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Supramolecular Chemistry

DOI: 10.1002/anie.200503128

A Supramolecular Bundling Approach toward the Alignment of Conjugated Polymers**

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Exploring new methods for controlling the orientation and electronic state of π -conjugated oligomers and polymers is of importance for the production of materials with optimized properties and for their ultimate assembly into molecular circuitry. In addition to supramolecular assembly schemes,^[1-4] methods for aligning conjugated polymers, which lead to many new photophysical functions, include the use of metastable states enforced by liquid-crystalline phases,^[5-7] Langmuir monolayers at the air–water interface,^[8] incorporation into prealigned host matrixes,^[9,10] and rubbing.^[11,12] Unlike synthetic macromolecular systems, the bundling

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[**]	We thank Dr. N. Fujita and Dr. M. Ikeda for fruitful discussions. M.T. and Y.K. thank Prof. A. Ikeda for kindly supplying compound 2 . Y.K.

and Y.K. thank Prof. A. Ikeda for kindly supplying compound **2**. Y.K. thanks the JSPS Research Fellowship for Young Scientists for financial support. This study was supported partially by a Sumitomo Chemical Award in Synthetic Organic Chemistry Japan, a Grant-in-Aid for Scientific Research B (17350071), and the 21st Century COE Program, "Functional Innovation of Molecular Informatics," of the Ministry of Education, Culture, Science, Sports, and Technology (Japan).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

proteins found in animal cells bind one-dimensional (1D) actin filaments in high affinity to elicit the formation of actin bundles.^[13] The bundling proteins possess two interactive modules for cross-linking actin filaments; their distinct properties determine the type of assembly. If one can reconstruct such modules interacting with 1D materials in a supramolecular manner, not only would these systems provide a new means of aligning the materials but also would create complex mesoscopic structures and networks akin to those found in nature. Herein, we report a new concept for aligning and assembling conjugated polymers through the action of supramolecular bundling ("aligner") molecules. We demonstrate this concept by utilizing the dative bonds formed between porphyrinatozinc and amine derivatives because of the high affinity and distinct bonding geometry of these species.^[14] We designed the aligner molecules 1 and 2, which are porphyrinatozinc oligomers,^[14,15] to elicit positive homotropic allosterism^[16-18] during their binding of the amino-functionalized conjugated polymers CP and CCP in an effort to organize the polymers into aligned, rather than random, assemblies (Figure 1). Although the distances between pairs of porphyrinatozinc units in 1 and 2 aligned in parallel can vary through conformational rearrangements about their rotational axes (the butadiyne unit for 1 and the ethylene bridges for 2), the distances between the binding subunits when in a cofacial orientation are 2.5 and 2.0 nm, respectively. Each pair of cofacially aligned porphyrinatozinc tweezers in 1 and 2 binds to a diamine moiety of the polymer in an allosteric manner to form polymer bundles (Figure 1B); in this process, the binding of the first polymer to an aligner molecule facilitates the second binding, which results in the ready formation of aligned assemblies (Figure 1C).

To confirm the cooperativity of the binding of CP and CCP by 1 and 2, we used MCP as a guest molecule for 1 and 2. We noted the formation of the [1·MCP] or [2·MCP] complexes in CHCl₃ from changes in the UV/Vis absorption spectra that occurred upon the successive addition of MCP (see the Supporting Information). The values of λ_{max} of the Soret and Q bands shifted to longer wavelengths with tight isosbestic points; these changes are consistent with those observed from studies of other porphyrinatozinc-amine coordination systems.^[14] We estimated the stoichiometries of the complexes formed between MCP and both 1 or 2 from molar ratio plots, which clearly indicated the formation of 1:2 $[1 \cdot (MCP)_2]$ and 1:3 $[2 \cdot (MCP)_3]$ complexes. Importantly, plots of absorbance at the Q band (607 nm) versus [MCP] possessed sigmoidal curvature. From analyses of these binding isotherm using nonlinear-curve-fitting and Hill-plot^[19] methods, we calculated the association constants (K_n/MCP) and Hill coefficients $(n_{\rm H})$ to be $K_1 = 1.6 \times 10^5$, $K_2 = 3.0 \times 10^5$, and $n_{\rm H} = 1.9$ for $[1 \cdot (\text{MCP})_2]$ and $K_1 = 8.8 \times 10^5$, $K_2 = 9.2 \times 10^5$, $K_3 =$ 4.8×10^6 , and $n_{\rm H} = 2.8$ for [2·(MCP)₃]. These results clearly indicate that highly cooperative binding occurs between MCP and both 1 and 2. Extrapolating from the cooperativity and high association constants in the binding of MCP with 1 and 2, we expected that the diamine moieties in CP and CCP would become juxtaposed and aligned by the clefts in the porphyrinatozinc units in 1 and 2 in a positive homotropic allosteric

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Figure 1. A) Chemical structures of the aligner molecules and conjugated polymers studied herein. CP: number-average molecular mass $(M_n) = 48000$; CPP: $M_n = 18000$. B) Schematic representation of the modes of bundling of the conjugated polymers with 1 (left) and 2 (right). Blue plates denote the porphyrinatozinc complexes in 1 and 2; sky-blue fibers and spheres denote the polymer backbones and methylaminomethyl moieties, respectively, in the conjugated polymers. C) Schematic illustration of the alignment of the conjugated polymer CP mediated by 1. The first polymer binding event to the porphyrinatozinc cleft preorganizes the second cleft (denoted by the asterisk) such that it has an even higher affinity toward the second polymer. The conjugated polymers are expected to be juxtaposed to each other to form aligned assemblies.

manner. That is to say that we expected the first polymer binding event to enhance the affinity of the second (and, for 2, the third) polymer binding event to form aligned supramolecular assemblies; such a process is necessary if we are to avoid the formation of random assemblies. In fact, the addition of CP to a solution of $1 (3.5 \,\mu\text{M})$ or $2 (0.43 \,\mu\text{M})$ in CHCl₃ at 25 °C resulted in similar bathochromic shifts in the Soret and Q bands as those observed for 1 or 2 upon the addition of MCP (see Figure 2 and the Supporting Information). The emission intensity of CP ($[CP_{unit}] = 24 \,\mu\text{M}$; $\lambda_{ex} = 400 \,\text{nm}$) in CHCl₃ decreased, without a change in its shape when it was mixed with **1** (see the Supporting Information). This phenomenon is due to efficient energy transfer from CP to **1** within the complex because the emission wavelength of CP overlaps considerably with the absorption of **1**. Deposition of a homogeneous solution of CP ($[CP_{unit}] = 240 \,\mu\text{M}$) in CHCl₃ containing 5.0 wt% polystyrene ($M_w = 200000$) on a quartz plate provided us with a solution-cast film. The emission

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Figure 2. A) UV/Vis spectra of 1 (3.7 μ M) upon addition of CP in CHCl₃ at 25 °C. Inset: magnified spectra about the Q bands. B) Fluorescence spectral change of CP ([CP_{unit}] = 240 μ M) in the presence and absence of **1** in the film cast from a solution of CHCl₃ containing polystyrene (5 wt%). The fluorescence intensity was normalized with respect to the absorption at 400 nm (λ_{ex}).

spectrum of this CP film is broadened relative to that recorded in dilute solution ($[CP_{unit}] = 24 \mu M$); this effect is probably due to random aggregation of the polymer main chains in the film. Interestingly, the addition of 1 turned the broad emission—even that obtained in the solid state—into the sharp one observed for a dilute solution of the [1·CP] complex (Figure 2B). Because the distance between the two distinct binding sites in 1 is 2.5 nm, the bundled assemblies of CP no longer emit the broad emission because of their random aggregation. Polarized optical microscopy images of [1·CP], as well as UV/Vis and fluorescence spectroscopic studies, also support the formation of ordered assemblies in the solid state (see the Supporting Information). These findings suggest that the structures of the supramolecular polymer bundles are maintained in the solid state; we further confirmed this situation by using atomic force microscopy (AFM) and transmission electron microscopy (TEM).

Figure 3 A displays an AFM image of CP (deposited from a 1.3 μ M solution in CHCl₃), in which the CP assembly is well dispersed in a rectangular shape on highly oriented pyrolytic graphite (HOPG). We calculated the average height to be 0.3 nm from the height profile. Polymer CP probably lies on HOPG in a monolayer with a face-on orientation (Figure 3 A). From the height profile of the deposition samples of **1** and **2**, their thickness was shown to be 0.6 nm, thus indicating that porphyrins in **1** and **2** lie on the HOPG in a face-on orientation as much as possible. By mixing CP ([CP_{unit}] = 1.2 μ M) with **1** (0.08 μ M), the assemblies assigned to CP or **1** itself disappeared, and we observed a 20–25-fold larger (in area ratio) homothetic shape for the CP assemblies



Figure 3. Representative AFM images of CP and [1-CP] assemblies deposited from solution of CHCl₃ onto HOPG. Compounds 1 and 2 formed amorphous assemblies on HOPG. The mixing ratio (α) is defined as $\alpha = [CP]/[1 \text{ or } 2]$ (mol/mol). A) CP ([CP_{unit}] = 1.3 µM); B) [1-CP] assemblies ($\alpha = 15$); C) [1-CP] assemblies ($\alpha = 9.1$); D) [1-CP] assemblies ($\alpha = 3.1$); E) [1-CP] assemblies aged for 24 h under the same conditions as those in (B); F) [2-CP] assemblies prepared under the conditions in which [CP_{unit}] = 1.3 µM and [2] = 0.17 µM ($\alpha = 5.9$).

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that had a height of 0.35 nm (see Figure 3B and the Supporting Information). Under the conditions in Figure 3B, every seventh repeating unit of CP on average was complexed with one porphyrin cleft of 1, thus showing that 1 was not so densely packed in $[1 \cdot CP]$ assemblies. The fact that the overall assembly height is larger than observed for CP itself shows that CP remain aligned in a porous-like solid-state morphology rather than collapsing on the surface. Given the degree of polymerization of CP, 1 must bundle with, and noncovalently splice, CP to form such aligned supramolecular assemblies. The polymer bundling and splicing caused by **1** is highly dependent upon the mixing ratio between CP and 1 and the aging period in solution. A higher molar ratio of 1 decreased the size of the assemblies (see Figure 3C and D); that is, the dimensions of the superstructure are readily controllable by changing the mixing ratio of CP and 1. Aging the [1·CP] complex for 24 h in CHCl₃ at 25 °C resulted in further growth of three-dimensional (3D) assemblies to a height of 1.5 nm (Figure 3E). From these results, we infer that the bundling and splicing processes caused by 1 in solution take place thermodynamically to form initially two-dimensional and then 3D aligned structures. Compound 2 also aligned CP into sheetlike assemblies that had an average height of 0.3 nm and 9-16-fold larger areas than that of CP itself (Figure 3F). The clefts of the porphyrinatozinc units in 1 and 2 are essential for the bundling and noncovalent splicing of the polymers, as evidenced by the fact that neither 3 nor 4 was capable of producing similar assemblies.

The electron micrograph images of the complexes provide information regarding how 1 and 2 align the polymer. We observed highly ordered structures in the TEM and highresolution TEM (HRTEM) images (see Figure 4 and the Supporting Information). We prepared solution-cast films of the polymer-in the presence and absence of 1 or 2-on a TEM grid without staining. An HRTEM image of the CP assemblies was observed (see the Supporting Information) in which the periodicity of the dark layers was 0.4 nm, as determined from the Fourier-filtered image. We suggest that the dark sections in the electron micrographs to be regions that contain the ordered π -stacked layers. This hypothesis is supported by the fact that the periodic distance of 0.4 nm is comparable with the distance between π -conjugated molecules that are associated through π - π stacking interactions.^[20] In the low-magnification micrograph, crystalline sheets (see the Supporting Information) and a multilamellar morphology (Figure 4A) with a periodicity of 2.0 nm over a 200-nm-wide distance was observed for the mixture of CP and 1; this superstructure is totally different from that formed from CP itself. We believe that the dark regions observed in the TEM images of the assembly of CP and 1 to be domains that contained ordered π -stacked layers and/or the heaviest atom (Zn) in 1; the results of energy dispersive X-ray spectroscopy (EDX) support this hypothesis (see the Supporting Information). The period of 2.0 nm corresponds to the distance between CP units when they are bundled in a parallel manner (Figure 5A). We recorded an HRTEM image of one of the sections of the assemblies constructed from CP and 1 to obtain additional evidence for the highly aligned nature of the polymer units. The micrograph in Figure 4B demonstrates



Figure 4. Electron micrographs (no staining) of conjugated polymers aligned by 1 or 2. A) A TEM image of aligned [1-CP] assemblies consisting of dark and light bands. The periodicity between the dark bands is 2.0 nm. B) An HRTEM image of [1-CP] assemblies with 0.2 nm periodicity, as revealed from the Fourier-filtered image. C) An HRTEM image of [2-CP] assemblies displaying multiwalled tubular and lamellar contrasts. The image in the inset displays a multiwalled tube that has bent from the back to the front. D) An HRTEM image of the [1-CCP] assemblies displaying a kagomé lattice contrast. The periodicity of the kagomé lattice is 0.8 nm.

that the film comprised many dark/light layers and that the periodicity of the dark contrast was 0.2 nm, which is much shorter than the π - π -stacking distances of common organic molecules. We infer that the dark/light contrast arises from the phase contrast provided by the zinc atoms in 1 aligned in [1·CP] assemblies when we observe the image in Figure 4 A at an oblique angle. Figure 4C displays the supramolecular assemblies formed from CP and 2, which we expected to bundle three CP strands to form 3D superstructures. We observe in this image unique supramolecular assemblies that possess both lamellar and multiwalled tubular contrast; the inside diameters of the tubes varied between 2 and 5 nm. The dark periodicities of the lamellar and multiwalled tubular assemblies were both 0.35 nm; this observation indicates that these assemblies were both constructed from the same structural unit (Figure 5B). Polymer CCP is also bound to 1 in CHCl₃ in a manner similar to that of CP and **1**. In addition to changes in the UV/Vis and fluorescence spectra, our circular dichroism (CD) spectroscopic measurements also support the formation of a complex between CCP and 1 (see the Supporting Information). The split-type CD signal that we observed in the Soret-band region indicates that the chiral side chains in CCP influence the orientation of the porphyrin plane in 1 to produce an induced-CD (ICD) signal, which should reflect the contrast pattern of the [1·CCP] assemblies. In fact, Figure 4D represents the HRTEM micrograph of the aligned assemblies constructed from CCP and 1; the kagomé lattice and triangular grid patterns^[21,22] with a 0.8-nm-

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Figure 5. Schematic representations of how A) 1 might align CP to form aligned assemblies and how B) [2-CP] assemblies might form multiwalled tubular structures.

periodicity dark contrast regions are clearly apparent. The differences between the contrast patterns of CP (lamellar) and CCP (kagomé lattice) might arise from the orientation of **1** in the assemblies being affected differently by the alkyl chains of CP and CCP.^[23] These micrographs demonstrate that the conjugated polymers were aligned by both **1** and **2** to form highly ordered supramolecular assemblies and that the spacings and arrangements of the polymer binding sites in the aligner molecules—and the nature of the peripheral alkyl chains of CP and CCP—should determine the mode of polymer assembly.

The exploitation of the supramolecular bundling that we have described herein was inspired by the mode of action of actin-filament bundling proteins. Our approach provides a new, general means of preparing complex, ordered assemblies of conjugated polymers. Introducing interactive sites for the aligner molecules at special positions along the conjugated polymers allows control over the dimensions, morphologies, and interpolymer spacings. The concepts that we have introduced complement the existing techniques for supramolecular and macromolecular assembly; in addition, they allow the interpolymer spacing and orientation to be controlled so that they can influence the photophysical properties of the conjugated polymer. Moreover, this approach permits the construction of alternating arrays of different conjugated polymers. We believe that such a system could be realized by utilizing an aligner molecule that displays positive heterotropic allosterism toward such polymers.

Experimental Section

All starting materials and solvents were purchased from Tokyo Kasei Chemicals or Wako Chemicals and used as received. The ¹H 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 Perseptive Voyager RP MALDI-TOF mass spectrometer and/ or a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV/Vis and fluorescence spectra were recorded using Shimadzu UV-2500 PC and Perkin-Elmer LS55 spectrophotometers.

Binding isotherm analysis: The cooperative guest-binding process was analyzed according to the Hill equation: $\log[y/(1-y)] = n\log[$ guest] + $\log K$, where K, y, and $n_{\rm H}$ are the association constant, the extent of complexation, and the Hill coefficient, respectively. The slope and the intercept of the linear (Hill) plots allow K and $n_{\rm H}$ to be estimated; these values are useful measures of cooperativity. A higher value of $n_{\rm H}$ is related to a higher degree of cooperativity; the maximum value is equal to the number of binding sites. In the analysis of the binding isotherm from the Hill plot, we evaluated the concentration of the unbound guest ([guest]) by assuming that the 1:2 complex of **1** is formed quantitatively when the absorption change is saturated.

Sample preparation for AFM and TEM measurements: The following provides a typical example of the approach. A solution of CP in CHCl₃ ($[CP_{unit}] = 290 \ \mu\text{M}$) and **1** (20.0 \ \mu\text{M}) was prepared; UV/ Vis spectroscopy confirmed that the [**1**·CP] complex had formed quantitatively. This solution was then diluted because the higher-concentration [**1**·CP] assemblies covered the whole area of the HOPG or TEM grid. The resultant dilute solution of [**1**·CP] assemblies in CHCl₃ was cast on HOPG or a copper TEM grid upon a holey carbon-support film.

TEM and HRTEM images were acquired using a JEOL TEM-2010 (accelerating voltage: 120 kV) and a TECNAI-20 FEI (accelerating voltage: 200 kV), respectively. A sample solution was placed on a copper TEM grid upon a holey carbon-support film. The TEM grid was dried under reduced pressure for 6 h prior to TEM observation.

AFM images were acquired in air using a Topo METRIX SPM 2100 (noncontact mode). The sample was cast on HOPG and dried for 1 h under reduced pressure prior to AFM observation.

Received: September 2, 2005

Keywords: alignment · allosterism · conjugated polymers · porphyrinoids · supramolecular chemistry

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