Self-Assembled Helical Nanofibers Made of Achiral Molecular Disks Having Molecular Adapter

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An achiral disk-shaped molecule (**2**) having one imidazole unit was found to be assembled into long and twisted nanoscopic fibers having 10 - 100 nm width as shown by transmission electron microscopy (TEM) and atomic force microscope (AFM). Compound **2** leads to spontaneous chiral symmetry breaking through the steric effect of imidazole units during the formation of one-dimensional stacks. The imidazole in **2** acts as a molecular adaptor to form hydrogen bonds and accumulate metal ions. The supramolecular connection of **2** with benzene-1,3,5-tricarboxylic acid through the hydrogen bonds exhibited a thermotropic liquid crystalline properties. Silver nanoparticles were deposited onto the self-assembled nanofibers by the photoreduction of silver ions.

Introduction

Self-assembled one-dimensional stacks composed of polyaromatic molecules have attracted increasing attention as potential molecular components in organic electronic and optoelectronic devices.[1] The decoration of polyaromatic molecules with flexible alkyl chains exhibits birefringent mesophases,[2] which correspond to a columnar arrangement of disklike molecules driven by the intermolecular $\pi-\pi$ interactions and local phase separation between flat rigid aromatic cores and peripheral side chains. The large $\pi-\pi$ overlap within the columnar stacks of disklike molecules provides a transport pathway for charge or energy.[3] A three-dimensionally ordered helical liquid crystalline phase of hexahexylthiotriphenylene exhibited a high mobility for photoinduced charge carriers of the order of 0.1 cm^2 V^{-1} s^{-1}, and this mobility in the liquid crystalline phase is comparable to that in organic single crystals.[4] Many attempts have been achieved in order to enhance the optoelectronic properties of the columnar stacks by exploring the chemical structures of disklike molecules.[5] The attachment of chiral segments with disklike molecules provides a bias in the direction of rotation within the stacks and form helical superstructures.[6]

The formation of chiral assemblies from achiral compounds in the absence of chiral influences has been reported.[7]

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The spontaneous breaking of mirror symmetry was observed though voltex motion during the self-assembly process of achiral water-soluble diprotonated porphyrins.[8] Achiral bent-core banana-shaped molecules exhibited macroscopic chirality in fluid smectic liquid crystals and assembled into helical nanofilaments.[9] Recent studies on the self-assemblies of bent-shaped bridging ligands having two imidazoles with $AgNO_3$ have revealed the formation of helical chiral tubular coordination polymers.[10] Here, we present an unusual example of helical stacks made of achiral disk-shaped triphenylenes attained because of the steric effect of imidazole segments. Although the investigations into the relationship between the molecular structures and supramolecular morphology have been reported,[11] self-assemblies with helical and chiral architectures have been achieved for the first time from achiral disklike molecules.

Furthermore, imidazoles have been utilized as building blocks to construct metallosupramolecular systems through the formation of coordination bonds.[12] We previously reported the self-organization of gold nanoparticles into three-dimensional network structures using thiol-terminated molecular components.[13] The thiol terminates served as an anchor to bind fibrous supramolecular assemblies to the surface of gold nanoparticles and the accumulation of gold nanoparticles around organic assemblies created a three-dimensional network assembly. Imidazole serves as a ligand for metal ions and the reduction of metal ions leads to the formation of nanoparticles. Here, we also discuss our demonstration of the assembly of silver nanoparticles along with stacks based on the self-assembly of disklike triphenylenes driven by $\pi-\pi$ interactions.

Experimental Section

General. NMR spectra were recorded on a Bruker AVANCE 400 FT NMR spectrometer at 399.65 and 100.62 MHz for ^1H and ^{13}C in $CDCl_3$ solution. Chemical shifts are reported relative to internal TMS. IR spectra were obtained on a SHIMAZU IR Prestige-21 with DuraSample IR II. UV–vis spectra and fluorescence spectra were measured on a JASCO V-650 and a JASCO FP-750. MALDI-TOF mass spectra were obtained on a PerSeptive Biosystems Voyager De Pro spectrometer with dithranol as matrix. The optical textures of the mesophases were studies a Nikon polarizing microscope equipped with a Mettler Toledo FP82 hot stage. The transition temperatures were measured by differential scanning calorimetry with a SII DSC 6200 operated at a scanning rate of 10 °C min^{-1} on heating and cooling. The apparatus was calibrated with indium as standard. The XRD patterns were obtained with a Rigaku XRD-DSC with Cu Kα radiation. Spacings were obtained from Bragg's law.

Atomic force microscopy images were acquired in noncontact mode by a JEOL JSPM-5400 system. The samples for AFM were prepared by the gel-transfer method. The freshly cleaved mica substrate was pressed against the gel surface for 10 min. The substrate was detached form the gel surface and observed by AFM. The specimens for TEM were prepared by drying a gel of **2** onto amorphous carbon-coated copper grids (400 mesh). The grids were observed in a JEOL JEM-2010 electron microscope at an acceleration voltage of 200 kV without any staining.

Materials. 3,4,3′,4′-Tetra(decyloxy)biphenyl and 4,7-dimethoxy-1,10-phenanthroline were synthesized according to the literature method.[14,15] All chemicals were purchased from commercial suppliers and used without purification. Column chromatography was performed with activated alumina (Wako, 200 mesh) or Wakogel C-200. Recycling preparative gel permeation chromatography was carried out by a JAI recycling preparative HPLC using $CHCl_3$ as an eluent. Analytical thin layer chromatography was performed with commercial Merck plates coated with silica gel 60 F_{254} or aluminum oxide 60 F_{254}.

2-Bromo-6,7,10,11-tetra(decyloxy)-3-methoxytriphenylene. 1: 3,4,3′,4′-Tetra- (decyloxy)biphenyl (2.0 g, 2.57 mmol) and 2-bromo-anisol (2.4 g, 12.9 mmol) were added in anhydrous CH_2Cl_2 (20 mL) and dissolved by standing the flask in warm water bath. $FeCl_3$ (4.2 g, 25.7 mmol) was added slowly to the reaction mixture. After being stirred for 2 h, the mixture was poured into stirred methanol (200 mL) and then allowed to cool for 8 h in a refrigerator. The solid was filtered off and washed with cold methanol. The crude product was purified using column chromatography (silica gel, eluting with petroleum ether/CH_2Cl_2 (1:1 v/v), $R_f = 0.5$) and HPLC to give a grayish solid. Yield: 1.2 g, 48%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.56 (1H, s, ArH), 7.85 (1H, s, ArH), 7.78 (4H, s, ArH), 4.22 (8H, s, $-O-CH_2-$), 4.11 (3H, s, $-OCH_3$), 1.93 (8H, m, $-O-CH_2-CH_2-$), 1.58 (8H, m, $-CH_2CH_3$), 1.28 (48H, m, $-CH_2-$), 0.88 (12H, t, $-CH_3$). MALDI-TOFMs for $C_{59}H_{93}O_5Br$: m/z 961.2.

2: **1** (0.2 g, 0.20 mmol), imidazole (0.17 g, 0.25 mmol), Cs_2CO_3 (98 mg, 0.30 mmol), poly(ethylene glycol) (M_n 3,400) (0.2 g), and CuO (48 mg, 0.34 mmol) were added in dried *N*-methylpyrrolidone (2.0 mL) and the reaction mixture was stirred for 48 h at 135 °C under N_2. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered through a plug of Celite, and eluted with additional CH_2Cl_2. The filtrate was concentrated and the resulting residue was purified using column chromatography (silica gel, eluting with ethyl acetate/CH_2Cl_2 (1:1 v/v), $R_f = 0.4$) and HPLC to give a white solid. Yield: 0.15 g, 75%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (1H, s, ArH), 7.93 (1H, s, ArH), 7.88 (1H, s, ArH), 7.86 (1H, s, ArH),

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Scheme 1
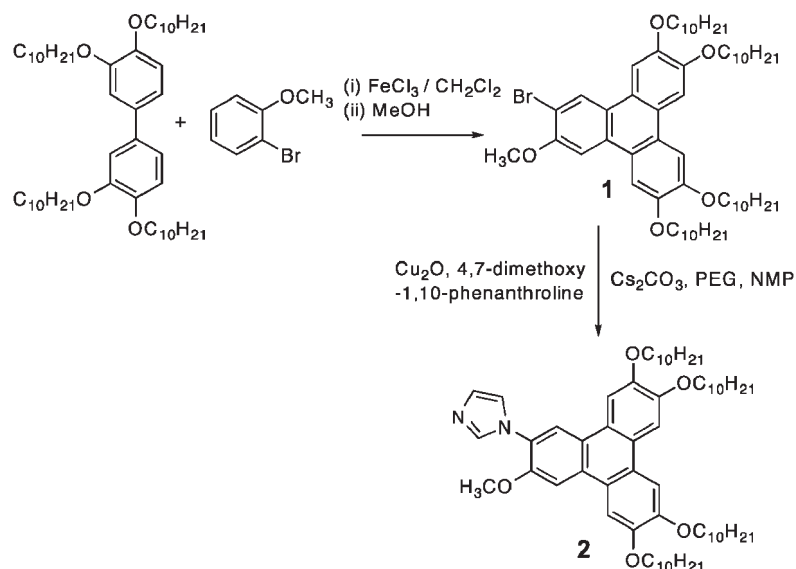
7.80 (2H, s, Ar*H*), 7.75 (1H, s, Ar*H*), 7.37 (1H, s, Ar*H*), 7.26 (1H, s, Ar*H*), 4.23 (8H, s, −O−C*H₂*−), 4.04 (3H, s, −OC*H₃*), 1.94 (8H, m, −O−CH₂−C*H₂*−), 1.58 (8H, m, −C*H₂*CH₃), 1.29 (48H, m, −C*H₂*−), 0.89 (12H, t, −C*H₃*). ¹³C NMR (100 MHz, CDCl₃): δ = 150.4, 149.4, 135.6, 130.1, 128.7, 120.1, 114.0, 106.7, 69.1, 55.8, 32.0, 29.7, 29.6, 29.5, 29.4, 26.7, 26.3, 26.2, 22.7, 14.1. MALDI-TOF-Ms for $C_{59}H_{93}O_5Br$: m/z 950.6.

Results and Discussion

Synthesis. We designed a new unsymmetrical substituted triphenylene **2**, which has four alkoxy groups and one imidazole group. Scheme 1 shows the synthesis of target triphenylene **2**. Compound **1** was synthesized by the oxidative coupling of biphenyl with 2-bromoanisole using iron(III) chloride, followed by a methanol reductive-workup procedure.[14] Compound **2** was synthesized by the copper-catalyzed *N*-arylation reaction of imidazole with **1** in the presence of 4,7-dimethoxy-1,10-phenanthroline.[15] Bromide in **1** was converted to imidazole in a 75% yield. Compounds **1** and **2** were identified by ¹H and ¹³C NMR, and MALDI-TOF-Ms.

Self-Assembly of Achiral Disklike Molecules in Solution. When **2** was heated in 2-methoxyethanol and then cooled slowly, the molecules strongly aggregated to a transparent supramolecular gel take place. Compound **2** can form a transparent gel in alcohols such as n-butanol, n-hexanol, n-decanol, and 2-methoxyethanol. Although **1** formed a turbid gel in 2-methoxyethanol, the gel with **1** was relatively weaker than that with **2**.[16] The critical gelation concentrations (CGC) of **1** and **2** in 2-methoxyethanol were 0.10 wt % (100 μM) and 0.04 wt % (41 μM). The transparent gel with **2** was stable over a period of several months. The gel-to-solution phase-transition temperature (T_g) of **2** was

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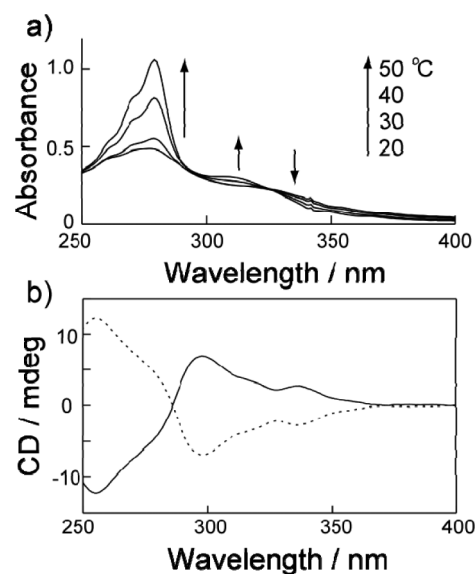

Figure 1. (a) Absorption spectral changes of **2** in 2-methoxyethanol at various temperatures. (b) CD spectra obtained in different batches at 20 °C. [**2**] = 2.5 mM.

48 °C at 0.04 wt % in 2-methoxyethanol. The observed CGC value for **2** was significantly smaller than the reported values of supramolecular gelators,[16] suggesting that **2** assembled into stable stacks in 2-methoxyethanol.

UV−vis spectrum of homogeneous CHCl₃ solution of **2** was typical for triphenylene chromophore.[17] In the 2-methoxyethanol gel of **2**, the absorption peak at 277 nm was significantly broadened and the shoulder peak assigned to transition $S_0 \rightarrow S_1$ shifted to a longer wavelength (Figure 1a).[17] The intensity of the absorption peak at 279 nm increased with a rise of temperature and the absorption spectrum at 50 °C had identical features to that in CHCl₃. This spectral change was reversible and synchronized with the formation or collapse of gels. These results consistently

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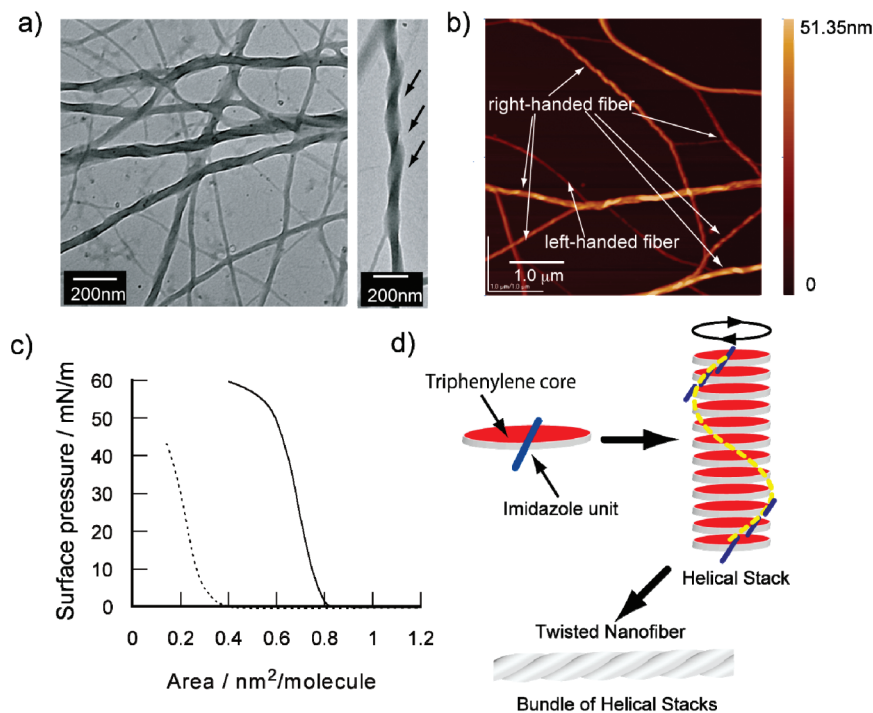
Figure 2. (a) TEM and (b) AFM images of twisted nanofibers made of **2**. (c) Surface pressure vs area per molecule isotherms for **1** (dashed line) and **2** (solid line) on triply distilled water at 20 °C. (d) Schematic representation of self-organized process of **2** into twisted nanofibers.

provided evidence that the triphenylene core in **2** formed a stacked aggregate in the gel phase through $\pi-\pi$ interaction. Solution of **2** in CHCl$_3$ and the 2-methoxyethanol gel of **1** were circular-dichroism (CD) inactive, as expected for an achiral molecule. However, the CD spectra of achiral **2** in 2-methoxyethanol (2.5 mM) showed an exciton-coupled Cotton effect with the $\theta = 0$ crossing wavelength at 285 nm (Figure 1b).[18] A couplet was present in the CD spectra at the same wavelength of the UV−vis spectra and the $\theta = 0$ crossing wavelength was in agreement with the absorption maximum of the chromophore. To check the linear dichroism (LD) effect, we measured the CD spectra in the same locations for rotation of 90 °. Because no differences were observed for the two CD spectra, we concluded that the LD contribution was almost negligible for the observed CD activity in the gel of **2**. These results clearly indicate the presence of a helical arrangement of the triphenylene cores within a stack, suggesting the chiral symmetry breaking. The gel of **2** had the same CD spectrum after being stored for several months, thus the racemization did not occur after the helical stacks had formed. The CD signals completely disappeared above 45 °C because of the disassembly of helical stacks. After cooling into room temperature, the resulting gel showed opposite CD signals. Further repeating experiments revealed a statistical distribution for CD signals, indicating that the CD activity was governed by chance in the self-assembly process of **2**. Ribó et al. demonstrated the introduction of a chiral sign of porphyrin assemblies by controlling the direction of stirring.[8] We also tried to control the sign of CD signals for helical stacks that were prepared by stirring

samples at 200 rpm clockwise or anticlockwise during the cooling process from 50 °C to room temperature. Although all samples were CD active, the sign of the CD signals was not controlled by the stirring direction. However, the addition of 1 mol % L-tartaric acid into **2** resulted in a CD signal with positive and negative Cotton effects.[19] L-Tartaric acid could form a complex with **2** through a hydrogen bonding formation between two carboxylic acids in L-tartaric acid and imidazole in **2**, and the angle between two triphenylene rings in the complex may have determined the helical sense of stacks.

TEM image indicates that the gel from 2-methoxyethanol is composed of long twisted fibers at the macroscopic level, which are approximately 10−100 nm wide and several micrometers long with a pitch of approximately 180 nm (Figure 2a). Although twisted fibers have been observed in many supramolecular assemblies of molecular components bearing chiral substituents,[20] the formation of twisted fibers from achiral molecular components

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is rare. The observed widths of the fibers are wider than the molecular length of **2** (about 2.8 nm estimated from the computer-simulated molecular model). This suggests that the fibrous structures observed by TEM may be composed of bundles of one-dimensional stacks of **2**. The chiral symmetry breaking at the stacking of achiral disklike molecule **2** affects the hierarchical organization process from numerous one-dimensional helical stacks into a macroscopic ropelike fiber. The tapping-mode AFM height image of **2** shows the presence of mainly right-handed fibers along with a few left-handed fibers within the same area and reveals a three-dimensional network structure composed of twisted fibers having heights of 10−40 nm (Figure 2b). In contrast, the left-handed fibers are dominant in the other specimen. The helical sense of twisted fibers is undermined for different batches, which is in agreement with the statistical distribution of CD signals. Compound **1** also formed fibrous assemblies, but the resulting fibers were not twisted (see the Supporting Information, Figure S1) . Therefore, we concluded that the origin for the formation of helical stacks and macroscopic twisted fibers was the introduction of imidazole unit into the triphenylene ring. The dimensions of the synthesized disklike molecules **1** and **2** were estimated from the analysis of a surface pressure versus area ($\pi{-}A$) isotherm on pure water as the subphase (Figure 2c). The limiting surface areas per molecule of **1** and **2** were estimated at 0.35 and 0.78 nm^2 determined by extrapolating the slope of the $\pi{-}A$ isotherm in the liquid-condensed region to zero pressure. The observed area of **2** was almost twice of that of **1**, suggesting a large stacking distance between triphenylene rings within the one-dimensional stacks by the attachment of imidazole unit. Powder X-ray diffraction of the gel state provided a diffraction peak at 0.35 nm corresponding to the stacking distance between the triphenylene cores within the stacks. The steric hindrance of imidazole provides a rotation bias for triphenylene rings during the assembling process of **2** into helical one-dimensional stacks through intermolecular $\pi{-}\pi$ interaction (Figure 2d). The chirality arises from a twist between the triphenylene core and the imidazole unit in **2**. This results in a helical stacking of the triphenylene cores with a stacking distance of 0.35 nm, where the triphenylene cores are rotated in the same direction along with the stack axis.

Self-Assembly in Bulk. The thermal behavior of **2** was performed by differential scanning calorimetry (DSC), temperature-controlled optical polarizing microscope (OPM), and X-ray diffraction pattern (XRD). One reversible transition was detected at 94 °C in the second heating and at 78 °C in the first cooling run (Figure 3a). The XRD pattern of **2** at room temperature displayed many deflections in the small angle region and no mesomorphic behavior was observed by OPM studies. From these results, the transition in the DSC measurements could be attributed to the melting point. Recently, new types of liquid-crystalline materials have been obtained by the formation of supramolecular assemblies made up of two or more different molecular components
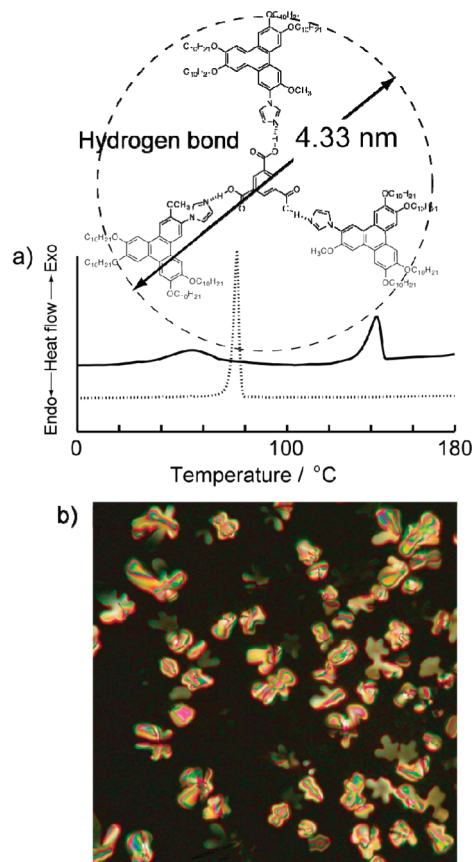

Figure 3. (a) DSC thermograms of **2** (dotted line) and a mixture of **2** and benzene-1,3,5-tricarboxylic acid (solid line) in first cooling scans at rate of 10 °C/min. (b) Birefringence texture micrograph of the mixture of **2** and benzene-1,3,5-tricarboxylic acid at 125 °C. The domains were grown from the isotropic phase as the sample was being annealed.

using various intermolecular noncovalent interactions.[21] Among these noncovalent interactions, hydrogen bonding has been widely used to construct well-defined organized structures. Kawakami and Kato reported the formation of hydrogen bonding liquid crystalline side chain polymers and networks from mesogenic compounds having imidazoles and poly(acrylic acid). Hydrogen bonding between imidazole and carboxylic acid can function as supramolecular connectors for the assembly of different molecular components.[22] The imidazole group in **2** acts as a hydrogen acceptor in the hydrogen-bonding formation with carboxylic acids, and the supramolecular connection of **2** leads to the construction of well-defined organized structures. Hydrogen-bonded complexes were prepared by mixing of **2** with benzene-1,3,5-tricarboxylic acid at 150 °C at a molar ratio of 3:1. Bezene-1,3,5-tricarboxylic acid was completely dissolved in melted **2** as confirmed by OPM and the carbonyl band of benzene-1,3,5-tricarboxylic acid in the FT-IR measurements shifted from 1691 to 1707 cm^{-1} after complexation with **2** because of the formation of thea hydrogen bond between carboxylic acid and imidazole in **2**. Figure 3b shows the DSC curves for cooling runs for

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the hydrogen-bonded complex. The melting points of **2** completely disappeared for the DSC trace of the hydrogen-bonded complex and new phase transitions were detected at 43 and 134 °C upon cooling. A birefringence texture appeared at 130 °C upon slowly cooling down from 240 °C observed under OPM. Figure 3b shows the texture of the mixture of **2** and benzene-1,3,5-tricarboxylic acid at 125 °C. The observed texture has characteristics of the hexagonal columnar mesophase D_h. The XRD study of the complex at 120 °C yielded three Bragg reflections at 3.75, 2.15, and 1.85 nm with a spacing ratio of $1:1/\sqrt{3}:1/2$, indiacating that the mesophase consisted of a two-dimensional hexagonal lattice of columnar stacks with a lattice constant of $a = 4.33$ nm. The lattice constant was much larger than the estimated diameter of single **2** and almost agreeed with the diameter estimated for a large disklike complex in which three **2**s were connected with benzene-1,3,5-tricarboxlic acid through the hydrogen bonding between imidazole and carboxylic acid. In addition, the complex revealed a sharp peak at 0.34 nm due to the stacking distance between aromatic disklike cores, suggesting the presence of long-range periodicity along the columnar axis. The current observations support that **2** and benzene-1,3,5-tricarboxylic acid self-assemble into a disklike complex decorated with 12 hydrocarbons through intermolecular hydrogen bonds, and that the supramolecular disk exhibits a thermotropic liquid crystalline behavior.

Photochemical Deposition of Silver Nanoparticles. The self-organization of **2** induces the aggregation of imidazoles along with one-dimensional triphenylene stacks.[23] We expected the accumulation of metal ions around fiber aggregates through the formation of coordination bonds with the imidazole group in **2**. A solution of $AgNO_3$ in 2-methoxyethanol (20.0 mM, 0.5 mL) was added to the transparent gel of **2** ([**2**] = 0.2 mM in 1.0 mL 2-methoxyetahnol) in the dark and the mixture was allowed to stand for 6 h at room temperature. The gel retained its size and transparency after Ag^+ was added, and no precipitation occurred after one week. The complexation of **2** with $AgNO_3$ was confirmed by fluorescence, MALDI-TOF mass, and ^1H NMR spectra. The self-assembled **2** in 2-methoxyethanol emitted a fluorescence peak at 425 nm with excitation at 350 nm. This fluorescence was completely quenched by the addition of Ag^+, indicating the highly efficient energy transfer within the complex. On the other hand, the self-assembled **1** lacking the imidazole unit did not show any fluorescence changes by the addition of $AgNO_3$. The MALDI-TOF mass spectrum of the gel after $AgNO_3$ was added revealed a mass ion peak at m/z 1057 corresponding to the 1:1 complex between **2** and Ag^+ (see the Supporting Information Figure S). ^1H NMR spectrum of **2** with $AgNO_3$ in $CDCl_3$ indicated that all proton resonances corresponding to the imidazole group had shifted downfield due to the complexation with Ag^+ (see the Supporting Information,
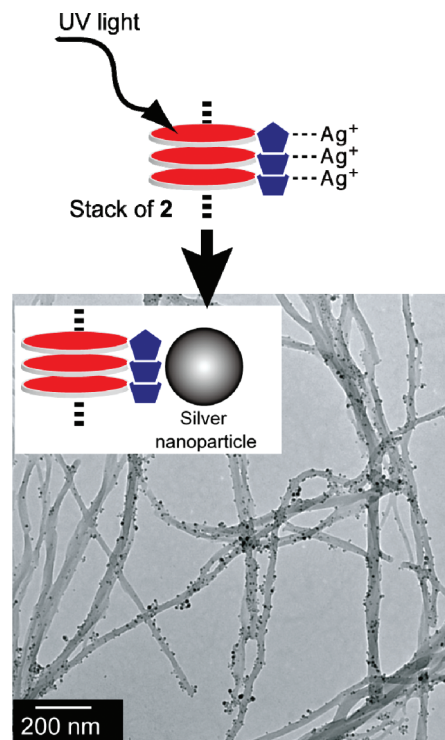

Figure 4. TEM image of self-assembled nanofibers with deposited silver nanoparticles.

Figure S3). These observations indicate that Ag^+ ions diffuse into gel and form the metal complexes with imidazole in **2**. This would produce a local accumulation of Ag^+ ions around the nanofibers, which would lead to growth of silver nanoparticles localized at the fiber after exposure of UV light.

In the absence of UV light, Ag^+ ions are stable and no silver nanoparticles form in the mixture of $AgNO_3$ and **2**. Photochemical reduction has been used previously to prepare metal colloids.[24] UV irradiation of Ag^+ solution induced photoreduction of solvents by excited Ag^+, resulting in the formation of silver atoms Ag^0. Subsequent aggregation of Ag^0 produced silver nanoparticles. When the Ag^+-containing gel in a 1.0 cm quartz cell was subjected to irradiation for 5 min with a 365 nm UV light (4 W) at 25 °C from a distance of 5 cm (light intensity: 510 $\mu W/cm^2$) under air at room temperature, the colorless gel turned gray. The absorption band of **2** did not significantly change and a new broad absorption band was appeared in the region of 400−700 nm. This absorption band coincided in position with the silver plasmon band of silver nanoparticles.[24] A small piece of the gel was placed on a carbon-coated grid and the solvent was allowed to evaporate under reduced pressure at room temperature. The TEM image showed that spherical silver nanoparticles having an average diameter of 8.0 nm

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deposited onto the surface of self-assembled fibers (Figure 4).[13,25] The fiber widths were comparable with those of organic fibers made of only **2**. Love et al. reported the formation of gold nanoparticles within the three-dimensional network of self-assembled fibers under irradiation of UV light.[26] The fibrous network structure made of dendritic gelator lacking sulfur segments stabilized the formation of metal nanoparticles. However, the irradiation of **1** gel that contained $AgNO_3$ did not afford silver nanoparticles under the same condition for more than 1 h. When the gel of **1** with $AgNO_3$ was irradiated with a 100 W mercury vapor UV lamp, a small portion of the silver nanoparticles was attached with the self-assembled nanofibers. These results clearly support the view that the coordination of Ag^+ with imidazole in **2** promotes the growth of silver nanoparticles along the surface of self-assembled nanofibers by the photoreduction with a 4W UV light irradiation. The formation of silver nanoparticles would occur though a UV absorbing of triphenylene stacks and a highly efficient energy transfer from stacks to Ag^+. Energy transfer has been widely demonstrated in one-dimensional alignment of chromophore molecules in supramolecular gel nanostructures.[27] Ajayaghosh et al. have shown energy transfer from stack of oligo(*p*-phenylenevinylene)s to entrapped organic dyes.[28] The excitation of triphenylenes by UV irradiation stores energy within the stacks and the stored energy transfers to Ag^+ through a ligand-to-metal energy transfer process. The reduction of Ag^+ to Ag^0 may proceed by the energy transfer process and the silver nanoparticles form by the aggregation of Ag^0 around the triphenylene stack.

Conclusion

In conclusion, we demonstrated that an achiral disklike molecule **2** could induce a helical stack by introducing an imidazole group, which formed a three-dimensional network structure of twisted flexible nanofibers. In addition, the imidazole in **2** acted as a molecular adaptor to form hydrogen bonds and accumulate metal ions. The supramolecular connection of **2** with benzene-1,3,5-tricarboxylic acid through the hydrogen bonds exhibited a thermotropic liquid crystalline properties. The accumulation of metal ions and photoreduction enabled metal nanoparticles to be deposited onto the self-assembled nanofibers. The present findings provide a rational approach to the hierarchical organization of complex nanostructures and they open up new possibilities for the design of integrated molecular components in optical and electronic nanodevices.

Supporting Information Available: MALDI-TOF mass and ^{1}H NMR spectra of **2** with $AgNO_3$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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