

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

Md. Akhtarul Alam, Yeong-Sang Kim, Saho Ogawa, Akihiko Tsuda,* Noriyuki Ishii, and Takuzo Aida*

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 176MoO₃ 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[−]⋯H⁺) groups on its surface, it can interact with NH₂ and NH₃⁺ 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⊃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 (BocPB₁) was subjected to Cu^{II}-mediated Glaser–Hey coupling. The high-molecular-weight fraction of the resultant polymer (BocPB_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 BocPB_n and its polydispersity were estimated as 14 and 1.5, respectively.

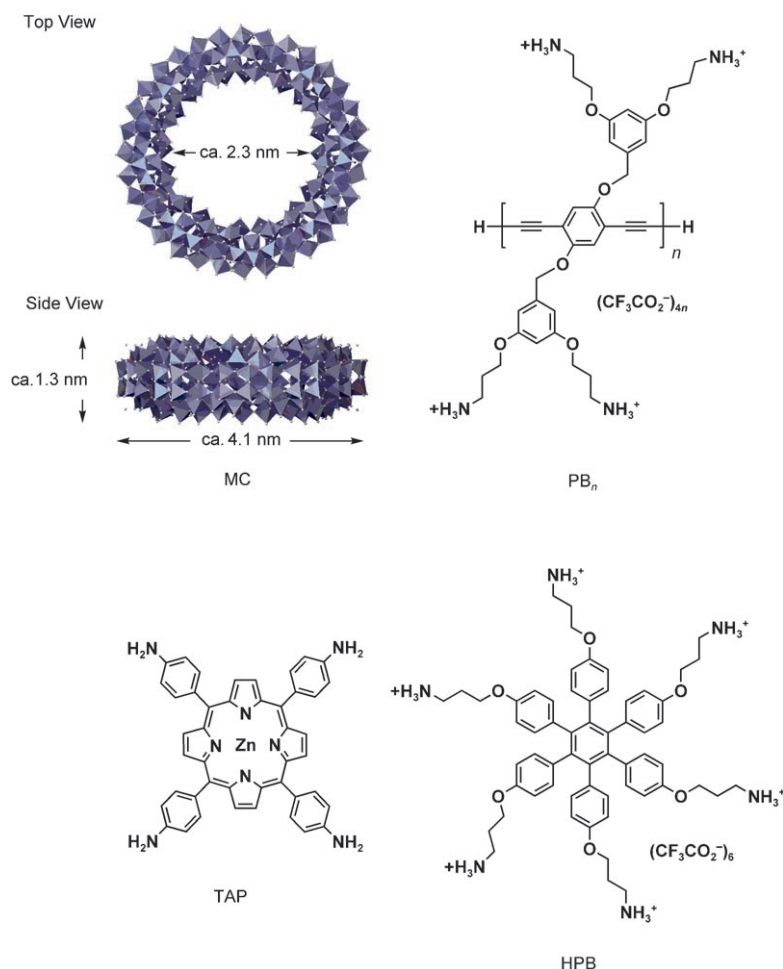
For the coassembly of MC with PB₁₄, a solution of PB₁₄ in MeOH ([PB unit] = 6.0 × 10^{−5} M) was mixed with a solution of MC in MeCN (0.5 × 10^{−5} M)^[14] at [PB unit]/[MC] = 3:1 (MeCN/MeOH = 4:1 v/v), and the resulting mixture was stirred for 10 minutes at 20 °C. Dynamic light scattering (DLS) analysis 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 PB₁₄ (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 PB₁₄ showed only a great number of discrete nanodots with diameters of 3–5 nm (Figure 2b),^[4] while PB₁₄ 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 PB₁₄ likely plays an important role, since the mixing of MC with protonated polylysine, a rather flexible polymer having NH₃⁺ groups, resulted in the formation of an amorphous agglomerate, as observed by TEM.^[13]

When the MC was added to a solution of PB₁₄ in MeCN/MeOH (4:1 v/v) ([PB unit]/[MC] = 3:1), the visible absorption band of PB₁₄ became less intense and broadened.^[13] Furthermore, the addition of MC efficiently quenched the

[*] Dr. M. A. Alam, Dr. Y.-S. Kim, S. Ogawa, Dr. A. Tsuda, Prof. Dr. T. Aida
Department of Chemistry and Biotechnology
School of Engineering, and Center for NanoBio Integration
The University of Tokyo, 7-3-1 Hongo
Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7310
E-mail: tsuda@macro.t.u-tokyo.ac.jp
aida@macro.t.u-tokyo.ac.jp
Homepage: <http://macro.chem.t.u-tokyo.ac.jp/>
Dr. A. Tsuda
PRESTO, Japan Science Technology Agency (JST)
4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)
Dr. N. Ishii
(Responsible for TEM microscopy)
Biological Information Research Center, AIST, Tsukuba Central 6
1-1-1 Higashi Tsukuba, Ibaraki 305-8566 (Japan).

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Scheme 1. Compounds used in the study.

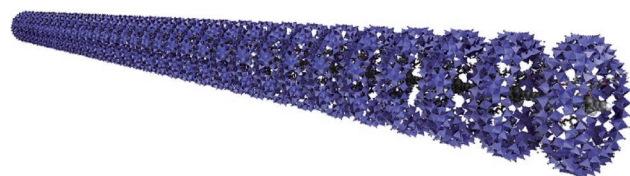


Figure 1. Schematic illustration of an inorganic/organic polypseudorotaxane derived from MC and PB_n.

photoexcited state of PB₁₄ (Figure 3 a): In the absence of MC, excitation of PB₁₄ at 440 nm resulted in a blue fluorescence centered at 480 nm. When MC was titrated with PB₁₄, the fluorescence emission from PB₁₄ did not occur until [PB unit]/[MC] exceeded 11:1 (Figure 3 b; filled circles). These results likely reflect that MC and PB₁₄ coassemble to form a complex. Compared with PB₁₄, PB₁ appears to have much less affinity toward MC, as judged from its fluorescence titration profile (Figure 3 b; open circles), where the characteristic fluorescence of PB₁ started to appear at a [PB₁]/[MC] ratio of 8:1 (which is smaller than in the case of PB₁₄).^[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 PB₁₄ disappeared completely upon mixing the solution with MC, which indicates

that PB₁₄ 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 PB₁₄: 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 PB₁₄? To address question (1), we attempted the coassembly of guest-included MC⊃TAP₁₋₃ ([TAP]/[MC]=3:1)^[6] with PB₁₄. The MC⊃TAP₁₋₃ 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⊃TAP₁₋₃ was mixed with PB₁₄ in MeCN/MeOH (4:1 v/v), the TAP recovered its red fluorescence (Figure 4), thus indicating that TAP binds MC less strongly than PB₁₄ and is “kicked out” of the MC cavity upon mixing MC⊃TAP₁₋₃ with PB₁₄ (Scheme 2). We also prepared MC⊃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 PB₁₄. In fact, mixing MC⊃TAP₁₋₃ 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⊃HPB was titrated with PB₁₄, the fluorescence of HPB

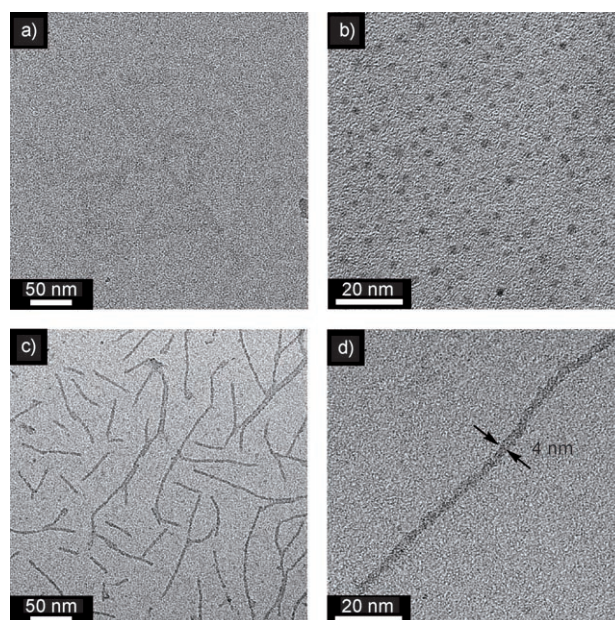


Figure 2. TEM micrographs of air-dried MeCN/MeOH (4:1 v/v) solutions of a) PB₁₄, b) MC, and c), d) a mixture of MC and PB₁₄ ([PB unit]/[MC]=3:1), deposited on a specimen grid covered with a thin carbon support film. [PB unit]=1.2×10⁻⁵ M, [MC]=0.4×10⁻⁵ M.

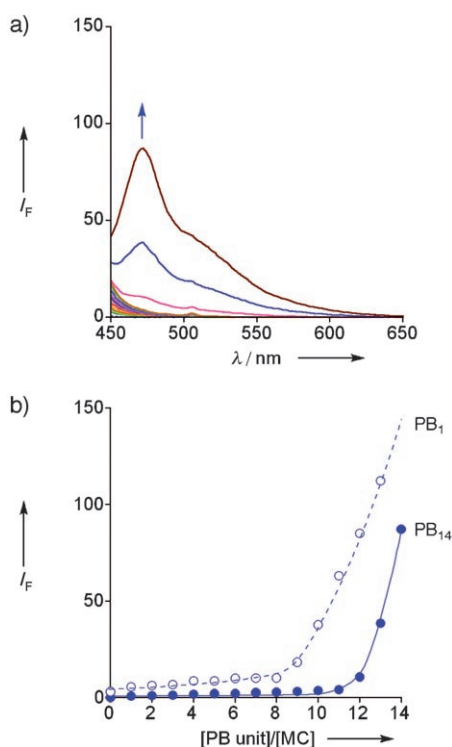


Figure 3. a) Fluorescence spectra of PB₁₄ (λ_{ext} : 440 nm) in MeCN/MeOH (4:1 v/v) at 20°C upon titration of MC with PB₁₄. b) Plots of the fluorescence intensities of PB₁₄ at 472 nm (filled circle) and reference PB₁ (λ_{ext} : 357 nm) at 450 nm (open circles)^[13] versus [PB unit]/[MC]. [MC] = 6.1×10^{-7} M.

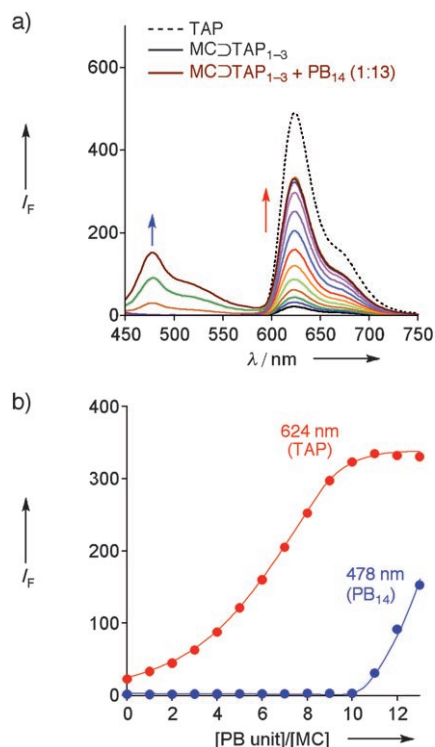
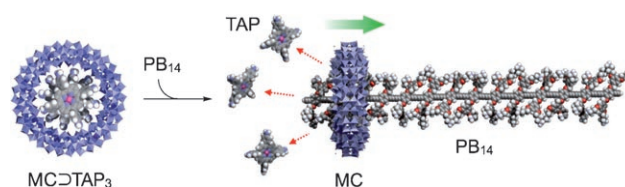


Figure 4. a) Fluorescence spectra of PB₁₄ (λ_{ext} : 435 nm) in MeCN/MeOH (4:1 v/v) at 20°C upon titration of MC⊃TAP₁₋₃ (1:3 mixture of MC and TAP) with PB₁₄. b) Plots of the fluorescence intensities of PB₁₄ at 478 nm (blue filled circles) and TAP at 624 nm (red filled circles) versus [PB unit]/[MC]. [MC] = 6.1×10^{-7} M.



Scheme 2. Schematic illustration of the possible liberation of TAP from MC⊃TAP₃ upon threading of PB₁₄.

remained quenched, even upon addition of a large excess of PB₁₄.^[13] Therefore, HPB indeed binds MC much more strongly than PB₁₄. Quite interestingly, while the mixing of MC⊃TAP₁₋₃ with PB₁₄ (Figure 4) resulted in the formation of fibrous (1D) objects, as observed by TEM, only aggregated dots formed when MC⊃HPB was mixed with PB₁₄.^[13] These contrasting results allow us to conclude for question (1) that the threading of the MC rings with PB₁₄ is essential for their controlled 1D coassembly. As for question (2), the fluorescence profiles of PB₁₄ in the titration experiments showed an interesting possibility in regard to the tube dimensions. In the competition experiment of MC⊃TAP₁₋₃ with PB₁₄ (Figure 4), the fluorescence of PB₁₄ 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 PB₁₄ (Figure 3b), we initially thought that it must be simply due to the threading interaction of MC with PB₁₄. However, despite no 1D coassembly and no threading interaction upon mixing PB₁₄ with MC⊃HPB, PB₁₄ showed an analogous fluorescence quenching profile.^[13] Therefore, PB₁₄ 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 PB₁₄, MC must be threaded by PB₁₄. We assume that the threaded MC units are “stitched” together by the surface adhesion of PB₁₄, 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 PB₁₄ used as a template (Figure 2c,d). From these observations, the 1D structure formed from MC and PB₁₄ 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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