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Supramolecular Device

Stimuli-Responsive Folding and Unfolding of a Polymer Bearing Multiple Cerium(IV) Bis(porphyrinate) Joints: Mechano-imitation of the Action of a Folding Ruler**

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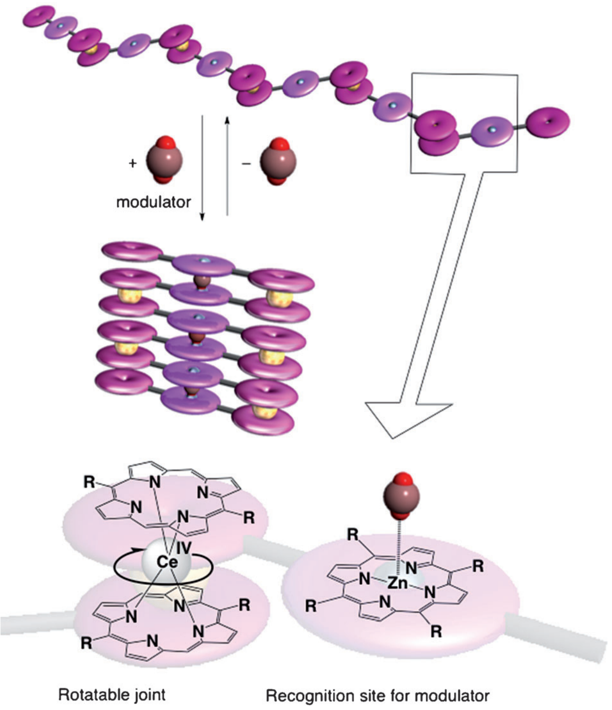
The design of molecular machines, in which the properties and functions are controlled by photo-, redox-, and host–guest-type interactions, has attracted growing attention.[1,2] Interest has been focused on synthetic actuating molecules that exhibit contraction/expansion motion, because a typical biological molecular machine, myosin, can directly convert chemical energy derived from ATP hydrolysis into mechanical motion with extremely high efficiency. In a synthetic system, it has been recently demonstrated that a sliding motion,[3,4] a spring-like motion,[5] and a conformational change[6] of synthetic molecules induce the contraction/expansion of their structures triggered by external stimuli. Challenges still remain in the design and synthesis of a new molecule toward organic mechano-responsive materials that deliberately undergo structural changes in length. It occurred to us that the rational combination of a pivoting motion,[2e,7] like a "folding ruler", and a stimuli responsive moiety enables us to construct a new class of actuating molecules.

We report herein the synthesis and dynamic guest response of a porphyrin polymer, poly(PorZn·DD), comprised of a porphyrinatozinc and a cerium(IV) bis(porphyrinate) double-decker complex as a repeating unit. In poly(PorZn·DD), porphyrinatozinc complexes recognize a divalent amine as a modulator to induce an intramolecular pivoting motion through the rotation of cerium(IV) bis(porphyrinate) complexes[8] that act as a joint and deliberately undergo structural changes in length (Scheme 1). Furthermore, we successfully monitored and visualized the reversible morphological changes that show folding and unfolding by transmission electron microscopy (TEM).

Poly(PorZn·DD) was synthesized by the reaction of **1** with tris(acetylacetonato) cerium(III) trihydrate in 1,2,4-trichlorobenzene under reflux conditions, as shown in Scheme 2; in this reaction, peripheral porphyrinatozinc moieties react intermolecularly to give poly(PorZn·DD). During the reaction, besides oligo- and poly(PorZn·DD), the intramolecularly cyclized compound **C1** was also formed; we hypothesized that **C1** would be an intermediate of this polymerization



Scheme 1. Schematic illustration of the folding action of a polymer with rotatable joints and recognition sites for a modulator; cerium(IV) bis(porphyrinate) is the joint and porphyrinatozinc is the modulator recognition site. Each porphyrin ligand in the cerium(IV) bis(porphyrinate)-based rotor undergoes a stepping rotation. Pivoting motion induced by the modulator binding gives rise to changes in the length of the polymer.

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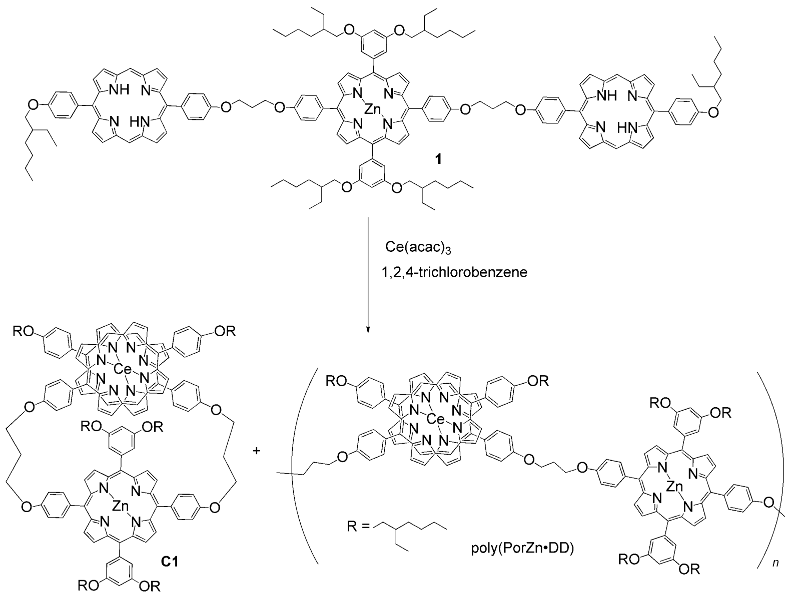

Scheme 2. Synthesis of poly(PorZn·DD).

reaction, however purified **C1** did not undergo further reaction to yield oligo- and poly(PorZn·DD). We thus purified the reaction mixture using gel permeation chromatography (GPC) to remove the low molecular weight fraction, and we obtained poly(PorZn·DD) with number-averaged molecular weight (M_n) of 27 000, calculated using a poly(styrene) standard (found a 10-mer on average for the poly(PorZn·DD)).

The Soret band of porphrinatozinc in poly(PorZn·DD) in chloroform appeared at 425.5 nm, which is identical to that of **1**. No band attributable to π–π stacking among porphyrin complexes in poly(PorZn·DD) was observed. In addition, the similarity between the UV/Vis spectrum of poly(PorZn·DD) and the additive sum of porphyrinatozinc and the double-decker complex indicates that intra- and interpolymer stacking of the porphyrin complexes does not occur in this system. To appraise the recognition-driven conformational change, we evaluated the formation of the poly(PorZn·DD) with divalent amine guest in chloroform using UV/Vis spectral changes that occurred upon the successive addition of a guest molecule. We chose 1,4-diazabicyclo[2.2.2]octane (DABCO) as a guest because the distance between two zinc metals in the sandwiched DABCO·(porphyrinatozinc)$_2$ was reported to be 7.0 Å,[9] which is slightly longer than the distance (5.1 Å) of *meso*-aryls in a cerium(IV) bis(porphyrinate) (Supporting Information, Figure S1); a slight difference would be negligible owing to the flexible propylene linkage inserted between porphyrinatozinc and cerium(IV) bis(porphyrinate). Given such a distance, we deduced that the successive DABCO binding induces the folded geometry of poly(PorZn·DD). Upon addition of DABCO, the λ_{max} values of the Soret and Q bands of the porphyrinatozinc moiety shifted to longer wavelengths with tight isosbestic points at 424.0 nm and 557.0 nm, whereas no spectral changes in the Soret band (397.0 nm) of cerium(IV) bis(porphyrinate) was observed (Figure 1 and Figure S2); these changes are consistent with those observed from studies of other porphyrinatozinc–amine coordination systems.[10] We estimated the stoichiometry of the complex formed between DABCO and PorZn·DD (PorZn·DD = 20 μM) from molar ratio plots, which clearly indicated the formation of a 1:2 DABCO/PorZn·DD complex and did not convert to a 1:1 complex, at

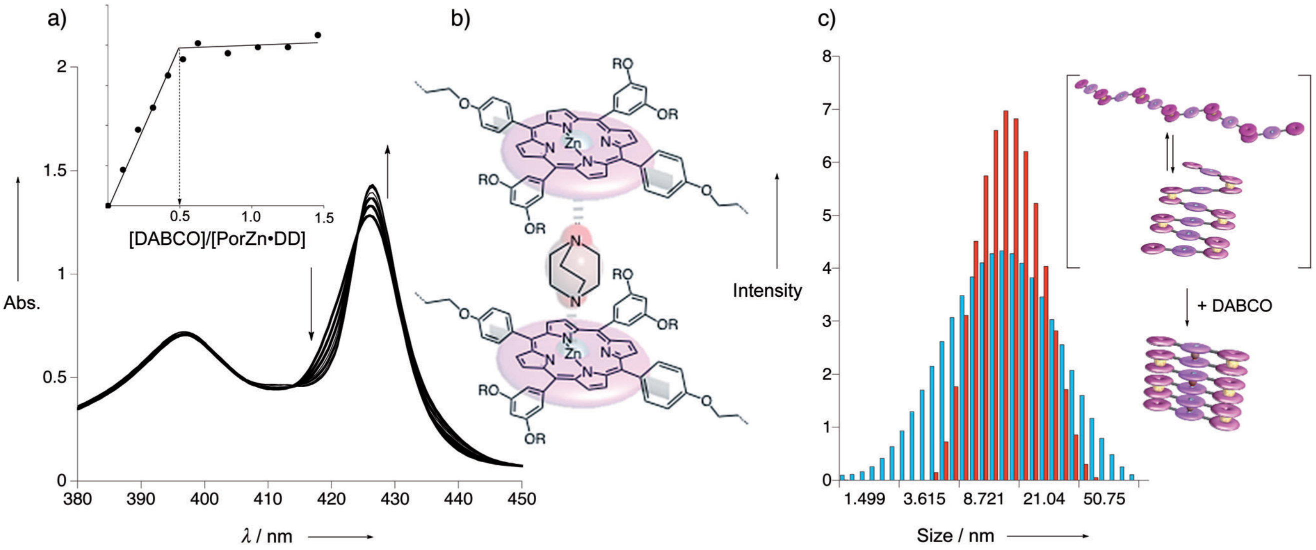

Figure 1. a) UV/Vis spectral changes of poly(PorZn·DD) upon addition of DABCO (0–28 μM) in chloroform at 25 °C ([PorZn·DD] = 20 μM, path length is 1 mm). Inset: A Plot of the absorbance at 561.5 nm of poly(PorZn·DD) versus [DABCO]/[PorZn·DD]. b) Schematic illustration of the poly(PorZn·DD)·DABCO complex. c) Hydrodynamic diameters of poly(PorZn·DD) with (red) and without (blue) DABCO analyzed by dynamic light scattering. The contracted form (calculated to be 7×6×1.6 nm in size, see Figure S7) retains some rotational freedom; we infer this would be one of the reasons why the average size did not change greatly.

least up to [DABCO] = 30 μM (even at a lower concentration of [PorZn·DD] = 1.0 μM corresponding to [poly(PorZn·DD)] = ca. 0.1 μM). A plot of the absorbance at 425.5 nm versus [DABCO]/[PorZn·DD] shows a linear relationship and is saturated at the ratio of 0.5 ($\log K_{ass}$ is assumed to be greater than seven), suggesting a 1:2 stoichiometry of DABCO and PorZn·DD (Figure S3). Neither piperidine nor 1,3-di(4-piperidyl)propane, which do not fit the folding geometry, showed such high affinities toward poly(PorZn·DD). The high association of DABCO suggests that the binding of DABCO to poly(PorZn·DD) most likely occurs intramolecularly, although interpolymer cross-linking or ladder formation[11] of polymers cannot be fully ruled out. We deduce, however, that full ladder formation rarely happens because it is difficult to construct a structural model for the ladder between DABCO and two poly(PorZn·DD)s owing to the steric hindrance between the DD moieties within a polymer chain.

The folding structures of poly(PorZn·DD) induced by DABCO binding in solution were further investigated using dynamic light scattering (DLS), atomic force microscopy (AFM), and TEM. The average size of poly(PorZn·DD) in chloroform at 25 °C was measured to be approximately 12 nm in chloroform ([PorZn·DD] = 20 μM) with a relatively large distribution, probably owing to its polymer structure having intrinsically rotatable joints (Figure 1 c). Upon DABCO addition ([DABCO] = 28 μM), we still observed an average size of ca. 12 nm, however, the size dispersity decreased, and this is consistent with the contraction of poly(PorZn·DD). Judging from the average size of 12 nm in the presence of DABCO, we would assume there is cross-linking or partial ladder formation of the polymers. Figure 2 shows an AFM image of poly(PorZn·DD) spin-coated from a 1.0 μM solution in chloroform, in which the linear- or granular-shaped poly(PorZn·DD) assembly is well dispersed on highly ordered pyrolytic graphite (HOPG), reflecting the larger distribution of the DLS profile. From the height profile we calculate the average height to be 1.4 nm; poly(PorZn·DD) probably lies on HOPG in a monolayer having an edge-on orientation. By mixing with DABCO ([DABCO] = 0.5 μM), instead, we only observed the dot or granular shape for the poly(PorZn·DD)·DABCO composites, which had a height of 1.6 nm (Figure 2 b); this unimolecular height strongly supports the view that the folding processes by the DABCO binding take place in solution to afford the dot morphologies.

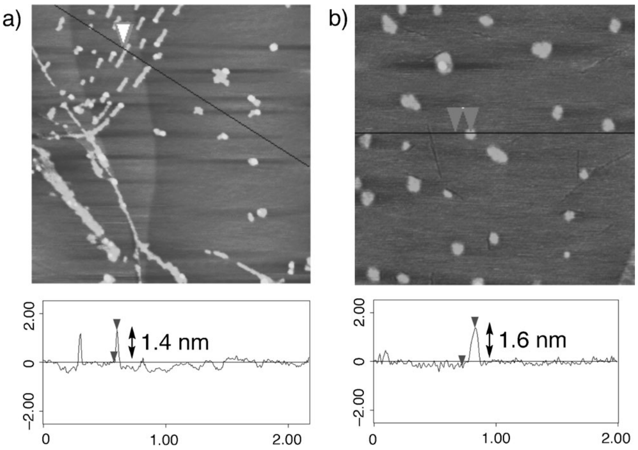

Figure 2. AFM images of poly(PorZn·DD) on HOPG spin-coated from a) a chloroform solution of poly(PorZn·DD) and b) a chloroform solution of a 1:2 mixture of DABCO and PorZn·DD in 2×2 μm.

Electron microscopic images of poly(PorZn·DD) present information regarding how poly(PorZn·DD) is folded and contracted by DABCO. As for the UV/Vis spectroscopy and DLS profile, we prepared a solution of poly(PorZn·DD) ([PorZn·DD] = 1.0 μM) and a solution with the addition of DABCO ([DABCO] = 0.5 μM); we then obtained solution-dip films on a TEM grid without staining. The samples were subjected to TEM. First, we confirmed that poly(PorZn·DD) forms fibrous morphologies that are approximately 10–20 nm in width and several hundred nanometers in length (Figure 3 a and Figure S7); this is probably because bundling of poly(PorZn·DD) occurs during the solution-dip process. Thin fibers can be seen faintly with a length of 50–100 nm on the TEM grid, however the contrast is not strong enough to confirm the width. Interestingly, when DABCO was added to the solution of poly(PorZn·DD) to form poly(PorZn·DD)·DABCO, the fibrous morphology assigned to poly(PorZn·DD) disappeared and we only observed dot structures having dimensions of 10–20 nm (Figure 3 b). Furthermore, an energy dispersive X-ray spectroscopic (EDX) study of poly(PorZn·DD)·DABCO revealed that the dot structure indeed contains cerium (Figure S6). Because the size of the dot morphologies is slightly larger than the calculated structure (Figure S7), we deduce that DABCO binding mainly takes place intramolecularly, however, some cross-linking and partial ladder formation could also occur, as shown in Figure 3 c. Addition of acid to poly(PorZn·DD)·DABCO should induce dissociation of the DABCO because of the formation of $\text{DABCO}\cdot 2\,H^+$; upon protonation with trifluoroacetic acid (TFA), the λ_{max} value of the Soret band for porphrinatozinc in poly-

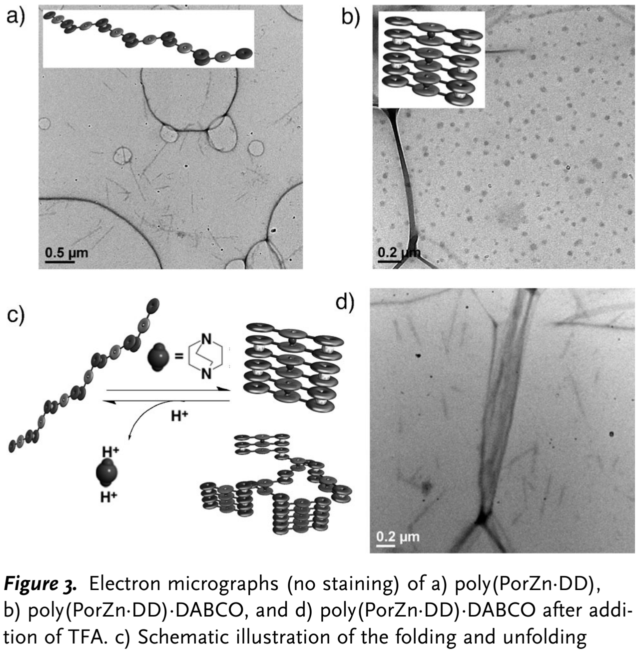

Figure 3. Electron micrographs (no staining) of a) poly(PorZn·DD), b) poly(PorZn·DD)·DABCO, and d) poly(PorZn·DD)·DABCO after addition of TFA. c) Schematic illustration of the folding and unfolding action of poly(PorZn·DD) upon addition of DABCO and then TFA.

(PorZn·DD)·DABCO shifts to a shorter wavelength of 425.5 nm with the same isosbestic points as those observed for the complexation process with DABCO (Figure S5). Eventually, this TFA treatment results in a reversal to uncomplexed poly(PorZn·DD), without demetallation of the porphyrinatozinc or decomposition of the cerium(IV) bis(porphyrinate). Figure 3 d shows a TEM image of the TFA-treated sample (10 equiv. to DABCO) in which once again the fibrous morphologies were the dominant feature. This confirms that DABCO association and dissociation induce the folding and unfolding actions of poly(PorZn·DD) and the resultant morphological changes.

In conclusion, we have successfully synthesized a new porphyrin polymer bearing porphyrinatozinc as the DABCO recognition site and cerium(IV) bis(porphyrinate) as the rotatable joints; successive DABCO binding to poly(PorZn·DD) modulates the distance between the two porphyrinatozinc moities and leads to the folded and contracted conformation. Furthermore, we visualized the morphological changes reflecting folded and unfolded structures by means of AFM and TEM. Such action resembles the pivoting motion of a folding ruler. Further efforts towards installing photoresponsive or redox moieties in addition to this molecular-recognition-based folding process could lead to the generation of a new class of actuating materials. Work along these lines is in progress.

Experimental Section

All starting materials and solvents were purchased from Tokyo Kasei Chemicals or Wako Chemicals and used as received. The ^{1}H NMR spectra were recorded on a Brucker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perceptive Voyager RP MALDI-TOF mass spectrometer and/or a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV/Vis spectra were recorded using Shimadzu UV-2500 PC spectrophotometer. Compound **1** and poly(PorZn·DD) were synthesized according to Scheme S1 and S2 in the Supporting Information. TEM images were acquired using a TECNAI-20 FEI (accelerating voltage: 200 kV). A sample solution was placed on a copper TEM grid upon a carbon support film. The TEM grid was dried under reduced pressure for 6 h prior to TEM observation.

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