Toward the alignment of conjugated polymers into anisotropically-ordered structure

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Recently, oriented polymers and/or polymer nanostructures have attracted a large amount of attention for their potential applications as, for example, electric devices such as FETs, LEDs, photovoltaic cells, and so forth. Besides several methods for organizing conjugated polymers, we have recently reported a novel concept for the alignment of conjugated polymers through the action of supramolecular bundling molecules. We here introduce two different approaches for aligning conjugated polymers; one is to utilize a crosslinking molecule ('aligner'), and the other is to use a twining polymer ('twimer') for organizing conjugated polymers. Aligner binds and crosslinks conjugated polymers in a positive allosteric manner to form organized supramolecular assemblies in solution. The cast film from the solution resulted in a crystalline sheet with periodicities corresponding to the distance between polymers, confirmed by several microscopic studies. On the other hand, twimer helically twins around the conjugated polymers to form one-dimensional (1D) complex in solution and the complex self-assembles into two-dimensionally (2D) aligned structure in drying process. The resulting film of conjugated polymer–twimer composites gave also highly ordered, crystalline structure. The principal results obtained both in solution and solid states and their future perspectives are discussed here.

Introduction

Orientation of π-conjugated systems

π-Conjugated molecules have been attracted a large amount of attention for their potential applications as molecular devices substitute for inorganic material.[1] Many attempts for fabrication of π-conjugated-molecule-based electronic devices, for example, field-effect transistors (FET)s,[2] light-emitting diodes (LED)s,[3] photovoltaic cells[4] and so forth, have been reported so far. In these systems, the orientation of π-conjugated molecules is an important factor for a high performance of devices because intermolecular electronic coupling significantly affects the performance efficiency. It is known that the alignment of conjugated polymers influences on the mobility in organic transistors,[5] and in addition, anisotropic electronic coupling is equally important for a macroscopic performance of electronic devices. Therefore, oriented π-conjugated polymers as well as oligomers have been widely studied recently.

Supramolecular self-assembly schemes of π-conjugated polymers have been reported, where intermolecular aggregations were regulated by, for example, solvent,[6] temperature[7] and host–guest interaction.[8] Other methods for aligning conjugated polymers include the use of metastable states enforced by rubbing, liquid-crystalline phases, Langmuir monolayers at the air–water interface and incorporation into prealigned host

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matrixes. Yoshino *et al.*[9] applied unidirectional rubbing to a poly(2,5-dinonyloxy-1,4-phenylene vinylene: NO-PPV) thin film spincoated on an ITO coated glass substrate, for the creation of an emissive layer of OLED. The rubbed NO-PPV film displayed polarized electroluminescence and the efficient dichroic electroluminescent light was observed with the electron-transporting/hole-blocking layer.[9] Swager *et al.*[10] mixed poly(phenylene vinylene) and poly(phenylene ethynylene) with rigid triptycene side chains in nematic liquid crystal solutions. To minimize the free volume, the polymers were aligned in the parallel direction of LC molecules. The anisotropic emission of the polymer film could be redirected by external electric field.[10] Akagi *et al.*[11] introduced liquid crystalline groups into poly(mono-substituted acetylene) side chains. The polymer chains aligned by external magnetic field showed the electrical anisotropy ranging $2 \sim 10^5$.[11] Swager *et al.*[12] showed conformational changes of surfactant poly(phenylene ethynylene) monolayers formed at the air–water interface. Their conformation and spatial arrangements were converted between face-on, zipper and edge-on structures depending on the chemical structures of polymers and the surface pressure.[12] Weder *et al.*[13] incorporated poly(2,5-dialkoxy-1,4-phenylene ethynylene) into ultra-high-molecular-weight polyethylene. The cast film from xylene solution of the mixture followed by drawing resulted in the uniaxially oriented PL films. In combination with randomly orientated sensitizers, which showed the isotropic absorption leading to the efficient energy transfer to oriented polymers, the emission from the film resulted in highly efficient and high degree of polarization.[13]

In addition to these macromolecular and supramolecular approaches, we here introduce a novel approach for aligning conjugated polymers utilizing supramolecular bundling scheme. This approach has a great advantage that the well-ordered supramolecular structures can be readily obtained by just mixing two components in homogeneous solution. The results obtained so far and the future perspectives are discussed.

Design scheme

As outlined above, anisotropic alignment of conjugated polymers (CPs) has been achieved to a certain degree by previously reported methods. The orientation of conjugated polymers, however, relies on the metastable states of CP themselves and/or the nature of host matrixes so far. From a supramolecular standpoint, we recently reported a supramolecular bundling approach toward the alignment of CPs.[14–16] One approach is to utilize a crosslinking molecule ('aligner') to bundle CPs into organized structure.[14,15] The other one is to use a twining polymer ('twimer'), which twines around CPs and then self-assembles into bundled architectures (Fig. 1).[16]

In animal cells, it is known that the bundling proteins interact with one-dimensional (1D) actin filaments in high affinity to elicit the formation of actin bundles that play an important role for muscle contraction. The bundling proteins possess more than two interactive modules for crosslinking actin filaments; their distinct properties determine the type of assembly (Fig. 2).[17] It is reasonable to expect that we may utilize this kind of crosslinking molecules, which possess several binding modules, to organize 1D polymers. In addition, we applied a dynamic molecular recognition concept, positive homotropic allosterism, to this system. In positive allosteric systems, the recognition of the first guest molecule facilitates the subsequent binding of guest(s);[18,19] for the

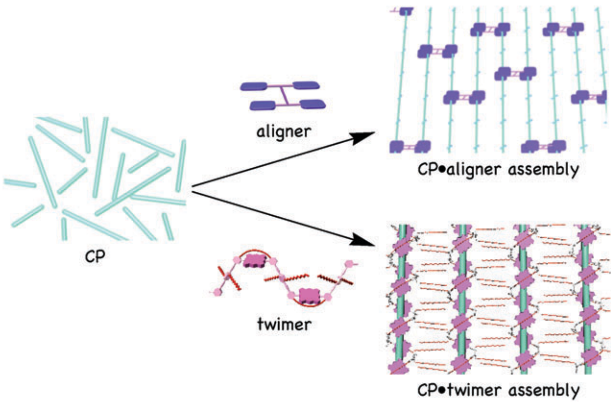


Fig. 1 Schematic illustration of the alignment of conjugated polymer CP mediated by aligner (top) and twimer (bottom).

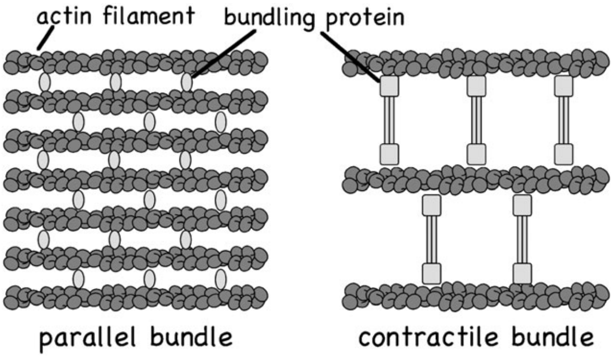


Fig. 2 Schematic illustration for the formation of two types of actin filament bundle (left: actin filament and fimbrin, right: actin filament and α-actinin). The spacing and the arrangement of actin filament binding sites in the bundling protein determine the type of assembly.

binding of CPs, the first CP binding event enhances the affinity of the second one to form aligned supramolecular assemblies. Such a process would be indispensable to avoid the formation of random, disordered assemblies (Fig. 3). This binding and bundling of CPs by aligners can be regarded as "supramolecular 2D polymerization" of 1D conjugated polymer with the aid of positive allosterism.

The other system, utilizing twimers, leads to sequential alignment of CPs.[16] Twimer, which is a 1D polymer with interactive moieties for CP binding at regular intervals, helically twins around (or wraps) the CPs in solution. Twimers are designed to possess aggregative moieties on their either side when they include CPs in their internal spaces; the resulting 1D complexes tend to self-assemble into 2D aligned structure, rather than a 3D structure, in the drying process (Fig. 4).[20]

We designed aligners and twimers based on the porphyrinatozinc moiety, which is often used for its facility of both spectroscopic and microscopic studies and for its functionality as π-conjugated molecule. Amino-functionalized conjugated polymers CP1, CP2 and CP3 were used because the coordination bonds formed between porphyrinatozinc and amine derivatives have high affinity and the distinct bonding geometry of these species (Scheme 1). Aligners **1**, **2** and **3** are porphyrinatozinc derivatives, which have two and three recognition sites for diamine guest molecules. Aligners can change its conformation by rotation around their axes (the butadiyne units for **1** and **2** and the ethynylene bridges for **3**), which leads to cooperative recognition of diamines by cofacially aligned porphyrinatozinc tweezers.[21] Aligner **2** has olefinic moieties at its peripheral position, and can be converted into bicyclic structure by ring-closing olefin metathesis (RCM). We recently reported this RCM reaction was

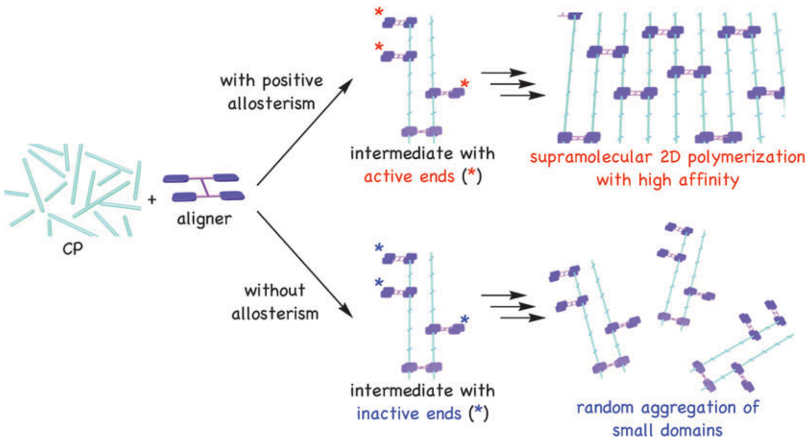


Fig. 3 Schematic representation how positive allosterism facilitates the formation of supramolecular assembly. (top) In a positive allosteric system, the first polymer binding event to the porphyrinatozinc cleft predisposes the second creft (denoted by the red asterisk) which results in an even higher affinity toward the second polymer. The conjugated polymers are expected to form aligned assemblies. (bottom) Without allosterism, the first polymer binding event does not enhance the second binding affinity (denoted by the blue asterisk), leading to formation of random aggregation of small domains, instead of large aligned assemblies.

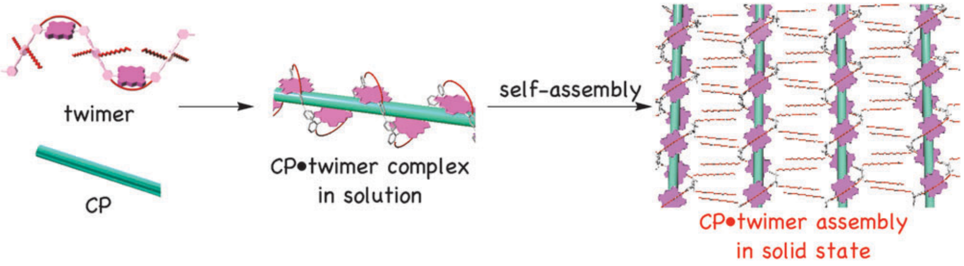
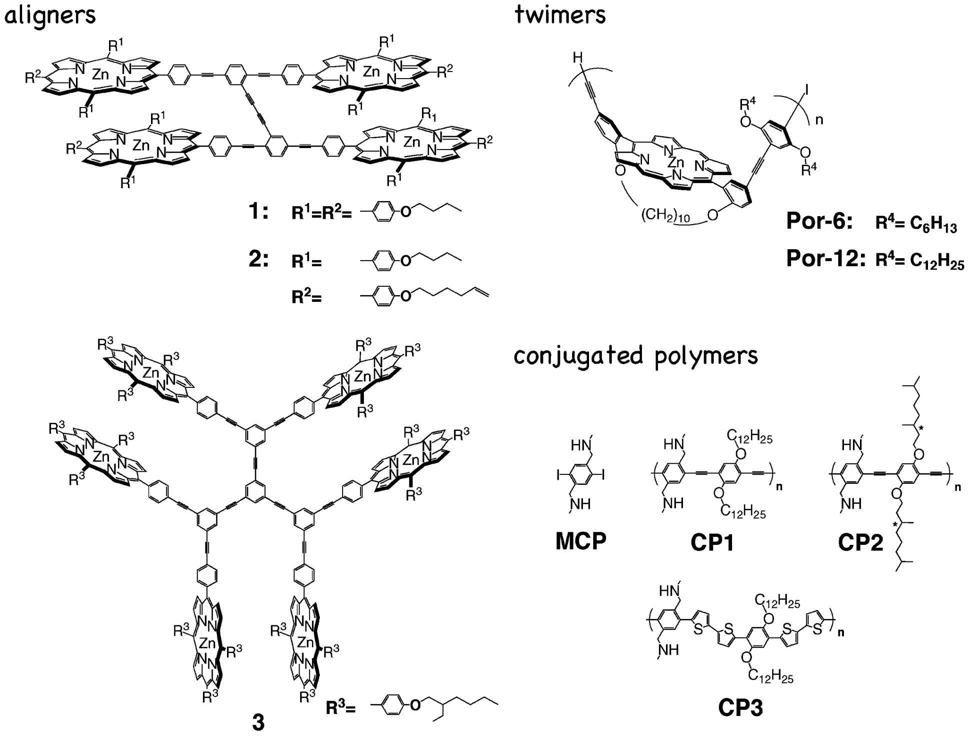


Fig. 4 Schematic representation of sequential alignment of conjugated polymers by twimer. CPs entwined by twimers tend to self-assemble into an aligned assembly in the drying process with the aid of the peripheral alkyl chains, aggregative moieties.



Scheme 1 Chemical structures of aligner and twimer molecules and conjugated polymers used in this study.

facilitated by addition of the template molecule to the predisposed reaction sites.[22] The RCM reaction was expected to proceed more efficiently after complexation with CPs as templates; the conversion to the poly-pseudo-rotaxane structures should stabilize the CP assemblies (Fig. 5).[15]

Twimers **Por-12** and **Por-6** are porphyrinatozinc polymers linked by phenyleneethynylene spacers.[16] In their energy-minimized states, these twimers tend to form a helical structure in which a coordinative open face of the zinc porphyrin unit (but not a non-coordinative face covered by a decamethylene strap[23]) is always turned inwards so that the central metal atom can interact with the included CP. We expected, therefore, that CPs possessing appropriate ligand groups, *e.g.*, CP1 and CP2 would become included within this helical strand through coordination with the porphyrinatozinc. The R groups in the twimers were introduced to control the spacing between Por–CP composites; the van der Waals interaction between these alkyl chains might be a major driving force of 2D organization of 1D Por–CP complexes in the drying process.

Aligner system[14,15]

The first method for aligning CPs is to use aligners, which bind and bundle CPs into the organized structure. Aligners were designed based on cofacial porphyrinatozinc moieties so that they could sandwich diamino-functionalized polymers within the clefts by coordination bonds with high affinity. In addition, aligners recognize diamino-functionalized CPs in a highly cooperative manner; CPs should be bundled in a parallel manner because of the cofacially aligned porphyrinatozinc moieties of aligners. The cooperative binding behaviors of

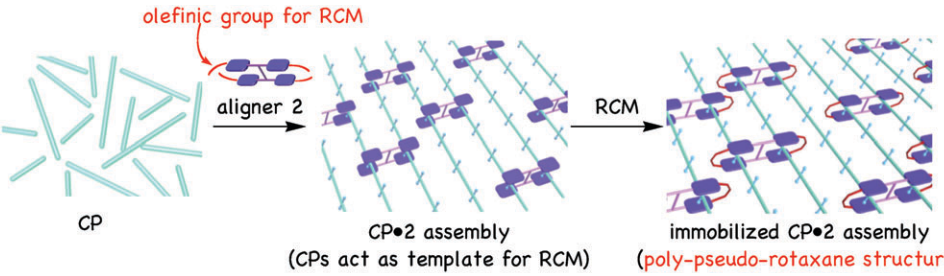


Fig. 5 Schematic illustration for the alignment and conversion of the CP · 2 assemblies into the poly-pseudo-rotaxane structures. The bundled CPs act as template molecules, which leads efficient RCM reaction.

aligners with CPs and the structural studies of resulting assemblies are discussed below.

Complexation behaviors between aligners and CPs in solution

We first observed the complexation behaviors between aligners and CPs by UV-vis spectroscopic method. Aligners are designed to possess several coequal binding sites mediated by rotational axes that play a role of binding information transducers; the first guest binding event suppresses the rotational freedom of the residual porphyrin tweezers to elicit the positive homotropic allosterism.[18,19] This positive homotropic allosterism during the binding of CPs plays a significant role in organizing the CPs into aligned, rather than random, assemblies; in the CP bundling process, the binding of the first CP to an aligner facilitates the second binding, which results in the ready formation of aligned assemblies. Aligners **1** and **2** have two recognition sites of diamino-functionalized CPs and form 1 : 2 complexes through coordination bonds between porphyrinatozinc and diamine moieties. Aligner **3** forms 1 : 3 complex with CPs by the same scheme as **1** or **2**.

To confirm the cooperativity in the binding process between CPs and **1**, we first used MCP, the monomer analogue of CPs, as a guest molecule for aligners. We noted the formation of the [**1** · MCP] complex in $CHCl_3$ from the bathochromic shifts in the Soret band and Q bands of **1** in the UV-vis absorption spectra upon the successive addition of MCP. The cooperative guest-binding process can be analyzed according to the Hill equation:[18] $\log(y/(1-y)) = n\log[\mathrm{guest}] + \log K$, where K and n are the association constant and Hill coefficient, respectively, and $y = K/([\mathrm{guest}]^{-n} + K)$. From the slope and the intercept of the linear plots, we obtained $\log K = 10.2$ ([**1** · $(MCP)_2$] complex) and $n = 1.9$. The plot was reanalyzed by a nonlinear least-squares method, assuming a two-step binding mechanism with K_1 and K_2. The K_1 and K_2 values were evaluated to be 1.6×10^5 and 3.0×10^6, respectively. From these Hill plot and nonlinear least-squares method analyses, it was found that **1** binds MCP in an allosteric fashion to form a 1 : 2 [**1** · $(MCP)_2$] complex. From this high affinity and cooperativity (in the binding of MCP with aligner), we inferred that the binding of CPs with aligners to become aligned by the clefts in the porphyrinatozinc moieties in a positive allosteric manner. In fact, the addition of CP1 to a solution of **1** in $CHCl_3$ resulted in the similar bathochromic shifts in the Soret band and Q bands as those observed for **1** upon the addition of MCP.

The complexation and bundling behaviors between CP1 and aligners were also supported by fluorescence spectroscopic studies. The emission intensity of CP1 in $CHCl_3$ decreased, without a change in its shape, when it was mixed with **1**. This phenomenon is probably due to the efficient energy transfer from CP1 to **1** within the complex because the emission wavelength of CP1 overlaps considerably with the absorption band of **1**.

Structural studies of CP · aligner assemblies

To obtain the insight into morphological properties of the CP · aligner complexes, we further investigated if the

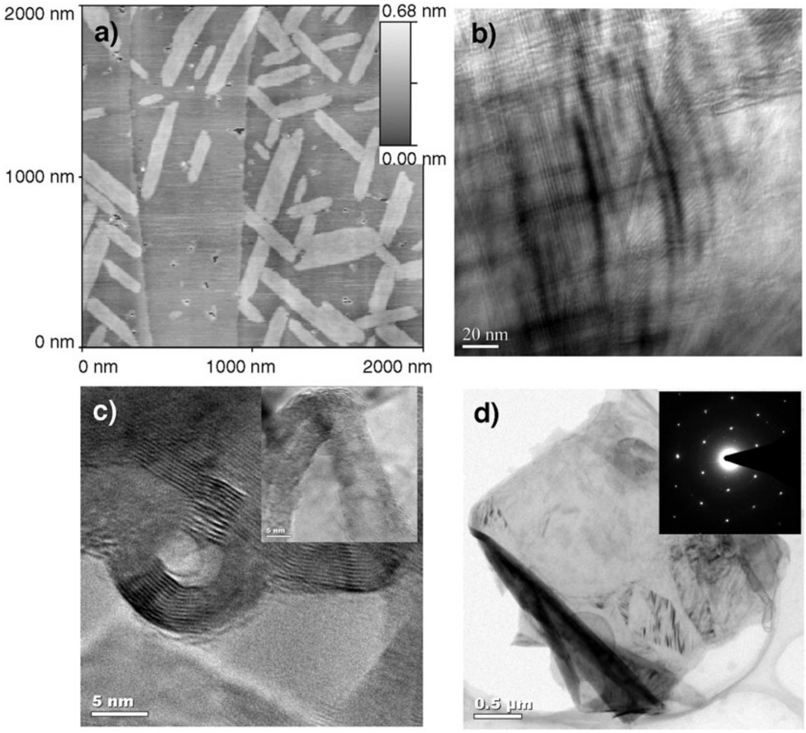


Fig. 6 (a) Representative AFM images of [**1** · CP1] assemblies grown up in solution of $CHCl_3$ onto HOPG. (b) A TEM image of aligned [**1** · CP1] assemblies ([**1**] = 0.07 μM, [$CP1_{unit}$] = 1.2 μM) consisting of dark and light stripes. (c) A HRTEM image of [**3** · CP1] assemblies ([**3**] = 0.1 μM, [$CP1_{unit}$] = 1.4 μM) displaying multi-walled tubular and lamellar contrasts. The image in the inset displays a multi-walled tube that features a bent structure from the back to the front. (d) HRTEM image of the immobilized [**2** · CP1] assemblies. Inset: electron diffraction pattern of (d), indicating that the immobilized assemblies show the crystalline nature.

supramolecular polymer bundles are maintained in the solid state by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM). Fig. 6a displays an AFM image of CP1 mixed with **1**, in which the assemblies are well dispersed in a rectangular shape on highly oriented pyrolytic graphite (HOPG). The observed area of the overall [**1** · CP1] assembly is a 20–25-fold larger homothetic shape, though the height is scarcely changed, than that observed for CP1 itself. Given this two-dimensional (2D)-polymerization of CP1, **1** must bundle with CP1 to form such aligned supramolecular assemblies as a solid-state morphology. Interestingly, the polymer bundling and splicing caused by **1** are highly dependent upon the mixing ratio between CP1 and **1** and the aging period in solution; a higher molar ratio of **1** decreased the size of the assemblies and longer aging of the [**1** · CP1] complex resulted in further growth of three-dimensional (3D) assemblies. The findings suggest that the dimensions of the superstructure are readily controllable by changing the mixing ratio between CP1 and **1** or the aging time of the complex. Porphyrinatozinc hexamer **3** also aligned CP1 into sheet-like assemblies that had an average height of 0.3 nm and 9–16-fold larger areas than that of CP1 itself. These AFM analyses indicate that the bundling and splicing processes caused by **1** in solution take place thermodynamically to form initially 2D and then 3D aligned structures.

The electron micrograph images of the [**1** · CP1] complex provide information regarding how aligners arrange the CP1. A HRTEM image of the assembly of CP1 and **1** was observed as a crystalline sheet, which features the multilamellar morphology with a periodicity of 2.0 nm over a 200 nm wide distance (Fig. 6b). The period of 2.0 nm corresponds to the distance between CP1 units when they are bundled in a parallel manner (see Fig. 7). We believe that the dark region observed in the HRTEM image of the assembly of CP1 and **1** is ascribed to the domain that contains ordered π-stacked layers and/or the heaviest atom (Zn) in **1**. CP2 with chiral side chains is also bound to **1** in a manner similar to that of CP1 and **1**, and the HRTEM image of the aligned assemblies constructed from CP2 and **1** represents the kagomé lattice and triangular grid pattern with 0.8 nm periodicity dark contrast regions. The differences between the contrast patterns of CP1 (lamellar) and CP2 (kagomé lattice) might arise from the orientation of **1** in the assemblies being affected differently between the alkyl chains of CP1 and CP2. Fig. 6c displays the supramolecular assemblies formed from CP1 and **3**, in which we observe unique supramolecular assemblies that possess both lamellar and multi-walled tubular contrasts. The fact that the dark periodicities of the lamellar and multiwalled tubular assemblies are both 0.35 nm indicates that these assemblies are both constructed from the same structural unit. From these TEM and HRTEM analyses, we supposed that aligner assembles CPs parallel to each other in its clefts to form the highly ordered structures that can be affected by both the geometry of aligner and the chemical structures of CPs.

Immobilization of the assembly

As discussed above, we proposed a new methodology for aligning CPs utilizing aligners and the resultant assemblies were found to be crystalline sheets with the periodicity corresponding to the distance of CPs. These supramolecular assemblies, however, are dissociated by the attenuation of the assemblies. We sought to immobilize the resulting CP assemblies to convert them into the permanent one. Aligner **2** possessing olefinic groups at the peripheral positions would lead the stabilization of the CP assemblies *via* the formation of pseudo-rotaxane structures after the RCM reaction.

The RCM reaction of the supramolecular [**2** · CP1] assemblies successfully proceeded, where the bundled CP1s are expected to act as templates (Fig. 5). The resultant polypseudo-rotaxane structures were stabilized enough to permit the separation of the assemblies of CP1 by size exclusion chromatography (SEC) (Fig. 8). We observed micro-metre size crystalline sheets in the HRTEM images of immobilized [**2** · CP1] complex (Fig. 6d). The multilamellar morphology with a periodicity of 2.0 nm is identical to that obtained for [**1** · CP1] assembly. Thus, RCM reaction affected neither the ratio of components nor the resultant sheet morphologies.

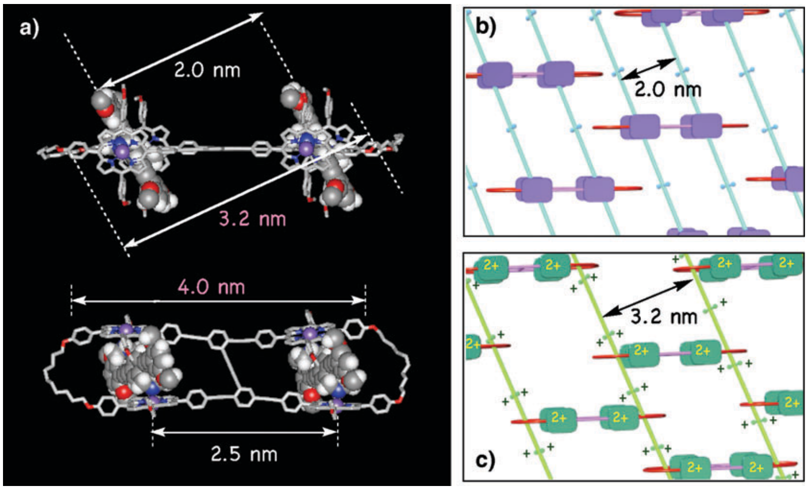


Fig. 7 (a) The energy minimized structure of immobilized [**2** · CP1] complex. Schematic representation of how (b) **2** might align CP1 (c) and how [**2** · CP1] assembly might change its periodicity.

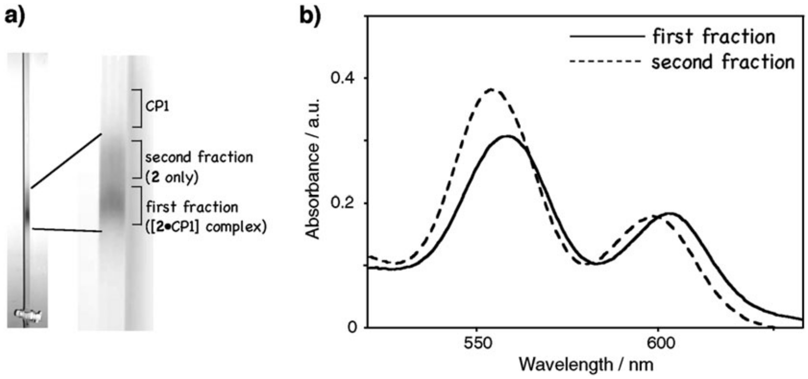


Fig. 8 (a) A photograph of SEC of the immobilized [**2** · CP1] assemblies. (b) UV-Vis spectra for the first and the second fraction in $CHCl_3$. The first fraction contains the [**2** · CP1] complex, which should be the immobilized assemblies by RCM reaction. The second fraction contains unreacted and/or uncomplexed **2**. (Reproduced with permission from ref. 15. Copyright 2006 American Chemical Society.)

CP3, poly(phenylenebithienylene) with diamine groups as interaction moieties, could also be aligned by **2** by the same scheme as CP1.

In our system, supramolecular CP assemblies are constructed through coordination bonds between aligners and CPs. Without RCM reaction, the addition of HCl aqueous solution to a chloroform solution should induce protonation of the amino groups in CP1 to produce CP1 · nH$^+$ units and demetalation of **2**. These reactions lead to the collapse of the [**2** · CP1] assemblies. The immobilized [**2** · CP1] assemblies by the RCM reaction in $CHCl_3$ remained as crystalline sheets even after the addition of HCl aqueous solution or trifluoroacetic acid (TFA), wherein all porphyrins of the [**2** · CP1] assemblies were protonated. The coordination bonds between porphyrinatozinc and diamine moieties of CP1 were no longer formed, and CP1 was bound to **2** only through steric effects; the poly-pseudo-rotaxane structures generated by RCM reaction are oparative to stabilize the assemblies under such conditions. The assemblies were observed as multilamellar morphologies with a periodicity of 3.3 nm, that was slightly expanded compared with that observed before the protonation. We estimate that the distance between CP1s is maximized to reduce the electrostatic repulsion because CP1 could move inside the clefts formed by RCM reaction of **2**. Since the distance from one end to the other end of **2** is *ca.* 4.0 nm, the distance between CP1s becomes *ca.* 3.2 nm when CP1s are complexed with **2** at the same tilt as that of [**2** · CP1] complex with coordination bond (Fig. 7c).

Twimer system[16]

Another approach for aligning CPs is to utilize twining polymers (twimers) that act as helical 'hosts' that would twine around and include within a single CP. Furthermore, we expected these 'hosts' to integrate chromogenic groups that could mediate electron or energy transfer to or from the CP. Taking these factors into consideration, we designed the oligomeric porphyrins **Por-12** and **Por-6** as twimers. These twimers tend to form helical structures in which a coordinative open face of the zincporphyrin unit is always turned inwards so that the central metal atom can interact with the included CP; a decamethylene group covers a non-coordinative face.[23] We expected that a CP with appropriate ligand groups, such as CP1 and CP2, would become included within this helical strand through coordination with the porphyrinatozinc. The R groups in the Por oligomers were introduced to increase their solubility in organic solvents and to control the spacing between Por/CP composites. We will discuss this system later.

Complexation behaviors between twimers and CPs in solution

UV-Vis absorption spectra of the [**Por-12** · CP1] complexes were measured in $CDCl_3$ at 25 °C.[24] The shifts to longer wavelengths for both the Soret band and Q bands of **Por-12** with isosbestic points occurred, indicating that the amino groups in CP1 coordinated to the porphyrinatozinc of **Por-12**. We confirmed the ratio between [diamino units in CP1] and [porphyrin units in **Por-12**] to be 1 : 1 from molar ratio plot, which suggests that only one of the two amino groups interacts with each porphyrin unit; that is, a single-stranded **Por-12** oligomer could wrap around a single CP1 chain, probably because the formation of a doubly stranded **Por-12**, in which all of the amino groups interact with porphyrin units, is sterically too crowded. In fluorescence spectra of **Por-12** and CP1 in $CDCl_3$, we observed that the emission intensity of CP1 was quenched upon increasing the **Por-12** concentration. This finding clearly indicates that the **Por-12** and CP1 units interact and that efficient energy transfer from CP1 to **Por-12** probably occurs in their complex.

Structural studies of CP · twimer assembly

We examined solid-state morphologies of [**Por-12** · CP1] assemblies using confocal laser scan microscopy (CLSM), polarized optical microscopy (POM) and HRTEM. We subjected a solution-cast film of the [**Por-12** · CP1] composite, constructed on an indium tin oxide (ITO) glass, for POM observation. The 2D assemblies with dimensions greater than 50 μm^2 were observed, and these assemblies exhibited a bright pattern, even between crossed polarizers. These findings indicate that **Por-12** and CP1 assemble into a highly ordered crystalline structure over the micron scale on the ITO glass. When we photoexcited a single large sheet-like aggregate (20 × 120 μm) at 354 nm, the CLSM image displays blue CP1 emission

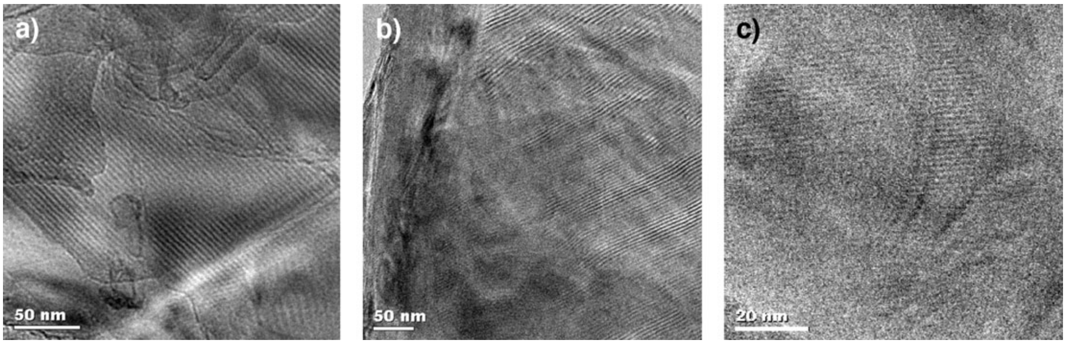


Fig. 9 Electron micrographs (no staining) of aggregates of the Por–CP composites. (a) HRTEM image of the [**Por-12**·CP1] composites that display dark and light stripes. The periodicity between the dark stripes is 4.0 nm. (b) HRTEM image of the [**Por-12**·CP2] composites. The periodicity between the dark stripes is 4.0 nm. (c) HRTEM image of the [**Por-6**·CP2] composites. The periodicity of the dark stripes is 2.7 nm. (Reproduced with permission from ref. 16. Copyright 2006 Wiley-VCH.)

(400–440 nm) and red **Por-12** emission (560–640 nm) in the same morphological domain. It is clear, therefore, that the micron-sized superstructure was assembled through interactions between **Por-12** and CP1.

In the HRTEM images of the aggregate obtained from the [**Por-12**·CP1] composite, several micro-meter size sheets with a 4.0 nm periodicity of the dark stripes, over a distance of a few hundred nanometers, were observed (Fig. 9a). Based on the results obtained from the [**1**·CP1] assemblies, the dark sections in the electron micrographs of the [**Por-12**·CP1] composites are attributed to the regions that contain ordered π-stacked layers and/or the heaviest atom (Zn). As mentioned above, the diamino groups in CP1 coordinate to these $\mathrm{Zn^{II}}$ atoms and, therefore, the CP1s are probably also ordered along these stripes. The addition of TFA to a solution of the [**Por-12**·CP1] composite in $\mathrm{CDCl_3}$ to decomplex the [**Por-12**·CP1] composite into **Por-12** and CP1·$n\mathrm{H^+}$ units in solution altered the overall morphologies of aggregates obtained from the [**Por-12**·CP1] composite on the TEM grid from sheetlike to amorphous structures. Neutralization through treatment of the acidified solution with 1.0 M aqueous NaOH resulted in retrieval of the sheet-like morphologies, the crystalline sheet structure of which is constructed from [**Por-12**·CP1] composites and is able to be formed reversibly.

CP2 also formed complexes with **Por-12** in a similar manner to the [**Por-12**·CP1] composite. Fig. 9b displays a HRTEM micrograph of the aggregates obtained from the [**Por-12**·CP2] composites. Since the striped pattern possesses the same 4.0 nm periodicity as that of [**Por-12**·CP1] composites, it appears that the side chains of CP2 do not influence the periodicity significantly. Then, what does this distance of 4.0 nm represent? To answer this question, we prepared a [**Por-6**·CP2] composite and its solution-cast film using the same procedure. Very interestingly, we observed a HRTEM image that depicts a similar striped structure, but the distance between stripes was

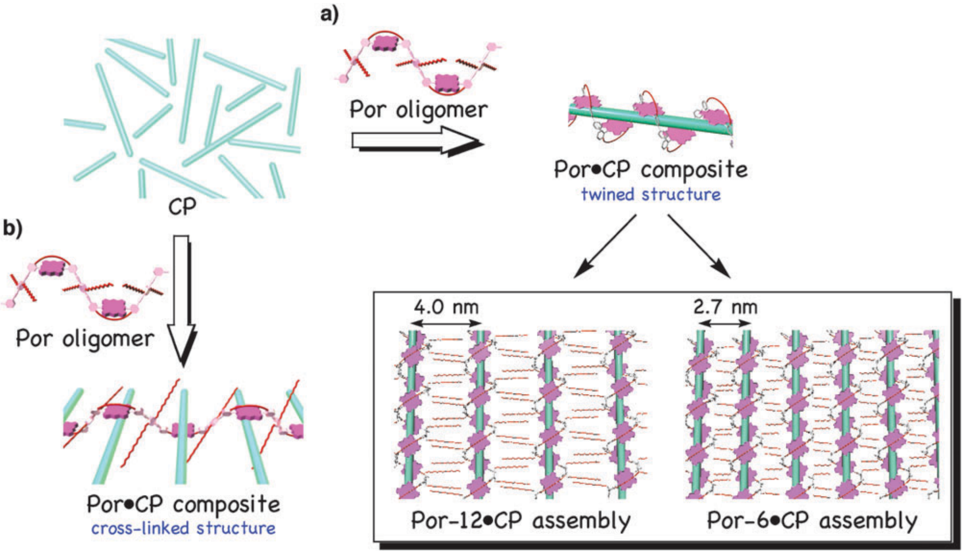


Fig. 10 (a) Schematic representation of the influence of the peripheral alkyl chains in the Por oligomers on the periodicity of the aligned assemblies. The peripheral alkyl chains in CP entwined within the Por oligomers, which are also considered to participate in the van der Waals packing among the composites in the solid state, have been omitted for clarity. (b) Schematic representation of the formation of the cross-linked network structure.

shortened to only 2.7 nm (Fig. 9c). This result clearly indicates that the distance reflects the length of the alkyl chains of the Por oligomer. In fact, if we assume that partially interdigitated packing of the alkyl groups of Por oligomers occurs in the [**Por** · CP] composites formed through the twining of Por oligomers around the CP, then we can estimate the Zn^{II}–Zn^{II} distance between adjacent composites to be 4.0 nm for the [**Por-12** · CP], in contrast, 2.7 nm for the [**Por-6** · CP] composites. The results support the view that the peripheral alkyl chains also participate in the packing among the composites.

From these findings, we proposed the following sequential growth mechanism for the preparation of these micron-sized, highly ordered assemblies. In the first step, the Por oligomer, which is preprogrammed for helix formation in the presence of the guest, twins around the CP strand and becomes stabilized through the formation of coordination bonds between the porphyrinatozinc and amino units in solution. In the second step, on the surface, the composites organize together through attractive van der Waals interactions between the alkyl groups during the solidifying process. In the final step, they construct 2D sheet-like assemblies that display distinctly striped patterns. It is unlikely that the random crosslinked network structure directly resulted in the formation of the crystalline assemblies on the ITO glass or the TEM grid during the solidification process (Fig. 10).

Application for 2D crystallization of flexible polymer

Here, we applied these concepts for aligning CPs to polymers with flexible backbones. For example, poly(vinyl-4-pyridine) (PPy) (M_w = 60 000) has both flexibility and functional groups coordinating to aligner and twimer; coordination bonds could be formed between porphyrinatozinc and pyridine moieties. The UV-vis spectra of **2** showed a change similar to those of [**2** · CP1] complex upon addition of PPy. We observed several micro-metre size crystalline sheets in the HRTEM images of immobilized [**2** · PPy] assemblies, in spite of the flexibility of original PPy backbone. This indicates that binding and bundling PPy by aligner **2** might lead to 2D supramolecular crystallization (Fig. 11a). PPy also complexed with **Por-12** in a manner similar to its assembly with CP1 through coordination bonds. The TEM images and electron diffraction patterns from the solution-cast film clearly indicate that [**Por-12** · PPy] composites self-organized into crystalline supramolecular assemblies with the periodicity of 5.0 nm to form stacked thin 2D sheets (Fig. 11b).

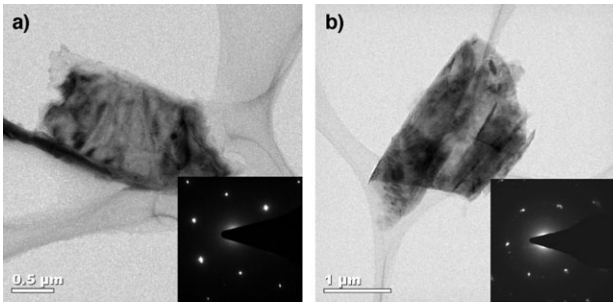


Fig. 11 (a) TEM image (obtained without staining) of immobilized [**2** · PPy] assemblies. Inset: Electron diffraction pattern of the image, indicating that the immobilized assemblies show the crystalline nature. (b) TEM image (obtained without staining) of [**Por-12** · PPy] composite. Inset: an electron diffraction pattern indicating that the [**Por-12** · PPy] composite is crystalline.

Conclusions and future perspectives

In summary, we proposed a novel concept for aligning CPs through the action of supramolecular bundling molecules. One of the two approaches is to utilize crosslinking molecule, aligner. Aligners bind and bundle CPs by coordination bonds formed between porphyrinatozinc and amine moieties. The high affinity and cooperativity through the binding events lead to the well-organized and aligned CP structures. Although the supramolecular assemblies are thermodynamically formed in solution to give transient architectures, they can be immobilized to permanent architectures through post-modification RCM reaction of the olefinic moieties in the aligner. The immobilized assemblies could maintain the architecture under the acid conditions, even though the coordination bonds were no longer formed. The second one is to use twining polymer, twimer. Twimer helically twines around CPs through coordination bonds between porphyrinatozinc and amine moieties in solution and then the 1D complex self-assembles into 2D-ordered structure in the drying process. The solid state morphology expressed crystalline sheets with the emission of both twimers and CPs. Very interestingly, the spacing between CPs could be regulated by the lengths of peripheral R groups of twimers. Finally, this system was extended even to the 2D pseudo-crystallization of flexible polymer, PPy. Through these systems, we confirmed that HRTEM becomes a powerful tool to analyze supramolecular soft materials when they have periodicities in their assemblies.

In our system, introducing interactive moieties to aligning molecule (aligner or twimer) leads to the control over the dimensions, morphologies, and interpolymer spacing of CP assemblies. Furthermore, this approach would resolve two critical issues associated with conjugated polymer-based devices, the segregation of polymers in individual chains and controlled alignment. We believe, therefore, that the present system to create the well-ordered, huge structures from polymers by just mixing in solution is very attractive as a new methodology useful for designing functional soft materials and conjugated polymer-based devices.

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