Fibrous Self-Organization of an Azopyridine Carboxylic Acid through Head-to-Tail Hydrogen Bonds

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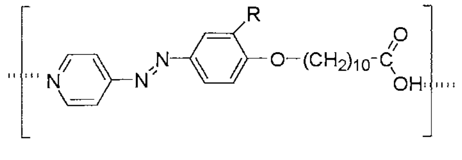
Fibrous materials were formed from an alkaline solution of an azopyridine carboxylic acid as a result of the intermolecular head-to-tail hydrogen bonding and of the suppressive effect of an alkyl side chain on the π-π stacking of the molecules.

Morphological features of molecular assemblages are influenced significantly by inherent chemical structures of component molecules, since the precisely controlled molecular self-organization is specifically determined by the position, orientational direction and number of intermolecularly as well as intramolecularly interactive sites of component molecules.[1,2] Several kinds of amphiphiles self-organizing bilayers or micelles change into well-defined fibrous architectures as reviewed by Fuhrhop *et al.*[1] It has been claimed that the hydrogen bonding of a secondary amide incorporating in amphiphilic molecules plays a key role in the generation and stabilization of the fibrous assemblages,[3-5] while dipole-dipole interactions prevent the formation of fibrous assemblages because of the preferential crystal growth.[5] To authors' knowledge, however, there has been no general guideline to produce fibrous aggregates starting from relatively simple molecules. We report here the first example of the formation of self-organized fibrous materials derived from a simple azopyridine carboxylic acid through the head-to-tail hydrogen bonding.

Our initial motivation to prepare azopyridine carboxylic acids (**1**-**2**) [6] was to determine the possibility of the self-organization to give rise to linear polymers[7] exhibiting photofunctionality through head-to-tail hydrogen bonds in suitable matrices. During the course of sample preparation of **1** in an alkaline solution, we happened to observe the deposition of fine fibers from the aqueous solution. When 1 ml of 1 mmol dm^{-3} aqueous solution of **1** containing 10 mmol dm^{-3} NaOH placed in a 2 ml vial capped with an aluminum foil with small holes was kept standing for several days, micro-fibers of several 100 μm in length were deposited. Figure 2(a) shows an optical micrograph of the fibers. It was found that the deposition of micro-fibers occurs at about pH=9, being irrespective of initial concentration of NaOH. This fact suggests that the neutralization of alkaline solution of **1** with atmospheric carbon dioxide leads to the precipitation of fibers. It followed that there is essentially no dependence of concentrations of **1** on the morphology of fibers in the range of 2×10^{-5} - 10^{-2} mol dm^{-3}. The resulting micro-fibers were stable for more than several months. Atomic force microscope observation revealed that the fibers are comprised of bundles of submicro-fibers of a diameter of 200 nm, as shown in Figure 2.



1: R=C_3H_7, **2**: R=H

Figure 1. Head-to-tail coupled and hydrogen-bonded azopyridine derivatives (**1**-**2**).

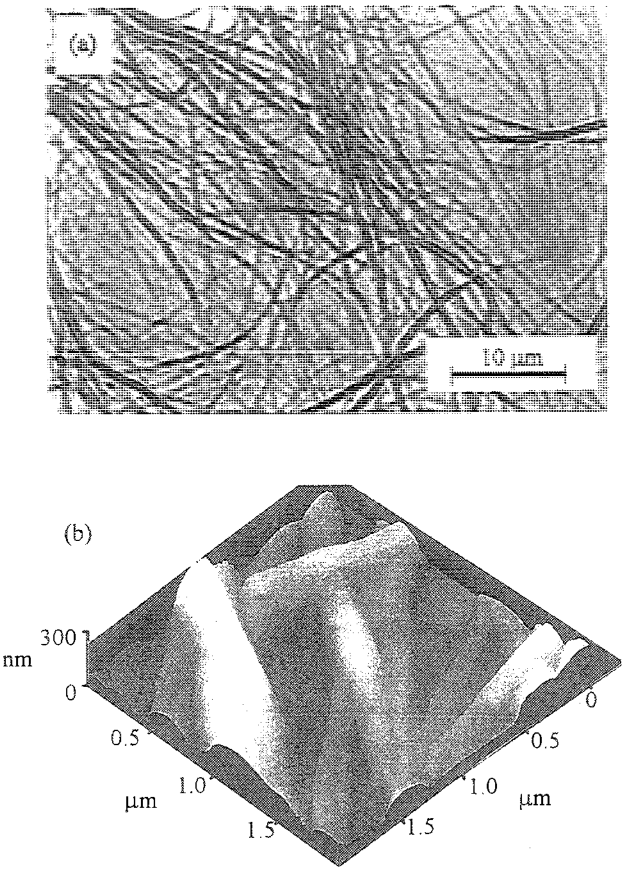


Figure 2. Optical microscope (a) and AFM (b) images (2×2 μm) of micro-fibers formed from **1**.

FT-IR spectra of the fibers displayed $\nu_{C=O}$, ν_{OH} and its Fermi resonance at 1707, 2500 and 1930 cm^{-1}, respectively, suggesting the occurrence of intermolecular hydrogen-bonds of **1** in a head-to-tail manner between the pyridyl and carboxyl groups to form supramolecular assemblages, as depicted in Figure 1.[8] **1** dissolved in an alkaline solution as a carboxylate anion exhibiting ν_{as,COO^-} = 1566 cm^{-1} is so gradually neutralized by carbon dioxide that the fibrous assemblages with a relatively homogeneous diameter is formed through the intermolecular hydrogen bonds.[9]

Polarized FT-IR microscope measurements were performed to elucidate the arrangement of molecules of **1** in the fibers.[10] As shown in Figure 3, the $\nu_{\phi\text{-}O}$ band at 1263 cm^{-1} exhibits a maximum intensity at an angle of 0°, when the angle is contained by the polarization plane of a probe light and the long axis of a fiber. On the other hand, the $\nu_{C=O}$ band shows a minimum at 0° in the intensity, indicating that the long axis of azopyridine moieties of **1** is aligned in parallel with the long axis of fibers.

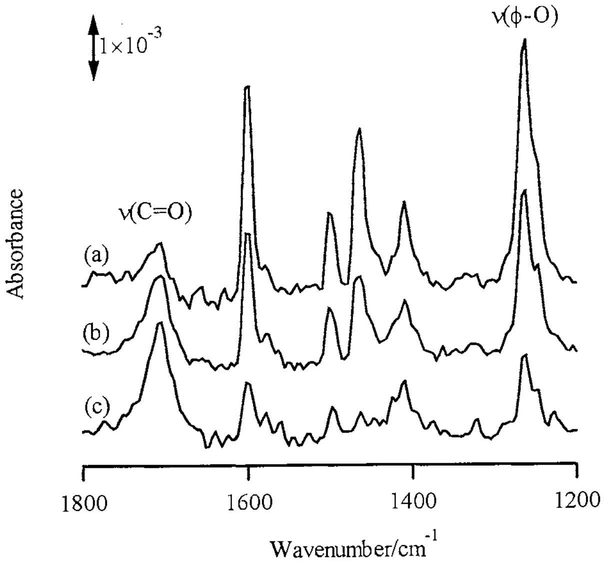


Figure 3. Polarized FT-IR spectra at (a) 0°, (b) 45° and (c) 90° of a micro-fiber self-organized from **1**. The polarization plane of probing light at 0° is parallel to the long axis of fiber.

In contrast to **1**, the azopyridine carboxylic acid **2** having no propyl substituent formed leaflet crystals under the same preparation conditions. When compared with the crystals of **2**, powder X-ray diffraction (XRD) patterns of the micro-fibers of **1** possessed no clear peak in the wide angle region ($2\theta > 22°$, $d <$ 0.4 nm)[6], suggesting that the introduction of the propyl group plays a critical role to inhibit π-π stackings among the azopyridine moieties. Taking these structural analyses into account, the formation of the fibers occurs as follows. The dipole moment of each molecule of **1** is enhanced by the head-to-tail linkage to form pseudo-polymer linear chains, which assemble tightly each other in an unti-parallel manner. As the results, the molecules are aligned uniaxially in parallel with the long axis of the fibers. The suppressive effect of the propyl substituent on the π-π stacking of the chromophores is also essential to prevent the crystal growth.

In conclusions, stable fibrous assemblages with a uniform diameter of 200 nm were self-organized from an alkaline solution of the azopyridine carboxylic acid **1**. The intermolecular head-to-tail hydrogen bonds and the inhibition of π-π stacking due to the substituent are critical factors for the self-organization to form fibrous materials with a high length-to-diameter ratio. It is assumed that objective architectures of molecular assemblages are available by designing subtle balances of total molecular interactions among molecular components.

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Reference and Notes

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6 Azopyridine carboxylic acids (**1-2**) were synthesized through three steps involving the azo-coupling of a phenol derivatives with 4-aminopyridine, the Williamson ether synthesis with ω-bromoalkanoate and subsequent alkaline hydrolysis.
1; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.77 (2H, dd, J = 4.5, 1.6 Hz), 7.77-7.89 (2H, m), 7.68 (2H, dd, J = 4.5, 1.6 Hz), 6.94 (1H, d, J = 8.6 Hz), 4.07 (2H, t, J = 6.4 Hz), 2.67 (2H, t, J = 7.2 Hz), 2.36 (2H, t, J = 7.0 Hz), 1.24-1.90 (18H, m), 0.98 (3H, t, J = 7.2 Hz). Anal. Calcd for $C_{25}H_{35}N_3O_3$: 70.56; H, 8.29; N, 9.87%. Found: C, 70.12; H, 8.28; N, 9.97%. XRD (CuKα): 2θ/deg = 4.6, 6.9, 8.1, 9.1, 11.1, 11.7, 14.3, 14.9, 16.1, 17.0, 18.8, 20.9, 22.1.
2; ^{1}H-NMR (200 MHz, pyridine-d_5): δ 8.79 (2H, d, J = 6.3 Hz), 7.95 (2H, d, J = 8.8 Hz), 7.71 (2H, d, J = 6.1 Hz), 7.16 (2H, d, J = 9.0 Hz), 4.11 (2H, t, J = 6.4 Hz), 2.19 (2H, t, J = 7.2 Hz), 1.20-1.93 (16H, m). Anal. Calcd for $C_{22}H_{29}N_3O_3$: C, 68.90; H, 7.62; N, 10.96%. Found: C, 68.75; H, 7.40; N, 11.20%. XRD (CuKα): 2θ/deg = 3.4, 6.7, 7.1, 9.9, 10.6, 16.5, 17.4, 18.9, 19.8, 21.3 23.1, 26.4, 29.8, 33.3, 36.6.
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10 Polarized FT-IR microscope measurements were carried out using Bio-Rad UMA-500 and FTS-575C equipped with a MCT detector. The measured size was 8 × 250 μm.