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Tunable Coordinative Assembly of a Disc-Like Molecule and Metal Ions: From Mirospheres to Microtubes and Microrods

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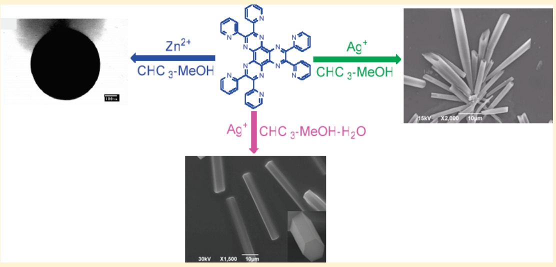
Supporting Information

ABSTRACT: This study reports a tunable metallo-supramolecular assembly strategy to construct microscaled objects with different morphologies. Three well-defined discrete microstructures—microspheres, microtubes, and microrods—have been fabricated through metal—organic coordination between the same organic unit and different transition metal ions or the same organic unit and metal ion processed in different solvents. The formations of microspheres, microtubes, and microrods have been readily evidenced by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Encapsulation experiments revealed that those microspheres could entrap rhodamine B and might be used as carrier materials. It was also found that the microrods and microtubes could be transformed into each other by adding or removing water to or from the solution. The formation mechanisms of these microstructures have also been discussed on the basis of spectroscopic and crystallographic studies.



KEYWORDS: tunable, coordination-directed self-assembly, microspheres, microtubes, microrods

INTRODUCTION

The self-assembly driven by the metal—organic interaction has received considerable attention during the last decades because of their useful applications in the fabrication of functional materials for gas storage, catalysis, optics, recognition, and separation.[1] Originating from the construction of relatively simple coordination compounds,[2] this strategy has now been widely employed to fabricate more complicated inorganic—organic hybrid materials, such as metal—organic frameworks (MOFs),[3] coordination polymers (CPs),[4] and metallogels.[5] Furthermore, the coordination-directed assembly has also become a powerful tool to fabricate well-defined micro/nanoscaled materials.[6] Although different organic units might lead to discrete morphologies of the assembled entities, changes in the bridged metal ions might also cause remarkable structural variations because of the different strength and geometry of the corresponding coordination bonds. However, most studies to date have mainly focused on creating organic ligands with novel chemical structures and then coassembling them with selected transition metal ions to fabricate ordered supramolecular entities with controlled size and shape. In contrast, examples of producing ordered supramolecular entities from one organic ligand and different metal ions are quite limited,[7] even though the latter strategy might be more efficient and economic by avoiding the time-consuming organic synthesis required for the former approach.

Since the discovery of the carbon nanotube by Iijima,[8] more and more attention has been paid to the construction of tubular structures in the range of nano to micro size because of their potential applications in chemistry, biology, and material sciences.[9] Micro/nanotubes fabricated from inorganic as well as organic compounds have been reported in large numbers during last two decades.[10,11] Although a broad variety of micro/nanoentities such as spheres,[12] vesicles,[13] cubes,[14] rods,[15] and wheels[16] fabricated from metal—organic complexes have been reported, examples of discrete microtubes constructed from metal—organic hybrids are extremely limited.[17] We herein report the construction of three distinct well-ordered microstructures —microspheres, microtubes, and microrods—through coassembly of hexa-2-pyridyl hexaazatriphenylene (HPHAT) with different types of metal ions or with the same metal ion in different solvents. HPHAT was developed in our lab recently by merging six pyridine units into a hexaazatriphenylene (HAT) core, a disc-like conjugated heterocycle that has been used for developing *n*-type semiconductors,[18] magnetic materials,[19] nonlinear optic chromophores,[20] and liquid crystals.[21] We have previously reported the construction of microwires through coassembly of HPHAT and primary alkyl ammoniums with hydrogen bonding as a major driving force.[22] In this paper, we describe the construction of well-defined microscaled objects based on metal—organic interactions between HPHAT and transition metal ions.

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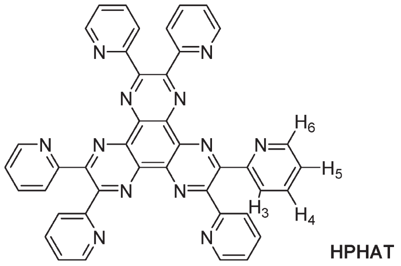

EXPERIMENTAL SECTION

All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. The ^{1}H NMR spectra were recorded with a Varian 300 MHz spectrometer in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual proton resonances of the deuterated solvents as the internal standards ($CDCl_3$, 7.26). Scanning electron microscopy (SEM) experiments were conducted on a JEOL JSM-6390-LV microscope. Transmission electron microscopy (TEM) images were recorded on JEOL JEM-2010 or CM200EFG microscopes working at 200 kV. The energy dispersive X-ray (EDX) spectroscopy was obtained on a CM200EFG microscope equipped with energy dispersive X-ray spectroscopy. UV−vis spectra were recorded on a Varian Cary100 spectrometer. Powder XRD spectra were obtained on a X'Pert PROX system using monochromated Cu Kα (λ = 0.1542 nm).

Synthesis. The preparation of HPHAT follows the procedure reported previously.[22]

Procedure for the Preparation of HPHAT−Zn(II) Metal−Organic Microspheres. A solution of $Zn(OAc)_2 \cdot 2H_2O$ (3.27 mg, 1.5×10^{-2} mmol) in methanol (1 mL) was added to a solution of HPHAT (3.45 mg, 5.0×10^{-3} mmol) in chloroform (1 mL). After vigorous stirring at room temperature for 2 h, *n*-hexane (8 mL) was added to the resulting dark purple solution to precipitate the formed complex, which was then collected by centrifugation (3000 rpm, 20 min), and finally dispersed in chloroform/methanol to a certain concentration.

Encapsulation Study. Encapsulation of rhodamine B with metal−organic spheres was performed in a similar way, except that a solution of rhodamine B (1%) in chloroform/methanol (1/1, 0.1 mL) was added before the stirring. The rhodamine B-encapsulated spheres stood after being washed with chloroform/methanol and dialysis for 2 days.

For the contrast experiment, rhodamine B (1% in chloroform/methanol, 0.1 mL) was added after the metal−organic spheres were fabricated. In this case, rhodamine B was virtually gone after being washed with chloroform/methanol and dialysis.

Procedure for the Preparation of a HPHAT−Ag Microtube. A solution of HPHAT (6.9 mg, 1.0×10^{-2} mmol) in chloroform (1 mL, distilled with CaH_2) and a solution of anhydrous CF_3SO_3Ag (7.7 mg, 3.0×10^{-2} mmol) in methanol (1 mL, distilled with magnesium) were stirred at room temperature for 1 h (the final concentration for HPHAT is 5 mM). After standing for 2 h, the mixture was subjected to SEM analysis, which showed the formation of microtubes of hollow structures in large majority. The structures of the microtubes were further confirmed by TEM analysis (a few microrods were also formed).

Procedure for the Preparation of HPHAT−Ag Microrods. To a solution of HPHAT (6.9 mg, 1.0×10^{-2} mmol) in chloroform (1 mL) was added a solution of anhydrous CF_3SO_3Ag (7.7 mg, 3.0×10^{-2} mmol) in methanol (1 mL) and water (0.2 mL) at room temperature. The mixture was stirred for 1 h, allowed to stand for 2 h, and then was analyzed with SEM and TEM, which revealed that microrods were formed, and no microtubes were formed.

Procedure for the Microtubes-to-Microrods Transformation. A solution of HPHAT (6.9 mg, 1.0×10^{-2} mmol) in chloroform (1 mL, distilled with CaH_2) was added to a solution of anhydrous CF_3SO_3Ag (7.7 mg, 3.0×10^{-2} mmol) in methanol (1 mL, distilled with magnesium). The mixture was stirred at room temperature for 1 h (the final concentration for HPHAT is 5 mM), allowed to stand for 2 h, and then subjected to SEM analysis, which supported the formation of hollow microtubes in large majority. For the next step, water (0.2 mL) was added to the mixture. The mixture was stirred for another 1 h, stood for 2 h, and analyzed with SEM and TEM again, which showed that all the microtubes disappeared, and microrods were generated.

Procedure for the Microrods-to-Microtubes Transformation. To a solution of HPHAT (6.9 mg, 1.0×10^{-2} mmol) and anhydrous CF_3SO_3Ag (7.7 mg, 3.0×10^{-2} mmol) in chloroform (1 mL) and methanol (1 mL), water (0.1 mL) was added. The mixture was stirred for 1 h, allowed to stand for 2 h, and then subjected to SEM and TEM analysis, which confirmed that microrods were generated, and no microtubes generated. Upon evaporation of the solvent, the resulting yellow residue was dried in vacuum for 24 h. Then a suspension of the residue in anhydrous chloroform/methanol (1/1, 2 mL) was stirred for 1 h, allowed to stand for 2 h, and again subjected to SEM analysis, which confirmed the formation of microtubes.

Growth of Single Crystals of HPHAT−AgOTf. HPHAT (7.0 mg) was dissolved in chloroform (0.5 mL) in a test tube. A solution of AgOTf (8.0 mg) in methanol (0.5 mL) was carefully added to the top of the HPHAT chloroform solution. After one week, bar-shaped crystals were generated on the wall of the tube. The crystals, which were stable in air, were collected for X-ray diffraction analysis. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as CCDC 759865. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: t44 (0) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Assembly with Zn^{2+}. The coordinative assembly of HPHAT and divalent metal ions were first investigated. It was found that mixing HPHAT with zinc acetate in methanol and chloroform led to the formation of spherical entities. These metal−organic spheres were prepared by adding a methanol solution of $Zn(OAc)_2 \cdot 2H_2O$ to a vigorously stirred solution of HPHAT in chloroform, which led to the formation of a purple solution. After stirring at room temperature for 2 h, *n*-hexane was added to precipitate the formed aggregates, which were then collected by centrifugation, washed with chloroform and methanol, and finally dispersed in methanol again to generate a purple colloid solution. This as-prepared material was characterized with SEM and TEM, both of which clearly indicated the spherical nature of the aggregates (Figure 1a, b). The TEM images also suggested that the microspheres were interiorly solid because no contrast was observed throughout the sphere. The presence of the zinc ion was confirmed by the energy dispersive X-ray spectroscopy (EDX) (Figure S1 of the Supporting Information). The potential application of the microspheres as carriers has also been examined. The experiment was conducted by adding the solution of $Zn(OAc)_2 \cdot 2H_2O$ and rhodamine B both in methanol into a solution of HPHAT in chloroform. Following the process described above for the preparation of the microspheres, the resulting mixture was dialyzed in chloroform/methanol for 2 days. The residue was then subjected to fluorescence microscope analysis. The fluorescence images readily showed discrete red spheres, suggesting rhodamine B was entrapped by the microspheres. The entrapment of rhodamine B inside the microspheres,

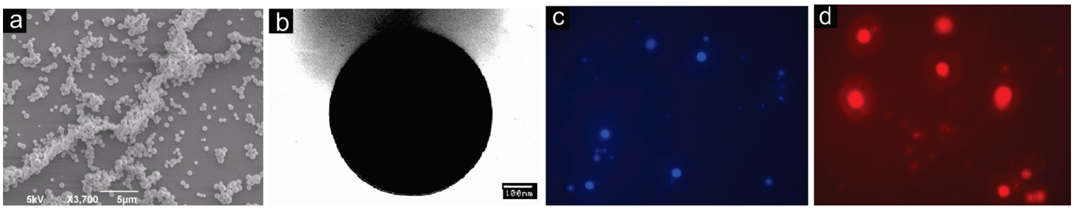

Figure 1. (a) SEM and (b) TEM images of the microspheres constructed from the HPHAT/Zn^{2+} mixture and the fluorescence micrographs of the microspheres (c) before and (d) after the encapsulation of rhodamine B.

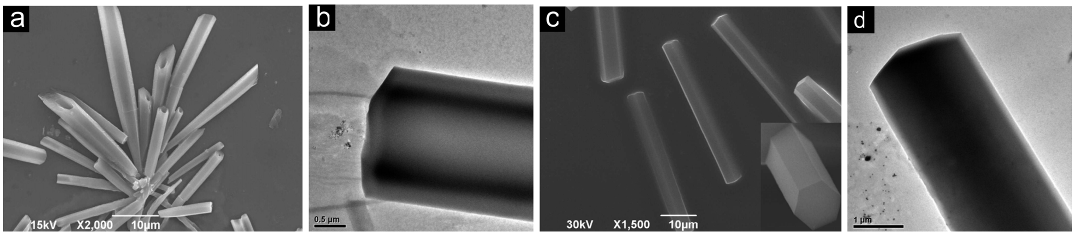

Figure 2. (a) SEM and (b) TEM images of HPHAT/Ag^+ microtubes and (c) SEM and (d) TEM images of HPHAT/Ag^+ microrods. Inset of panel (c): selected area to demonstrate the cross-section of the microrod.

instead of on their surface, was confirmed by a contrast experiment. In the contrast experiment, rhodamine B was added after the microspheres were generated. After dialysis, the fluorescence microscope showed that almost no rhodamine B was adsorbed (Figure S2 of the Supporting Information). This result clearly indicates that the rhodamine B was entrapped in the inner portion of the spheres in the entrapment experiment. Considering the versatility of HAT, novel composite materials might also be created if nanoparticles with other functions are encapsulated. Similar transition metal−organic spheres could also be fabricated by mixing HPHAT with the acetates of Cu (II), Ni (II), and Co (II) in methanol (Figure S3 of the Supporting Information), which suggested that this is a general approach to the construction of spherical microstructures from HPHAT.

Assembly with Ag^+. We then investigated the self-assembly behavior of HPHAT with monovalent metal ions. For this purpose, silver triflate (AgOTf) in anhydrous methanol was introduced into a solution of HPHAT in anhydrous chloroform, followed by stirring at room temperature for 1 h. Different from the preparation of the Zn−HPHAT microspheres, no hexane was added because solids already precipitated out from the resulting pale yellow solution during stirring. Notably, the resulting Ag−HPHAT aggregates displayed a totally different morphology as compared to that of their Zn−HPHAT counterpart. As shown by the SEM images (Figure 2a), microtubes with different inner diameters were formed; the hollow nature was readily demonstrated by their open-ended features. It should be noted that a little amount of microrods could also be observed, which coexisted with the microtubes. Both the precipitate and the solid material obtained by evaporation of the solution were characterized by SEM, which showed the same tubular morphology (Figure S4 of the Supporting Information). This result suggested that the microtubes were originally formed in solution. TEM images provided further evidence for the formation of tubular structures by displaying a clear contrast between the wall and the inner part of the microtube (Figure 2b).

Interestingly, it was found that the morphology of the HPHAT−Ag entity could be tuned by the introduction of water. When 10% water was added into the above methanol solution of AgOTf under identical conditions, discrete hexagonal cross-section microrods of several micrometers in width and more than 50 μm in length were formed exclusively (Figure 2c). TEM images displayed nearly no contrast throughout the rods, suggesting that the as-prepared microrods were solid (Figure 2d). Furthermore, EDX spectrum of the microrods also corroborated the presence of the silver (Figure S5 of the Supporting Information).

Moreover, the microtubes and microrods could be transformed into each other reversibly. Adding water (10%) to a solution of the as-prepared microtubes led to the transformation of microtubes to microrods (see Experimental Section for detailed procedure), as evidenced by SEM images, which indicated that all the microtubes disappeared while microrods were formed. The microrod-to-microtube transformation could be realized by simply redissolving the microrods (dried in vacuum at 25 °C for 24 h to remove water before use) in anhydrous chloroform/methanol (see Experimental Section for detailed procedure).

Mechanisms for the Formation of Microspheres, Microtubes, And Microrods. To obtain insight into the mechanism for the formation of the above microstructures, both spectroscopic and crystallographic investigations were carried out. Adding $Zn(OAc)_2 \cdot 2H_2O$ into the chloroform solution of HPHAT immediately led to a color change, suggesting the formation of a strong interaction between HPHAT and Zn^{2+}. The UV−vis absorption of HPHAT before and after the addition of the salt was then examined. As expected, upon the incremental introduction of $Zn(OAc)_2 \cdot 2H_2O$, the UV−vis absorption of HPHAT was decreased, while a broad peak between 425 and 600 nm was generated gradually (Figure S6 of the Supporting Information). Adding AgOTf also caused the absorption of HPHAT to decrease (Figure S7 of the Supporting Information). However, different from that of the HPHAT−Zn system, no absorption in the visible region was observed, suggesting a different coordination manner. ^{1}H NMR titration experiments were further conducted to obtain insight into the organic−metal complexes. Upon titration with Zn^{2+}, the signals of the H-4, H-5, and H-6 protons of the pyridine unit of HPHAT shifted downfield, while the signal of the H-3 proton shifted upfield. These observations could be attributed to the coordination of HPHAT with Zn^{2+} (Figure 3). In contrast, the addition of 1 equiv of AgOTf resulted in the signals of protons of HPHAT to broaden. Upon addition of 3 equiv of salt, HPHAT gave rise to seven well-separated peaks (Figure S8 of the Supporting Information), suggesting the formation of a stable entity of well-defined structure between them.

The as-prepared microspheres and microrods were also investigated with the powder X-ray diffraction (XRD) experiments. The powder XRD diagram exhibited a featureless diffraction pattern for the microspheres, suggesting that the resulting spherical materials were amorphous (Figure S9 of the Supporting Information). The result also implied that the spherical structures might be derived from infinite coordination polymers formed through the pyridyl—Zn coordination.[12] For the case of Ag^+, the powder XRD revealed that the microrods displayed strong and sharp diffraction peaks, suggesting a highly crystalline character (Figure 5, vide infra). Single crystals suitable for X-ray crystallographic analysis were also obtained by slow diffusion of AgOTf (in methanol) into a solution of HPHAT in chloroform. The X-ray crystal structure of the HPHAT—AgOTf complex revealed a cage structure formed from two HPHATs and six Ag^+ ions through six N—Ag complexes, in which one Ag^+ ion was coordinated to three nitrogen atoms of one HPHAT unit, one pyridyl nitrogen of another HPHAT, and one triflate anion (Figure 4). The two HAT units of one cage stacked in a staggered face-to-face pattern with a distance of about 3.6 Å. The cages were one-dimensionally packed along the *c* axis of the crystal cell (Figure 4b), connected by a cyclic hexameric water cluster with a chair information through six hydrogen bonds between protons of water and oxygen atoms of triflates.[23] Such an arrangement of the cages dictates a one-dimensional growing process and causes the formation of the microtubes/microrods.

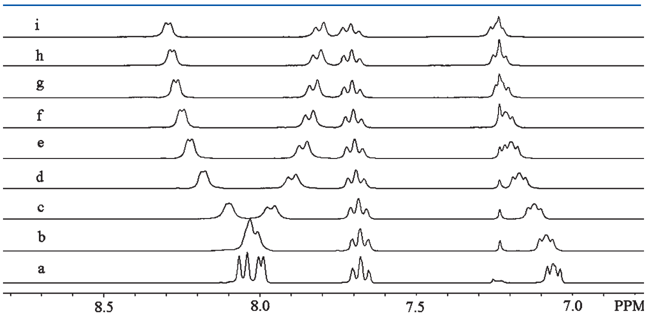

Figure 3. Partial ^1H NMR spectra of titration of HPHAT with (a) 0, (b) 0.2, (c) 0.5, (d) 1.0, (e) 1.5, (f) 2.0, (g) 2.5, (h) 3.0, and (i) 3.5 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in $CDCl_3$—CD_3OD (1:1) at 25 °C.

The structural relationship between the microtubes and microrods was then investigated. The solutions of complexes prepared by mixing HPHAT and AgOTf in the mixture of methanol and chloroform with or without the addition of water (5% and 10%) exhibited almost the identical UV—vis spectra (Figure S10 of the Supporting Information). Furthermore, the UV—vis spectra of the microtubes and microrods dispersed in hexane also showed similar absorption patterns, although their intensities were a little bit different probably because of the difference of the amount of the microrods and microtubes in the suspensions (Figure S11 of the Supporting Information). The sample of the tubular structures was also characterized with the XRD analysis. It was found that the diffraction pattern of the X-ray diffraction of the as-prepared microtubes matched well with that of microrods (Figure 5b, c). These results supported that the arrangement of the HPHAT—Ag complexes in the microtubes and microrods were very similar. Their XRD profiles were further compared with the theoretical pattern calculated from the single-crystal data of the HPHAT—Ag complex. The calculated diffraction of the single crystal exhibited quite similar patterns as those of the microtubes (microrods) (Figure 5a), if

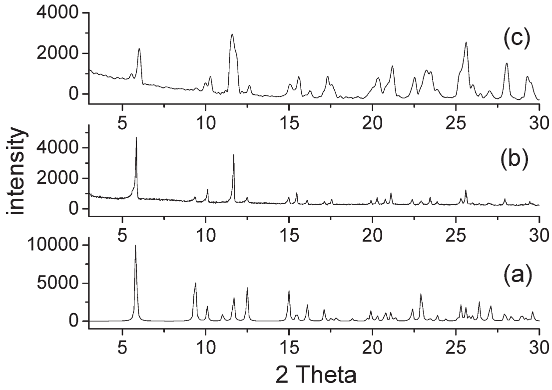

Figure 5. Powder XRD patterns of (a) theoretical profile calculated from X-ray crystallographic data, (b) experimental result of the microtubes, and (c) experimental result of the microrods.

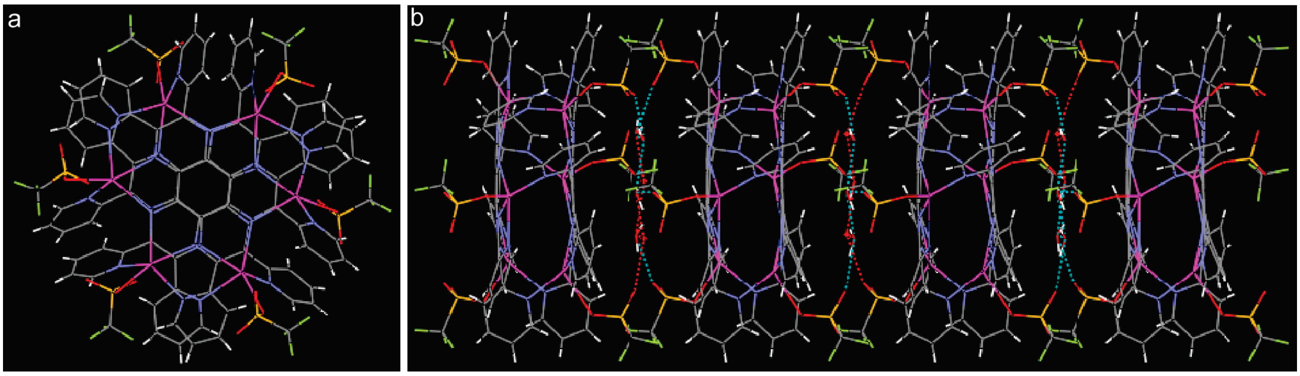

Figure 4. (a) Crystal structure (view down crystallographic *c* axis) and (b) packing pattern of HPHAT—Ag+ (view down crystallographic *b* axis). The water molecules in the former one have been omitted for clarity.

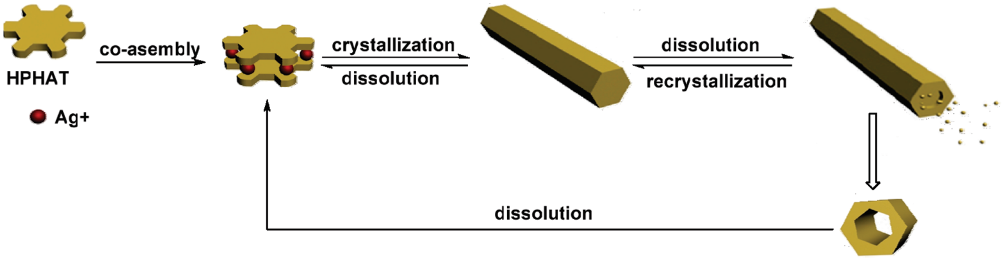

Figure 6. Proposed formation mechanisms of microtubes and microrods and the transformation between them.

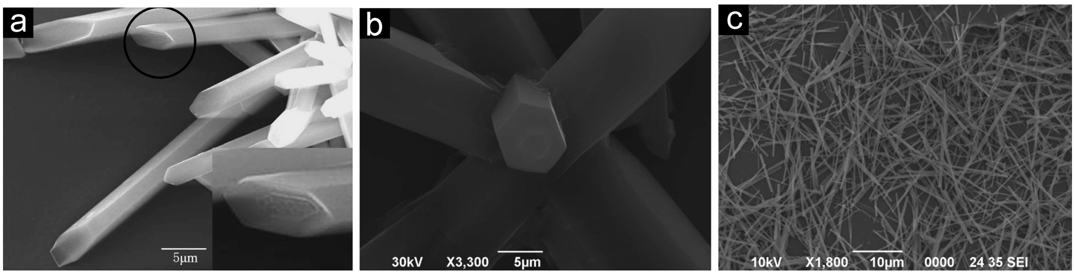

Figure 7. SEM images of (a) and (b) microrods of HPHAT−Ag fabricated from chloroform−methanol−water (1:1:0.2). Inset of panel (a): magnification of the selected area and (c) wire-like structures of HPHAT−Ag prepared from chloroform−methanol−hexane (1:1:0.2).

the influence of the loss of solvents on the diffraction of XRD of the samples was taken into account. On the basis of the result, it could be deduced that a similar molecular packing manner existed in the microtubes (microrods) and the single crystals of the complex.

Because the building units as well as their arrangement were identical in the microtubes and microrods, a crystallization−dissolution mechanism was proposed for their transformation. As illustrated in Figure 6, the microrods were first formed in methanol through packing of the cages of HPHAT−Ag complexes mainly along the ⟨001⟩ direction, which was the direction for quicker growth.[17b,24] The resulting microrods were always in a equilibrium of exchange for the building blocks (cages) between those in solution and those in the microrods. Because the quick growth direction is usually the fast dissolving direction, the dissolution along the ⟨001⟩ direction was also favored over other directions. Therefore, the central part of the microrods dissolved, and the tubular structures were generated. On the other hand, inner parts of rod-like structures were reported to usually form with a higher density of defects than the peripheral part, which also induced a higher local dissolution rate at the center and led to the formation of the tubular structures.[17a,25] This process was supported by the etching part that could be observed at the centers of some microrods (Figure 7a, b), suggesting that the rod-like structure should be a precursor for the tubular morphology. When water was introduced, the solubility of the HPHAT−Ag complex was decreased, which resulted in retardance of the dissolution of the HPHAT−Ag cages from the central part of the rods. As a result, the rod-like structures were retained. The proposed process was supported by the two following experiments. First, with an increase in water content in the solution, it was found that the population of the microrods was also increased at the expense of the amount of microtubes (Figure S12 of the Supporting Information). Second, when water was replaced by even 1% (v/v) of anhydrous *n*-hexane, which is also poor for the coordination complex, tubular structures could be observed. However, when 10% of hexane was added, wire-like structures with high aspect ratio were generated (Figure 7c). This result revealed again that the one-dimensional crystallization process along the ⟨001⟩ direction overwhelmingly dominated the growing progress of the aggregates. A time-resolved SEM investigation on the samples at different stages was also conducted to try to track the microrods-to-microtubes transformation. It was found that the formation of the tubular structures was so quick that the microtubes could be observed just 5 min later after mixing the HPHAT and AgOTf solutions, suggesting that the crystallization−dissolution process was extremely fast. For the tube-to-rod transformation in the presence of water, it might be achieved by a quick crystallization−slow dissolution process at the inner part of the microtubes or through deconstruction of microtubes into building units (cages) and then recrystallization to form the microrods because there is always an equilibrium established between dissolution and crystallization.

■ CONCLUSION

Coordination-directed self-assembly has been a powerful tool for the fabrication of materials of nano/microscales. While the construction of micro/nanomaterials that exhibit novel features and morphologies could be achieved by coordination-directed self-assembly of selected transition metal ions and organic units with different chemical structures, this study demonstrates that microscaled objects of different morphologies could be fabricated by simply assembling an identical organic unit with discrete metal ions or could be controlled by changing the environmental conditions. Deriving from the same organic unit, the resulting microspheres and microtubes (microrods) exhibit dramatic difference in dimension (0D vs 1D) as a result of different coordination manners of zinc and silver with HPHAT because of different coordination numbers and size. This strategy might be extended to other organic molecules that bear coordination sites because organic−metal interactions generally exist no matter what type of transition metal ions is employed. Although it is not guaranteed if such interactions could always lead to the formation of well-defined micro/nanoscaled entities, this approach represents a promising method to construct self-organized molecular assemblies in a tunable way. More investigations on tunable coordinative self-assembly should be expected in the future, considering that this approach needs less synthetic work, and the organic component can be utilized to the greatest extent.

■ ASSOCIATED CONTENT

S Supporting Information. Additional microscope images, ^{1}H NMR, UV/vis spectra, XRD profile, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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