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One-Dimensional Chiral Self-Assembly of Pyrene Derivatives Based on Dendritic Oligopeptides

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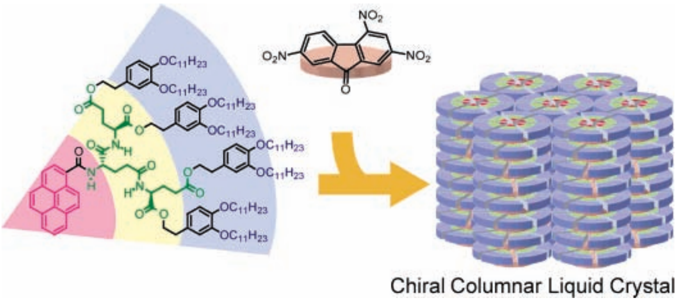
ABSTRACT



Supramolecular chiral columnar liquid crystals have been formed through one-dimensional self-assembly of pyrene-containing oligopeptides. Supramolecular chirality is further tuned by cooperation of intermolecular hydrogen bonding and electron donor–acceptor interactions.

Self-assembly of columnar liquid crystals through specific molecular interactions can be used for the development of one-dimensional dynamically functional nanomaterials.[1,2] In these liquid-crystalline materials, chiral assemblies have been studied to develop asymmetrically ordered dynamic superstructures with attractive features such as chiral amplification, ferroelectricity, and nonlinear optical properties.[2] Intensive work has focused on chiral organization of π-conjugated molecules in the solution states.[3] Our intention here is to achieve one-dimensional chiral organization of a π-conjugated molecule in ordered bulk states. In the present study, we have chosen pyrene for this type of organization. Pyrene is known to form an electron donor−acceptor complex with electron-acceptor molecules such as 2,4,7-trinitrofluorenone (TNF)[4] and already has been incorporated into self-assembled systems.[5] Until now, only a limited number of pyrene-containing liquid crystals have been reported.[6]

We have recently reported that dendritic oligopeptides can act as useful building blocks for chiral supramolecular liquid crystals.[1k,2a,b,7] These dendritic architectures are intensively studied to form designed nanostructures with a variety of functions.[8] To achieve one-dimensional organization of pyrenes, the liquid-crystalline dendritic oligo(glutamic acid)s[1k,2a,b,7] can be used because of their self-assembling behavior and hierarchical molecular chirality.

Furthermore, it is of interest to tune chiral supramolecular structures where noncovalent interactions are involved such

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Table 1. Thermal Properties and X-ray Results of **1**, **2**, and Their Complexes with TNF

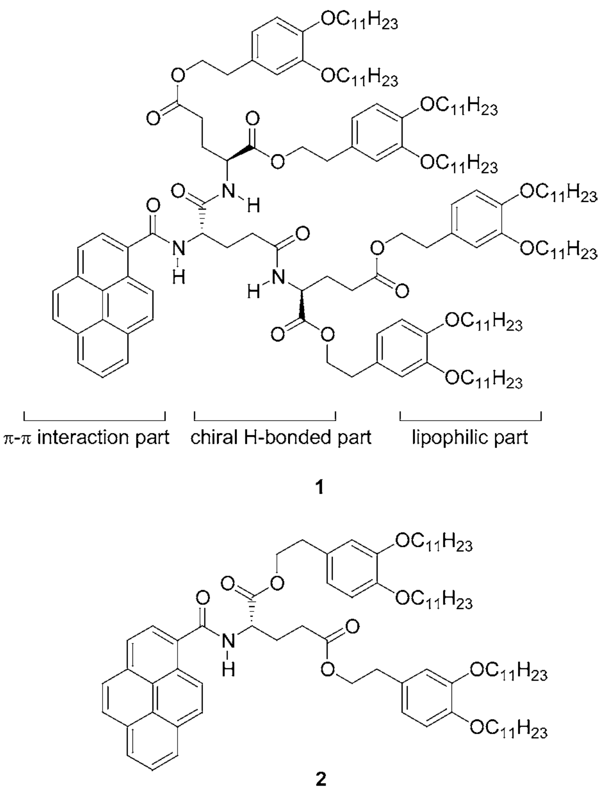
							X-ray results				
compd[a]	phase transition behavior[b]						T (°C)	phase	lattice parameter (Å)	activity on CD spectra	H-bond
1/TNF	Cr	−10	Col$_h$	57	Iso		30	Col$_h$	60.4	ON	ON
1			Cr	113	Iso						
2/TNF	G	−5	Col$_{tet}$	50	Iso		25	Col$_{tet}$	62.8	OFF	OFF
2	Cr	76	Col$_h$	86	Iso		80	Col$_h$	51.3	ON	ON

[a] Molar ratio of TNF to **1** and **2** is 1.0. [b] Transition temperatures (°C). Cr: crystalline. G: glassy. Col$_h$: hexagonal columnar. Col$_{tet}$: tetragonal columnar. Iso: isotropic.

as hydrogen bonding,[1a,b,9,10] $\pi-\pi$ interactions,[1c,d,2e] and electron donor−acceptor interactions.[2i,11]

Here we report on tuning of supramolecular chirality of a π-conjugated molecule through cooperative hydrogen bonding and electron donor−acceptor interactions. We prepared compounds **1** and **2** having molecular triblock structures: pyrene moieties at focal points, glutamic acid and branched oligo(glutamic acid)s as chiral hydrogen-bonded parts, and lipophilic alkyl parts (Figure 1). These molecules were expected to form cylindrical columns by nanosegregation between the molecular block structures.

Thermal properties of compounds **1** and **2** are summarized in Table 1. Compound **2** shows a hexagonal columnar phase from 76 to 86 °C, while compound **1** is nonmesomorphic (Table 1).



1

2

Figure 1. Molecular structures of oligo(glutamic acid)s derivatives having pyrene moieties **1** and **2**.

The addition of an equimolar amount of TNF to nonmesomorphic compound **1** results in the formation of an electron donor−acceptor complex of dark red color. A hexagonal columnar phase is induced for the complex of

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1/TNF. The thermal properties and self-assembled structures of compounds **1** and **2** and their complexes with TNF were studied with use of differential scanning calorimetry and X-ray diffraction (XRD) measurements (Table 1). The XRD pattern of **1**/TNF shows two sharp peaks at 51.9 and 30.4 Å, and a broad reflection at 3.4 Å, respectively (Figure 2).

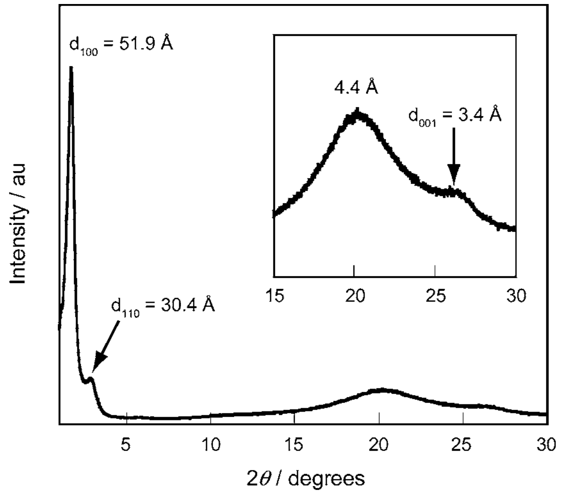

Figure 2. XRD profile of the complex of **1**/TNF at 30 °C.

The intercolumnar distance of **1**/TNF is calculated to be 60 Å. The peak at 3.4 Å corresponds to the stacking distances between pyrene derivatives and TNF molecules, indicating the formation of alternately stacked structures. The formation of the electron donor−acceptor complexes is further confirmed by the UV−vis spectra.

The CD (circular dichroism) and UV−vis spectra of the complexes have been obtained to study their chiral structures (Figure 3). Complex **1**/TNF induces a bisignate Cotton effect with a positive extreme at 296 nm and a negative extreme at 276 nm (Figure 3). The split-type CD spectrum indicating chiral orientation of the pyrene chromophores is maintained after the intercalation of TNF molecules. On the other hand, **2**/TNF having one amino acid residue only shows an inactive CD spectrum (Figure 3). Although both compounds **1** and **2** form similar columnar liquid crystals in the presence of TNF, the resulting chiral structures of the columns are apparently different.

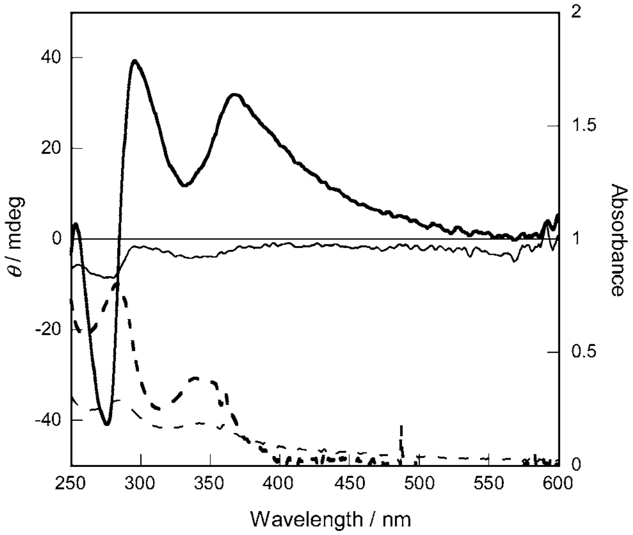

Figure 3. CD spectra of **1**/TNF at 30 °C (thick solid line) and **2**/TNF at 30 °C (thin solid line); UV spectra of **1**/TNF at 30 °C (thick broken line) and **2**/TNF at 30 °C (thin broken line).

The hydrogen-bonded states of the peptide residues were examined by IR measurements. In the LC state, the peaks of the amide group of complex **1**/TNF show significant shifts to 3288 (NH stretching band) and 1633 cm^{-1} (CO stretching band) from those observed in the isotropic state, due to the formation of intermolecular hydrogen bonds. These values of **1**/TNF are comparable to those observed for compound **1** alone in the crystalline state. For complex **1**/TNF, a hydrogen-bonded array of peptide groups stabilizes self-assembled inner column structures formed through electron donor−acceptor interactions between alternate molecular stacks (Figure 4). The cooperation of hydrogen-bonding and electron donor−acceptor interactions should lead to the induction of supramolecular chirality. In contrast, the spectrum of **2**/TNF exhibits an NH stretching band at 3406 cm^{-1} and a CO stretching band at 1657 cm^{-1}, whereas for the spectrum of compound **2** alone the amide bands appear at 3288 and 1633 cm^{-1}. It is evident that a hydrogen-bonded array of the amide groups of **2** is not formed in the electron donor−acceptor complex. For the complex **2**/TNF, smaller peptide dendrons are not appropriate for inducing both hydrogen-bonded and electron donor−acceptor interactions. To confirm the role of hydrogen bonds in the chiral self-assembly process, the CD spectra of the single component of compound **2** were measured in the bulk state (Figure 5). Until now, several columnar liquid crystals[6] containing pyrenes have been reported. Of these materials, only one pyrene-based compound was chiral.[6a] However, no CD spectrum was reported for this compound. A positive Cotton

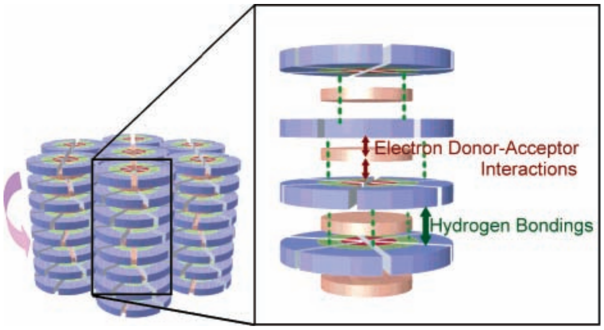

Figure 4. Schematic illustration of the cooperation of hydrogen bondings and electron donor−acceptor interactions for the chiral self-assembly of complex **1**/TNF.

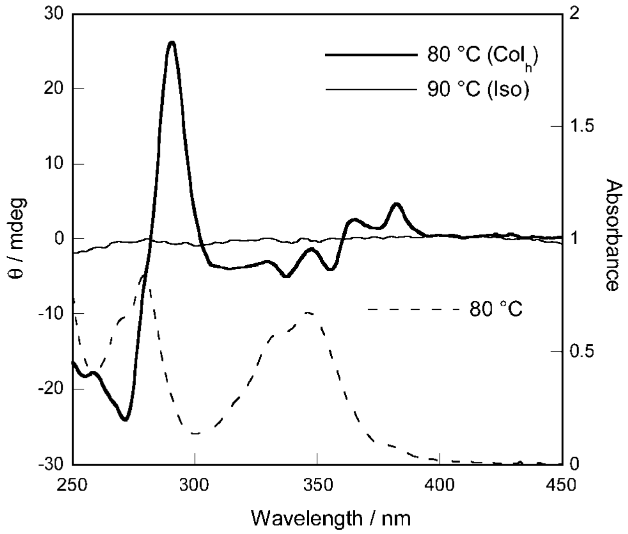

Figure 5. CD spectra of **2** in the hexagonal columnar (thick line) and isotropic liquid state (thin line); UV spectrum of **2** in the columnar state (broken line).

effect is observed for **2** in the LC state, and disappears in the isotropic liquid state. The active CD spectra are induced by the formation of hydrogen bonds. However, the intensities of the Cotton effects of **2** alone are far weaker than those observed for the complex **1**/TNF. In the columnar phase of **1**/TNF, hydrogen bonds of the amide groups are formed in parallel to the columnar axes of pyrene derivatives to induce helical organization of the molecules, and the supramolecular chirality is further enhanced by cooperative electron donor–acceptor interactions.

In summary, pyrene-containing oligo(glutamic acid)s derivatives exhibit thermotropic chiral columnar LC phases. On using this kind of material design, the properties of the functional moieties such as luminescence, electron conductivity, and ferroelectricity may be tuned by chiral supramolecular structures formed through several intermolecular interactions.

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Supporting Information Available: Experimental procedures, UV–vis spectra of compound **2** in the presence and absence of TNF, XRD profile of compound **2** and the complex **2**/TNF, FT-IR spectra of compounds **1** and **2**, polar plot of compound **2**, and variable-temperature CD spectra of the complex **1**/TNF. This material is available free of charge via the Internet at http://pubs.acs.org.

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