VIP Nanotube Assembly

DOI: 10.1002/anie.201008193

Coordination-Polymer Nanotubes and Spheres: A Ligand-Structure Effect**

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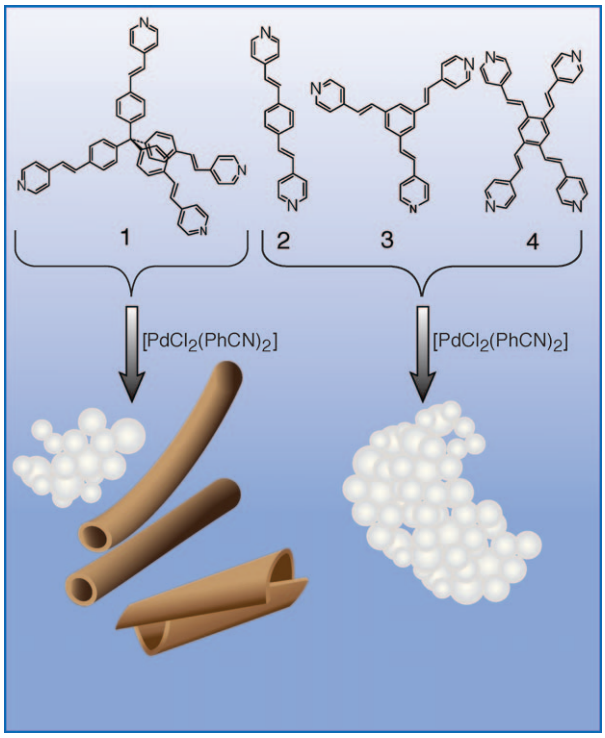
Metal–organic frameworks (MOFs) and coordination polymers (CPs) exhibit a high level of structural tailorability.[1] The rich coordination chemistry of metal ions with multidentate ligands offers versatility from both the structural and functional aspects.[2] The molecular structures of the formed complexes dictate the formation, organization, and function of discretely defined assemblies at the micrometer scale. In addition, the applied assembly process and reaction parameters also play key roles.[3] Fundamental research resulted in the formation of functional metal–organic materials,[4] some of which have already been developed into commercially available products. Regardless of the remarkable recent progress in this field, it is still a challenge to design MOFs, CPs, and related materials with a desired structure and function based on a given set of metal complexes and ligands. For example, the bottom-up assembly of coordination-polymer nanotubes (CPNTs) from multidentate ligands and metal salts is largely unexplored.[5–7] These CPNTs might possess functionalities not readily attainable with other materials.

We present herein a systematic molecular approach for forming amorphous and flexible CPNTs and networks of interconnected spheres by varying the ligand geometry (2D versus 3D) and symmetry, and the number of binding sites (2–4). The CPNTs were formed with multidentate ligand **1** and a palladium precursor, along with interconnected spheres and misfolded sheets (Scheme 1). The use of the ligands **2**–**4** resulted in the formation of interconnected spheres. CPNTs are generated by mixing a solution of $[PdCl_2(PhCN)_2]$ with a suspension of ligand **1** in toluene in a 2:1 molar ratio, followed by heating to 95 °C for three days in a glass pressure tube under nitrogen (see the Supporting Information for experimental details). The metal–ligand ratios used are suitable for forming fully formed networks.[8,9] The benzonitrile ligands of the metal complex precursor are readily replaced by pyridine and its derivatives. Indeed, an orange precipitate formed immediately upon combining the two components. This solid turned light yellow during the subsequent thermal treatment.



Scheme 1. Molecular structures of ligands **1**–**4**[8–10] and the assemblies generated with $[PdCl_2(PhCN)_2]$. Coordination-polymer nanotubes (CPNTs) were only obtained with ligand **1** at elevated temperatures.

Scanning electron microscopy (SEM) measurements revealed the formation of single-wall CPNTs, sheets, spheres, and their aggregates (Figures 1 A–C and Figure S1 in the Supporting Information). The diameters of the CPNTs and the spheres are 70–150 nm and 20–25 nm, respectively. Large-diameter nanotubes might be used as nanoreactors.[11] The length of our CPNTs reaches several micrometers. Transmission electron microscopy (TEM) analysis unambiguously confirmed the formation of amorphous and hollow tubes (Figure 2). Their amorphous nature is somewhat expected because the applied assembly process does not involve slow crystallization from solution. The wall thickness of the CPNTs is uniform and about 25 nm. This width can be achieved by assembling approximately 15 molecules of **1** and palladium. Both capped and open-ended CPNTs are formed. Examples of open-ended CPNTs are shown in Figures 1 A, B and S2, whereas Figure 2 B displays a capped structure. Time-dependent SEM analysis showed that the CPNTs are flexible.[12]

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[**] This research was supported by the Helen and Martin Kimmel Center for Molecular Design and by the Minerva Foundation. The transmission and scanning electron microscopy studies were conducted at the Irving and Cherna Moskowitz Center for Nano and Bio-Nano Imaging at the Weizmann Institute of Science.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008193.

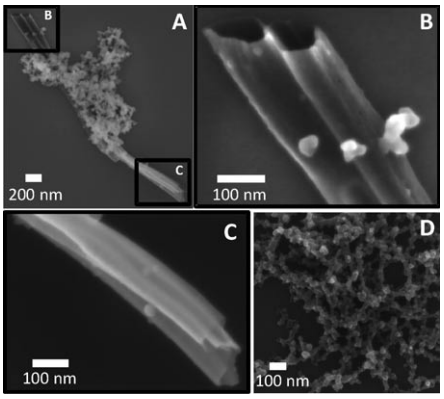

Figure 1. Representative SEM micrographs for assemblies formed by reacting $[PdCl_2(PhCN)_2]$ with ligands **1** (A–C) and **3** (D) upon heating. A) Representative image of CPNTs, misfolded sheets, and a network of interconnected spheres. B) A close-up image of two open-ended tubes from (A) with a diameter of about 100 nm. C) A close-up image of a folded sheet from (A). D) Representative network of interconnected spheres with diameters of 20 to 25 nm.

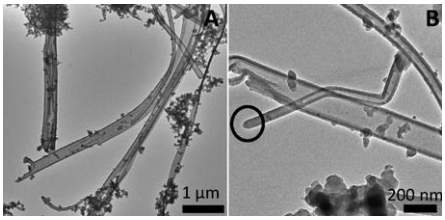

Figure 2. Representative TEM micrographs for CPNTs formed by reacting $[PdCl_2(PhCN)_2]$ and ligand **1** upon heating (A and B). The CPNT wall thickness is about 25 nm. An example of an end-capped CPNT is shown in B (circle).

Frames of bending CPNTs were taken by scanning segments of 3–5 seconds under an electron beam of 3 kV (Figures 3 and S3).

Nanoprobe X-ray energy dispersive spectrometry (EDS) indicated a Pd/N ratio of 0.50:1 and 0.65:1 for the CPNTs and the aggregates of the spheres, respectively (Figure S4). These ratios suggest the formation of coordinatively saturated networks where two pyridine moieties are bound to one metal center,[8,9] although other binding motifs cannot be rigorously excluded. This coordination mode has been thoroughly explored and used for forming palladium–pyridine-based assemblies in solution,[13] and more recently, for forming thin films.[8,9,14] Such complexes generally have a square-planar geometry around the metal center with the pyridine groups mutually *trans*. A recent computational study showed that ligands **3** and **4** and palladium can form closed ring structures, which are well-suited to form extended networks.[8]

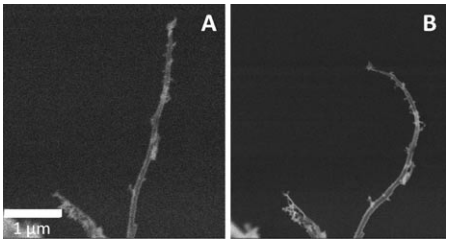

Figure 3. Representative time-dependent SEM micrographs of a CPNT before (A) and after (B) bending upon irradiation with a 3 kV beam (see Figure S3 for further details).

Mechanistically, the formation of carbon and inorganic nanotubes involves the assembly of sheets followed by a rolling/folding process.[15] A similar pathway might be operating in our system. We observed misfolded sheets that have structures not suitable for forming CPNTs under the applied reaction conditions (Figures 1 C and S1 C,D). Their dimensions are similar to the circumferences, wall thicknesses, and lengths of the CPNTs. No CPNTs and sheets were observed when performing the reaction at room temperature. SEM and TEM measurements indicated only the formation of rods and interconnected spheres (Figure S5), which rearrange upon thermolysis in the apparently thermodynamically preferred products. The palladium–pyridine bond dissociation energy (BDE) is approximately 33 kcal mol^{-1},[16] suggesting that the macromolecules (partly) disassemble upon heating to afford the observed CPNTs.[17] The CPNTs generated at elevated temperatures are stable for at least three months at room temperature. CPs are known to form spheres in solution in order to minimize the interfacial free energy.[18] The formation of the sheets implies a relatively fast growth along one of the axes. This anisotropic behavior is probably induced by the molecular structure of ligand **1**.

The key role of the tetrahedral geometry of ligand **1** in the assembly of the CPNTs is apparent from the different assemblies obtained with ligands **2**–**4** (Scheme 1). These compounds, having essentially 2D structures and two to four pyridine moieties, do not form CPNTs and sheets under identical reaction conditions. Regardless of the different numbers of coordination sites, no considerable structural differences were observed for the macromolecules formed from ligands **2**–**4** with $[PdCl_2(PhCN)_2]$ (Figures 1 D and S6–S8). SEM analysis revealed the formation of spheres and mostly their aggregates. SEM images of the **3**-based assemblies indicate a secondary aggregation process upon aging. Relatively dense aggregates of smooth spheres having diameters between 50 and 70 nm were observed after two months at room temperature (Figure S7). This solid-state conversion resembles to some extent the initial stages of the formation of particles from infinite coordination polymers.[18]

Our observations indicate that the dominant factor in this metal–ligand-directed assembly is strongly related to the 3D geometry of compound **1** and its propensity to form sheets to generate the observed CPNTs. The reaction outcome is further controllable by varying the reaction temperature, with higher temperatures favoring the formation of the CPNTs. The number of ligand binding sites (2–4) does not drastically affect the reaction outcome. These findings indicate that the molecular architecture, combined with a bottom-up approach, can be effectively used to direct the formation of flexible CPNTs of up to several micrometers long with circumferences approaching 500 nm. The large range of metals that can coordinate to the used ligands opens up

opportunities to control the structure and properties of the CPNTs.

Received: December 26, 2010
Published online: March 4, 2011

Keywords: coordination polymers · nanotubes · scanning probe microscopy · self-assembly

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