Metal-mediated coordination polymer nanotubes of 5,10,15,20-tetrapyridylporphine and tris(4-pyridyl)-1,3,5-triazine at the water–chloroform interface†

Bing Liu,[a] Dong-Jin Qian,*[a] Meng Chen,[a] Tatsuki Wakayama,[b] Chikashi Nakamura[b] and Jun Miyake[b]

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Coordination polymer nanotubes have been prepared by using the Hg^{2+}-mediated co-assembly of two ligands, tetrapyridylporphine (TPyP) and tris(4-pyridyl)-1,3,5-triazine (TPyTa), at the water–chloroform interface.

Tubular nanomaterials have attracted remarkable interest in the fields of material science, nanotechnology, molecular sieves, sensors, and biomimetic processes.[1] Within the last decade, numerous reports have described the synthesis and properties of carbon nanotubes, inorganic and non-fullerene organic nanotubes.[2–5] The preparation methods include chemical vapor deposition,[6] sol–gel coating,[7] self-assembly,[8] template assembly,[9] and so on.[10] Recently, efforts have been directed toward molecular assembly of tubular materials based on supramolecular interactions, among which metal-mediated coordination building blocks are being developed to assemble inorganic–organic coordination nanotubes.[11,12]

Coordination building blocks are generally constructed from metal ions as connectors and ligands as linkers.[13] Depending on the metals and their oxidation states, coordination numbers can range from 2 to 7, giving rise to various geometries.[13] The linkers, including neutral and anionic organic ligands, afford a wide variety of linking sites with tuned binding strength and directionality. Molecules including di-, tri- and tetrapyridyls are typical neutral linkers, with which many interesting frameworks have been constructed.[13,14] Tetrapyridylporphine (TPyP) and tris(4-pyridyl)-1,3,5-triazine (TPyTa) (Fig. 1) are typical tetra-/tripyridyl derivatives, with which a large number of building blocks have been assembled.[14–18]

We present here Hg^{2+}-directed assembly of HgTPyP–HgTPyTa coordination polymer nanotubes. To the best of our knowledge, although porphyrin nanotubes based on porphyrin dendrimers, nonplanar porphyrins and the ionic self-assembly of cationic/anionic porphyrins have very recently been prepared,[5,12,17] there is no report on metal-mediated assembly with two functional species at the liquid–liquid interface. As having been pointed out, large numbers of building blocks have been constructed from molecules including di-, tri- and tetrapyridyls. We suggest that the suitable design and selection of the metal ions and ligands for use in present assembly method could open a route for a new class of tubular materials—coordination polymer nanotubes.

The HgTPyP–HgTPyTa coordination polymer nanotubes were assembled at the interface of a $HgCl_2$ aqueous solution and a TPyP–TPyTa chloroform solution. Regular nanomaterials have been assembled at the liquid–liquid interface because the particles at the fluid interface are highly mobile and can rapidly achieve an equilibrium assembly.[18] The rapid diffusion of nanoparticles and reagents in either phase lead to a very efficient interfacial reaction and molecular assembly. Moreover, the interfaces between two immiscible solutions provide a defect-free junction, which is very important for products with high purity. A typical experiment in the present work was performed as follows: 20 mL 2.5 mM $HgCl_2$ solution was slowly added onto the surface of 30 mL TPyP–TPyTa chloroform solution (TPyP, 0.3 mM; TPyTa changed with different molar ratios of TPyP–TPyTa; see details in the supporting materials†). The reaction system was left undisturbed at room temperature for 5–30 min depending on the concentration of $HgCl_2$. As control experiments, the interfacial assembly of $HgCl_2$ with pure TPyP or TPyTa was also performed. The products obtained at the interface were transferred onto copper and quartz substrate surfaces using the Langmuir–Blodgett (LB) method for transmission electron microscope (TEM), electron diffraction (ED), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), UV-vis and fluorescence spectroscopy measurements. Samples for the elemental analysis were filtered from the interface and well washed with plenty of pure water and chloroform to remove unreacted $HgCl_2$, TPyP, and TPyTa.

TEM images of the HgTPyP–HgTPyTa nanotubes (Fig. 2 and Fig. S1†) revealed that the nanotubular structure formed only

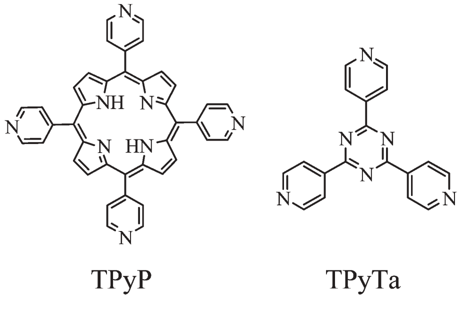

Fig. 1 Structure of the ligands used for assembling nanotubes.

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[a] *Department of Chemistry and Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, China. E-mail: djqian@fudan.edu.cn; Fax: +86 21 5566 4192; Tel: +86 21 6564 3666*
[b] *Research Institute of Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), Amagazaki 661-0974, Hyogo, Japan*

† Electronic supplementary information (ESI) available: Experimental details; TEM and SEM images at various molar ratios of TPyP–TPyTa; XPS and fluorescence spectra; elemental analysis results. See DOI: 10.1039/b606967c

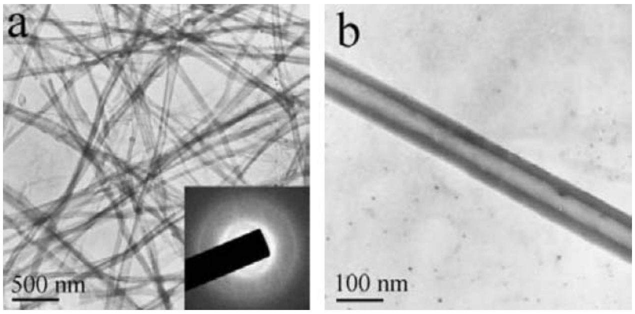

Fig. 2 TEM images of the HgTPyP–HgTPyTa nanotubes.

when the molar ratios of TPyP : TPyTa were in the range of 1 : 3 to 1 : 4. The phenomena were well reproducible. The outer diameter of most nanotubes was about 60–80 nm and inner diameter about 30–40 nm. The wall thickness of the nanotubes was about 15–25 nm (Fig. 2). When the molar ratios of TPyP : TPyTa were below 1 : 2, rod-like and irregular particles were formed, conversely, when the ratios were above 1 : 6, nanowires were formed (Fig. S1†). SEM images confirmed the formation of a large amount of nanowires, as shown in Fig. S2.† Due to its sensitivity, it was hard to observe tubular structures in the SEM images. XPS spectra indicated that the nanotubes were composed of following elements: Hg, Cl, C, N (Fig. S3†), which are in agreement with the multiporphyrin arrays assembled on solid surface and will be discussed later with elemental analysis below.

To clarify the formation process for such nanotubes, the interfacial reaction of $HgCl_2$ with pure TPyP or TPyTa was also performed. The TEM images showed that HgTPyP formed nanowires with thickness up to about 200 nm and length over 10 μm (Fig. 3a).[19] On the other hand, irregular cubed nanocrystals were formed for $HgCl_2$ reacting with pure TPyTa with the length about 1 μm and width in the range of 20 to 100 nm (Fig. 3b). These TEM images confirmed that the structure of either HgTPyP or HgTPyTa was very different from that of their mixtures HgTPyP–HgTPyTa, indicating that unique coordination features dominated the formation of nanotubes.

Electron diffraction patterns for the HgTPyP–HgTPyTa nanotubes, HgTPyP nanowires and HgTPyTa nanorods are inserted in Fig. 2 and 3. An arc diffraction pattern was recorded for the nanotubes (Fig. 2a), which was much similar to the ED patterns of multiwalled carbon nanotubes,[20] and nanofibers of phenyleneethynylenes.[21] The ED pattern of HgTPyTa was close to that of HgTPyP–HgTPyTa nanotubes though the second-order reflection was not so clear as that of nanotubes. On the other hand, irregular dots were observed from the ED image of HgTPyP nanowires, which was however similar to that of CdTPyP nanocrystals.[19] The *d* spacing was about 3.4, 4.0 and 3.4 Å for HgTPyP–HgTPyTa, HgTPyP and HgTPyTa, respectively. Similar *d* values and shapes of the ED patterns of nanotubes compared to those of HgTPyTa nanorods indicated that the structure of the nanotubes may be dominated by the ligand of TPyTa or the coordination unit of HgTPyTa. This may be the reason why the tubular structure was observed only when the molar ratios of TPyP : TPyTa were about 1 : 3 to 1 : 4.

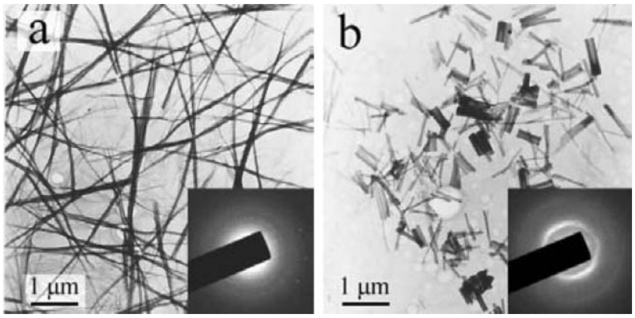

Fig. 3 TEM images of (a) HgTPyP nanowires and (b) HgTPyTa nanorods.

The composition of the HgTPyP–HgTPyTa nanotubes was estimated by elemental analysis. During the experiments, various concentrations of $HgCl_2$ were used for the interfacial assembly. As summarized in Table S2,† the amount of elements C, H and N in the HgTPyP–HgTPyTa nanotubes increased with the decrease in $HgCl_2$ concentration. Compared with the theoretical value from the composition of $Hg_2TPyP–Hg_6TPyTa_4$ (TPyP : TPyTa = 1 : 4, one Hg^{2+} coordinates with two pyridyls), we find that, under the present experimental conditions, the best concentration of $HgCl_2$ was about 2.5 mM. When the $HgCl_2$ concentration was too low, some TPyP (TPyTa) molecules were not coordinated with Hg^{2+} ions, thus the amount of C, H and N was higher than the theoretical value; conversely, when the $HgCl_2$ concentration was too high, some Hg^{2+} ions coordinated with only one TPyP (TPyTa) ligand, leading to a low content of C, H, N elements.

Absorption spectra for the LB films of HgTPyTa, HgTPyP, and HgTPyP–HgTPyTa showed maximum absorption at 245, 437 and 430 nm, respectively (Fig. 4). We have pointed out that the TPyP Soret band appeared at 417 nm for its monomer form, red shifted to 442 nm for its J-aggregates.[22] Here, this Soret band appeared at 430 nm for the HgTPyP–HgTPyTa nanotubes, thus, there is a smaller red shift in comparison with not only the J-aggregate but also the HgTPyP nanocrystals. As it has been well known that the red shift for the Soret band is due to the π–π* interaction between porphyrin rings,[23] we can conclude that porphyrin–porphyrin interaction in the present nanotube is weaker than that in the J-aggregates and HgTPyP nanocrystals. This weakened interaction is due to the co-assembled TPyTa ligand; in the nanotubes the minor component of TPyP is immersed in the HgTPyTa arrays.

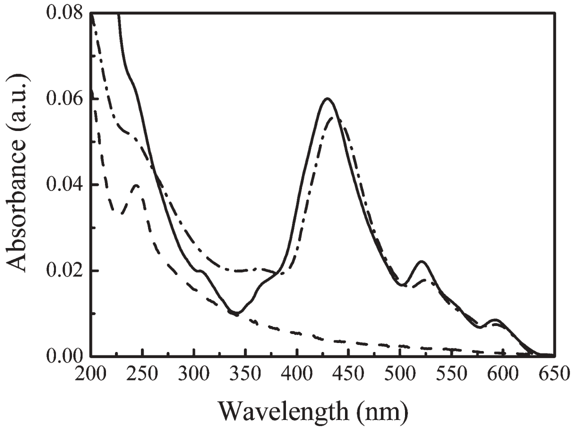

Fig. 4 Absorption spectra for the HgTPyP nanowires (-·-·-), HgTPyTa nanorods (- - - -), and HgTPyP–HgTPyTa nanotubes (—).

Close inspection of Fig. 4 revealed that, compared to the HgTPyP nanowires, the nanotubes showed stronger relative intensity at around 245 nm to the Soret band. This difference may be ascribed to the absorption of co-assembled HgTPyTa.[24]

Two emission bands were recorded for the LB films of HgTPyP–HgTPyTa (λ 700 and 723 nm) and HgTPyP (λ 698 and 718 nm) (Fig. S4†). The spectra were similar to those reported in the literature,[16,25] but a little red shifted. No significant fluorescence change was recorded between the HgTPyP–HgTPyTa nanotubes and HgTPyP nanowires, indicating that the inserted TPyTa ligands had no significant influence on the excited state of the porphyrins. These absorption and fluorescence spectra together with TEM images and ED patterns suggested that the nanotubes as prepared were composed of both TPyP and TPyTa ligands.

It has been known that Hg^{2+} ions are in the common distorted tetrahedral geometry,[26] with a Cl–Hg–Cl angle of 115.97° and an N–Hg–N angle of 101.96° when forming a coordination polymer with 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms).[27] Zur Loye and co-workers found that this coordination feature is necessary for completing a rectangular tube structure with bbimms.[27] We have revealed that nanowires could be formed by an interfacial reaction of Hg^{2+} with TPyP,[19] since one Hg^{2+} ion coordinates with two pyridyl groups from two different TPyP molecules.[16]

Here, this tetradentate ligand TPyP was co-assembled with another tridentate ligand TPyTa. With the use of TPyTa and metal ions, Fujita *et al.* have assembled boat-/bowl-shaped or encapsulated coordination polymers.[28] Moreover, they constructed a 3.5 nm coordination nanotube by using $enPd(NO_3)_3$ coordination with a ligand containing hexapyridine.[11] It has been revealed that the shaped structure is dominated by the triangular binding sites of TPyTa molecules. Thus, we can suggest that, in the present work, the Hg^{2+} ions coordinate with two pyridyl groups from neighboring ligands (TPyP or TPyTa) to form a nonplanar TPyTa–Hg–TPyP coordination unit. This nonplanar unit can result in a curved surface of the produced coordination polymer arrays. Such a curved surface takes an important role in the formation of a ring or a tube of porphyrins.[12] When the interfacial reaction continues, more and more metal ions and ligands assembled, the curved coordination polymer layer rolled into the tubular structure.[12,27,28]

In summary, we have demonstrated a metal-mediated assembly of nanotubes with the use of two different ligands at the interfaces. Such a unique nanotube formation was strongly dependant on the geometries of metal ions and ligands. However, due to the difficulty to get large enough crystals, we were unable to provide detailed structural data of the nanotube by X-ray crystallography. Efforts are underway to assemble nanocrystals by using Hg^{2+} with other ligands and to clarify how varying the ligand structure leads to different nanostructures, with a goal of better understanding the assembly process, especially clarifying the formation mechanism of these unique nanostructures.

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