored all-carbon-based systems and inorganic nanotubes.[25]

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