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Electrically conductive hybrid nanofibers constructed with two amphiphilic salt components†

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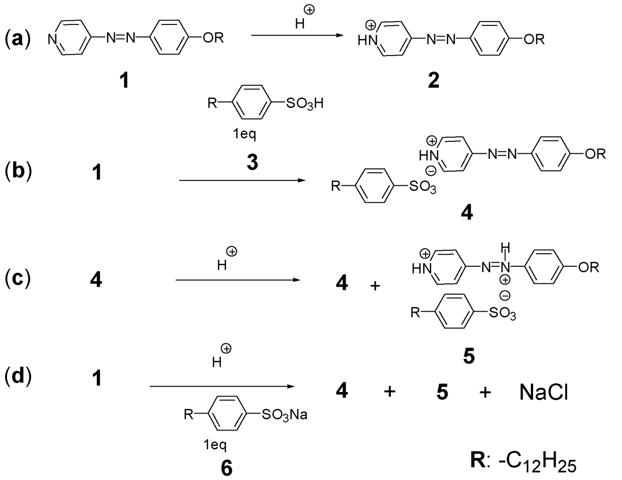
Electrical conductivity was obtained in hybrid organic nanofibers fabricated with low-molecular-weight amphiphilic azopyridinium and dodecylbenzenesulfonic acid or its salt.

Supramolecular self-assembly is one of the powerful approaches being explored for creation of novel nanostructures.[1] In the last few decades, fabrication of self-assembled nanofibers has been widely studied and developed in the fields of electronics and biomaterials.[2] Fabrication of nanofibers using amphiphilic salts has become one of the most popular procedures. Recently, Kimizuka *et al.* summarized diverse ways of creating organic nanofibers using the amphiphilic salts as single, double, triple, quadruple chains, as well as bola-amphiphile, gemini amphiphile, catanionic amphiphile, and amphiphilic metal complex types. These nanofibers exhibiting heat-set gel-like networks in organic media were also studied.[3] However, special functionalities like electrical conductivities of these self-assembled nanofibers are desired from the viewpoint of applications.[2a–c,3] It is necessary to design novel nanofibers constructed with different salt components in order to achieve these unique properties, because it is difficult to realize these functions for the nanofibers having one single salt in self-assembled processes.

Generally, conductive nanofibers were fabricated with conductive polyaniline or polyheterocycle polymers by using various plates.[4–7] Gupta *et al.* created carbon nanofiber composites with excellent conductivity by dispersing carbon nanofibers in a polystyrene (PS) matrix.[8] Moreover, nanowires, nanoribbons, and nanoplates containing polyaniline were formed by self-assembly in the process of oxidative chemical polymerization. Their fabrication needed a relatively long time and their conductivities were acquired by doping with acids.[9,10] Compared with these nanofibers assisted by conductive polymers, it is difficult to achieve electrically conductive nanofibers with single low-molecular-weight (LMW) amphiphilic components because their molecular arrangement of bilayer structures in the nanofiber formation does not benefit the flow of electric current.[2a–f] However, LMW nanofibers have advantages of being quickly formed in simple self-assembly processes at room temperature. In this communication, we report a robust method of fabricating novel hybrid nanofibers by using different components of LMW amphiphilic azopyridinium salts and sulfonic-acid based surfactants, and supplying the obtained nanofibers with electrically conductive function *via* improved π–π stacking interactions. This simple method would help development in fabrication of conductive LMW nanofibers.



Scheme 1 Synthesis of LMW compounds for fabricating organic nanofibers.

As shown in Scheme 1a, LMW azopyridine compounds were chosen due to their capability of nanofiber formation.[2c] Although compound **1** is hydrophobic, it was easily converted to amphiphilic azopyridinium **2** by addition of excess HCl into its THF solution. After this azopyridinium-forming reaction, a new broad peak at 2581 cm^{-1} was observed in the FT-IR spectrum due to the formation of pyridinium structures (Fig. S1, ESI†). Such a structural change is also reflected in the ^{1}H NMR spectra (Fig. S2, ESI†). Compared with the results of compounds **1** and **2**, the chemical shift of proton b was obviously shifted from 7.88 to 8.16 ppm when azopyridine groups were changed into azopyridiniums.

Different from the azopyridine compound reported by Nakagawa *et al.*,[2e,f] the azopyridinium **2** lacks hydrogen-bonding functions. However, its distinctive amphiphilic

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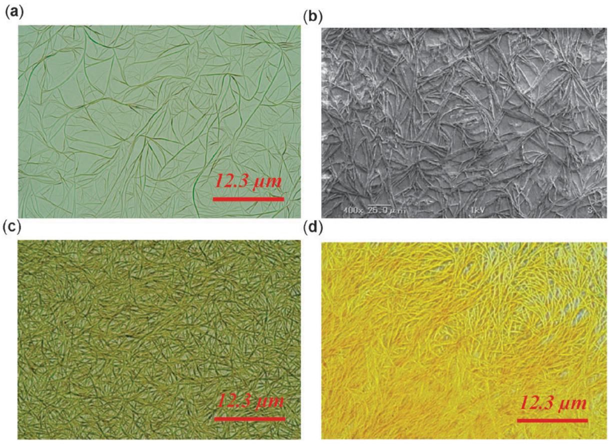

Fig. 1 Characterization of fabricated nanofibers. (a) and (b) are optical and SEM images of nanofibers formed with **2**. (c) and (d) are optical images of hybrid nanofibers formed with **4** and **5**, or **4** and **5** plus NaCl.

structure and π–π stacking interactions still enable it to self-assemble into organic nanofibers. As shown in Fig. 1a, the nanofiber formed spontaneously upon evaporation of a THF solution of **2** dropped on the surface of glass substrates. Furthermore, an obvious birefringence was observed with a polarizing optical microscope (POM, Fig. S7, ESI†). Both the optical micrograph and the SEM image (Fig. 1b) clearly indicate the formation of nanofibers with **2**.

As shown in Fig. S5a (ESI†), a high and sharp peak was observed at 4.53 nm in the X-ray diffraction (XRD) pattern of the nanofibers formed with **2**, which is the width of the monolayer sheet.[2g] Other peaks at 0.46 nm, 0.43 nm and 0.41 nm were attributed to the packing of the long hydrocarbon chain (the dodecyl group). The broad peak at around $2\theta > 20^\circ$ was ascribed to the suppressive effect of π–π stacking interactions among the azopyridine chromophores.[11] Therefore, the nanofibers obtained with **2** possessed lamellar structures and π–π stacking interactions.

To investigate the intermolecular interactions of **2**, UV-vis absorption spectra were measured at its different states. As shown in Fig. 2a, the maximum absorption peak (λ_{max}) was observed at the band of 356 nm in its THF solution, whereas λ_{max} appeared at 371 nm in its film state (Fig. 2b). This red shift of 15 nm further demonstrates the existence of π–π stacking interactions of **2** in the solid state of nanofibers.

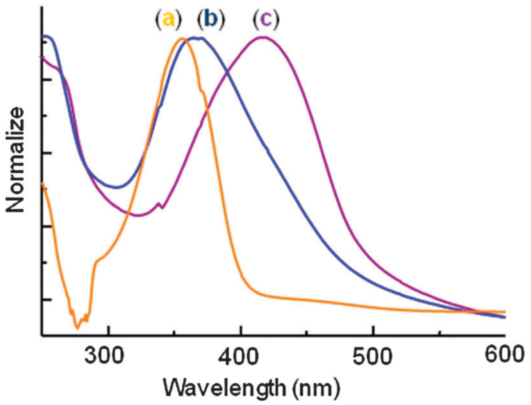

Fig. 2 UV-vis absorption spectra of LMW compounds for fabricating nanofibers. (a) **2** in THF solution, (b) **2** in the film state, (c) a mixture of **4** and **5** plus NaCl salts in the film state.

Accordingly, the organic nanofibers could be formed by the following processes. Addition of excess HCl into THF solution of **1** introduced both proton and water, and azopyridinium **2** was formed spontaneously by the reaction in Scheme 1a. Upon evaporation of solvent, molecular aggregation was induced. Since THF is more volatile than water, the hydrophobic hydrocarbon chain should contract and exist in the inner part of the aggregates. Then the repulsion of positive charges occurred among the hydrophilic azopyridinium moieties, leading to the formation of head–tail structures by molecular arrangement, as shown in Fig. S13a (ESI†). Moreover, π–π stacking interactions existed in the nanofibers obtained with **2**.

To provide the fabricated nanofibers with special functionalities like electrical conductivity, a hybrid method was developed by introducing different components of amphiphilic salts. These hybrid nanofibers were obtained by the reactions of **1** with dodecylbenzene-sulfonic acid (DBSA) **3** or its sodium salt (DBSNa) **6** (Scheme 1c and d). Here, the addition of excess HCl in the THF solution played a key role in fabricating hybrid nanofibers. Without this treatment, nanofibers did not form.

To elucidate these processes, the reaction of **3** with **1** (molar ratio, 1 : 1) in THF solution was first carried out, and then compound **4** was obtained (Scheme 1b). In the ^{1}H NMR spectra (Fig. S3, ESI†), all the peaks and their assignments to **2** and **3** were observed, indicating the formation of a salt structure shown in Scheme 1c. However, hybrid nanofibers were not obtained by using compound **4**, because its hydrophilic part influenced the molecular aggregation, leading to poor capability of nanofibers formation (Fig. S9, ESI†). In contrast, a mixture of **5** with **4** was prepared by addition of excess HCl into THF solution of **4**. Generally, the DBSA anion should combine with the azopyridinium cation by electrostatic interactions, as confirmed by the obvious changes of the chemical shift of protons in its ^{1}H NMR spectrum (Fig. S4, ESI†). As the shielding effect of aromatic-ring current existed between the benzene and pyridine in **5**, the chemical shift of protons (a–e in Fig. S4, ESI†) shifted to high field. Combining with previous results of Goswami *et al.*,[12] the structure of **5** is described in Scheme 1c. Meanwhile, the peaks of **4** were also observed, which indicated that a mixture of **4** and **5** was obtained. The integral ratio of protons (e and e′) of methylene groups ($-CH_2O$) in **4** and **5** was calculated as 1 : 1.5, which is the molar ratio of **4** to **5** in the resulted mixture. In their FT-IR spectra (Fig. S1, ESI†), the characteristic peak of DBSA **3** at around 907 cm^{-1} disappeared in the resulted mixture because of the formation of salts upon combination of the anion and the cation. More interestingly, the hybrid nanofibers were successfully fabricated with this mixture (Fig. 1c), which might be attributed to the existence of amphiphilic structures of **5** in this mixture.

Similarly, the hybrid nanofibers were also fabricated with another mixture, obtained by a reaction of DBSNa **6** with **1** (molar ratio 1 : 1) upon treatment with excess HCl (Scheme 1d). The optical image in Fig. 1d shows their fibrous morphologies. Likewise, the hybrid nanofibers were not obtained without additional treatment of HCl (Fig. S10, ESI†) because no azopyridinium was formed in this case. This indicated that the hydrophilic azopyridinium was one of the most important factors in the fabrication of nanofibers and their hybrids.

Besides, two other compounds such as sodium lauryl sulfate without the aromatic ring and *p*-toluenesulfonic acid monohydrate (TSAM) with a short alkyl chain were also utilized for fabrication of hybrid nanofibers. Although the same reactive conditions were used, neither of them showed nanofiber formation (Fig. S11, ESI†). For TSAM, solids preferably precipitated from the solution upon addition of excess HCl. These indicate that both π–π stacking interactions of aromatic rings and a long alkyl chain in benzenesulfonic groups are necessary for fabrication of the hybrid nanofibers.

Then, electrical conductivity of the fabricated nanofibers was evaluated *via* a standard four-probe method. All the nanofiber films were prepared with a thickness of about 0.4–0.5 mm, but two contrary results were obtained. The nanofibers with **2** had no electrical conductivity, whereas the hybrid nanofibers with a mixture of **4** and **5** (or **4**, **5** plus NaCl) showed an electrical conductivity of 1.1×10^{-7} S cm^{-1} (or 1.3×10^{-7} S cm^{-1}). Undoubtedly, this additional conductive property should be achieved from the hybridizing process.

In the UV-vis absorption spectrum of a mixture of **4**, **5** plus NaCl in the solid state (Fig. 2c), $\lambda_{\max}$ was obtained at 417 nm. In its solution, $\lambda_{\max}$ appeared at 357 nm (Fig. S12, ESI†), almost the same as that of Fig. 2a, indicating that π–π stacking interactions existed in the solid state of the hybrid nanofibers. Moreover, $\lambda_{\max}$ in Fig. 2c showed a remarkable red shift of 46 nm compared with that in Fig. 2b. This demonstrates that the π–π stacking interactions were strongly enhanced in the hybrid nanofibers than that without a hybrid, which might be responsible for the obtained conductivity.

XRD of the obtained hybrid nanofibers is shown in Fig. S5b (ESI†). Two broad peaks at $2\theta > 20^\circ$ and $15^\circ < 2\theta < 20^\circ$ were observed. The former was attributed to π–π stacking interactions among the azopyridine chromophores, similarly to that of Fig. S5a (ESI†). The latter is an additional peak, originated from the hybridization process by introduction of DBSA or its salt, which should be responsible for the enhancement of π–π stacking interactions. The sharp peak at 0.28 nm was ascribed to NaCl (Fig. S5b, ESI†). Therefore, a possible schematic illustration of the enhanced π–π stacking in the hybrid nanofibers is given in Fig. S13b (ESI†). It is the strong π–π stacking interactions improved by the hybrid method that resulted in the additional electrical conductivity.

In summary, hybrid organic nanofibers were successfully fabricated with LMW amphiphilic azopyridinium and DBSA or its salt by a simple self-assembled process. The formation of azopyridinium salts played an important role in the fabrication of nanofibers and their hybrids. Interestingly, electrical conductivity was obtained by the enhanced π–π stacking interactions using this robust hybrid method. It is expected that more variations of hybrid nanofibers with multi-components such as various organic and inorganic compounds can be created *via* this simple method, which would advance their future applications in conductive nanomaterials.[2]

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