Supramolecular Fibers and Microbelts from a Phthalhydrazide Derivative of Crown Ether with Alkyl Chains

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Assemlbing behaviors of some crown ether derivatives with alkyl chains were investigated. It was found that a phthalhydrazide derivative was unique among them in that it assembles into fibers in solution, which transform into microbelts on the surface of highly oriented pyrolytic graphite.

Nature uses ions, rather than electrons, for information processing. Artificial molecular devices may also be envisaged, which are established on the basis of ions as information carriers. In this context, nano/microarchitectures, especially fibers, containing crown ethers merit special attention for their potential use in ion selective components. To date, very limited classes of compounds containing a crown ether moiety are known to form fibers,[1–3] phthalocyanine derivatives being prominent examples.[1] Herein, we present our finding that a phthalhydrazide derivative of crown ether bearing alkyl chains form fibers by self-assembly, which transform into microbelts on a surface.

We examined four dibenzocrown ether derivatives bearing alkyl chains on one benzene ring and various functionalities on the other, two of them having hydrogen-bonding capability, as shown in Chart 1 (see Supporting Information (SI) for preparation).[4] We also used a model compound with a hydrogen-bonding capability but without alkyl chains (PHC).[5]

^{1}H NMR was employed to probe the association behavior in $CDCl_3$ solution (1 mM). All proton peaks for DBCA and PNCA, which lack hydrogen-bonding capability, were sharp. Also, the peaks for PICA were sharp regardless of the hydrogen-bonding capability of the imide group. However, the peaks in both of the aromatic and crown ether parts for PHCA were significantly broadened, as shown in SI.[4] A similar spectral shape was observed for a 0.1 mM solution as well. The broadened spectra suggest that aggregation of the molecules involving the whole crown ether moiety occurs in the solution. The spectrum sharpened up upon addition of an aliquot of CD_3OD to the $CDCl_3$ solution, which provides evidence that the aggregation is primarily due to hydrogen-bond formation. The ^{1}H NMR spectrum for PHC, which has a common phthalhydrazide head group as PHCA but lacks alkyl chains, showed that the aromatic protons and crown ether protons close to the head group were broadened, while the farthest protons from the head group remained sharp. The spectral behavior indicates that the aggregation is due to the head group association. The comparison of the spectra for PHCA and PHC reveals that alkyl chains also play an important role in the formation of larger aggregates.

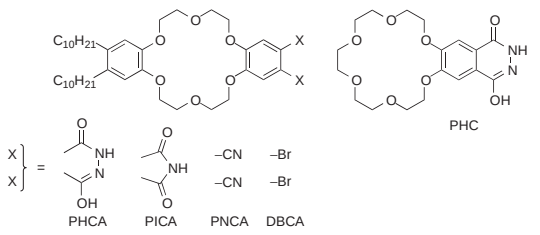

Chart 1. Crown ether derivatives used in this study. In the codes, "PH", "PI", "PN", "DB", "C", and "A" represent phthalhydrazide, phthalimide, phthalonitrile, dibromo, crown ether, and alkyl groups, respectively.

PHCA gelated toluene when a 1 mM or more concentrated solution made at an elevated temperature was cooled down to room temperature. Any other compounds listed in Chart 1 did not gelate toluene. Gelation by PHCA implies that a fibrous network is formed in solution that traps solvent molecules. A transmission electron microscopy image for a sample cast and air-dried from 0.1 mM toluene solution on a carbon-coated TEM-grid is shown in Figure 1. Fibers with various diameters in a range from several nanometers to tens of nanometers are observed.

To gain insight into the unique behavior of PHCA, solutions of PHCA were subjected to electrospray ionization mass spectrometry. The spectrum for 0.1 mM solution of PHCA in $CHCl_3$, with a spray temperature of 80 °C, showed peaks at $m/z = 746.9$ ($[PHCA + Na]^+$), 1472.4 ($[PHCA_2 + Na]^+$), and 2196.9 ($[PHCA_3 + Na]^+$) with relative intensities being 100, 8, and 2. The mass spectrum under lower temperature conditions with a spray temperature of 23 °C (coldspray ionization mass spectrometry)[6] gave the intensity ratios of 100, 16, and 18, with additional small peaks for higher oligomers as shown in SI.[4] The marked increase in intensity for the trimer is indicative of an exceptional stability of the trimeric assembly as compared to other aggregates.

Phthalhydrazides can, in principle, exist as an equilibrium mixture of three tautomeric forms: lactam–lactam, lactim–lactam, and lactim–lactim forms. The lactim–lactam isomer, which is the most stable,[7] can assemble into a trimer via multiple complementary hydrogen bonds. The trimeric structure is found in the crystal of luminol.[8] Phthalhydrazides modified with

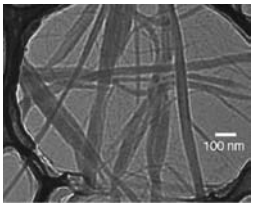

Figure 1. TEM image of the fibers from PHCA. The grey fibrous features are the molecular fibers. The black shadow encircling the image is the carbon-coated TEM grid.

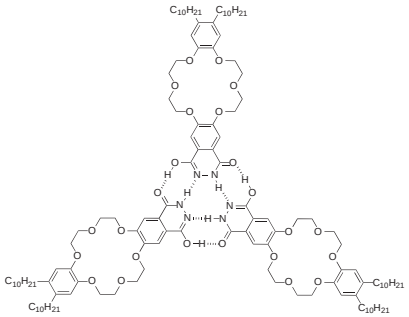

Figure 2. Likely structure of the trimer of PHCA in solution.

dendrons or alkyl chains also form trimers.[9] The trimer structure consistent with the present data and literature results[8,9] is shown in Figure 2. The diameter of the circle encompassing the extended alkyl chains is estimated to be ca. 5 nm by MM3 calculations.

Fibers were also observed on highly oriented pyrolytic graphite (HOPG). A drop of toluene solutions with a concentration in a range of 0.1–1 mM was cast onto HOPG, which was then air-dried. Samples thus prepared were observed by means of dynamic force mode atomic force microscopy (DFM). Representative DFM images are shown in Figure 3. In some places, fibers similar to those observed in TEM were observed as shown in Figure 3a. The diameter of the fibers, as judged from the DFM height, varied in a wide range, with the thinnest fibers being ca. 4 nm. The same procedure using PHC or a 1:1 mixture of PHCA and PHC resulted only in globular aggregates. These model experiments show that the alkyl chains are indispensable for the fiber formation. The coincidence between the diameters of the trimer model and the thinnest fibers suggests that the trimer units stack into the fibers with the aid of intermolecular alkyl–alkyl interactions.

It is noted that the background of fibers in Figure 3a is not the surface of HOPG, but is covered by a molecular layer. The analysis of the image indicates that the layer is extremely flat, the heights being multiples of a unit thickness of 3.3 ± 0.4 nm, as the height profile taken along the line between the pair of arrows A and B across a fiber clearly shows. The fiber is located just on the border of the first layer on the A side and the second layer on the B side. It appears that the fiber was transforming into the layer at this site, when the solvent dried up. It is likely that the affinity of the alkyl chains toward the HOPG surface promotes the transformation.

Figure 3b shows one of the places where only the first layer is observed. The long meandering morphology suggests that the fibers formed in solution merge into wider belt-like first layer. The crevices observed in the belts are directed parallel to the belts, which supports the picture that the belts are made of aligned fibers. Also, belts are not disrupted at the step edges of the basal HOPG surface, as indicated by the arrows in the figure, evidencing that the formation of the belts are not initiated at the surface but rather preformed fibers are deposited and transformed on the surface.

Summarizing, we have examined the aggregation behaviors of several structurally related compounds containing a crown ether moiety. The phthalhydrazide derivative is unique among them in that it has a strong tendency to aggregate into fibers in solution, likely through the formation of trimers via multiple

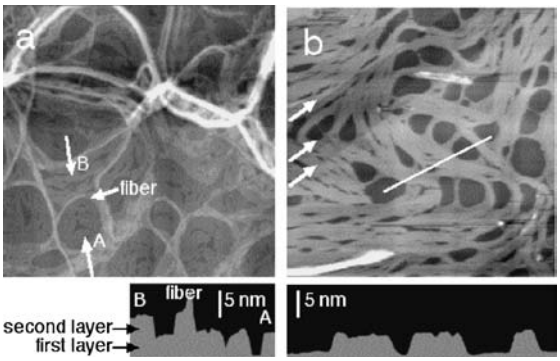

Figure 3. Representative DFM images ($5 \times 5\,\mu m^2$) of the assemblies of PHCA on HOPG. (a) Fibers and layers. The height profile between the pair of arrows A and B is given. (b) A region where only the first layer is present. The arrows indicate steps of the HOPG substrate. The height profile along the straight line is given.

complementary hydrogen bonds. The fibers, which are formed in solution and gelate toluene, transform into microbelts on the HOPG surface. Ion uptaking and transporting properties of these assemblies are of interest as materials for molecular ionics.

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4 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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