## Supramolecular Chemistry

## 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.<sup>[1]</sup> To enhance their expediency for materials science, the controlled assembly of POMs with nanometric precision is one of the important goals.<sup>[2,3]</sup> We took notice of the ring-shaped polyoxomolybdate (MC) developed by Müller et al.,<sup>[4]</sup> 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.<sup>[5]</sup> Herein we report that MC coassembles with a rigid *p*-phenylenebuta-diynylene polymer (PB<sub>n</sub>, 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  $176 \text{ MoO}_3$  units and adopts a 1.3-nmthick ring-shaped structure, with external and internal diameters of roughly 4.1 and 2.3 nm, respectively.<sup>[4]</sup> Since the MC has many acidic OH (O<sup>-...</sup>H<sup>+</sup>) groups on its surface, it can interact with NH<sub>2</sub> and NH<sub>3</sub><sup>+</sup> groups through hydrogenbonding and electrostatic interactions, respectively. In fact, as reported previously,<sup>[6]</sup> MC can accommodate 1–3 molecules of a metalloporphyrin with aminophenyl side groups (TAP, Scheme 1) within its cavity, thereby forming the inorganic/

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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.<sup>[7-11]</sup>

For the synthesis of PB<sub>n</sub>, a 1,4-diethynylbenzene derivative with four *tert*-butoxycarbonyl-protected amino groups (<sup>Boc</sup>PB<sub>1</sub>) was subjected to Cu<sup>II</sup>-mediated Glaser–Hey coupling. The high-molecular-weight fraction of the resultant polymer (<sup>Boc</sup>PB<sub>n</sub>) was isolated by preparative size-exclusion chromatography (SEC) and then deprotected with trifluoroacetic acid (TFA).<sup>[12,13]</sup> 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 <sup>Boc</sup>PB<sub>n</sub> 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] =  $6.0 \times 10^{-5}$  M) was mixed with a solution of MC in MeCN  $(0.5 \times 10^{-5} \text{ m})^{[14]}$  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).<sup>[13]</sup> 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<sub>14</sub> (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.<sup>[4]</sup> In sharp contrast, TEM analysis of MC alone under identical conditions but without PB<sub>14</sub> showed only a great number of discrete nanodots with diameters of 3–5 nm (Figure 2b),<sup>[4]</sup> 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<sub>14</sub> likely plays an important role, since the mixing of MC with protonated polylysine, a rather flexible polymer having NH<sub>3</sub><sup>+</sup> groups, resulted in the formation of an amorphous agglomerate, as observed by TEM.<sup>[13]</sup>

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.<sup>[13]</sup> Furthermore, the addition of MC efficiently quenched the



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Scheme 1. Compounds used in the study.

TAF



*Figure 1.* Schematic illustration of an inorganic/organic polypseudorotaxane derived from MC and PB<sub>n</sub>.

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

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)<sup>[6]</sup> with PB<sub>14</sub>. 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 > TAP<sub>1-3</sub> was mixed with PB<sub>14</sub> 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<sub>14</sub> and is "kicked out" of the MC cavity upon mixing  $MC \supset TAP_{1-3}$  with  $PB_{14}$  (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 PB<sub>14</sub>. In fact, mixing MC \(\)TAP1-3 with HPB resulted in the recovery of the fluorescence of TAP and quenching of the HPB fluorescence,<sup>[13]</sup> 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  $PB_{14}$ , the fluorescence of HPB



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

NH,

HPB

## Communications



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



**Figure 4.** a) Fluorescence spectra of PB<sub>14</sub> ( $\lambda_{ext}$ ; 435 nm) in MeCN/ MeOH (4:1 v/v) at 20 °C upon titration of MC $\supset$ TAP<sub>1-3</sub> (1:3 mixture of MC and TAP) with PB<sub>14</sub>. b) Plots of the fluorescence intensities of PB<sub>14</sub> at 478 nm (blue filled circles) and TAP at 624 nm (red filled circles) versus [PB unit]/[MC]. [MC] = 6.1 × 10<sup>-7</sup> м.



**Scheme 2.** Schematic illustration of the possible liberation of TAP from  $MC \supset TAP_3$  upon threading of  $PB_{14}$ .

remained quenched, even upon addition of a large excess of PB<sub>14</sub>.<sup>[13]</sup> Therefore, HPB indeed binds MC much more strongly than PB<sub>14</sub>. Quite interestingly, while the mixing of MC \(\)TAP<sub>1-3</sub> with PB<sub>14</sub> (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<sub>14</sub>.<sup>[13]</sup> These contrasting results allow us to conclude for question (1) that the threading of the MC rings with PB<sub>14</sub> is essential for their controlled 1D coassembly. As for question (2), the fluorescence profiles of PB<sub>14</sub> in the titration experiments showed an interesting possibility in regard to the tube dimensions. In the competition experiment of MC $\supset$ TAP<sub>1-3</sub> with PB<sub>14</sub> (Figure 4), the fluorescence of PB<sub>14</sub> 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 guestfree MC with  $PB_{14}$  (Figure 3b), we initially thought that it must be simply due to the threading interaction of MC with PB<sub>14</sub>. However, despite no 1D coassembly and no threading interaction upon mixing PB<sub>14</sub> with MC⊃HPB, PB<sub>14</sub> showed an analogous fluorescence quenching profile.<sup>[13]</sup> Therefore, PB<sub>14</sub> 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 PB<sub>14</sub>. We assume that the threaded MC units are "stitched" together by the surface adhesion of PB<sub>14</sub>, 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 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 templateassisted 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.<sup>[16]</sup>

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