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Communication

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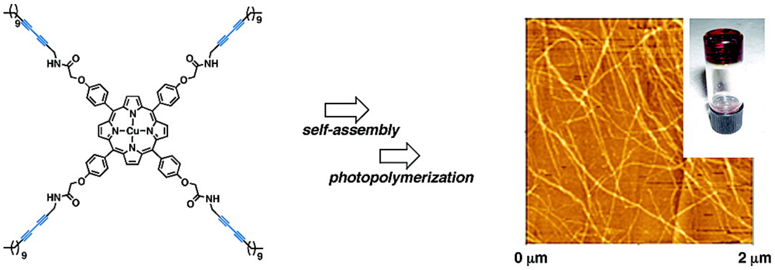

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A Stable Single Piece of Unimolecularly π-Stacked Porphyrin Aggregate in a Thixotropic Low Molecular Weight Gel: A One-Dimensional Molecular Template for Polydiacetylene Wiring up to Several Tens of Micrometers in Length

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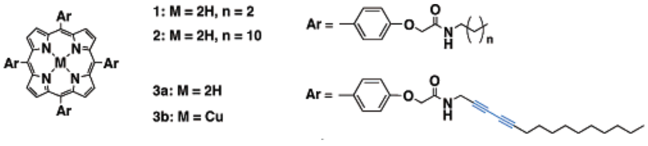
Molecules with one-dimensional (1-D) projection are the most promising materials for nanodevices. Carbon nanotubes[1] have been already raised as a candidate for such purposes, which show unique electron conductivity and physical strength indispensable to those 1-D chemical and electronic structures.[2] On the other hand, a programmed supramolecular approach to design and construct such 1-D nanodevices has received much attention in the last couple of decades; however, it is still a challenging subject since most of the examples have been carried out in the solution state where these supramolecules have a character of time-averaged factors. Recently, it has been recognized that low molecular weight gels give well-defined 1-D assemblies with a high structural aspect ratio, which can be directly imaged by microscopic observations.[3]

We have found that alkylamide group-tethered tetraphenyl porphyrins including **1** and **2** act as excellent gelators with[4a] or without guest molecules.[4b] In the 1-D **2** gel tissue, **2** molecules adopt an H aggregation mode where amide−amide hydrogen bonding and porphyrin π-stacking are working efficiently. The structural insights have fully been characterized by UV−vis and IR spectroscopy and X-ray crystallographic analyses.[4] In the course of this study, we have recognized that the alkylamide group-tethered tetraphenyl porphyrin skeleton is a promising candidate of a 1-D aggregative template for nanostructuring. On the basis of these lines of information, we introduced diacetylene units as polymerizable monomers into the 1-D aggregative core, expecting creation of a novel supramolecular architecture, in which the porphyrin π-stacking column is fabricated by conductive polymers.



The gelation properties of **3** containing diacetylene units have been tested for 12 kinds of solvents.[5] Although **3a** does not act as a gelator for the solvent tested herein, **3b** successfully triggers molecular aggregation leading to formation of very transparent gels in cyclohexane and decahydronaphthalene (Decalin). This transparency offers a suitable condition for efficient photochemical reactions without any scattering of the light.

Interestingly, the Decalin gel of **3b** (10 g dm^{-3}) shows very unique physical behaviors called thixotropy (Figure 1a−d). Generally, once low molecular weight gels are shaken to break these gel states, they turn to solution with or without precipitates and never return to the gel states unless the broken gels are heated to give solution once. The thixotropic behavior in low molecular weight gel[7] is best explained by the specific nature that the gel fibers are extremely thin, extended, and stable, and have low crystallinity. The fact that the Decalin gel of **3b** shows this unique "thixotropy" phenomenon implies that this thin and stable 1-D aggregate is very suitable for template-directed synthesis of polydiacetylens.

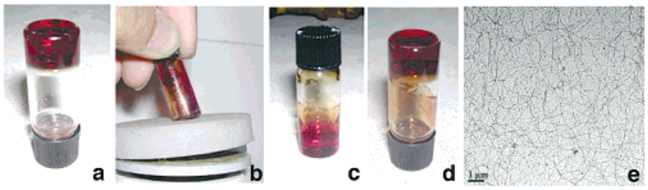


Figure 1. Photographs showing the thixotropic behavior of the Decalin gel of **3b** and its TEM image: (a) the Decalin gel of **3b** ([**3b**] = 10 g dm^{-3}), (b) shaking the gel with a vibrator, (c) leaving the gel for several seconds, (d) the regenerated gel state, and (e) TEM image of the Decalin gel of **3b** ([**3b**] = 1.0 g dm^{-3}).

In the UV−vis spectra, the Soret band observed in the Decalin gel of **3b** shows a blue shift compared with that of the solution state of **3b** (418 nm → 404 nm).[6] As expected, **3b** molecules having a 1-D motivated skeleton adopt an H aggregation mode in the gel phase. IR spectral analyses of the xerogel prepared from the cyclohexane gel of **3b** allowed us to evaluate the hydrogen bonding fashion of the amide groups in the gel phase. In both amide I and amide II regions, several split peaks appeared, which means that there are a few patterns of hydrogen bondings.[6] This observation is well-consistent with the low crystallinity of the **3b** gel as well as with the high transparency and the thixotropic behavior.

An XRD analysis of the xerogel prepared from the cyclohexane gel of **3b** shows a strong peak at $2\theta = 3.6°$ (2.5 nm), which is ascribable to the distance between the carbon atoms that neighbor the amide groups at the distal position of porphyrin.[6] This observation further confirms that the gel consists of H-aggregated porphyrin stacks. The foregoing findings based on spectroscopic analyses and XRD studies consistently support the view that **3b** has a strict nature to grow up into a 1-D aggregate.

To obtain a direct image of the gel tissue, we performed electron microscopic analyses.[6] Figure 1e shows an image of the Decalin gel of **3b** taken by transmission electron microscopy (TEM). It is clearly seen from this TEM picture that well-developed fibers, whose diameter is almost consistent with the size of a few **3b** molecules, are entangled. The elongated 1-D tissues reach to several tens of micrometers in length, which is ascribed to several 10 000 **3b** molecular stacks into the 1-D direction. Scanning electron microscopic (SEM) observation of the Decalin gel of **3b** also shows the linear morphology of the gel tissue.[6]

Given such 1-D arrays of the polymerizable units in hand, we conducted photopolymerization of the diacetylene units covalently attached to the porphyrin template. The Decalin gel of **3b** (4.0 g

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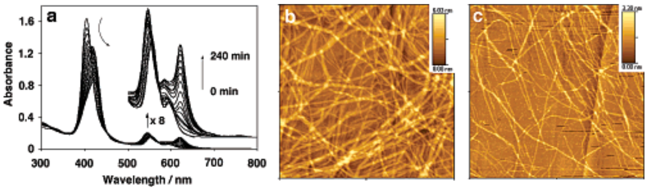

Figure 2. (a) Time dependence of the UV−vis spectral change of the Decalin gel of **3b** upon UV irradiation ([**3b**] = 4.0 g dm^{-3}) by a 500 W high-pressure mercury lamp at 25 °C. AFM images of (b) the Decalin gel of **3b** and (c) the Decalin gel of **3b** after UV irradiation and chloroform rinsing; these processes were conducted on HOPG, [**3b**] = 1.0 g dm^{-3}, a 500 W high-pressure mercury lamp, 25 °C. Edges of the AFM images are 2-μm long.

dm^{-3}) in a 0.1-mm quartz cell was subjected to photoirradiation with a 500 W high-pressure mercury lamp at 25 °C from a distance of 8 cm. The time-dependence of the UV−vis spectral change in this photoirradiation process (Figure 2a) shows that the Soret band at 404 nm gradually disappears concomitant with an appearance of a new Soret band at 420 nm. This observation evidences that assembled porphyrinic monomers undergo the structural perturbation as photopolymerization proceeds at the periphery of the porphyrins. The spectral change shows that all diacetylene units should join the polymeryzation along the extremely long aggregate template. In addition, two new absorption bands appeared at 580 and 620 nm, which are assigned to those of π-conjugated polydiacetylene. Judging from the absorption maxima, the effective conjugation length seems to be very long.[8]

IR spectra of the **3b** gel sample before and after photoirradiation also confirmed completion of photopolymerization of the polydiacetylene units. When the Decalin gel of **3b** was photoirradiated, the mass of the gel was gradually broken and purple insoluble solid precipitated. IR analysis of this solid material[6] shows that the absorption band at 2250 cm^{-1} characteristic of diacetylene monomers completely disappeared. Unfortunately, this insolubility of this photopolymerized solid material makes TEM and SEM observations difficult.

To obtain structural images by microscopic analysis, we conducted photopolymerization of the 1-D **3b** array directly on the surface for atomic force microscopic (AFM) measurements. First, we tested whether the surface photopolymerization proceeds completely with the aid of UV−vis spectroscopic analysis. The Decalin gel of **3b** (1.0 g dm^{-3}) was cast on the glass surface and left for 12 h under the ambient conditions. This treatment resulted in a filmlike material. This material shows the blue-shifted Soret band which is similar to that of the bulk gel material. Upon UV irradiation for 4 h, the red shift of the Soret band (404 → 420 nm) and the appearance of 580 and 620 nm absorption bands were observed. These spectral changes are consistent with the previous bulk experiments (Figure 2a), which show successful photopolymerization on the surface.[6] Second, the Decalin gel of **3b** (1.0 g dm^{-3}) was cast on highly oriented pyrolytic graphite (HOPG). The cast gel was washed with cyclohexane (a poor solvent for the **3b**) to remove the solvent Decalin. An AFM image of this sample shows dense accumulations of straight tissues on the surface (Figure 2b). Next, the cast gels on the HOPG surface with or without 4 h of UV irradiation were washed with chloroform (a good solvent for **3b**) to remove unreacted monomers **3b**. As seen in Figure 2c, an AFM image of the photoirradiated sample shows that straight fiber structures still remain on the HOPG surface without dissolution by chloroform washing because of the insolubilized diacetylene polymers. An AFM image of the sample without photoirradiation lost its original image after chloroform washing. A height profile of this photoirradiated sample revealed that each fiber is about 3-nm thick, which is consistent with the molecular width of **3b**. These AFM observations strongly support the nature of this templated polymerization, that is, **3b** molecules are arranged in a 1-D structure, the diacetylene units of which are photopolymerized in situ. Further striking is the finding that each unimolecularly polymerized polydiacetylene fiber is elongated to more than several micrometers in length without any defect. This implies that the distance between 1-D arranged **3b** molecules is suitable for the topochemical reaction among the peripheral diacetylene groups.

In conclusion, this work shows that the low molecular weight gel is a specific medium for generating highly elongated materials with a unimolecularly stacked array. By using this material as a photopolymerization template, unimolecularly segregated polydiacetylene nanowires are easily obtained. Despite many attempts concerning template-directed polymerization of diacetylene derivatives in gels, unimolecularly segregated polymerization several micrometers in length has thus far been unsuccessful.[9] We believe that this is the first example of such a programmed bottom-up system.

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Supporting Information Available: Experimental details. IR and UV spectra and XRD profile of assembled **3b** before and after photopolymerization. Magnified pictures of Figures 1e and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) For synthetic procedures of **3a** and **3b**, see Supporting Information. Solvents tested for gelation properties: methanol, ethanol, 1-propanol, acetone, ethyl acetate, tetrahydrofuran, *tert*-butyl alcohol, benzene, 1,2,3,4-tetrahydronaphthalene, anisole, cyclohexane, and Decalin.
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