Organic nanotubes assembled from isophthalamides and their application as templates to fabricate Pt nanotubes†

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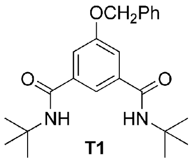
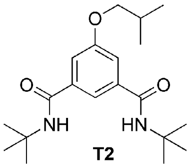
A new class of organic nanotubes have been assembled from simple isophthalamide derivatives and their surface can be conveniently coated with Pt, which form new Pt nanotubes after the inside organic materials are removed with hot methanol.

Tubular nanostructures have drawn considerable attention in recent years because of their potential applications in sensors, catalysis, gene and drug-delivery, biological separation and transport. Since the first reports of carbon nanotubes in 1991[1] and inorganic nanotubes in 1992,[2] numerous methods have been developed for the preparation of various inorganic nanotubes.[3] Although several approaches have been reported for assembling organic nanotubes from cyclic molecules,[4] examples of using acyclic molecules for this purpose are relatively limited.[5] Among others, Pt-nanotubes are potentially useful in studies in catalysis and electrochemistry,[6] but their preparations have been mainly limited to the inorganic templates approach.[7] We herein report the preparation of a novel type of organic nanotubes through the self-assembly of simple isophthalamide derivatives. In addition, the new organic nanotubes have been successfully used as templates for fabricating well-ordered Pt nanotubes.



T1



T2

During our study of the self-assembly of aromatic amide oligomers,[8] we found that compounds **T1** and **T2** could self-assemble into nano-scaled tubular structures. These well-ordered organic nanotubes could be generated in methanol or its mixtures with water or chloroform. The procedure is quite simple. Compound **T1** or **T2** was dissolved in hot methanol. The resulting clear solution was allowed to cool gradually to room temperature and stand overnight to give the tubular structures. SEM and TEM were employed to characterize the morphologies of the assembled structures (Fig. 1). SEM images clearly showed the tubular structures. The tubes were packed into bundles and their hollow nature was readily evidenced by their open-ended features (Fig. 1(b)). The nano-tubes formed by **T2** also had a hexagonal cross section, which was not observed for those of **T1**. The hollow nature of the nanotubes was further confirmed by TEM, which showed a clear contrast between their inner and outer areas (Fig. 1(e) and (f)). The sizes and wall thickness of the nanotubes from both compounds were concentration-dependent. Reducing the concentration remarkably decreased the diameters of the nanotubes (Fig. 1(c) and (d)). Therefore, the size of the new organic nanotubes can be tuned readily by simply changing the concentration of the initial solutions.

Aromatic amides have a great tendency to form intermolecular $C{=}O\cdots H{-}N$ hydrogen bonds and to stack in polar solvents. Therefore, it is reasonable to postulate that the driving forces for the self-assembly of the nanotubes by **T1** and **T2** mainly came from these two interactions. The IR spectra of the tubes, upon removal of the solvent under reduced pressure, exhibited the N–H stretching vibrations at $<3380\ \text{cm}^{-1}$, which indicated that the NH units were involved in the intermolecular H-bonding.[9] The single-crystal X-ray

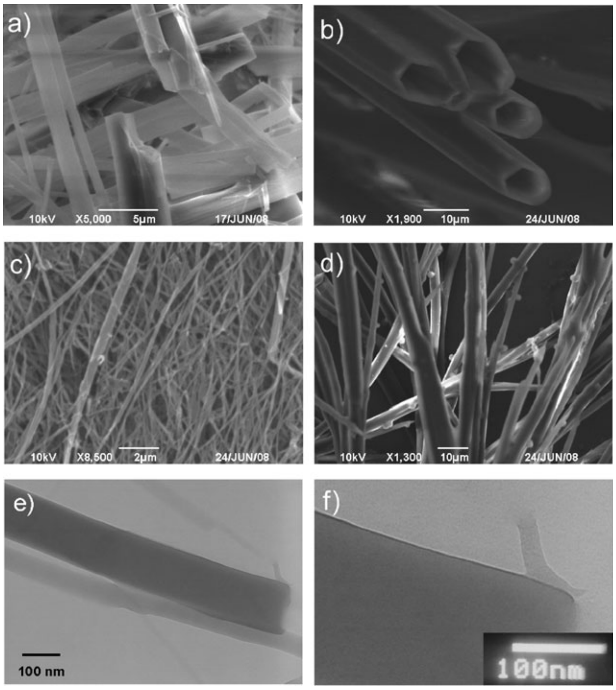


Fig. 1 SEM images of (a) **T1** (10 mM), (b) **T2** (28 mM), (c) **T1** (0.58 mM) and (d) **T2** (2.6 mM) and TEM images of (e) **T1** (8.4 mM) and (f) partial magnification of the former image. All the samples were obtained from their solution in methanol.

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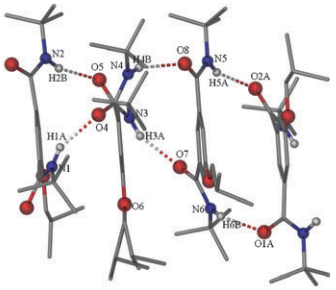

Fig. 2 The packing structure of **T2** in the single crystal (along the *b* axis), highlighting the dislocated feature of the stacking molecules stabilized by hydrogen bonds. Please see ESI† for lengths and angles of H-bonds.

structure of **T2**‡ also revealed that, in the solid state, the molecules stacked with each other, with a torsion angle of 60° (Fig. 2). The stacked aromatic rings had an $\text{aryl}_{\text{centriod}}$–$\text{aryl}_{\text{centriod}}$ distance of 3.45 Å, which is typical for the columnar stacking of aromatic amides.[10] The stacking was further stabilized by two pairs of intermolecular C$=$O···H–N hydrogen bonds between each molecule and its two stacked neighbours. The hydrogen bonds forced the stacked molecules to dislocate slightly, which might play a role in the formation of the tubular structures. The powder X-ray diffraction (XRD) of the nanotubes of **T2** also exhibited a stacking pattern that was very similar to that calculated from the crystal structure,[11] indicating that the molecules in the nanotubes adopted a similar packing mode as that in the crystal structure (Fig. 3). The XRD of the nanotubes of **T1** displayed a similar pattern as that of **T2** for most peaks, suggesting that, to some extent, their stacking patterns in the nanotubes were similar. However, the XRD of the nanotubes of **T1** also exhibited several extra peaks ($2\theta = 6.57, 8.09$ and 24.49) (Fig. S1, ESI†), which might be produced by the ordered stacking of its benzyl unit.

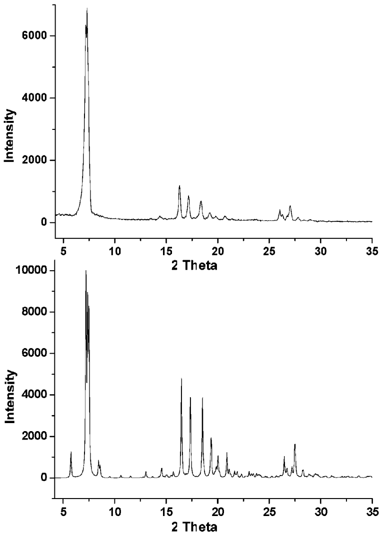

Fig. 3 XRD patterns of (a) the nanotubes of **T2** (top) and the theoretical profile calculated from its X-ray crystallographic data (bottom).

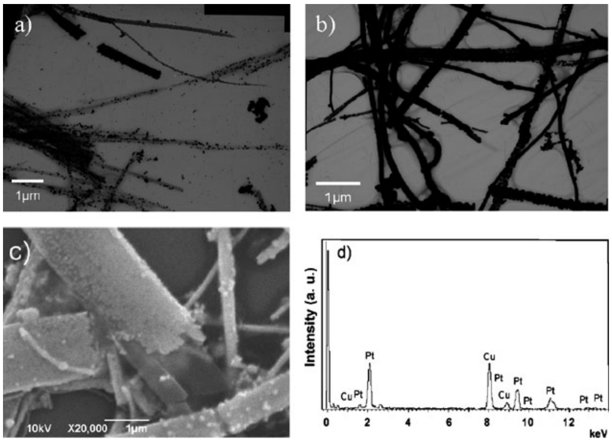

Fig. 4 TEM images of Pt–organic nanotubes of **T1** formed from methanol–water solution at (a) 4.2 mM and (b) 0.5 mM. (c) SEM image and (d) EDX spectrum of Pt–organic nanotubes, both of which were obtained from a solution of **T1** (0.5 mM) in methanol–water. The copper peaks were generated from the copper support grid.

It was reported that the N and O atoms of amides have a high affinity towards Pt(II).[12] The new O- and N-rich organic nanotubes are therefore potentially useful in templating the fabrication of Pt nanotubes, if Pt(II) ions are anchored on their surface through the weak metal ion–O or –N interactions and further reduced to Pt(0) *in situ*. Based on this consideration, we further studied the possibility of using organic nanotubes of **T1**, which were found generally more stable than those of **T2**, to template the growth of Pt nanotubes. The typical process is as follows. To a solution of **T1** (0.5–4.2 mM, 0.3 mL) in methanol and water (5 : 1, v/v) was added a solution of K_2PtCl_4 in water (20 mM, 0.1 mL). The mixture was stirred slowly for 5 min and then a solution of ascorbic acid in water (0.15 M, 0.1 mL) added.[13] The mixture was gently shaken and the resulting homogeneous solution was incubated at room temperature for 10 h. The solution turned from light yellow (that of K_2PtCl_4) to black, indicating that the salt was reduced to metal Pt(0).

The morphologies of the resulting materials were first studied by TEM, which showed that Pt was coated on the surface of the nanotubes (Fig. 4). The surface coverage significantly depended on the amount of the added salt, even though the salt was always used in excess. For example, at the ratio of 1.6 : 1, the organic nanotubes were only partially covered by the Pt particles (Fig. 4(a)). When the ratio was increased to 13.3 : 1 by reducing the concentration of **T1** from 4.2 to 0.5 mM, the surface of the organic nanotubes was almost completely covered by the Pt nanoparticles, which aggregated together to form new Pt–organic nanotubes of micrometer length with diameters ranging from 100 to 500 nm (Fig. 4(b)). Fig. 4(a) also indicated that the Pt nanoparticles were formed on the outside of the organic nanotubes, from which additional evidence came from SEM (Fig. 4(c)). It can be seen that a layer of the Pt nanoparticles were packed on the surface of the thickest organic tube, while its naked end clearly showed that it was hollow. The formation of the Pt metal was further confirmed by an energy dispersive X-ray (EDX) experiment, which exhibited strong peaks of Pt (Fig. 4(d)).[5e]

The new Pt–organic hybrid nanotubes were stable over weeks (Fig. S2, ESI†). Removal of the organic tubes from

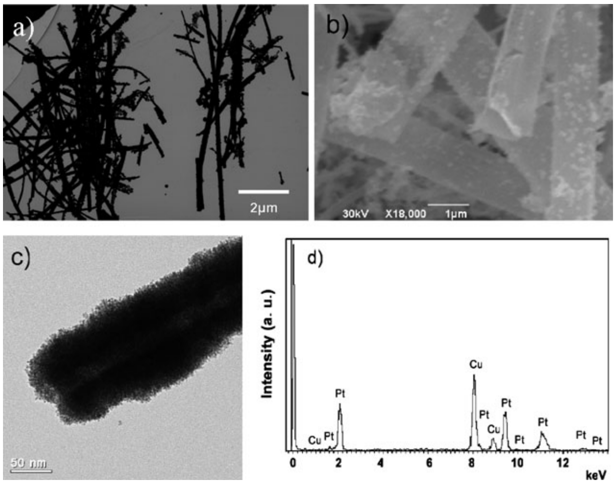

Fig. 5 (a) TEM, (b) SEM and (c) high-resolution TEM images and (d) EDX spectrum of Pt nanotubes, which were obtained after the internal organic templates were removed with hot methanol.

the Pt tubes was realized by simply immersing the hybrid tubes in hot methanol (30 min) and then removing the solvent by centrifugal purification. After repeating three times, **T1** was completely removed, as evidenced by the elemental analysis of the resulting tubes, which showed that only Pt remained. Both TEM and SEM supported that the tubular feature of Pt was maintained after the organic templates were removed (Fig. 5(a)–(c)). The new Pt nanotubes were also very stable and the high-resolution TEM showed their hollow nature (Fig. 5(c)), indicating that Pt existed as nanotubes with or without the support of the organic templates. The EDX spectrum of this tubular material was similar to that of the above Pt–organic nanotubes (Fig. 5(d)).

In summary, we demonstrate that simple isophthalamide derivatives can self-assemble in methanol to form new well-ordered organic nanotubes through cooperative intermolecular hydrogen bonding and stacking interaction. The new organic nanotubes are good supporting materials to template the formation of Pt nanotubes by efficient absorption of K_2PtCl_4 on their surface, followed by *in situ* reduction. While inorganic template-based techniques, which usually need chemical modifications, but can offer a high degree of control over the pore size and the wall thickness have traditionally been used to produce Pt-nanotube arrays,[7a–i] and peptide- or surfactant-based templates been recently employed to generate Pt-nanotubes with specific characteristics,[14a,b] the method reported here provides an alternative approach that can produce Pt-nanotubes with comparable quality. Given the advantages of structural variety and ready modification of small organic molecules, this strategy may offer great flexibility for the construction of nanoscaled materials with various morphologies and should be applicable for many other transition metals. Currently we are investigating this potential.

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Notes and references

‡ *Crystal data* for **T2**: $C_{60}H_{96}N_6O_9$, M = 1045.43, monoclinic, space group $P2_1/n$, a = 14.1075(8), b = 20.1933(11), c = 23.5204(13) Å, β = 91.509(2)°, V = 6698.1(6) Å^3, T = 173(2) K, Z = 4, D_c = 1.037 g cm^{-3}, μ = 0.069 mm^{-1}, $R1$ = 0.0706, $wR2$ = 0.1812 ($I > 2\sigma(I)$), $R1$ = 0.1113, $wR2$ = 0.2335 (all data). Reflections collected/unique: 75 209/ 11 753 (R_{int} = 0.0471), GOF = 1.903. Disorders at the isobutyl were found.

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