Coordination polymer nanocombs self-assembled at the water–chloroform interface†

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

Received (in Montpellier, France) 6th February 2007, Accepted 6th April 2007
First published as an Advance Article on the web 20th April 2007
DOI: 10.1039/b701839h

We report the $HgCl_2$-mediated interfacial self-assembly of coordination polymer nanocombs composed of (zinc, palladium) tetrapyridylporphyrin and 4,4′-bipyridyl ligands. Scanning electron microscopic images revealed that lengths and widths of the core stems of the nanocombs were about 10 and 1 μm, respectively. Needle-like branches grew out perpendicularly from both sides of the core stems, with branch lengths of about 1–10 μm and diameters of about 0.1–15 μm. Both the X-ray photoelectron spectroscopic and energy dispersive X-ray spectroscopic measurements confirmed that the as-prepared nanocombs were composed of Hg, Cl, C and N elements. When the 4,4′-bipyridyl ligand was replaced by its derivatives, 2,2′-bipyridyl or 4,4′-trimethylenedipyridine, coordination polymer nanocombs could not be obtained. The results revealed that formation of such nanocombs was closely dependent on the structure of the bipyridyl, the mixed molar ratios of porphyrin and 4,4′-bipyridyl, as well as the interfacial reaction time.

Introduction

Molecular self-assembly of one-dimensional (1D) nanostructures has recently received great interest because the specific structures of crystals determine their unique physical and chemical properties.[1,2] Inorganic nanotubes, nanowires and nanocomb materials, consisting of pure carbon, metal oxides and boron nitride, have been the focus of many research efforts for their potential applications in electronics and photonics.[3–5] Similarly, many advances have been reported in the realm of organic–inorganic hybrids, in particular, in coordination polymers with backbones constructed from metal ions and organic ligands.[6,7] For instance, with a choice of ligand structure and morphology, zur Loye and co-workers recently reported a design of coordination architecture of neutral tetranuclear nanotubes $[Hg_4Cl_8(bbimms)_4]$ (bbimms: 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene).[8] Fujita and co-workers constructed several coordination nanotubes with the sizes ranging from 2 to 3.5 nm by the reaction of penta- or hexapyridine ligands with ethylenediamine-protected Pd^{II} ions.[9] Moreover, Shelnutt and co-workers exploited the ionic self-assembly of oppositely-charged porphyrin tectons to synthesize porphyrin nanotubes in aqueous solution and porphyrin nanofiber bundles in an aqueous–organic two phase system, and the re-precipitation method to synthesize porphyrin nanosheets.[10]

Coordination polymers contain two central components: connectors and linkers. Transition metal ions are often used as versatile connectors, with coordination numbers ranging from 2 to 7, dependent on the oxidation states of the metal ions.[6] Multidentate ligands are often used as linkers, which can afford a wide variety of linking sites, tuned binding strength and directionality. Thus, by using different connectors and linkers, one can design and prepare large numbers of 1D, 2D and 3D coordination polymers with various structural frameworks.

4,4′-Bipyridyl (BPy), tris(4-pyridyl)-1,3,5-triazine (TPyTa) and 5,10,15,20-tetrapyridylporphyrin (TPyP) are typical bidentate, tridentate and tetradentate ligands. By using these ligands to coordinate with metal ions or metal-complex ions, large numbers of supramolecular building blocks have been constructed.[6,10–16] Bpy, the most frequently used neutral bridging ligand, is usually co-assembled with other ligands though it is possible to use it alone to form coordination polymers.[10] Fujita and co-workers designed and synthesized many TPyTa-based coordination polymers, which can be used as a host (or a cage) to encapsulate some solvent molecules, even ferrocene and its derivatives, or as a cage for cavity-directed synthesis.[12] When TPyP or its derivatives are used as linkers the products are usually termed multiporphyrin arrays. In this research area, Drain, Rogers, Alessio and some other research groups have published large numbers of multiporphyrin arrays with unique structural or optical properties in the past several years.[13–16]

In recent studies, we have demonstrated controlled growth of regular cubic nanocrystals and nanowires of multiporphyrin arrays, the shapes of which were dominated by the geometries of the metal ions.[17] We further found that hybrid nanotubes could be built from Hg^{2+}-mediated coordination oligomers with TPyTa and TPyP.[18] A significant difference of our work from that reported in the literature is that our molecular self-assembly was performed at the water–chloroform interface.[17–19] Our purpose was to reveal the intrinsic

[a] *Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, P. R. 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: XPS patterns and TEM images. See DOI: 10.1039/b701839h

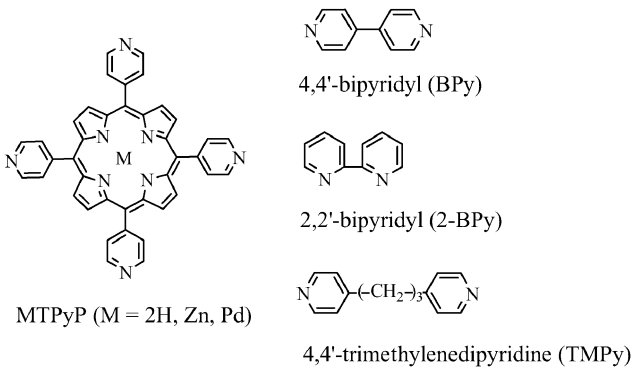

Fig. 1 Molecular structures of porphyrins and bipyridyl ligands.

relationship between the morphologies of nanocrystals or microcrystals produced at the interfaces and the structural features of the metal ions and multidentate ligands (coordination numbers and coordination geometries). The two immiscible solutions provided a defect-free junction, where the produced nanocrystals are highly mobile and can rapidly achieve an equilibrium assembly.[20] In the present work, we describe the assembly and characterization of a novel coordination architecture of nanocombs by an interfacial reaction of $HgCl_2$ in aqueous solution with the mixtures of two ligands of BPy and MTPyP (Fig. 1) in chloroform. Shape control of the produced nanocrystals could be achieved by selecting suitable ligands and changing the molar ratios of the two ligands in the organic phase. We further found that, if the Bpy was replaced by its derivatives, 2,2′-bipyridyl (2-BPy) or 4,4′-trimethylenedipyridine (TMPy) (Fig. 1), comb-like crystals could not be obtained.

Experimental

Materials

4,4′-Bipyridyl, 2,2′-bipyridyl (2-Bpy), 4,4′-trimethylenedipyridine (TMPy), 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin (TPyP) and zinc 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin (ZnTPyP) were purchased from Aldrich Chemical Co.; palladium 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin (PdTPyP) from Frontier Scientific Porphyrin Products; $HgCl_2$ from Shanghai Chemical Reagent Co.; and chloroform from Fisher Chemicals Co. All chemicals were used as received without further purification. Double distilled water (firstly deionized) was used to prepare aqueous solutions.

Growth of coordination polymer nanocombs at the water–chloroform interface

Interfacial self-assembly of the nanocombs was performed as follows: 20 ml 10 mM $HgCl_2$ aqueous solutions were slowly added onto the surfaces of 30 ml chloroform solutions containing (Zn, Pd)TPyP and BPy mixtures in various molar ratios. The reaction systems were left undisturbed at room temperature for 5 min to 3 h. As control experiments, interfacial self-assembly of $HgCl_2$ with pure (Zn, Pd)TPyP, BPy, and TMPy was also performed.

Transfer of coordination polymer nanocombs onto solid surfaces

Layers of nanocombs or other nanomaterials grown at the interface were transferred to the freshly prepared mica, quartz, and Si substrate surfaces by using a dipper from KSV Instrument Co. (Finland). One layer referred to one transfer of the nanocrystals from the interfaces. The dipping rate was kept at 1 mm min^{-1}. The as-prepared substrates were dried in air at room temperature.

Characterization of coordination polymer nanocombs

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) measurements were performed on a Shimadzu SSX-550 electron microscope. The samples were deposited on either mica or Si(100) substrate surfaces.

Transmission electron microscopy (TEM) and electron diffraction (ED) were measured using a Jeol JEM-2010 electron microscope. The samples were transferred to the copper grids covered with Formvar.

X-Ray photoelectron spectroscopy (XPS) was carried out using a PHI-5600ci system with a monochromatic Al-Kα X-ray source (Perkin Elmer). Layers of coordination polymer nanocombs were deposited on the hydrophilic quartz substrate surface, which was prepared by immersing the cleaned quartz substrates in a 4% NaOH solution for 24 h.

UV-Vis absorption spectra for the layers of coordination polymer nanocombs, deposited on the hydrophilic quartz substrate surface by the method above, were measured using a Shimadzu UV-2550 UV-Vis spectrophotometer.

X-Ray diffraction (XRD) data for the nanocombs and other nanomaterial films on the Si(100) substrate surface were obtained with a Rigaku D/max-γb diffractometer in transition mode and Cu-Kα radiation. The scan range of 2θ was 10–67° with a step interval of 0.02°.

Results and discussion

HgTPyP–HgBPy coordination polymer nanocombs

Fig. 2 shows the SEM images of the HgTPyP–HgBPy materials synthesized at the molar ratios of TPyP : BPy from 2 : 1 to 1 : 8. These images revealed that regular comb-like nanocrystals could be formed when the molar ratios of TPyP : BPy were in the range 1 : 2 to 1 : 8. Lengths and widths for the core stems of the nanocombs were about 10 and 1 μm, respectively (Fig. 2c, d and e). Needle-like branches grew out perpendicularly from both sides of the core stems, with branch lengths of about 1–10 μm and diameters of about 0.1–1 μm, respectively. No significant change was recorded for the shapes of the nanocombs when the molar ratios of TPyP : BPy changed from 1 : 2 to 1 : 8, except for a slight increase in the core stem length. To date, and to the best of our knowledge, there have been some reports on the formation of nanocomb materials of inorganic compounds, such as ZnO, ZnS and AlN,[21] but few reports were found for other materials. Moreover, to obtain those inorganic comb-like materials, high temperature or low pressures were usually necessary. In the present work, the nanocombs could be obtained under very moderate conditions (normal atmosphere, room temperature), and no specific instrument was required.

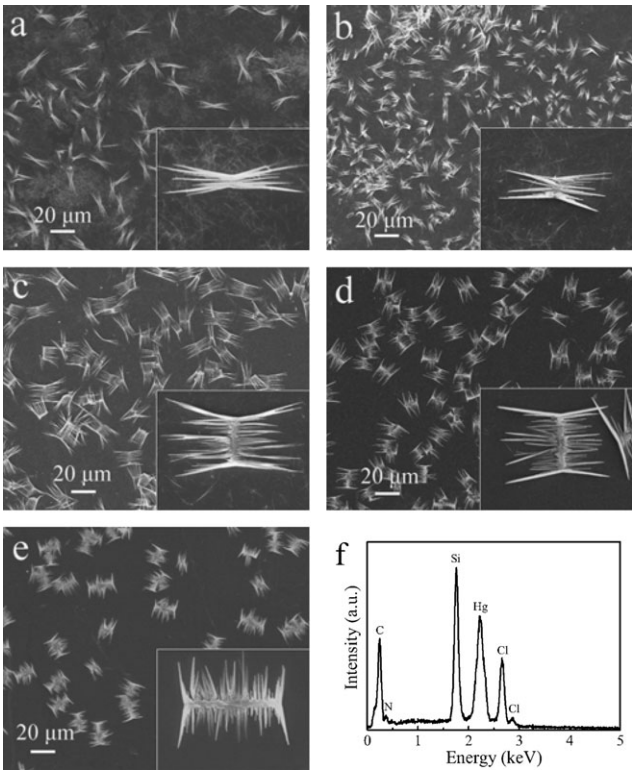

Fig. 2 SEM images of the HgTPyP–HgBPy coordination polymer nanocombs assembled at the molar ratios of TPyP : BPy: (a) 2 : 1, (b) 1 : 1, (c) 1 : 2, (d) 1 : 4 and (e) 1 : 8. (f) An EDS spectrum of the nanocombs.

EDS measurements on the nanocombs revealed that they are composed of C, N, Cl, and Hg elements (Fig. 2f). The Si peak was from the Si(100) substrate. It is known that $HgCl_2$ can react with either TPyP or BPy to form HgTPyP or HgBPy(L) (L: another ligand) coordination polymers,[6,7,13] thus we called the formed comb-like materials HgTPyP–HgBPy nanocombs.

The XPS spectra of the nanocombs exhibited several peaks in the binding energy between 100 and 600 eV (figures not shown), corresponding to the elements Hg, Cl, C, and N. The binding energies for each peak and identified elements were as follows:[22] Cl2p (198.2 eV), C1s (284.7 eV), $Hg4d\frac{5}{2}$ (360.2 eV), and N1s (401.1 eV), which were in agreement with those from the EDS measurements and with the composition of HgTPyP–HgBPy nanocombs. As a control experiment, we also measured the XPS spectra of TPyP and BPy powders, which revealed that the N1s binding energies were 399.1 and 399.6 eV for the compounds TPyP and Bpy, respectively. (The XPS spectra of N1s in the nanocombs, TPyP and Bpy are shown in Fig. S1†).

When the molar ratios of TPyP : BPy were about 2 : 1 and 1 : 1, the nanomaterials formed consisted of both comb-like materials and nanowires (Fig. 2a and b, images of nanowires were not so clear as those of nanocombs). Interestingly, more nanowires formed when the molar fraction of BPy was lower (Fig. 2a). As the molar fraction of BPy increased in the reactants, nanowires became less prevalent while (irregular) comb-like materials became more so, indicating that the

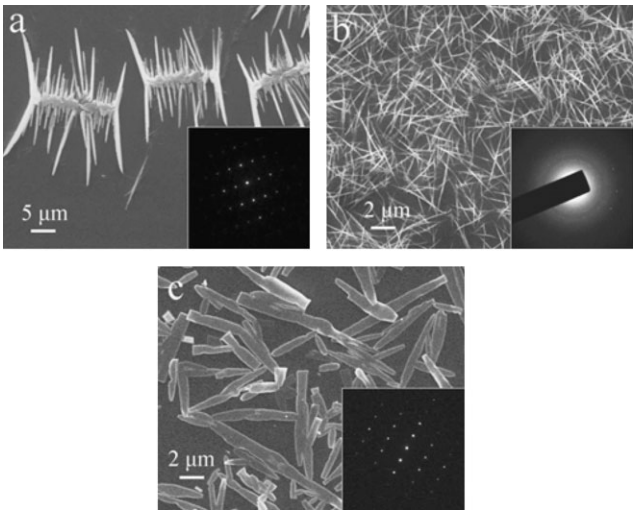

Fig. 3 SEM images of (a) HgTPyP–HgBPy nanocombs, (b) HgTPyP nanowires and (c) HgBPy nanorods. Inserted images are ED patterns corresponding to each nanomaterial.

structures of the nanomaterials are closely dependent on the mixing ratios of the ligands. To reveal the relationships between such structural features and each ligand, we further carried out interfacial reactions of $HgCl_2$ with either pure TPyP or BPy as control experiments.

Fig. 3 compares the SEM images and electron diffraction patterns of the HgTPyP–HgBPy nanocombs with those of HgTPyP and HgBPy coordination polymers. Completely different SEM morphologies of these nanomaterials were observed. The HgTPyP formed nanowires with diameters of up to about 200 nm and lengths over 10 μm (Fig. 3b),[17] while the HgBPy formed irregular nanorods with widths about 1–2 μm and lengths in the range 2 to 20 μm (Fig. 3c). These features indicated that the nanowires in Fig. 2a and b were composed of HgTPyP coordination polymer, while the comb-like nanomaterials were HgTPyP–HgBPy hybrids, which grew into more regular nanocombs when the molar fractions of BPy in the reactants were increased. Hence, we concluded that the coordination polymer nanocombs could be assembled at the interface by changing molar fractions of TPyP and BPy.

Electron diffraction patterns of both HgTPyP–HgBPy nanocombs and HgBPy nanorods showed regular patterns while those of the HgTPyP nanowires showed only some irregular dots (Fig. 3, inserted images. The TEM photos of the nanocombs and nanorods are shown in Fig. S2†), which indicated that the nanocombs and nanorods were single-crystalline but that the HgTPyP nanowires were microcrystals or of non-crystalline structure. Small dark spots in Fig. S2c may be some HgBPy particles segregated from the nanorods.† These ED patterns revealed that the crystallographic parameters of the nanocombs were about 3.9 and 6.0 Å (Fig. 3a), which were in agreement with those of the HgBPy nanorods (Fig. 3c).

In order to get more structural information on the nanocombs, we also measured the X-ray diffraction spectra of the HgTPyP–HgBPy nanocombs, HgBPy nanorods, and HgTPyP nanowires on the Si(100) substrate surfaces. No obvious Bragg peaks were recorded for the HgTPyP nanowires, which may be due to its non-crystalline nature and in agreement with their

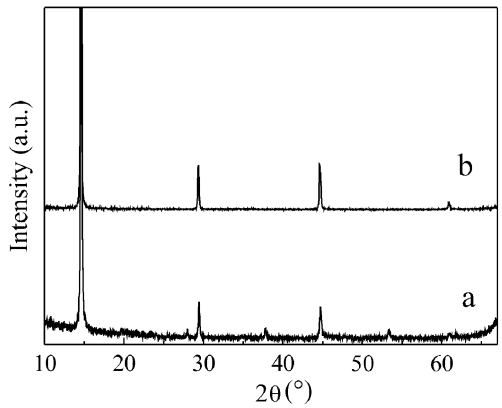

Fig. 4 XRD spectra of (a) HgTPyP–HgBPy nanocombs and (b) HgBPy nanorods.

ED pattern. On the other hand, very similar XRD spectra were recorded for the HgTPyP–HgBPy nanocombs and HgBPy nanorods, both of them showed a group of strong and sharp peaks (Fig. 4). These diffraction peaks appeared at the 2θ values of 14.6°, 29.4°, and 44.7°, corresponding to the lattice spacing d = 6.05 Å according to Bragg's equation ($2d\sin\theta = \lambda/n$). This d spacing was in very good agreement with one crystallographic parameter (6.0 Å) from the ED spectra. Hence, we suggest that the structural nature of the nanocombs might be similar to that of the HgBPy nanorods.

The Soret band shift of porphyrin rings has often been used to reveal the electronic coupling of the porphyrins based on the exciton theory.[23] That is, when two porphyrin rings are closely packed in the films or form aggregates, the Soret band is usually red- or blue-shifted compared with that in the monomer state; the stronger the electronic coupling the larger the red-/blue-shift.

Fig. 5 shows absorption spectra for the films of HgTPyP and HgTPyP–HgBPy nanocombs, together with that of TPyP in dilute chloroform solution. We have pointed out that the TPyP Soret band appears at 417 nm for its monomer form, and red-shifted to 442 nm for its J-aggregates.[16] Here, this Soret band appeared at 437 and 427 nm for the HgTPyP and HgTPyP–HgBPy nanocombs; thus, compared with the Soret absorption in the monomer state, the extent of red-shift increases in the following order: HgTPyP–HgBPy nanocombs (10 nm), HgTPyP (20 nm) and TPyP aggregates (25 nm). As it is well known that the red-shift for the Soret band is due to the π–π^* interaction between porphyrin rings,[24] we can conclude that porphyrin–porphyrin interaction in the present nanocombs is weaker than that in the TPyP J-aggregates and HgTPyP nanowires. This weakened interaction is due to the co-assembled BPy ligand.

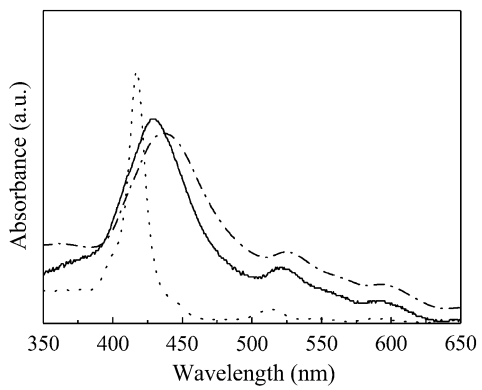

Fig. 5 Absorption spectra for the films of the HgTPyP–Hg2-BPy nanocombs (—), the HgTPyP nanowires (--) and dilute TPyP chloroform solution (···).

Interfacial reaction time effect on the nanocombs

Although the HgTPyP–HgBPy nanocombs could form within several minutes after the interfacial reaction had started, both the shapes and sizes of the nanocombs slightly changed when the interfacial reaction time was over 1 h. Fig. 6 shows several SEM images of the nanocombs at reaction times from 5 min to 3 h, which reveal that the lengths of the core stems did not largely increase with the reaction time while those of the branches became longer and longer. The needle-like branches were no longer perpendicular to the core stems but formed curved wires, especially at the two sides of the core stems. Moreover, the sharp tips of the branches split into many fine-curved wires, and some tips looked like a broom (Fig. 6b, inserted image).

Ligand structure effect on the nanocombs

It has been shown that the frameworks of coordination polymers are largely dependent on the geometries of metal ions and ligand structures.[6,7] For example, when a tridentate ligand TPyTa was co-assembled with TPyP, the nanocrystals produced were hybrid nanotubes.[18] To reveal the importance of BPy on the formation of nanocombs, we used its derivatives, 2-Bpy and TMPy (Fig. 1) as co-assembling ligands with TPyP as control experiments.

Fig. 7a and b show the SEM images of HgTPyP–Hg(2-BPy) and HgTPyP–HgTMPy nanomaterials, both of which were composed of some nanowires but no nanocombs; that is, comb-like materials could not be formed when 2-Bpy or

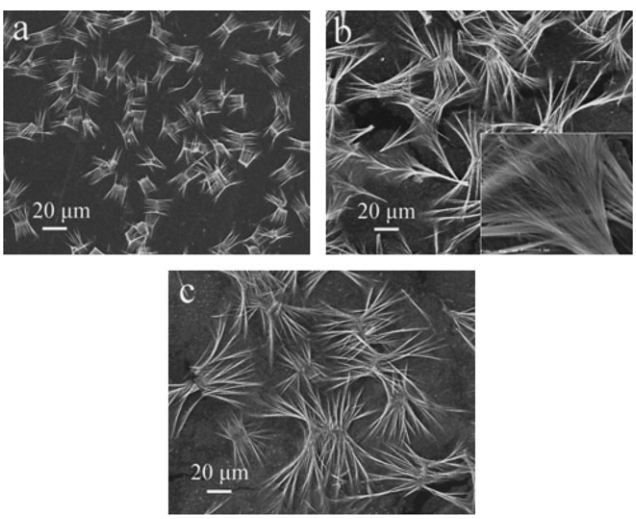

Fig. 6 SEM images of the HgTPyP–HgBPy nanocombs prepared at various interfacial reaction times: (a) 5 min, (b) 1 h and (c) 3 h. Inserted image in (b): tip of the branches after 1 h interfacial reaction.

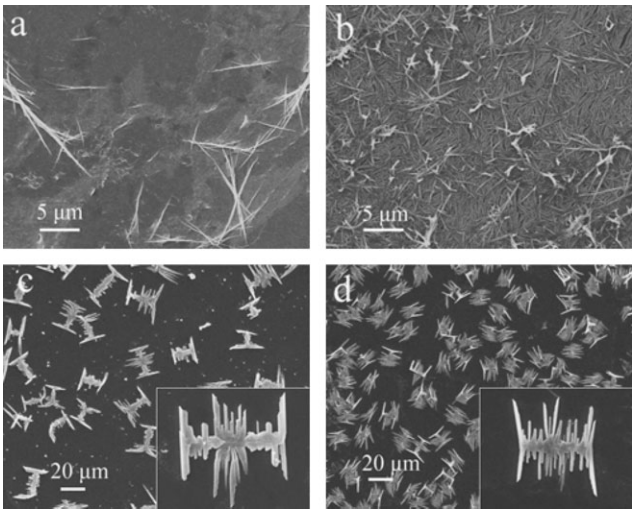

Fig. 7 SEM images of (a) HgTPyP–Hg2-BPy, (b) HgTPyP–HgTMPy, (c) HgZnTPyP–HgBPy and (d) HgPdTPyP–HgBPy coordination polymer nanocrystals.

TMPy were used to co-assemble with TPyP. This may be ascribed to the following reasons. (1) Although 2-BPy contains two pyridyl groups, they are not in an opposite position like 4,4′-bipyridyl and usually form five-coordinate complexes with transition metal ions,[25] which leads to a difficulty in forming bridging binding, thus, coordination polymer hybrids could not be assembled. (2) For the TMPy ligand, there is a $(CH_2)_3$ spacer between the two pyridyl ligands, resulting in the loss of the rigid and linear structural features.[26] The results indicated that the rigid BPy ligand, with linear and opposite binding sites, was necessary for the formation of hybrid nanocombs.

For the porphyrin ligands, when the metal-free porphyrin (TPyP) was replaced by its metalated derivatives of ZnTPyP or PdTPyP, again the coordination polymer nanocombs could be assembled at the interface (Fig. 7c and d), though the branches of Hg(Zn)TPyP–HgBPy nanocombs seem to be easily broken from the core stems. The results indicated that central metal ions of metalloporphyrins had little influence on the formation of the Hg(M)TPyP–HgBPy nanocombs.

Conclusions

We have demonstrated $HgCl_2$ mediated self-assembly of coordination polymer nanocombs composed of (metallo)porphyrins and 4,4′-bipyridyl at the water–chloroform interface. These nanocombs could be formed within several minutes. Formation of the coordination polymer nanocombs closely depended on the molecular structures of the bipyridyl ligands, the mixed molar ratios of porphyrins and bipyridyls in the reactants, as well as the interfacial reaction time. The central metal ions of tetrapyridylporphyrins had little influence on the nanocombs assembled.

Acknowledgements

We thank the National Science Foundation of China (20473024, 20421303) for financial support.

References

1 (*a*) J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435; (*b*) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353; (*c*) P. Gao and M. Liu, *Langmuir*, 2006, **22**, 6727; (*d*) P. Gao, C. Zhan and M. Liu, *Langmuir*, 2006, **22**, 775; (*e*) T. Jiao and M. Liu, *Langmuir*, 2006, **22**, 5005.
2 (*a*) M. Ornatska, S. Peleshanko, B. Rybak, J. Holzmueller and V. V. Tsukruk, *Adv. Mater.*, 2004, **16**, 2206; (*b*) B. H. Hong, J. Y. Lee, C.-W. Lee, J. C. Kim, S. C. Bae and K. S. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 10748.
3 (*a*) S. Iijima, *Nature*, 1991, **354**, 56; (*b*) H. M. Cheng, *Carbon Nanotubes: Synthesis, Microstructure, Properties and Applications*, Chemical Industry Press, Beijing, 2002, (in Chinese).
4 (*a*) Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, R. Yang and Y. Zhang, *Adv. Funct. Mater.*, 2004, **14**, 943; (*b*) H. Huang, S. Yang, J. Gong, H. Liu, J. Duan, X. Zhao and R. Zhang, *J. Phys. Chem. B*, 2005, **109**, 20746; (*c*) H. Yan, R. He, J. Johnson, M. Law, R. J. Saykally and P. Yang, *J. Am. Chem. Soc.*, 2003, **125**, 4728; (*d*) Y. Hao, G. Meng, Z. L. Wang, C. Ye and L. Zhang, *Nano Lett.*, 2006, **6**, 1650.
5 (*a*) N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, *Science*, 1995, **269**, 966; (*b*) A. Loiseau, F. Willaime, N. Demoncy, G. Hug and H. Pascard, *Phys. Rev. Lett.*, 1996, **76**, 4737; (*c*) W.-Q. Han, C. W. Chang and A. Zettl, *Nano Lett.*, 2004, **4**, 1355.
6 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
7 J. Wojaczyski and L. Latos-Grayski, *Coord. Chem. Rev.*, 2000, **198**, 133.
8 C.-Y. Su, M. D. Smith and H.-C. zur Loye, *Angew. Chem., Int. Ed.*, 2003, **42**, 408.
9 T. Yamaguchi, S. Tashiro, M. Tominaga, M. Kawano, T. Ozeki and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 10818.
10 (*a*) Z. Wang, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2004, **126**, 15955; (*b*) Z. Wang, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2004, **126**, 16720; (*c*) Z. Wang, K. J. Ho, C. J. Medforth and J. A. Shelnutt, *Adv. Mater.*, 2006, **18**, 2557; (*d*) Z. Wang, Z. Li, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2007, **129**, 2440.
11 (*a*) M.-L. Tong, H.-J. Chen and X.-M. Chen, *Inorg. Chem.*, 2000, **39**, 2235; (*b*) M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; (*c*) E. Colacio, F. Lloret, M. Navarrete, A. Romerosa, H. Stoeckli-Evans and J. Suarez-Varela, *New J. Chem.*, 2005, **29**, 1189; (*d*) C. Genre, G. S. Matouzenko, E. Jeanneau and D. Luneau, *New J. Chem.*, 2006, **30**, 1669.
12 (*a*) T. Kusukawa and M. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576; (*b*) M. Yoshizawa, Y. Takeyama, T. Okano and M. Fujita, *J. Am. Chem. Soc.*, 2003, **125**, 3243; (*c*) M. Yoshizawa, S. Miyagi, M. Kawano, K. Ishiguro and M. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 9172.
13 (*a*) C. M. Drain and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1994, 2313; (*b*) C. M. Drain, F. Nifiatis, A. Vasenko and J. D. Batteas, *Angew. Chem., Int. Ed.*, 1998, **37**, 2344; (*c*) C. M. Drain, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5178; (*d*) K. F. Cheng, N. A. Thai, K. Grohmann, L. C. Teague and C. M. Drain, *Inorg. Chem.*, 2006, **45**, 6928.
14 C. V. K. Sharma, G. A. Broker, J. G. Huddleston, J. W. Baldwin, R. M. Metzger and R. D. Rogers, *J. Am. Chem. Soc.*, 1999, **121**, 1137.
15 (*a*) E. Iengo, E. Zangrando, S. Geremia, R. Graff, B. Kieffer and E. Alessio, *Chem.–Eur. J.*, 2002, **8**, 4670; (*b*) E. Iengo, E. Zangrando and E. Alessio, *Eur. J. Inorg. Chem.*, 2003, 2371.
16 (*a*) S. J. Lee and J. T. Hupp, *Coord. Chem. Rev.*, 2006, **250**, 1710; (*b*) J. L. Ruggles, G. J. Foran, H. Tanida, H. Nagatani, Y. Jimura, I. Watanabe and I. R. Gentle, *Langmuir*, 2006, **22**, 681; (*c*) D.-J. Qian, C. Nakamura and J. Miyake, *Langmuir*, 2000, **16**, 9615; (*d*) D. J. Qian, T. Wakayama, C. Nakamura and J. Miyake, *J. Phys. Chem. B*, 2003, **107**, 3333.
17 B. Liu, D.-J. Qian, H.-X. Huang, T. Wakayama, S. Hara, W. Huang, C. Nakamura and J. Miyake, *Langmuir*, 2005, **21**, 5079.
18 B. Liu, D.-J. Qian, M. Chen, T. Wakayama, C. Nakamura and J. Miyake, *Chem. Commun.*, 2006, 3175.
19 D.-J. Qian, C. Nakamura, T. Wakayama and J. Miyake, *J. Porphyrins Phthalocyanines*, 2003, **7**, 415.

20 Y. Lin, H. Skaff, T. Emrick, A. D. Dinsmore and T. P. Russell, *Science*, 2003, **299**, 226.
21 (*a*) W. P. Zheng, M. M. Shannon, D. Sheng and H. L. Douglas, *Nano Lett*., 2005, **5**, 723; (*b*) Y. H. Leung, A. B. Djurisic, J. Gao, M. H. Xie, Z. F. Wei, S. J. Xu and W. K. Chan, *Chem. Phys. Lett*., 2004, **394**, 452; (*c*) C. Ma, D. Moore, J. Li and Z. L. Wang, *Adv. Mater*., 2003, **15**, 228; (*d*) L.-W. Yin, Y. Bando, Y.-C. Zhu, M.-S. Li, Y.-B. Li and D. Golberg, *Adv. Mater*., 2005, **17**, 110.
22 *NIST Standard Reference Data*, NIST, Gaithersburg, USA, 2003, http://srdata.nist.gov/xps/bindE_query_res.asp.
23 R. Rubires, J. Crusats, Z. El-Hachemi, T. Jaramillo, M. López, E. Valls, J.-A. Farrera and J. M. Ribó, *New J. Chem*., 1999, **23**, 189.
24 R. F. Khairutdinov and N. Serpone, *J. Phys. Chem. B*, 1999, **103**, 761.
25 (*a*) Y. Niu, Y. Song, H. Hou and Y. Zhu, *Inorg. Chim. Acta*, 2003, **355**, 151; (*b*) S. Ching and C. M. Elliott, *Langmuir*, 2006, **15**, 1491.
26 (*a*) Y. Y. Niu, Y. L. Song, H. W. Hou, H. G. Zheng, H. K. Fun and X. Q. Xin, *Wuji Huaxue Xuebao*, 2001, **17**, 727; (*b*) E. Freire, S. Baggio, R. Baggio and L. Suescun, *J. Chem. Crystallogr*., 1999, **29**, 825.

