

Conductive Hybrid Nanofibers Self-Assembled with Three Different Amphiphilic Salts

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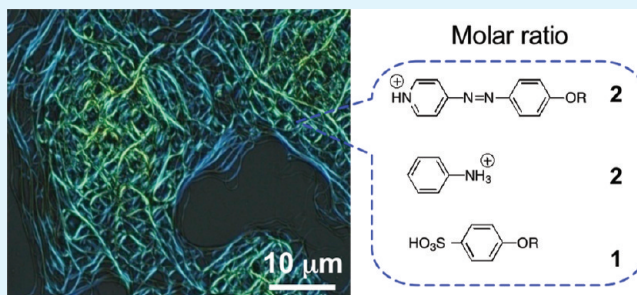
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S Supporting Information

ABSTRACT: Upon supramolecular self-assembly, novel conductive hybrid nanofibers were successfully fabricated using three amphiphilic salts, azopyridinium, aniline hydrochloride, and alkylbenzenesulfate-based anionic surfactants. The interactions like π - π stacking and ionic bonding among the different compounds played important roles in preparation of these multicomponent hybrid nanofibers. These were demonstrated by measurements of XRD, UV-vis absorption, and FTIR spectra. Interesting conductivity in an order of magnitude of 1×10^{-7} to 1×10^{-5} S/cm was observed in films of the fabricated hybrid nanofibers, which was attributed to the existence of freely movable ions, showing their possible applications as bionanomaterials and nanoelectronic devices. The fabrication processes of the conductive nanofibers might provide references for simulation of nerve fibers in nature.

KEYWORDS: hybrid nanofibers, conductive materials, supramolecular self-assembly, azopyridine, π - π stacking interactions



1. INTRODUCTION

The concept of "hybrid" has been widely used in fabrication of organic-inorganic hybrid materials by introduction of special functionalities such as optical, electrical, thermal responsiveness, which is difficult to be achieved in organic or inorganic materials having one single component.¹ In the last few decades, amphiphilic salt materials were intensively studied in fabricating soft functional nanomaterials such as nanofibers, nanoparticles, nanoplates, et al.² In nature, the elaborate nanofibers with pivotal biological significance are one of the most important components of neurons. Their fundamental task is to receive, conduct, and transmit signals. These nerve fibers show a high surface area and a highly interconnected porous architecture, which facilitates the colonization of cells in the scaffold and the efficient exchange of nutrients and metabolic waste between the scaffold and its environment.³

Normally, the nanofibers for potential applications as artificial neurons have been fabricated by an electrospinning approach using biocompatible polymers such as poly(L-lactic acid) (PLLA).⁴ However, the size of the obtained nanofibers was limited by the assembled conditions and equipments in the electrospinning processes. In fact, the self-assembled method is more close to the forming process of natural nerve fibers.⁵ From the viewpoints of transmission functions and electric signals of neurons, conductive nanofibers fabricated with self-assembled processes are of important significance in preparation of artificial neurons.

Generally, fabrication of nanofibers using one single compound by inter- or intramolecular interactions such as

hydrogen bonds and π - π stacking interactions are common strategies in self-assembled processes.⁶ For instance, Kaner et al. reported fabrication of conductive nanofibers by using polyaniline.⁷ However, a long time was necessary because of the polymerization of aniline monomers. Recently, we successfully fabricated hybrid nanofibers using two components of azopyridinium salt and dodecylbenzenesulfonic acid (DBSA) or its salt (DBSNa) upon supramolecular self-assembly.⁸ The obtained nanofibers showed interestingly electric conductivity, which was not observed in nanofibers containing one component of azopyridinium salt. These hybrid nanofibers have advantages of simple processing and quick fabrication (within several minutes) over other preparation methods of conductive nanofibers.⁷

However, these fabricated hybrid nanofibers in our previous studies difficultly exhibited good conductivity,⁸ because of the limitation of the π - π stacking interactions. To realize the function of quickly transferring electric signals in the obtained hybrid nanofibers, the components of hybrid nanofibers should be converted. Referring to the reports that conductive nanofibers showing excellent conductivity have been fabricated using polyaniline,⁷ here we introduced aniline hydrochloride as one of amphiphilic salts into the self-assembled processes in fabrication of these hybrid nanofibers to enhance their conductivity.

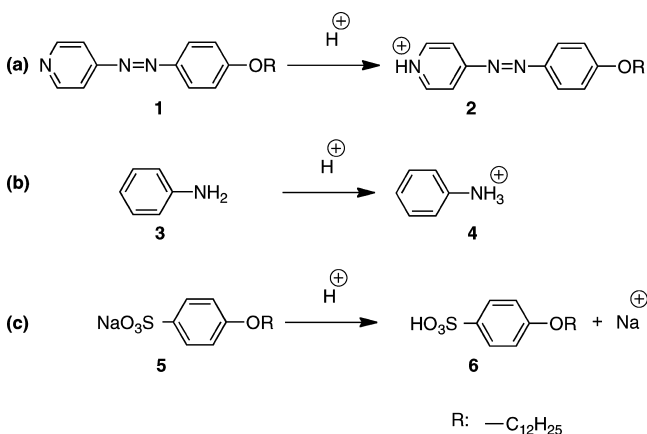
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In this paper, we reported fabrication of novel hybrid nanofibers having three components of azopyridinium, aniline hydrochloride, and alkylbenzenesulfate-based surfactants. We first prepared novel hybrid nanofibers having two components of azopyridinium **2** and anilinium chloride **4** (Scheme 1). Then

Scheme 1. Synthesis of Low-Molecular-Weight Compounds for Fabrication of Hybrid Nanofibers



the third component of amphiphilic salt (DBSNa **5**) was added in the fabrication process to prepare multicomponent hybrid nanofibers (Scheme 1). Different from the general method of fabrication of low-molecular-weight nanofibers using one component of an amphiphilic compound, we realized the fabrication of novel hybrid nanofibers with various amphiphilic components. Moreover, it is expected that their conductivity should be improved by this novel hybridization processes. The fabricated conditions of the multicomponent hybrid nanofibers were also discussed, which might provide references for stimulating nerve fibers in nature.

2. RESULTS AND DISCUSSION

The materials for fabrication of the hybrid nanofibers were synthesized from the treatment of mixtures of **1** and **3**, or mixtures of **1**, **3**, and **5** in THF solution with an excess of hydrochloride acid (HCl) (Scheme 1). As shown in Figure S1 in the Supporting Information, the hybrid nanofibers were spontaneously formed upon evaporation of their THF solutions having the resulted mixtures of **2** and **4** or **2**, **4** and **6** dropped on the surface of glass substrates. Similarly to our previously reported results,⁸ the hybrid fibers were first fabricated using a mixture of **1** and **3** (molar ratio, 1:1) by treatment of excess HCl. Their morphologies were clearly observed in an optical microscopic picture, as shown in Figure 1c. Especially, an obvious birefringence of the hybrid nanofibers was obtained upon observation with a polarizing optical microscope (POM, Figure 1d).

The composition of the fabricated two-component nanofibers was examined with ¹H NMR spectrum (see Figure S2 in the Supporting Information). Because the mixture of **2** and **4** is composed of salt, it is difficult to isolate them by usual methods as column chromatography and recrystallization. The ¹H NMR spectra were directly measured without further purification. The integral ratio of **2** and **4** in ¹H NMR (see Figure S2 in the Supporting Information) was the same as the molar ratio of the reactive mixture of **1** and **3** (1:1), indicating that no side reactions occurred in the fabrication process. Thus, the two-

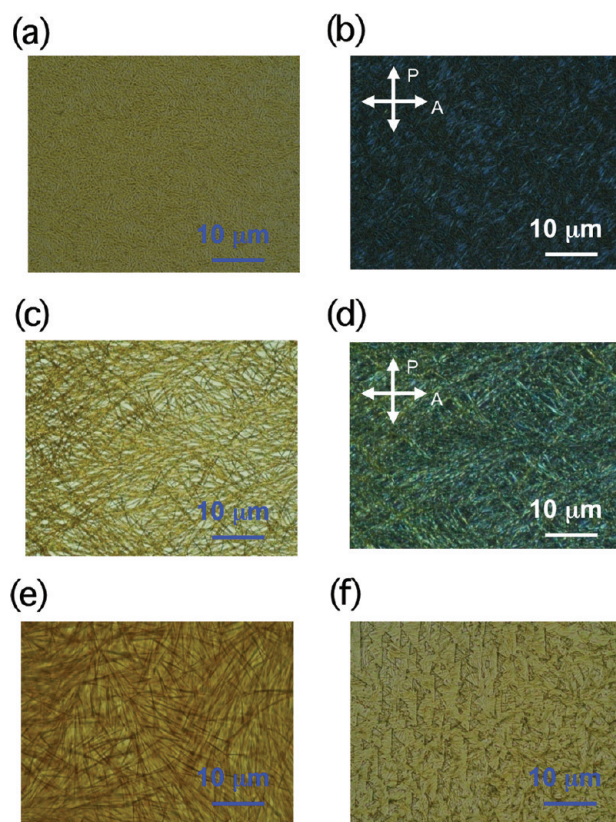


Figure 1. Characterization of fabricated hybrid nanofibers using the resulting mixture of **2** with **4** having different molar ratios of (a, b) 2.5:1, (c, d) 1:1, (e) 1:1.5, and (f) 1:2. a, c, e, and f are optical images. b and d are POM images. P, polarizer; A, analyzer.

component nanofibers were simply constructed with two amphiphilic salts of **2** and **4**.

Figure 2 shows UV–vis absorption spectra of the fabricated nanofibers in film and solution states. In the solid state of nanofibers composed of **2** and **4** (Figure 2b), the maximum absorption peak was observed at 365 nm, a slight red shift of 10 nm compared with their maximum absorption in THF solution (Figure 2a). These results are similar to the changes of the absorption spectra of azopyridinium **2** in solid and solution states.⁸ Likewise, the red shift of 10 nm was attributed to the π – π stacking interaction exist in the obtained hybrid nanofibers. Such π – π stacking interactions were also observed in the results of X-ray diffraction (XRD) (Figure 3). In the XRD of a film containing **2** and **4** (Figure 3b), the broad peak at around $2\theta > 20^\circ$ was ascribed to the suppressive effect of π – π stacking interactions among the azopyridine chromophores.⁹

Compared with the XRD of aniline hydrochloride in Figure 3a, two points should be emphasized. First, the peak at $2\theta = 22^\circ$ (correlate with 0.41 nm) of **4** remarkably weakened in the hybrid nanofibers, indicating that **4** was consumed in the self-assembled process for fabrication of the hybrid nanofibers. Second, the especial peak of aniline hydrochloride at $2\theta = 35^\circ$ (0.26 nm) was still observed in XRD of the two-component hybrid fibers (Figure 3b). This demonstrates that the special aggregative form of anilinium **4** also existed in the hybrid nanofibers. Therefore, anilinium **4** might partly coaggregate with **2** in the hybrid nanofibers, which could be described in Figure S9 in the Supporting Information. In the hybrid

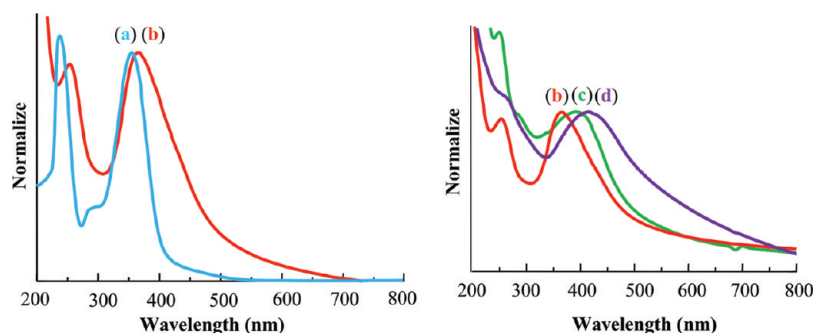


Figure 2. UV-vis absorption spectra of compounds for fabricating nanofibers. The mixture of **2** and **4** (1:1) in (a) THF solution and (b) film state. Films containing the mixture of **2**, **4**, and **6** with a molar ratio of (c) 2.8:1.4:1 and (d) 2:2:1.

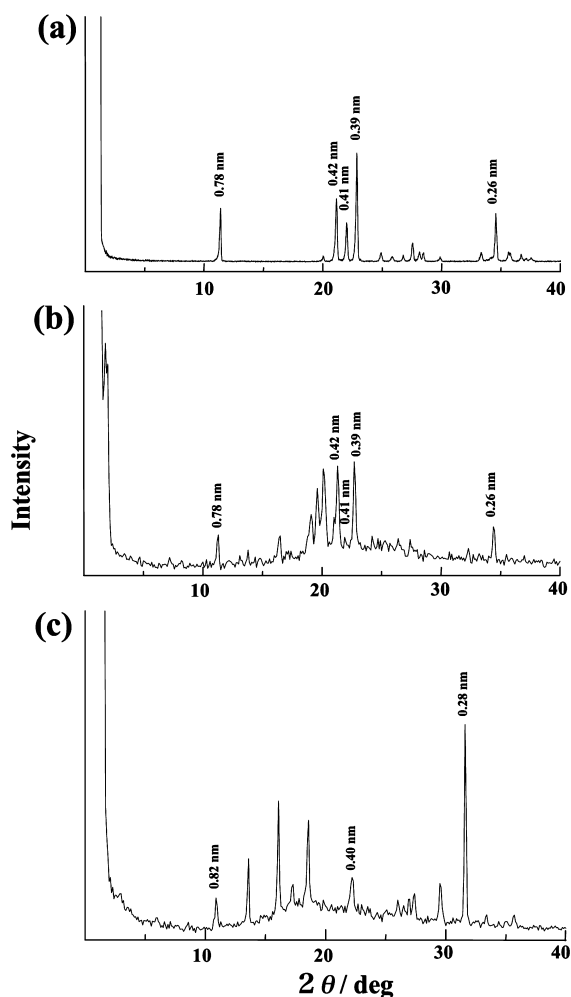


Figure 3. X-ray diffraction patterns of the fabricated nanofiber films containing (a) **4**, (b) a mixture of **2** and **4** (1:1), and (c) a mixture of **2**, **4**, and **6** (2:2:1).

nanofibers with two components, the possible aggregations can be classified as three kinds of patterns, **2** with **2**, **2** with **4**, and **4** with **4**, respectively.

Via a standard four-probe method, conductivity of the hybrid nanofibers formed with **2** and **4** (1:1) was measured as 1.2×10^{-7} S/cm. This conductivity was attributed to the introduction of **4** into the nanofibers because the nanofibers with **2** has no conductivity.⁸ Similarly to the analysis of ¹H NMR and FT-IR results of polyaniline,¹⁰ the peaks of water were also observed in nanofibers containing the mixture of **2** and **4** (see Figures S2

and S3 in the Supporting Information). Although the hybrid nanofibers were spontaneously dried in air at room temperature for one day, the small residue of water still existed. In addition, no remarkable change was observed in the π - π stacking interactions in Figure 2b, demonstrating that the conductivity of hybrid nanofibers might be attributed to the transfer of freely movable ions in amphiphilic salt.

To investigate the influence factors in fabrication of the hybrid nanofibers and improve their conductivity, we converted the reactive mixture ratio of **1** and **3** into 2.5:1, 1:1.5, 1:2, respectively. As shown in Figure 1b,d and Figure S4 in the Supporting Information, these hybrid nanofibers exhibited notable birefringence upon POM observation. However, a large quantity of crystalline materials was observed in fabrication of hybrid nanofibers using a mixture of **2** and **4** (1:2) (Figure 1f).

To investigate the influence of **4** for amphiphilic salts of **2** with **4**, we measured their contact angle with pure water. Films containing **2** and a mixture of **2** and **4** (1:1) showed contact angles of 22 and 8°, respectively, indicating that the introduction of anilinium **4** into nanofibers increased their hydrophilic properties. The conductivity of the hybrid nanofibers fabricated using **2** and **4** with a molar ratio of 2.5:1 and 1:1.5 was observed at 7.7×10^{-8} and 7.7×10^{-5} S/cm, respectively. These indicate that excess amount of **4** is beneficial for improving the conductivity of the two-component hybrid nanofibers.

Generally, the self-assembly of neurons with different components is one of the most complicated processes in nature. To further understand the complicated self-assembled processes, we studied the fabrication of multicomponent nanofibers using three different amphiphilic compounds. Especially, we added **5** into the reactive mixture of **1** and **3** (Scheme 1 and Figure S1 in the Supporting Information). The hybrid nanofibers were successfully fabricated using the resulted mixtures obtained from **1**, **3**, and **5** (molar ratio as 2:2:1 and 2.8:1.4:1) by treatment of their THF solutions with excess HCl (Figure 4a, c). Similarly, the formed nanofibers also showed a remarkable birefringence (Figure 4b, d). However, the hybrid nanofibers were not completely formed using the other resulted mixtures with molar ratios of 1:1:1, 1:1:2, 1:2:1, 2:1:1 and 2:1:2 (Figure 4e-1).

As mentioned above, two-component hybrid nanofibers have been fabricated with the mixture of **1** and **3**. However, hybrid nanofibers were not successfully obtained with another two components of **3** and **5** (reactive molar ratio of 1:1) treated by excess HCl in THF, and only crystallization was observed as shown in Figure 4k. These indicated that a large amount of components of **1** and **3** in the reactive mixtures is beneficial to

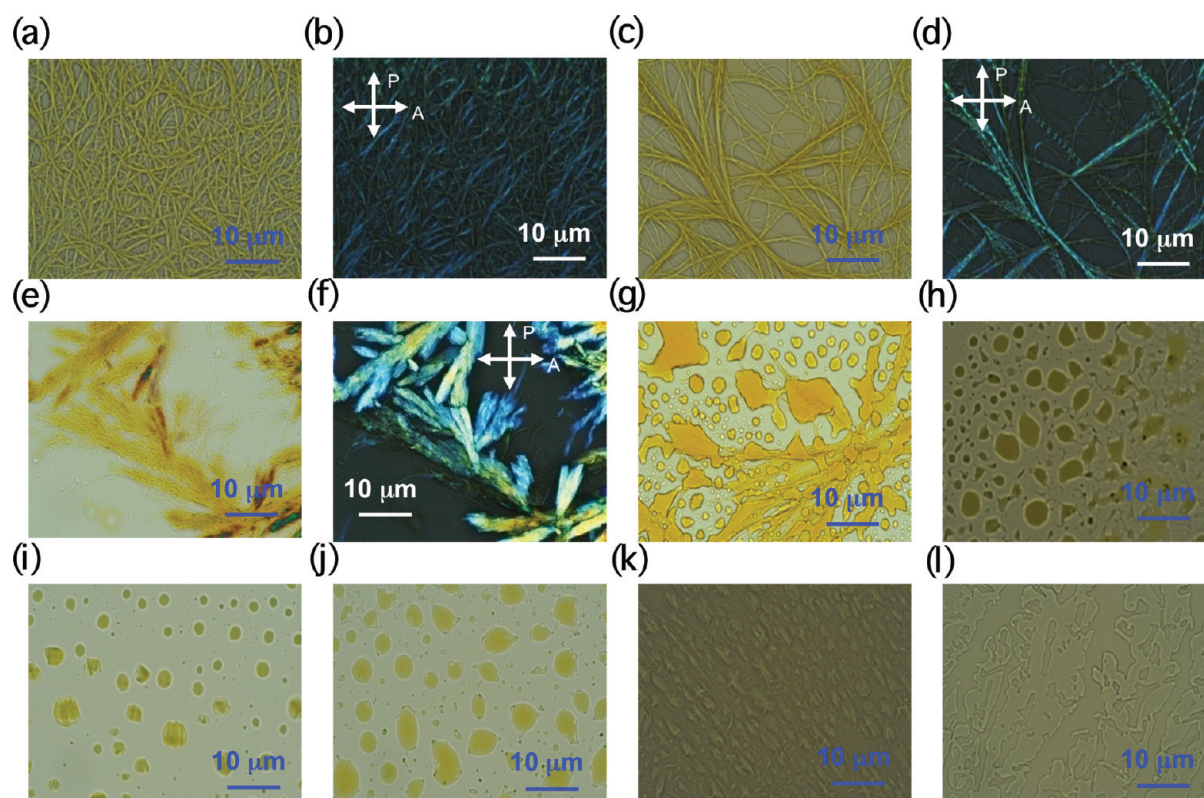


Figure 4. Characterization of the fabricated hybrid nanofibers with three components of **2**, **4**, and **6** having different molar ratios, such as (a, b) 2:2:1, (c, d) 2.8:1.4:1, (e, f) 2:1:2, (g, h) 2:1:1, (i) 1:1:1, (j) 1:2:1. (k) Obtained from a mixture of **4** and **6** (1:1). (l) Picture of **4**. (a, c, e, g, h, i, j, k, l) Optical images. (b, d) are POM images.

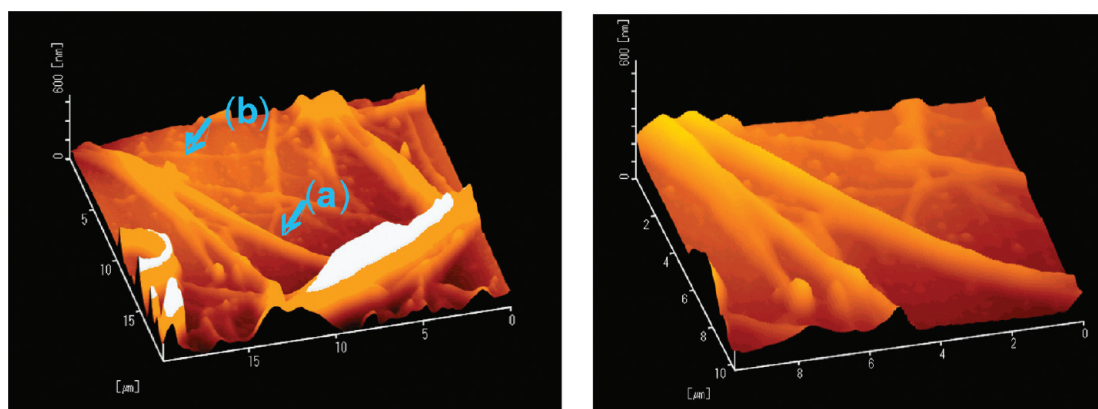


Figure 5. AFM images of the fabricated hybrid nanofibers using three components of **2**, **4**, and **6** (2:2:1).

the fabrication of three-component hybrid nanofibers. Namely, the mixture of **1** and **3** play an important role in adjusting the amphiphilic properties of hybrid mixture of **2**, **4**, and **6**.

To investigate the influence of introducing **5** on the amphiphilic properties of the mixture containing the three amphiphilic salts, we measured contact angles of the resulted mixtures obtained from the reactive mixture of **1**, **3**, and **5** with molar ratios of 2:2:0, 2:2:1, 2:2:2. Their contact angles were observed at 8, 12, and 30°, respectively, indicating that the hydrophobicity was remarkably increased with increasing the amount of **5** in the reactive mixtures. The morphologies of hybrid nanofibers were also demonstrated by AFM images shown in Figure 5. The mountainous shape of hybrid nanofibers was clearly observed, and the size of the obtained nanofibers were different from that of the nanofibers fabricated

by Nakagawa et al.⁹ For example, the width and height of a and b in Figure 5 were obtained at (900 nm, 118 nm) and (500 nm, 24 nm), showing that the fabricated hybrid nanofibers were in nanoscale. The different diameters of the obtained nanofibers might be attributed to the influence of glass substrate in the fabrication system.

In ¹H NMR of the mixtures obtained from reactive mixtures of **1**, **3**, and **5** (2:2:1), the characteristic peaks of the three salt components were observed (see Figure S6 in the Supporting Information). Their integral ratios were the same as the molar ratio of the reactive mixture, indicating that the fabricated hybrid nanofibers were composed of the three salts with the same composition of their reactive mixtures. Moreover, the peaks of protons in aromatic-rings did not shifted to a high field (see Figure S6 in the Supporting Information), which is

different from our previous results.⁸ It was possibly attributed to the electrostatic interactions of the anilinium cationic combined with alkylbenzenesulfate anion, which are stronger than the interactions of alkylbenzenesulfate anion with azopyridinium in a strongly acidic environment.¹¹ Thus, the resulted hybrid nanofibers were simply constructed with three amphiphilic salts (**2**, **4**, and **6**), and no side reactions occurred.

Likewise, π - π stacking interactions also existed in these hybrid nanofibers having three amphiphilic salt components, which were verified by measurements of XRD and UV-vis adsorption spectra. As shown in Figure 3c, the broad peak at around $2\theta > 20^\circ$ appeared, which could be ascribed to the suppressive effect of π - π stacking interactions among the azopyridine chromophores. Compared with Figure 3a, c, the characteristic peaks (0.26, 0.41, and 0.42 nm, correlated with 2θ at 35, 23, and 22°) of **4** weakened remarkably upon fabrication of the hybrid nanofibers because **4** aggregated with **2** and **6** in the hybrid nanofibers. These indicated that the electrostatic interactions among ions greatly influenced the aggregation behaviors upon nanofiber formation when **6** was introduced into the system. Therefore, molecular interactions involving in fabrication of the hybrid nanofibers with three components can be summarized as π - π stacking and ion bonding.

On the basis of the morphological observation by POM, AFM, and the measurements of contact angles and XRD, the possible scheme of hybrid nanofibers with three components (**2**:**4**:**6** = **2**:**2**:**1**) are given in Figure S10 in the Supporting Information. Here, two aggregation patterns might be included in the fabricated hybrid nanofibers. The first is aggregation formed with **2**, **4**, and **6** in a molar ratio of 1:1:1. The second one is obtained from the accumulation of the residue parts of **2** and **4** in a molar ratio of 1:1. These two types of aggregated structures should be in a mutual arrangement in the hybrid nanofibers since the hybrid nanofibers were not successfully obtained using the three components **2**:**4**:**6** = 1:1:1 (Figure 4h). It can be inferred that such mutual aggregative forms between the two aggregation patterns (**2**:**4**:**6** = 1:1:1 with **2**:**4** = 1:1) are in abundance upon the self-assembled process for fabrication of the three-component hybrid nanofibers.

Figure 2d gives the UV-vis absorption spectrum of the film containing a mixture of **2**, **4** and **6** (**2**:**2**:**1**). The maximum absorption peak appeared at 415 nm of Figure 2d, demonstrating a red shift of 60 nm than that in THF solution (see Figure S8b in the Supporting Information). This indicates strong π - π stacking interactions existed in the hybrid nanofibers with three components. Compared it with the maximum absorption peak of nanofibers films with two components (**2**:**4** = 1:1, λ_{\max} = 365 nm, Figure 2b) and another three components (**2**:**4**:**6** = **2.8**:**1.4**:**1**, λ_{\max} = 404 nm, Figure 2c), remarkable red shifts of 50 and 11 nm were obtained for Figure 2d. These strongly suggest that the π - π stacking interactions are strongly enhanced by introduction of **6** into the two-component hybrid nanofibers containing **2** with **4**.⁸

Accordingly, the hybrid nanofibers with three components also possessed relatively excellent conductivity. The results of 8×10^{-6} S/cm (**2**:**4**:**6** = **2**:**2**:**1**) and 4×10^{-6} S/cm (**2**:**4**:**6** = **2.8**:**1.4**:**1**) were obtained, respectively. Although the conductive process of three-component hybrid nanofibers is complicated, it is easy to deduce that the amphiphilic salt **6** played an important role in increasing the free movable ions and π - π stacking interactions in these hybrid nanofibers. In contrast, the amphiphilic salt **4** mainly enhanced the free movable ions at the

existence of small amount of water in the solid films (see Figures S2 and S6 in the Supporting Information). The residual amount of water was attributed to the introducing of **4** having strong hydrophilic properties, as demonstrated by the measurement of contact angles. Therefore, conductive capability of the fabricated multicomponent nanofibers can be classified into electrics and ions.

The conductivity of three-component hybrid nanofibers was more excellent than that of the hybrid nanofibers with two components having the same composition (1×10^{-7} S/cm, **2**:**6** = 1:1),⁸ indicating that movable ions remarkably due to the introduction of the third constituent **4** influence the conductivity of multicomponent hybrid nanofibers. However, the conductivity of three-component hybrid nanofibers (**2**:**4**:**6** = **2.8**:**1.4**:**1**, **2**:**2**:**1**) was still lower than of hybrid nanofibers containing mixture of **2** and **4** (1:1.5) (7.7×10^{-5} S/cm). This also demonstrates that amount of movable ions (owing to **4**) play a pivotal role in improving the conductivity of the hybrid nanofibers fabricated using low-molecular-weight amphiphilic salts.

3. CONCLUSIONS

In summary, hybrid organic nanofibers were successfully fabricated with three components of amphiphilic salts as azopyridinium, aniline hydrochloride, and alkylbenzenesulfate-based anionic surfactants. This supramolecularly self-assembled method shows characteristics of easy processing and quick fabrication. The amphiphilic balance is one of the most important factors in fabrication of hybrid nanofibers with two and three amphiphilic salts. The enhanced conductivity of the obtained hybrid nanofibers was mainly attributed to the freely movable ions. Furthermore, the present fabricated method provided a novel concept for fabricating strategy of functional low-molecular-weight nanofibers, which would promise for their future applications in nanoconductive materials and bionanomaterials.

More interestingly, the present study of three-component hybrid nanofibers possessing conductivity might provide references for the complex processes of artificial fabrication and working of nerves fibers. On the basis of the present studies, rational adjustment and optimization of various interactions like π - π stacking and ionic bonding among the different compounds play important roles in fabrication of these multicomponent hybrid nanofibers. Following these principles, other materials such as peptides, amino acids, and monoamines could be possibly applied to assemble artificial nerve fibers, because they are more rational and beautiful conductive biomaterials in nature.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and further characterization of the hybrid nanofibers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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