Self-Assembly

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Hierarchical Assembly of a Phthalhydrazide-Functionalized Helicene**

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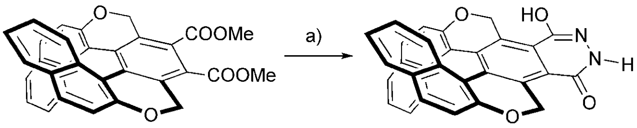
Exploration of a general principle to control the morphology and electronic states of assemblies based on π-conjugated molecules in order to create various functional materials with optimized π-electronic properties has been an important research target in supramolecular chemistry.[1] Among π-conjugated molecules, helicenes, which consist of *ortho*-annulated aromatic rings that have a helical chirality,[2] have attracted much attention because of their inherent chirality, which has recently led to promising applications in asymmetric catalysis, enantioselective molecular recognition, and chirooptical or electrooptical functional materials.[3] For example, nonracemic helicene molecules form supramolecular architectures in organogels, the liquid-crystalline phase, and crystals to form aggregates that exhibit second-order nonlinear optical (NLO) and chirooptical properties.[4] In these assemblies, helicenes accumulate around 1D structures. In order to construct such a system, we chose a disk-shaped trimer formation of phthalhydrazide units, in which the resulting trimeric disk is known to assemble into 1D structures.[5,6] Rational introduction of a helicene moiety into the phthalhydrazide unit would lead to a new supramolecular assembly of helicenes, which would exhibit intriguing chirooptical properties. Herein we report a new helicene **1** that bears a phthalhydrazide unit as a multiple-hydrogen-bonding site (Scheme 1). We found that the trimeric disk formation of **1** induces the creation of 1D chiral fiber structures. Furthermore, the assembly exhibits superior circularly polarized luminescence (CPL) properties with the value of $|g_{\text{lum}}| = 0.035$ at 476 nm, which is, to the best of our knowledge, the highest value reported to date for organic chiral molecules without a host matrix.



(*M*)-**2** (*M*)-**1**

Scheme 1. Synthesis of (*M*)-**1**. a) NH_2NH_2, dry EtOH.

Compound **1** was synthesized from the corresponding precursor helicene **2**, which was prepared enantioselectively by a rhodium-catalyzed [2+2+2] cycloaddition reaction.[7] Enantiopure (*M*)-**1** and (*P*)-**1** were isolated by recrystallization and enantiomeric separation by column chromatography on a chiral support. The trimeric disk formation of **1** was first observed by ^{1}H NMR spectroscopy (Figure 1 and Figure S3 in the Supporting Information). In polar solvents such as [D$_6$]dimethylsulfoxide or [D$_4$]methanol, which disrupt hydrogen-bonding interactions, the sharp proton signals of **1** that corresponds to the molecularly dispersed state were observed. In contrast, in nonpolar solvents such as [D$_1$]chloroform or [D$_8$]toluene, two broad signals at low magnetic fields were observed for (*M*)-**1** ($\delta = 13.0$ and 13.8 ppm in [D$_1$]chloroform, $\delta = 13.3$ and 13.9 ppm in [D$_8$]toluene) that can be attributed to the hydrogen-bonded protons of the phthalhydrazide moiety in a lactim–lactam trimeric disk, where the N−H−N

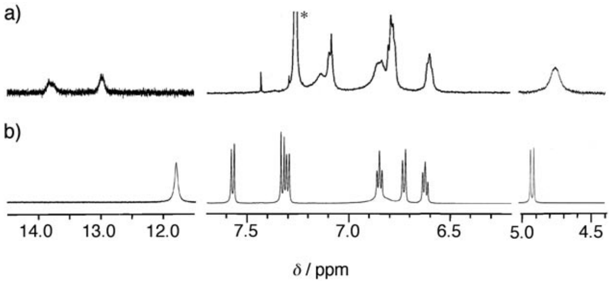


Figure 1. ^{1}H NMR spectra of (*M*)-**1** (1.0 mM) in a) [D$_1$]chloroform and b) [D$_6$]dimethylsulfoxide. * indicates the signal for the solvent.

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protons show a different signal from the O–H–O protons. It is known that a phthalhydrazide moiety exists as a mixture of tautomers in equilibrium, namely lactam–lactam, lactim–lactam, and lactim–lactim forms (Figure S7), and the equilibrium in nonpolar solvents is slow enough to be detected by ^{1}H NMR spectroscopy.[5a] In addition to trimeric disk formation, broad proton peaks of the helicene moiety also appeared, which indicate the formation of aggregates comprised of trimeric disks (Figure S4). The formation of trimeric disks was further confirmed by using dynamic light scattering (DLS). The average size of aggregates in freshly prepared solutions of **1** at 20 °C was measured to be 2.5 nm in chloroform ([**1**] = 0.09 mM) and 1.2 nm in methanol ([**1**] = 0.42 mM; Figure S6). The average aggregate size of 2.5 nm in chloroform is consistent with the diameter of the trimeric disk calculated by molecular modeling (Figure S7), while the average size of 1.2 nm in methanol was in good agreement with the size of monomeric **1**.

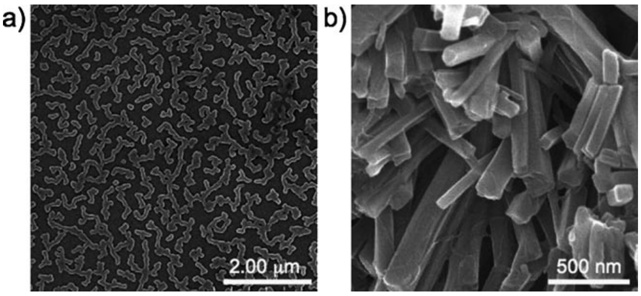

Figure 2. SEM images of (*M*)-**1** (1.0 mM) prepared in chloroform; a) 0 h and b) 12 h after sample preparation.

Assemblies of (*M*)-**1** ([**1**] = 0.50 mM) prepared from various solvents were observed by SEM and AFM. In nonpolar solvents such as chloroform, the hydrogen-bonding interaction should be operative, which should facilitate spontaneous production of the trimeric disk. However, we only observed amorphous aggregates from a freshly prepared solution of (*M*)-**1** in chloroform, thus suggesting that the trimeric disk requires time to stack and form larger supramolecular aggregates in solution. Figure 2 shows SEM images for drop-cast sample on Si wafers from a solution of (*M*)-**1** in chloroform that was left for 0 and 12 h; in the latter case, rectangular fibrous assemblies that were 200 nm wide and 3–4 micrometers long were obtained. Additionally, it can be clearly seen from the SEM and AFM images in Figure 3 that well-developed chiral fibers that were 50 nm wide and 10 µm long were formed when a solution of (*M*)-**1** in toluene was used. In contrast, amorphous or globular aggregates were mainly seen from samples prepared in methanol (Figure S9). Interestingly, AFM images revealed that fibrous assemblies of (*M*)-**1** consist of chiral fibers with a height of 2.5 nm, which is consistent with the size of the trimeric disk. From these findings, we propose the following mechanism for supramolecular fiber formation: firstly, the trimeric disk of (*M*)-**1** was formed by hydrogen-bonding interactions, then the trimeric unit stacked in a 1D manner so that the trimeric disks within the fibers are twisted with respect to each because of the complementary interaction between the helicenes (Figures 3 and 4). We tried to confirm the presence of such an interaction by UV/Vis and circular dichroism (CD) spectroscopy, however the UV/Vis and CD spectra were hardly affected upon formation of the assemblies (Figure S5). Given the unimolecular fiber structure of **1**, we infer that the outer helicene moieties need to interact with each other when stacked within the fiber and bundled with other fibers.[8] In such a manner of organization, the enantiomeric excess of the helicene unit should perturb the resulting morphologies.

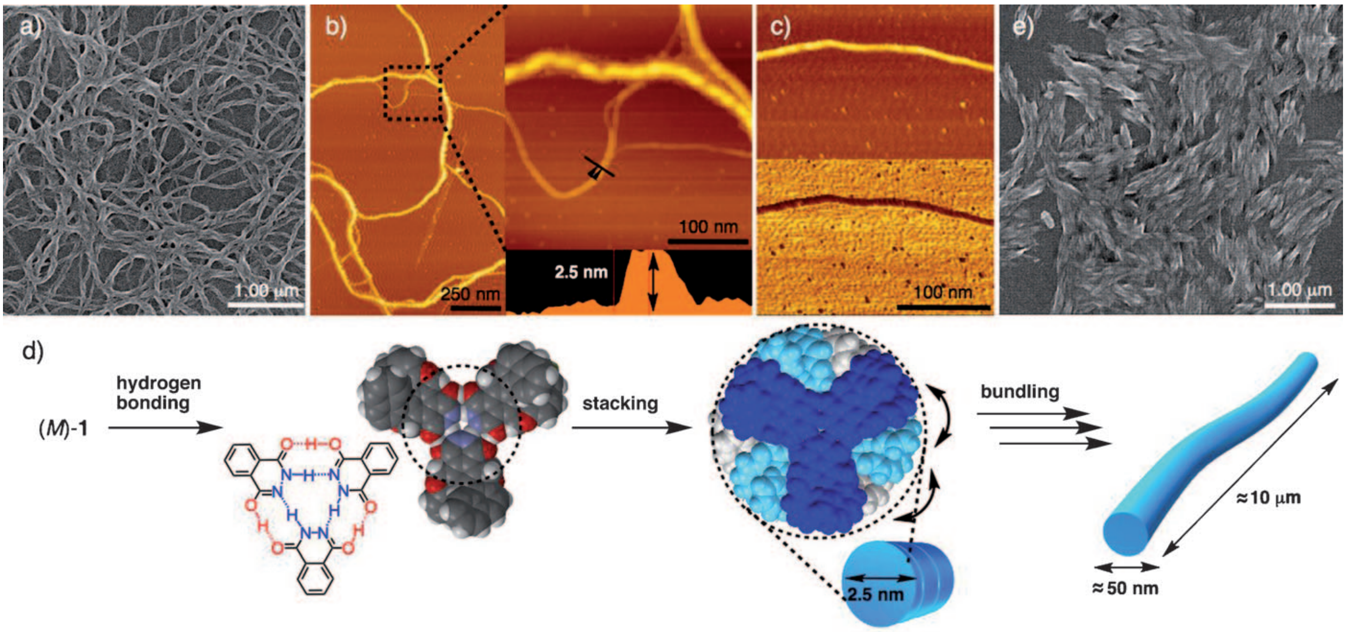

Figure 3. a) SEM image of (*M*)-**1** (0.5 mM) prepared in toluene; b,c) AFM images of (*M*)-**1** prepared in toluene, (c) is the (lower) phase image; d) plausible mechanism for the formation of fibrous aggregates from the trimeric disk of (*M*)-**1**; and e) SEM image of (*rac*)-**1** (0.5 mM) prepared in toluene.

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In order to confirm the effect of enantiomeric excess on the morphologies, we prepared samples with enantiomeric excesses of 100, 85, 70, 55, 33, and 0 % by mixing (*M*)-**1** with (*P*)-**1** (Figure S11).[9] The SEM image in Figure 3 e shows that racemic **1** formed smaller aggregates; the length and shape of the assemblies gradually changed as the enantiomeric excess decreased (see Figures S12 and S13). In the case of racemic **1**, the trimeric disk formation was confirmed by using ^{1}H NMR spectroscopy; in order to organize into well-developed fibrous structures, the molecules of **1** in the trimeric disk should have the same handedness. Furthermore, (*M*)-**1** and (*P*)-**1** do not undergo a lateral phase separation into the different chiral fibers. Instead, they are mixed homogeneously in the trimeric disk, then form a small aggregate structure.

Finally, CPL measurements (differential emission of right circularly polarized light versus left circularly polarized light in chiral molecular systems[10]) of a solution of **1** (0.4 mM) in chloroform were carried out. Figure 4 shows the corresponding UV/Vis absorption, fluorescence, CD, and CPL spectra. Compound **1** exhibits CPL activity as the CPL spectra of the *M* and *P* helicenes are mirror images. The degree of CPL is given by the luminescence dissymmetry ratio, which is defined as $g_{\mathrm{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the luminescence intensities of left and right circularly polarized light. The value of $g_{\mathrm{lum}} = -0.035$ at 476 nm for (*M*)-**1** in chloroform is found to be significantly larger than those of helicene derivatives reported to date.[11] Interestingly, the g_{lum} value of the fibrous assemblies is larger in chloroform than in methanol ($g_{\mathrm{lum}} = -0.021$ for (*M*)-**1**).

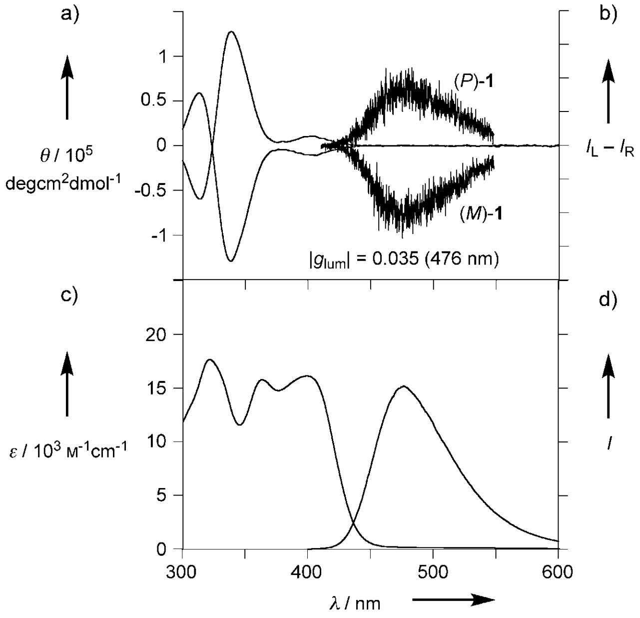

Figure 4. a) CD, b) CPL, c) UV/Vis absorption, and d) fluorescence spectra of (*M*)-**1** and (*P*)-**1** (0.40 mM) in chloroform.

In summary, we have demonstrated that a newly designed helicene, (*M*)-**1** and (*P*)-**1**, forms trimeric disks before forming screw-shaped fibrous assemblies in nonpolar solvents such as toluene and chloroform, and these morphologies of fibrous assemblies are highly dependent on the enantiomeric excess of the helicene unit. Furthermore, (*M*)-**1** and (*P*)-**1** assemblies exhibit superior CPL properties with the value of $|g_{\mathrm{lum}}| = 0.035$ at the peak maxima. To the best of our knowledge, this value is the highest among organic chiral molecules without a host matrix reported to date.[12,13] Introduction of this helicene unit to conjugated polymers, liquid-crystalline systems, and metal complexes would enhance its chirooptical properties. Research in this area is currently in progress.

Experimental Section

All chemicals were purchased from Aldrich, Kanto Chemical Co., Wako, or Strem Chemical Int. and used as received. NMR spectra were recorded on a Bruker Biospin DRX-600 spectrometer, and all chemical shifts are referenced to $(CH_3)_4Si$ (TMS; $\delta = 0$ ppm for ^{1}H) or DMSO ($\delta = 41$ ppm for ^{13}C). MALDI-TOF mass spectra were obtained with a Shimadzu AXIMA-CFR Plus instrument. High-resolution ESI mass spectra were obtained with a Bruker micrO-TOF II instrument. UV/Vis absorption spectra, fluorescence spectra, and CD spectra were obtained on a Hitachi U-2900 spectrophotometer, Hitachi F-7000 spectrophotometer, and JASCO J-725 spectrometer, respectively. Melting points were determined on a Yanaco NP-500P micro melting point apparatus. DLS measurements were performed on a Zetasizer Nano instrument (Malvern Instruments Ltd). Field emission scanning electron microscopy (FE-SEM) was performed with a Hitachi-4800 FE-SEM (accelerating voltage: 10 kV). All samples were shielded by Pt before measurement. AFM was performed with a SII E-Sweep, SPI4000 probe station (tapping mode). Molecular modeling was performed with the Spartan'08 package (Wavefunction, Inc., Irvine, CA). The initial model was then fully optimized by using AM1 calculations and further DFT calculations at the B3LYP/6-31G* level. Circularly polarized photoluminescent properties of the solutions were evaluated by excitation with linearly polarized 375 nm light from a diode laser beam (LDH-P-C-375 and PDL800-B, PicoQuant). The luminescence emitted from the solution cell was collected by a pair of achromatic doublet lenses, and the circular polarization was separated by the $\lambda/4$ plate and the linear polarizer. Circularly polarized photoluminescence spectra were recorded with a highly sensitive charge-coupled device (CCD) spectrometer (SR-303i and iDus420A, Andor technology; Figure S1).

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