Porphyrinoids

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Conjugated Polymers Complexed with Helical Porphyrin Oligomers Create Micron-Sized Ordered Structures**

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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.[1,2] In

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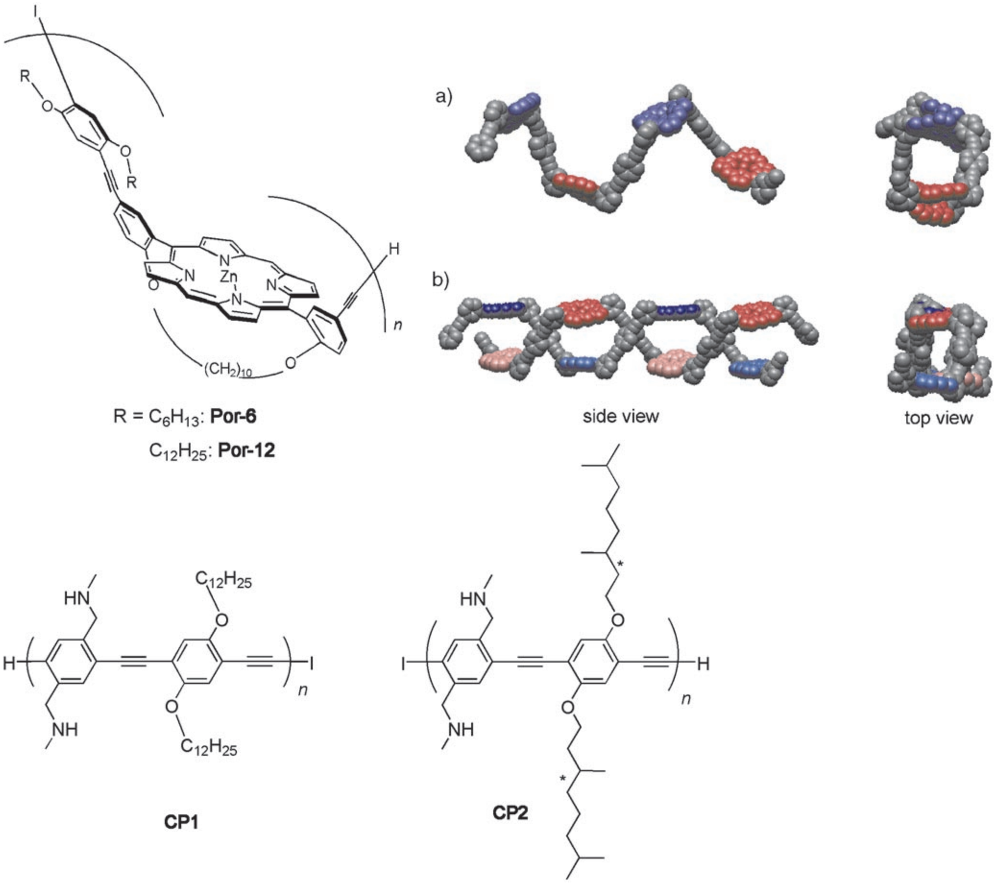
addition to supramolecular assembly schemes,[3–6] a number of approaches, including metastable states enforced by liquid crystalline phases,[7–9] Langmuir monolayers at the air–water interface,[10] incorporation into prealigned host matrixes,[11,12] and rubbing,[13,14] have been utilized to align conjugated polymers, thus 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.[15]

Herein, we present a new concept toward the alignment of CPs through the use of twining polymers (twimers) that act as helical "hosts" that would twine around and include within a single conjugated polymer. Furthermore, we wanted these "hosts" to integrate chromogenic groups that could mediate electron or energy transfer to or from the conjugated polymer. Taking these factors into consideration, we designed the oligomeric porphyrins **Por-12** and **Por-6** (Scheme 1). In their energy-minimized states, these oligomers tend to form helical structures in which a coordinative open face of the zinc porphyrin unit (but not a non-coordinative face covered by a decamethylene group[16]) is always turned inwards so that the central metal atom can interact with the included CP. We expected, therefore, that a CP that possesses appropriate ligand groups would become included within this helical strand through coordination with the porphyrinatozinc. We chose to use **CP1** and **CP2**, which bear coordinative amino groups, for the CPs.[15] The R groups in the Por oligomers were introduced to control the spacing between Por/CP composites and to increase their solubility in organic solvents. From studies using various spectroscopic and microscopic techniques, we proposed that the Por oligomers twine around the CP strands and that the resulting composites aggregate into relatively large two-dimensional (2D) structures in the solid state that exhibit well-oriented periodic striping.[17]

We used computational methods (Insight II, Discover) to evaluate whether the porphyrin units in the Por oligomers could be arranged in helical structures. We confirmed that the octamer of the Por series possessed helical turns and a 1D cavity with dimensions of 1.1 × 1.5 nm, which is adjustable through the oscillation of *meso*-aryl groups (note that Scheme 1 a illustrates only the tetramer for the sake of simplicity). Although it is also possible to construct a double strand with a 0.74 × 1.1 nm 1D cavity, this assembly is quite sterically crowded.

UV/Vis absorption spectra of the complexes formed between the **Por-12** oligomer and **CP1** were measured in $CDCl_3$ at 25 °C.[18] Figure 1 a indicates that shifts to longer wavelengths occur for both the Soret (411–420 nm) and Q bands (e.g., 537–550 nm) of **Por-12** with several isosbestic points, thus indicating that the amino groups in **CP1** have coordinated to the Zn^{II} atoms in **Por-12**. A molar ratio plot of A_{550} versus [diamino units in **CP1**]/[porphyrin units in **Por-12**] gives a break point at 1.0 (see the inset of Figure 1 a), 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 (in this case the break point would occur at 0.5), is sterically too crowded (Figure 1 c).



Scheme 1. Chemical structures of the Por oligomers and conjugated polymers used in this study. **CP1**: $M_n = 48000$; **CP2**: $M_n = 18000$; **Por-12**: $M_n = 12000$; **Por-6**: $M_n = 10000$ (M_n = number-average molecular mass). Energy-minimized structures of a) single- and b) double-stranded conformations of the Por oligomers. Hydrogen atoms and peripheral alkyl chains have been omitted for clarity.

When we photoexcited solutions of **Por-12** (0–0.072 mM unit) and **CP1** (0.036 mM unit) in $CDCl_3$

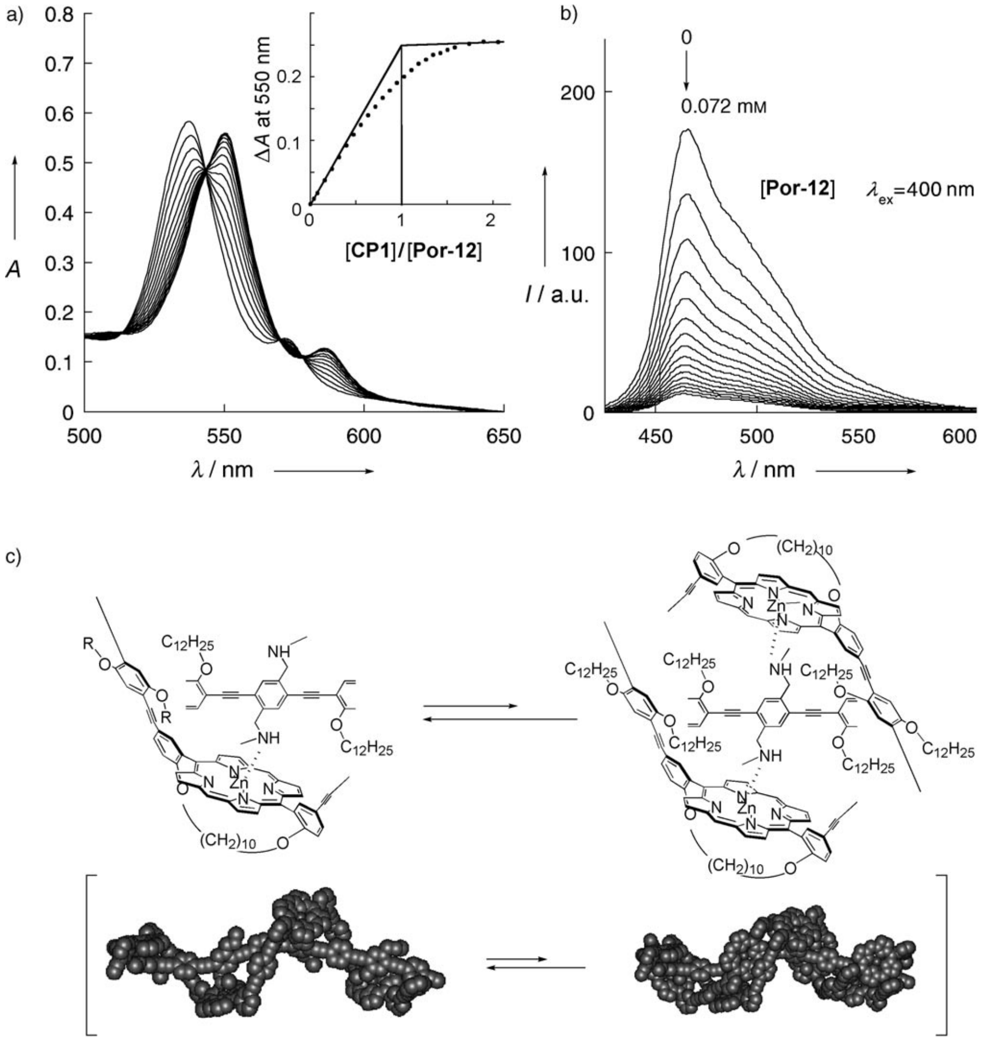


Figure 1. a) UV/Vis spectra of **Por-12** (0.050 mM unit) recorded after the addition of **CP1**. Inset: Plot of the absorbance change at 550 nm of **Por-12** (0.050 mM unit) versus [$\mathbf{CP1}_{\text{unit}}$]. b) Fluorescence spectra of **CP1** (0.036 mM unit) recorded in the presence and absence of **Por-12**. c) Schematic illustration of the equilibrium that exists between the singly and doubly complexed **Por-12**/**CP1** composites. Lower scheme of (c) is a schematic representation of the equilibrium that exists between the single- and double-stranded **Por-12**/**CP1** composites; the straps and peripheral alkyl chains have been omitted for clarity. The structures were calculated using Insight II, Discover, software.

at $\lambda_{ex} = 400$ nm (an isosbestic point in the UV/Vis spectrum) at 25 °C, we observed that the emission intensity ($\lambda_{em} = 465$ nm) of **CP1** decreased upon increasing the **Por-12** concentration (Figure 1 b). At [**Por-12**] = 0.072 mM, the fluorescence intensity of **CP1** decreased to 7 % of its value in the absence of **Por-12**. 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 as a result of the emission wavelength of **CP1** overlapping considerably with the absorption band of **Por-12**. We obtained a solution-cast film after deposition of a homogeneous solution of **CP1** (0.30 mM unit) in $CDCl_3$ containing 5.0 wt % polystyrene ($M_w = 200000$) on a quartz plate. The emission spectrum of this **CP1** film was broad in comparison with that recorded in dilute solution ([**CP1** unit] = 0.03 mM). This effect probably is due to random aggregation of the polymer main chains in the film.[15] Interestingly, the addition of **Por-12** transformed the broad emission obtained in the solid state into the sharp one similar to that observed for a dilute solution of **CP1** (see the Supporting Information), that is, random aggregates of CP no longer exist. With this experiment, we also confirmed the bathochromic shift of the Q bands of **Por-12** in the solid state, thus indicating that **Por-12** formed the complex with **CP1** (see the Supporting Information). The UV/Vis and emission spectra of the solution-cast film of the composite formed between **Por-12** and **CP1** in $CDCl_3$ suggest that the structure of the composite is maintained in the solid state.

To obtain visual images, we examined the composite formed between **Por-12** and **CP1** in $CDCl_3$ using confocal laser scan microscopy (CLSM), polarized optical microscopy (POM), and high-resolution transmission electron microscopy (HRTEM). From the HRTEM image, we confirmed that the **Por-12**/**CP1** composites grew into large aggregates (several microns in size) that possess stacked sheetlike 2D structures (see below). In a separate study, we confirmed that the aggregates of **Por-12** or **CP1** alone are amorphous[15] and cannot organize into 2D structures as large as that presented in Figures 2 and 3.

We subjected a solution-cast film of the **Por-12**/**CP1** composite, constructed on an indium tin oxide (ITO) glass, to POM observation. In Figure 2, we observe a 2D structure with dimensions greater than 50 µm². Very interestingly, this structure exhibits a bright pattern, even between crossed polarizers, thus indicating that this aggregate displays birefringence; that is, **Por-12** and **CP1** assemble into a highly ordered crystalline structure on the micron scale on the ITO glass. When we photoexcited a single large sheetlike aggregate (20 × 120 µm) at 354 nm, the CLSM image displays a blue **CP1** emission (400–440 nm) and a red **Por-12** emission (560–640 nm) in the same morphological domain (see the Supporting Information). It is clear, therefore, that the micron-sized superstructure was assembled through interactions between **Por-12** and **CP1**.

The electron micrographs of the composite provide information regarding how the **Por-12**/**CP1** composite self-organizes. We prepared solution-cast films of the **Por-12**/**CP1** composite on a TEM grid without staining. Figure 3 displays HRTEM images of the aggregate of the **Por-12**/**CP1** composite in which the periodicity of the dark stripes, over a distance

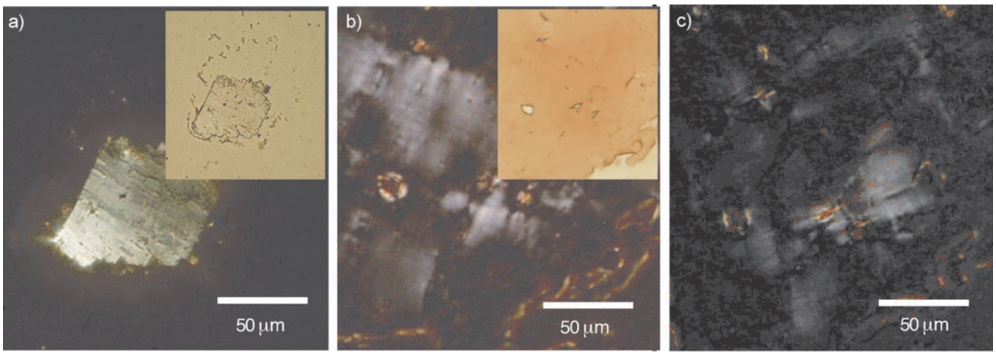


Figure 2. Optical microscopy images of the assemblies of the a) **Por-12/CP1** ([**Por-12**$_{unit}$] = 0.020 mM; [**CP1**$_{unit}$] = 0.036 mM) and b) **Por-12/CP1** ([**Por-12**$_{unit}$] = 0.20 mM; [**CP1**$_{unit}$] = 0.40 mM) composites on ITO as observed between crossed polarizers. c) Optical microscopy image of the assemblies observed after 45° rotation of the sample b). Inset: Images obtained without polarizers. Samples were prepared by drop-casting a solution of the **Por-12/CP1** composite in $CDCl_3$ on the ITO surface and then drying.

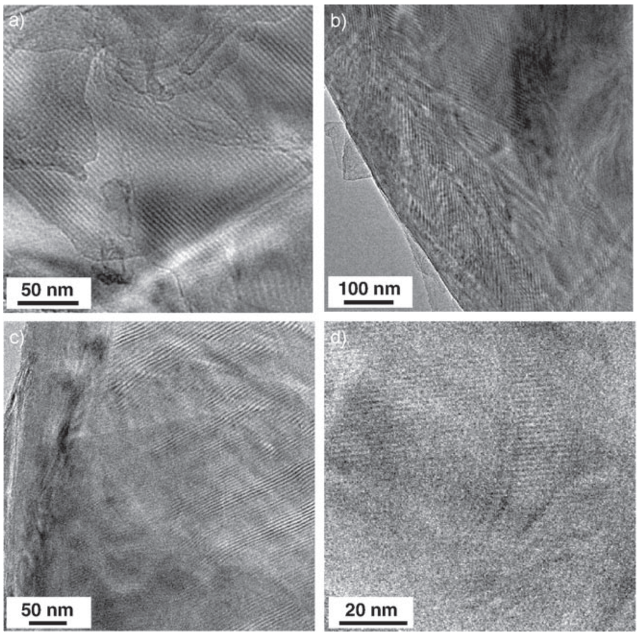


Figure 3. Electron micrographs (no staining) of aggregates of the Por/CP composites. a) HRTEM image of the **Por-12/CP1** composites that display dark and light stripes. The periodicity between the dark stripes is 4.0 nm. b) HRTEM image of a thick plate of **Por-12/CP1** composites. The crossed dark stripes suggest the overlap of a few thin plates that possess striped structures. c) HRTEM image of the **Por-12/CP2** composites. The periodicity between the dark stripes is 4.0 nm. d) HRTEM image of the **Por-6/CP2** composites that display dark and light stripes. The periodicity of the dark stripes is 2.7 nm.

of a few hundred nanometers, was 4.0 nm, as determined from the Fourier-filtered image (Figure 3a). In the image of a thick plate (Figure 3b), we observe crossed dark-stripe contrast, thus indicating that a few thin plates with striped structures were overlapped. We infer that the dark sections in the electron micrographs of the **Por-12/CP1** composites are regions that contain ordered π-stacked layers and/or the heaviest atom (Zn). As mentioned above, the diamino groups in **CP1** coordinate to these Zn^{II} atoms and, therefore, the **CP1** are probably also ordered along these stripes. Given the degree of polymerization of **CP1**, the **Por-12** oligomers must splice **CP1** noncovalently to form such aligned supramolecular assemblies. The addition of trifluoroacetic acid to a solution of the **Por-12/CP1** composite in $CDCl_3$ (namely, to protonate the amino groups of **CP1**) altered the overall morphologies of aggregates of the **Por-12/CP1** composite on the TEM grid from sheetlike to amorphous structures (see the Supporting Information for further details). This phenomenon is due to decomplexation of the **Por-12/CP1** composites into **Por-12** and **CP1**·nH$^+$ units in solution, which we confirmed from the appearance of the UV/Vis absorption spectrum of **Por-12** (the value of the λ_{max} value of the Soret band was 412 nm; see Figure 1). Neutralization through treatment of the acidified solution of **Por-12/CP1** in $CDCl_3$ with 1.0 M aqueous NaOH resulted in the Soret band of **Por-12** shifting to 420 nm. Through a process that we ascribe to recomplexation between **Por-12** and **CP1**, TEM analysis clearly indicates that reorganization occurred to form the sheetlike morphologies (see the image given in the Supporting Information). These results indicate that the crystalline sheet structure is constructed from **Por-12/CP1** composites.

Polymer **CP2** also formed complexes with **Por-12** in a manner similar to that occurring between **Por-12** and **CP1**. The UV/Vis and fluorescence spectra support the formation of a composite between **Por-12** and **CP2** (see the Supporting Information). Figure 3c displays a HRTEM micrograph of the aggregates of the **Por-12/CP2** composite; because the striped pattern possesses a 4.0-nm periodicity, it appears that the side chains of **CP2** do not influence the periodicity significantly. The following question arises: What does this distance of 4.0 nm represent? In an attempt to answer this question, we prepared a composite from **Por-6** and **CP2** and its solution-cast film using the same procedure. Interestingly, we observed an HRTEM image that depicts a similar striped structure, but with a distance between stripes of only 2.7 nm (Figure 3d). This result indicates clearly that the distance reflects the length of the alkyl groups of the Por oligomer. In fact, if we assume that partially interdigitated packing of the alkyl groups of Por occurs in the Por/CP composites that were formed through the twining of Por oligomers around the CP, then we estimate the $Zn^{II}\cdots Zn^{II}$ distance between adjacent **Por-12/CP** composites to be 4.0 nm and that for the **Por-6/CP** composites to be 2.7 nm (Figure 4), in which the peripheral alkyl chains are also thought to participate in the packing among the composites but to be indecisive.

From these findings, we propose the following sequential growth mechanism for the preparation of these micron-sized,

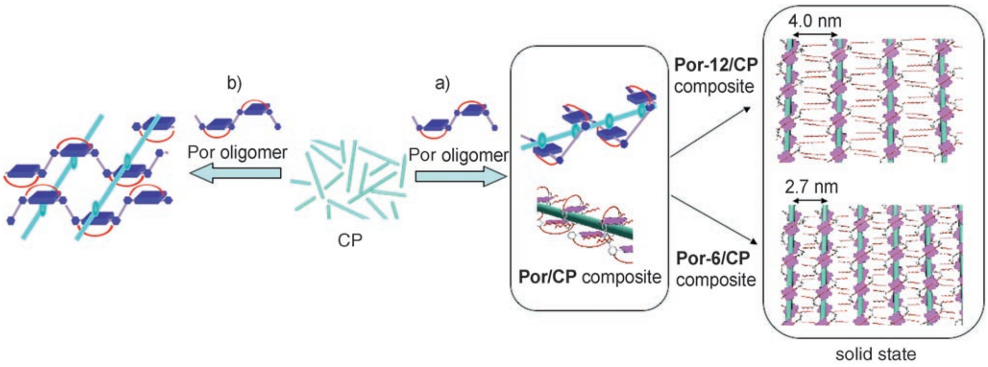


Figure 4. a) Schematic representation of the influence of the peripheral alkyl chains in the Por oligomers on the periodicity of the aligned assemblies. The peripheral alkyl chains in CP entwined within the Por oligomers, which are also considered to participate in the van der Waals packing among the composites in the solid state, have been omitted for clarity. b) Schematic representation of the formation of the crosslinked network structure.

highly ordered assemblies (Figure 4a). In the first step, the Por oligomer, which is preprogrammed for helix formation in the presence of the guest, twines around the CP strand and becomes stabilized through the formation of dative 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 third step, they construct 2D sheetlike assemblies that display distinctly striped patterns. Other systems that form a crosslinked network structure constructed from the Por oligomer and CP (Figure 4b) could not elucidate the effect of the alkyl chain length in the Por oligomers on the periodicities and the contrast patterns observed in the electron micrographs.[19] It is unlikely that the random crosslinked network structure resulted in the formation of the crystalline assemblies on the ITO glass and the TEM grid during the solidification process.

The assembly/aggregation approach we present herein is also readily applicable for use with nonconjugated, flexible polymers bearing coordinating moieties. For example, poly(4-vinylpyridine) ($M_w = 60\,000$) also complexed with **Por-12** in a manner similar to its assembly with **CP1** through dative bonds, and the stoichiometry between [pyridine units in poly(4-vinylpyridine)] and [porphyrin units in **Por-12**] was clearly determined to be 2:1 (see the Supporting Information). TEM images and electron diffraction patterns indicate clearly that the poly(4-vinylpyridine)/ **Por-12** composites self-organized into crystalline supramolecular assemblies with the periodicity of 5.0 nm that formed stacked thin 2D sheets (see the Supporting Information).

Herein, we have demonstrated that porphyrin oligomers (Por series) form homogeneously dispersed composites with conjugated polymers (**CP1** or **CP2**) and poly-4-vinylpyridine in $CDCl_3$; the resulting micron-sized aggregates on the surface possess highly ordered, crystalline structures.[20] It is quite astonishing that such large, highly ordered assemblies could be created simply by mixing two polymeric components together and then drop-casting on a surface. Modification of the lengths of the alkyl chains in the Por series allows control over the intercomposite spacing. The concepts that we introduce herein are complementary to the techniques that exist currently for the preparation of supramolecular and macromolecular assemblies. Furthermore, our results imply that “molecular programming”—that is, utilizing weak intermolecular interactions that tend to occur through reversible processes in a search for the thermodynamically most stable state—can play crucial roles during such organization processes. This twining association/aggregation event is a rare example of a molecular assembly technique that results in a visually recognizable ordered structure; in this regard, our process is reminiscent of some of the self-assembly and self-organization events that occur in biological systems. The application for other 1D polymeric materials is now under investigation.

Experimental Section

All starting materials and solvents were purchased from Tokyo Kasei Chemicals or Wako Chemicals and used as received. ^1H NMR spectra were recorded on a Bruker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, 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.

A typical example of sample preparation for TEM and POM measurements: A solution of **CP1** ([**CP1** unit] = 36 μM) and **Por-12** ([**Por-12** unit] = 20 μM) in $CDCl_3$ was prepared. UV/Vis spectroscopy confirmed that the porphyrinatozinc units in **Por-12** had formed complexes quantitatively. This solution was then cast onto a copper TEM grid upon a holey carbon support film or onto the ITO glass.

TEM and HRTEM: The images were acquired using JEOL TEM-2010 (accelerating voltage: 120 kV) and TECNAI-20 FEI (accelerating voltage: 200 kV) microscopes, respectively. The 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.

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[1] a) G. A. Ozin, A. C. Arsenault, *Nanochemistry*, RSC, Cambridge, **2005**; b) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537 – 2574.
[2] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Shenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546.
[3] J.-M. Lehn, *Supramoleculer Chemistry*, VCH, New York, *1995*.
[4] S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384 – 389.

[5] S. Park, J.-H. Lim, S.-W. Chung, C. A. Mirkin, *Science* **2004**, *303*, 348–351.

[6] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685–688.

[7] H. Goto, K. Akagi, H. Shirakawa, *Synth. Met.* **1997**, *84*, 373–374.

[8] T. M. Long, T. M. Swager, *J. Am. Chem. Soc.* **2002**, *124*, 3826–3827.

[9] K. P. Fritz, G. D. Scholes, *J. Phys. Chem. B* **2004**, *108*, 10141–10147.

[10] J. Kim, T. M. Swager, *Nature* **2001**, *411*, 1030–1034.

[11] A. Montali, C. Bastiaansen, P. Smith, C. Weder, *Nature* **1998**, *392*, 261–264.

[12] W. C. Molenkamp, M. Watanabe, H. Miyata, S. H. Tolbert, *J. Am. Chem. Soc.* **2004**, *126*, 4476–4477.

[13] M. Hamaguchi, K. Yoshino, *Appl. Phys. Lett.* **1995**, *67*, 3381–3383.

[14] P. Dyreklev, M. Berggren, O. Inganas, M. R. Anderson, O. Wennestrom, T. Hjertberg, *Adv. Mater.* **1995**, *7*, 43–45.

[15] Y. Kubo, Y. Kitada, R. Wakabayashi, T. Kishida, M. Ayabe, K. Kaneko, M. Takeuchi, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1578–1583; *Angew. Chem. Int. Ed.* **2006**, *45*, 1548–1553.

[16] a) A. Osuka, F. Kobayashi, K. Maruyama, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1213–1225; b) N. C. Maiti, M. Ravikanth, *J. Photochem. Photobiol. A* **1996**, *101*, 7–10.

[17] C. Kubel, M. J. Mio, J. S. Moore, D. C. Martin, *J. Am. Chem. Soc.* **2002**, *124*, 8605–8610.

[18] The spectroscopic data were not as reproducible when we used $CHCl_3$ as the solvent, probably because the amino groups induced decomposition of $CHCl_3$ to generate some acidic species; in contrast, the use of $CDCl_3$, which is somewhat less reactive than $CHCl_3$, resulted in very reproducible data.

[19] Dynamic light scattering (DLS) analysis of a solution of the composite in $CDCl_3$ indicated that by mixing the Por oligomer and CP, somewhat larger assemblies with a high aspect ratio assignable to the Por/CP composite exist in solution (see the Supporting Information). At the present stage, we can not fully rule out the competitive association system (the intersected model) depicted in Figure 4b; however, we infer that the formation of the composite as illustrated in Figure 4a is more likely.

[20] The assemblies of the composites may form a mesophase or organogel; however, we could not observe gelation phenomena under the conditions used and liquid crystalline phases.