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Olefin Metathesis of the Aligned Assemblies of Conjugated Polymers Constructed through Supramolecular Bundling

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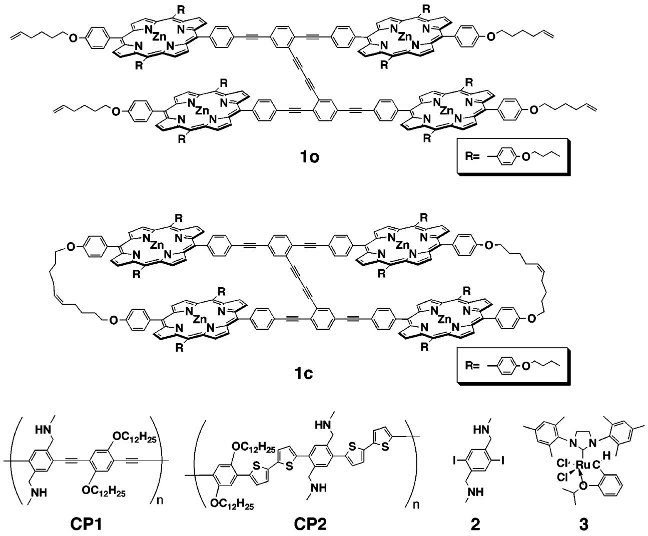
Recently, oriented polymers and/or polymer nanostructures have attracted a large amount of attention. Of particular interest are structures that consist of conjugated polymers (CPs) because of their potential applications as, for example, electrochemical switches, electric devices, and sensors.[1] In addition to supramolecular assembly schemes,[2] several approaches[3,4] have been utilized to align conjugated polymers, leading to some unprecedented and fascinating photophysical functions. From a supramolecular standpoint, we recently proposed a supramolecular bundling approach toward the alignment of CPs. In this approach, aligner molecules, which elicit positive homotropic allosterism, are used to bundle, noncovalently splice, and align CPs to form ordered assemblies of CPs.[5] This process can be regarded as two-dimensional "supramolecular polymerization" utilizing a cooperative function of the bundling molecules (aligners). These unique assemblies, however, are constructed under thermodynamic control and therefore dissociated by the attenuation of the assemblies of CPs. It occurred to us that our recent finding regarding "template-assisted olefin metathesis facilitated by allostery" [6] of compound **1o** could be applied in order to stabilize these CP assemblies from a temporary architecture to a permanent one.[7]

In this paper, we report that the ordered structures constructed from an aligner molecule **1o**[6] and CPs[5] were efficiently converted into the poly-pseudo-rotaxane structures[8] by the template-assisted ring-closing olefin metathesis (RCM)[9] of olefinic groups at the peripheral positions of **1o** (Scheme 1, Figure 1). The poly-pseudo-rotaxane structures were stabilized enough to permit the separation of the crystalline ordered assemblies of **CP** by size exclusion chromatography (SEC) and the preservation of the sheet morphologies even after the acid treatment. It was also confirmed that the morphologies and the periodicities of the assemblies were maintained after the retrieving treatments by SEC.

Scheme 1. Chemical Structures of the Aligner Molecules and Conjugated Polymers Used in This Study



As previously reported,[6] compound **2**, the monomer unit of **CP1**, was cooperatively recognized by **1o** with a Hill coefficient of 1.8 and association constants of $K_1 = 4.7 \times 10^5$ M^{-1} and $K_2 = 3.6 \times 10^5$ M^{-1}. The complexation between **1o** (2.0 μM) and **CP1** was confirmed by a UV−vis spectroscopic method as evidenced by the fact that the bathochromic shifts in the Soret and Q-bands (from 557.0 and 599.0 to 564.0 and 607.0 nm, respectively) are similar to those observed for **2** (Figure S1, Supporting Information) and the recent related system.[5] One can expect, therefore, that the diamine moieties in **CP1** would become juxtaposed and aligned by the clefts of the porphyrinatozinc units in **1o** to form the aligned superstructures. Thus, we applied this system to the template olefin metathesis to convert them into poly-pseudo-rotaxane structures. Compound **1o** (0.57 mM) was complexed with **CP1** ([**CP1**$_{\text{unit}}$] = 8.6 mM) in chloroform-*d* at 25 °C for 24 h because the size of CP assemblies is highly dependent on not only the mixing ratio between **1o** and **CP1** but also the aging period in solution;[5] we confirmed by UV−vis spectroscopy that **1o**·(diamine unit in **CP1**)$_2$ complex is formed quantitatively and that no spectral change is induced during the aging period. Hoveyda−Grubbs catalyst **3** (60 mol % with respect to **1o**; see Supporting Information) was then added to the solution, and the resulting mixture was warmed at 60 °C with microwave irradiation[10] (110 W, 20 bar). We estimated, from the time course of the reaction monitored by ^{1}H NMR, that the conversion of terminal olefins reaches ca. 70% after 10 h; such a high conversion in the RCM reaction of the supramolecular assembiles is probably attributed to the bundled **CP1**s acting as templates.[6]

The reaction mixture was subjected to SEC (Bio-Beads SX-1, 10 × 600 mm, chloroform) to separate the assembly immobilized as poly-pseudo-rotaxanes and to remove the catalyst. We collected three fractions, and each fraction was analyzed by UV−vis spectroscopy (Figure S2). The UV−vis spectrum in Figure S2 indicated that the first fraction contains **1**·(diamine unit in **CP1**)$_2$ complex, which is assigned to the immobilized assemblies by RCM reaction; the second and the third fractions contain **1** (**1o** and **1c**) and **CP1**, respectively. Analysis of the absorbance at 387 nm for **CP1** and the absorbance at 599 nm for **1** in the first fraction allows us to estimate the ratio of [diamine unit in **CP1**] and [**1**] in these supramolecular assemblies to be 14.5:1, which is almost the same as the mixing ratio (15:1).

The electron micrographs of the first fraction provide information regarding how the immobilized assemblies maintain the structure constructed from **1** and **CP1**. We prepared solution-cast films from the first fraction on a transition electron microscopy (TEM) grid

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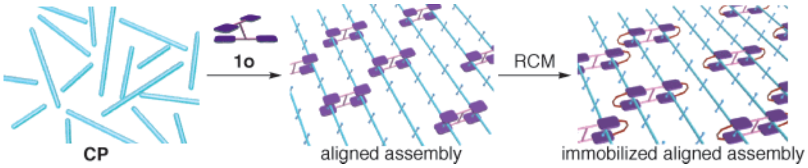

Figure 1. Schematic illustration for the alignment of the conjugated polymer **CP** mediated by **1o** and the conversion to the poly-pseudo-rotaxane structures. The first polymer binding to the porphyrinatozinc cleft preorganizes the second cleft, which has an even higher affinity toward the second polymer due to the allosteric effect.[5] The conjugated polymers are expected to be juxtaposed to each other to form aligned assemblies and then to be immobilized by RCM reaction.

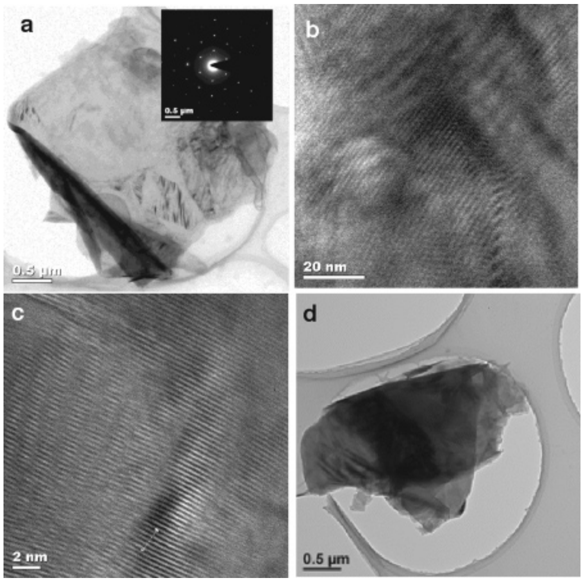

Figure 2. Electron micrographs (no staining) of conjugated polymers aligned and immobilized by **1**. (a) TEM image of the immobilized **1·CP1** assemblies. Inset: Electron diffraction pattern of (a), indicating that the immobilized assemblies show the crystalline nature. (b) HRTEM image of **1·CP1** assemblies consisting of dark and light stripes. The periodicity between the dark lines is 2.0 nm. (c) HRTEM image of the immobilized **CP·1** assemblies having 0.2 nm periodicity. (d) TEM image of the immobilized **CP·1** assemblies after TFA treatment.

without staining. In the TEM micrograph, we could observe the immobilized assemblies piled-up as micrometer-size crystalline sheets (Figures 2a and S3) with a multi-lamellar morphology (Figure 2b,c) having periodicities of 2.0 and 0.2 nm. These periodicities, consisting of dark layers, are identical to those we recently reported;[5] the dark regions observed in the TEM images of the assembly are assigned to the domains containing ordered π-stacking layers and/or the heaviest atom (Zn) in **1**. It is important to note that the RCM reaction did not affect the periodicities and the resultant two-dimensional sheet morphologies. The addition of trifluoroacetic acid (TFA) or HCl aqueous solution to a chloroform solution of the immobilized assemblies, which should induce protonation of the amino groups in **CP1** to produce **CP1**·nH$^+$ units and demetalation of **1**, did not alter the overall morphologies (Figures 2d and S4). We confirmed, from the appearance of the UV−vis absorption spectrum assignable to protopnated **1** **(1**·2H$^+$**)**, that all porphyrins of the **1**·(diamine unit in **CP1**)$_2$ in the assemblies are dissociated (Figure S5). These results indicate that the crystalline sheet contains the poly-pseudo-rotaxane structures generated by the RCM reaction.

The approach we present in this paper is more generally applicable to polymers bearing coordinating moieties. For example, polymer **CP2** and poly(4-vinylpyridine) (M_w = 60 000) also formed complexes with **1o** in a manner similar to that occurring between **1o** and **CP1** (Figures S6 and S7). Further studies on the use of the immobilized and aligned supramolecular assemblies will be reported in the future.

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Supporting Information Available: Experimental details and spectral data of the immobilized assemblies. This material is available free of charge via the Internet at http://pubs.acs.org.

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