Supramolecular Chemistry

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Directed 1D Assembly of a Ring-Shaped Inorganic Nanocluster Templated by an Organic Rigid-Rod Molecule: An Inorganic/Organic Polypseudorotaxane**

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Polyoxometalates (POMs) have attracted a great deal of attention because of their multielectronic redox activities and unique photochemical properties.[1] To enhance their expediency for materials science, the controlled assembly of POMs with nanometric precision is one of the important goals.[2,3] We took notice of the ring-shaped polyoxomolybdate (MC) developed by Müller et al.,[4] since MC is expected to display interesting physical properties that originate from its mixed-valent electronic structure. Polarz et al. have reported that coassembly of MC with a cationic surfactant results in the formation of a hexagonal array of MC rings.[5] Herein we report that MC coassembles with a rigid *p*-phenylenebutadiynylene polymer (PB$_n$, Scheme 1) bearing pendant ammonium ion groups to form a novel one-dimensional (1D) tubular assembly of cofacially connected MC rings (Figure 1).

The MC contains 176 MoO_3 units and adopts a 1.3-nm-thick ring-shaped structure, with external and internal diameters of roughly 4.1 and 2.3 nm, respectively.[4] Since the MC has many acidic OH ($O^-\cdots H^+$) groups on its surface, it can interact with NH_2 and NH_3^+ groups through hydrogen-bonding and electrostatic interactions, respectively. In fact, as reported previously,[6] MC can accommodate 1–3 molecules of a metalloporphyrin with aminophenyl side groups (TAP, Scheme 1) within its cavity, thereby forming the inorganic/organic nanocomposite $MC\supset TAP_{1-3}$. On the basis of this observation, PB$_n$ was designed with the expectation that it may connect multiple MC rings in a cofacial manner through electrostatic interactions to form a one-dimensional structure.[7–11]

For the synthesis of PB$_n$, a 1,4-diethynylbenzene derivative with four *tert*-butoxycarbonyl-protected amino groups ($^{Boc}PB_1$) was subjected to Cu^{II}-mediated Glaser–Hey coupling. The high-molecular-weight fraction of the resultant polymer ($^{Boc}PB_n$) was isolated by preparative size-exclusion chromatography (SEC) and then deprotected with trifluoroacetic acid (TFA).[12,13] By using the analytical SEC profile of an oligomeric fraction of the coupling product as a calibration standard, the average number of repeating PB units (*n*) of the isolated $^{Boc}PB_n$ and its polydispersity were estimated as 14 and 1.5, respectively.

For the coassembly of MC with PB$_{14}$, a solution of PB$_{14}$ in MeOH ([PB unit] $= 6.0\times10^{-5}$ M) was mixed with a solution of MC in MeCN (0.5×10^{-5} M)[14] at [PB unit]/[MC] = 3:1 (MeCN/MeOH = 4:1 v/v), and the resulting mixture was stirred for 10 minutes at 20 °C. Dynamic light scattering (DLS) analysis indicated that the mixture contains large objects with sizes ranging from 50 to 3500 nm (average radius; 347 nm).[13] As shown in Figure 2c,d, transmission electron microscopy (TEM) analysis of an air-dried sample of the solution clearly displayed the presence of one-dimensional (1D) objects with a high aspect ratio. While most of the 1D objects visualized by TEM are much longer than PB$_{14}$ (which has an average length of 14 nm, see below), they are characterized by a uniform diameter of 4 nm, which is nearly identical to that of MC.[4] In sharp contrast, TEM analysis of MC alone under identical conditions but without PB$_{14}$ showed only a great number of discrete nanodots with diameters of 3–5 nm (Figure 2b),[4] while PB$_{14}$ could not be visualized regardless of the presence or absence of MC (Figure 2a). From these contrasting observations, it is clear that the 1D objects in Figure 2c,d are composed of MC rings cofacially connected to one another. In this nanoscale aggregate, the rigidity of PB$_{14}$ likely plays an important role, since the mixing of MC with protonated polylysine, a rather flexible polymer having NH_3^+ groups, resulted in the formation of an amorphous agglomerate, as observed by TEM.[13]

When the MC was added to a solution of PB$_{14}$ in MeCN/MeOH (4:1 v/v) ([PB unit]/[MC] = 3:1), the visible absorption band of PB$_{14}$ became less intense and broadened.[13] Furthermore, the addition of MC efficiently quenched the

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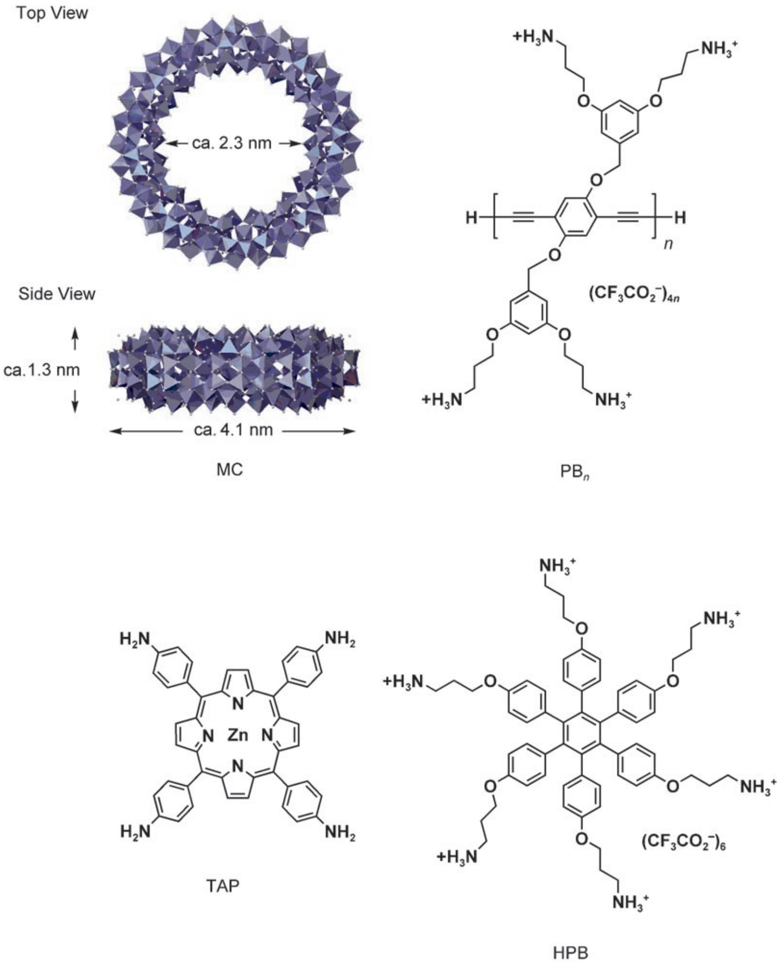


Scheme 1. Compounds used in the study.

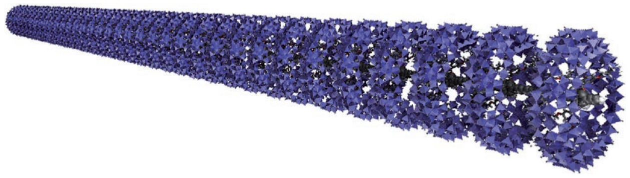


Figure 1. Schematic illustration of an inorganic/organic polypseudorotaxane derived from MC and PB_n.

photoexcited state of PB_{14} (Figure 3 a): In the absence of MC, excitation of PB_{14} at 440 nm resulted in a blue fluorescence centered at 480 nm. When MC was titrated with PB_{14}, the fluorescence emission from PB_{14} did not occur until [PB unit]/[MC] exceeded 11:1 (Figure 3 b; filled circles). These results likely reflect that MC and PB_{14} coassemble to form a complex. Compared with PB_{14}, PB_1 appears to be have much less affinity toward MC, as judged from its fluorescence titration profile (Figure 3 b; open circles), where the characteristic fluorescence of PB_1 started to appear at a $[PB_1]/[MC]$ ratio of 8:1 (which is smaller than in the case of PB_{14}).[13] This tendency indicates the importance of a multivalent interaction between PB_n and MC for the complexation.[15] The ^1H NMR signals corresponding to PB_{14} disappeared completely upon mixing the solution with MC, which indicates that PB_{14} likely loses its conformational freedom when deposited onto the MC surface.[13]

Two important issues need to be considered in regard to the mechanism of the 1D coassembly of MC with PB_{14}: 1) Does the doughnutlike structure of MC play a role and 2) why is the 1D coassembled structure much longer than the average length of PB_{14}? To address question (1), we attempted the coassembly of guest-included $MC \supset TAP_{1-3}$ ([TAP]/[MC] = 3:1)[6] with PB_{14}. The $MC \supset TAP_{1-3}$ coassembly showed only a slight red fluorescence at 600–750 nm originating from TAP (Figure 4), as a consequence of the photochemical quenching of the singlet excited state of included TAP by MC. However, when $MC \supset TAP_{1-3}$ was mixed with PB_{14} in MeCN/MeOH (4:1 v/v), the TAP recovered its red fluorescence (Figure 4), thus indicating that TAP binds MC less strongly than PB_{14} and is "kicked out" of the MC cavity upon mixing $MC \supset TAP_{1-3}$ with PB_{14} (Scheme 2). We also prepared $MC \supset HPB$ by mixing MC with hexaphenylbenzene (HPB) which carried six pendant ammonium ion groups at its periphery ([HPB]/[MC] = 3:1). This experiment was based on the expectation that HPB can bind MC more strongly than TAP and even PB_{14}. In fact, mixing $MC \supset TAP_{1-3}$ with HPB resulted in the recovery of the fluorescence of TAP and quenching of the HPB fluorescence,[13] which indicates that the TAP in the MC cavity can be kicked out by HPB. On the other hand, when $MC \supset HPB$ was titrated with PB_{14}, the fluorescence of HPB

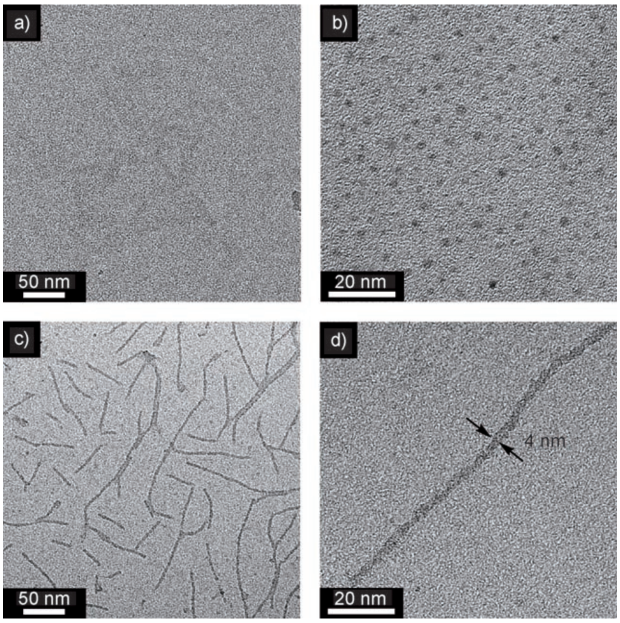


Figure 2. TEM micrographs of air-dried MeCN/MeOH (4:1 v/v) solutions of a) PB_{14}, b) MC, and c),d) a mixture of MC and PB_{14} ([PB unit]/[MC] = 3:1), deposited on a specimen grid covered with a thin carbon support film. [PB unit] = 1.2×10^{-5} M, [MC] = 0.4×10^{-5} M.

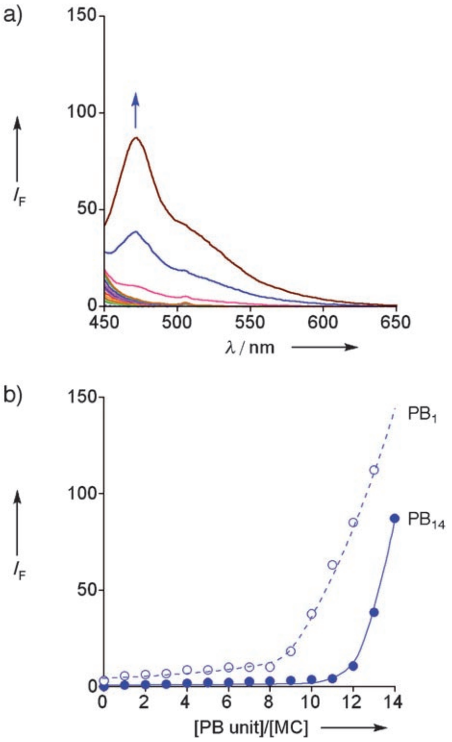


Figure 3. a) Fluorescence spectra of PB_{14} (λ_{ext}: 440 nm) in MeCN/MeOH (4:1 v/v) at 20 °C upon titration of MC with PB_{14}. b) Plots of the fluorescence intensities of PB_{14} at 472 nm (filled circle) and reference PB_1 (λ_{ext}: 357 nm) at 450 nm (open circles)[13] versus [PB unit]/[MC]. [MC] $= 6.1 \times 10^{-7}$ M.

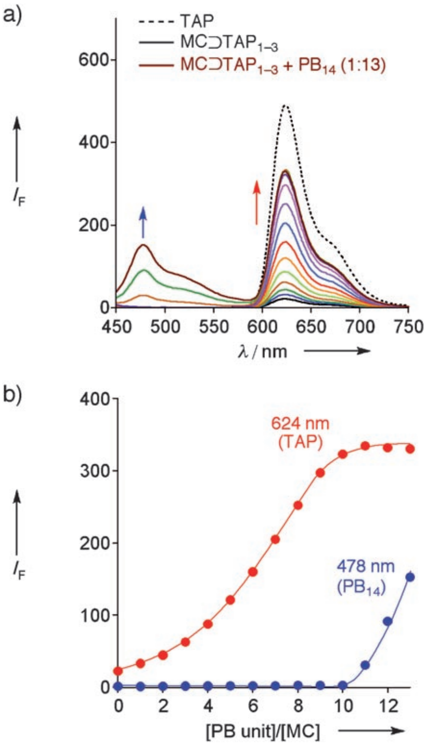
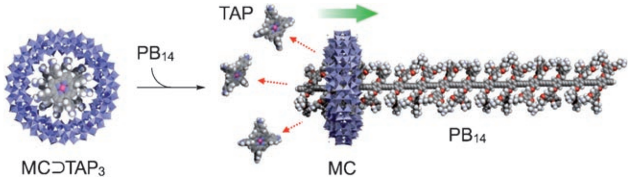


Figure 4. a) Fluorescence spectra of PB_{14} (λ_{ext}; 435 nm) in MeCN/MeOH (4:1 v/v) at 20 °C upon titration of MC⊃TAP_{1-3} (1:3 mixture of MC and TAP) with PB_{14}. b) Plots of the fluorescence intensities of PB_{14} at 478 nm (blue filled circles) and TAP at 624 nm (red filled circles) versus [PB unit]/[MC]. [MC] $= 6.1 \times 10^{-7}$ M.



Scheme 2. Schematic illustration of the possible liberation of TAP from MC⊃TAP_3 upon threading of PB_{14}.

remained quenched, even upon addition of a large excess of PB_{14}.[13] Therefore, HPB indeed binds MC much more strongly than PB_{14}. Quite interestingly, while the mixing of MC⊃TAP_{1-3} with PB_{14} (Figure 4) resulted in the formation of fibrous (1D) objects, as observed by TEM, only aggregated dots formed when MC⊃HPB was mixed with PB_{14}.[13] These contrasting results allow us to conclude for question (1) that the threading of the MC rings with PB_{14} is essential for their controlled 1D coassembly. As for question (2), the fluorescence profiles of PB_{14} in the titration experiments showed an interesting possibility in regard to the tube dimensions. In the competition experiment of MC⊃TAP_{1-3} with PB_{14} (Figure 4), the fluorescence of PB_{14} was hardly visible until the [PB unit]/[MC] ratio exceeded 10:1 (Figure 4b, blue filled circles). Since a similar trend was observed for the titration of guest-free MC with PB_{14} (Figure 3b), we initially thought that it must be simply due to the threading interaction of MC with PB_{14}. However, despite no 1D coassembly and no threading interaction upon mixing PB_{14} with MC⊃HPB, PB_{14} showed an analogous fluorescence quenching profile.[13] Therefore, PB_{14} likely adheres to MC, irrespective of whether the MC cavity is occupied by a guest molecule or not. Nevertheless, for the controlled 1D coassembly of MC and PB_{14}, MC must be threaded by PB_{14}. We assume that the threaded MC units are "stitched" together by the surface adhesion of PB_{14}, and such short-chain 1D objects are occasionally connected to one another. Consequently, they become much longer than expected from the average length (14 nm) of the PB_{14} used as a template (Figure 2c,d). From these observations, the 1D structure formed from MC and PB_{14} may be called an inorganic/organic polypseudorotaxane.[7–11]

In conclusion, we have demonstrated the formation of the first inorganic/organic polypseudorotaxane by the template-assisted cofacial assembly of a ring-shaped molybdenum cluster (MC) with a rigid-rod molecule having a high affinity toward the MC surface. Since the MC is a mixed-valent inorganic cluster with chromophoric characteristics, exploration of the optoelectronic properties of this novel 1D nanocomposite material is one of the subjects worthy of further investigation.[16]

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