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From Bola-amphiphiles to Supra-amphiphiles: The Transformation from Two-Dimensional Nanosheets into One-Dimensional Nanofibers with Tunable-Packing Fashion of n-Type Chromophores

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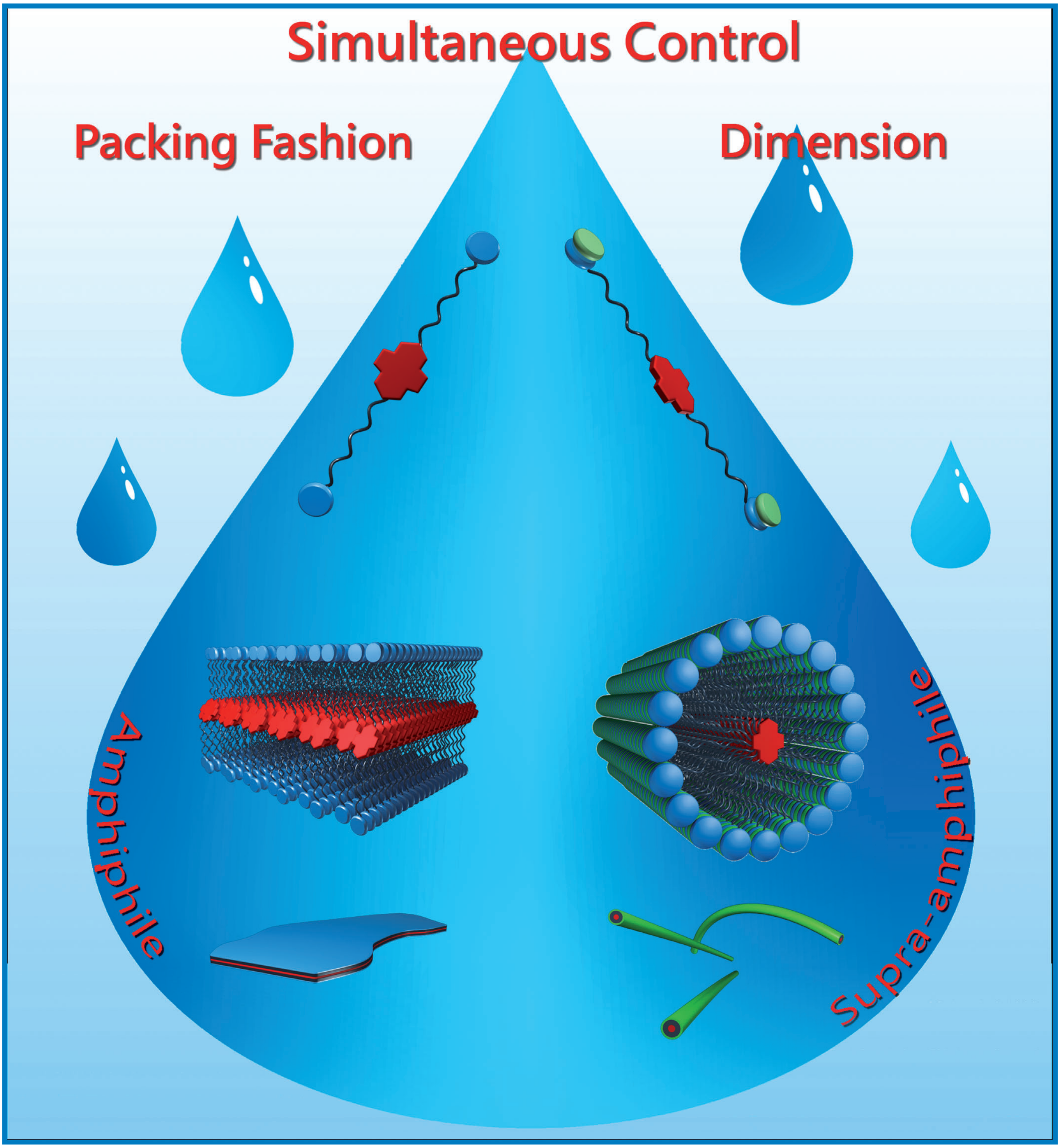

Abstract: With a rational design of the supra-amphiphiles, we have successfully demonstrated that not only the dimension of the self-assembled nanostructures, but also the packing fashion of the functional naphthalene diimide (a typical n-type chromophore), can be tuned in a noncovalent way in aqueous solution. Naphthalene diimide is incorporated into a bola-amphiphile as the rigid core, whereas viologen derivatives are used as the hydrophilic head. The bola-amphiphile self-assembles into two-dimensional nanosheets, in which naphthalene diimide adopts a "J-type" aggregation. Water-soluble supramolecular complexation between viologen derivatives and the 8-hydroxypyrene-1, 3, 6-trisulfonic acid trisodium salt is used as a driving force for the formation of the supra-amphiphiles. Upon formation of the supra-amphiphiles, the nanosheets transform into ultralong nanofibers with a close packing of naphthalene diimide. Notably, just by mixing the two building blocks of the supra-amphiphiles in aqueous solution, a dimension-controlled evolution of the nanostructures is formed that leads to a different packing fashion of the n-type functional chromophores, which is facile and environmental friendly.

Keywords: charge-transfer interaction · nanostructures · n-type chromophores · supra-amphiphiles · supramolecular chemistry

Introduction

The rational design and fabrication of dimension-controlled nanostructures containing organic functional π chromophores is very important for future nanoelectronics.[1] On one hand, the most fascinating features of π-conjugated materials are their variable optical and electronic properties when forming aggregates in organic or aqueous solution.[2] A different packing fashion of aromatic molecules may lead to completely different functions.[3] On the other hand, the dimension of nanostructures containing functional chromophores is very crucial for the dimension-controlled transportation of energies or charge carriers, which is significant for the microminiaturization of optoelectronic devices.[4] Various nanostructures containing functional chromophores have been fabricated in organic media, but rarely in aqueous solution.[5] In addition, the studies on the organization behaviors of n-type organic chromophores largely lag behind its p-type counterparts. Thus, it still remains a challenge for rational control over the dimension of the nanostructures with a tunable-packing fashion of the organic semiconductors, especially the n-type ones, in water.

Supra-amphiphiles refer to amphiphiles that are formed on the basis of noncovalent interactions, which may include π–π interactions, hydrogen bonding, charge-transfer interactions, and electrostatic interactions.[6] Supra-amphiphiles with various architectures can be fabricated by either small organic molecules or polymers. One advantage of supra-amphiphiles is their noncovalent-synthesized nature, by which the time-consuming chemical syntheses can be avoided to some extent. In addition, with elaborate tuning the chemical structures of the building blocks, supra-amphiphiles can be engineered to fabricate well-defined nanostructures.[7] Moreover, stimuli-responsive functional moieties can be easily incorporated into supra-amphiphiles, thus leading to the controlled self-assemblies and disassemblies.[8] The formation of supra-amphiphiles can be regarded as a first-order self-assembly, and by further second-order self-assembly, supra-amphiphiles can be utilized as building blocks for the construction of highly-ordered assemblies. The advance of supra-amphiphiles will not only enrich the family of conventional amphiphiles that are formed on the basis of covalent bonds, but will also provide a new avenue between the colloidal and supramolecular sciences.

Herein, with a rational design of the supra-amphiphiles, we have realized a simultaneous control over the packing fashion of naphthalene diimide and the dimension of self-assembled architectures in water. The nanosheets, in which naphthalene diimide is "J-aggregated", transform into ultralong nanofibers with a close packing of naphthalene diimide upon the formation of supra-amphiphiles. It should be noted that, just by mixing the two building blocks of the supra-amphiphile in water has led to a big change in the nanostructures as well as the packing fashion of n-type organic chromophores, which is facile and environmental friendly. We believe such strategy is promising for the design of functional materials with different optical and electronic properties, thus enriching the supramolecular engineering of functional nanomaterials.

Results and Discussion

Naphthalene diimide, a typical n-type chromophore, is incorporated into a bola-amphiphile (BNDIV, shown in Scheme 1) as the rigid core, whereas viologen derivatives are used as hydrophilic head. Water-soluble supramolecular complexation between viologen derivatives and the 8-hydroxypyrene-1, 3, 6-trisulfonic acid trisodium salt (PYR)[9] is

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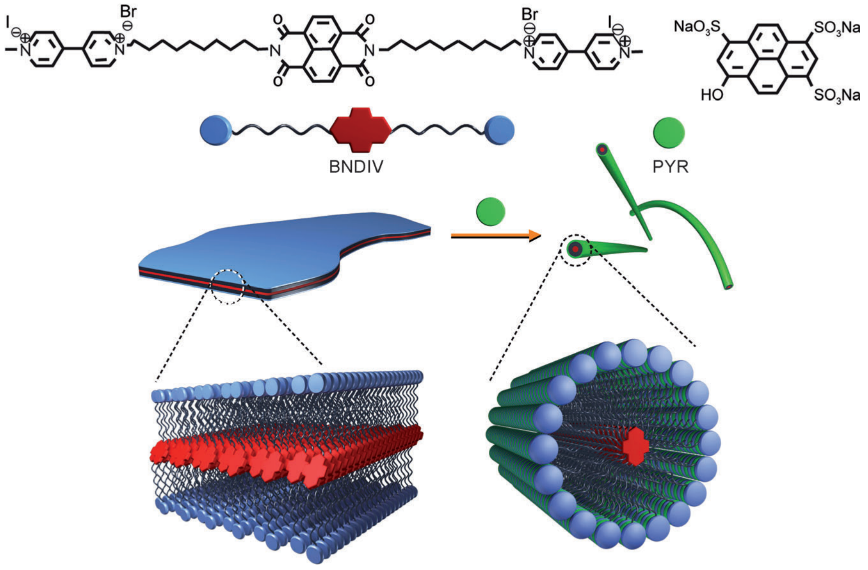

Scheme 1. Schematic representation of the formation of the supra-amphiphiles and the controlled evolution of the nanostructures as well as the packing fashion of the naphthalene diimide.

used as a driving force for the formation of the supra-amphiphiles. It has been reported by our group that the cooperativity of Coulombic attractions, charge-transfer interactions, and the hydrophobic effect are responsible for the formation of the "viologen derivative–PYR" supramolecular complex.[8a] It is anticipated that the formation of the supra-amphiphiles will not only lead to an dimension-controlled evolution of nanostructures, but also lead to a change of the packing fashion of naphthalene diimide, thus enriching the supramolecular engineering of functional nanomaterials.

As a typical bola-amphiphile, BNDIV itself self-assembles in water to form two-dimensional nanosheets, as revealed by TEM (Figure 1 a), which was confirmed by cryo-TEM (Figure 1 b) and AFM (Figure 1 c). The section analysis of Figure 1 c indicates that the thickness of the nanosheets is about 3.6 nm. XRD experiments also indicate that there exist layered structures with a thickness of about 3.9 nm (Figure 1 d). It should be noted that the extended length of the molecule is about 4.9 nm (estimated by Chem3D). The fact that the thickness of the nanosheets is shorter than the extended molecular length suggests that the BNDIV may adopt a tilted conformation in the nanosheets.

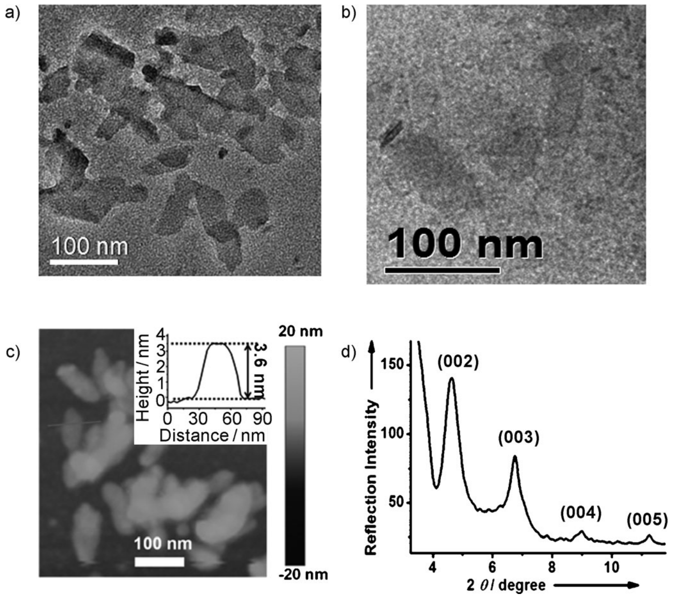

Figure 1. a) TEM, b) cryo-TEM, c) tapping mode AFM images (inset: height profile along the blue line) and d) XRD scan of the BNDIV assemblies in buffer solution (pH 9).

To gain further insight into the packing fashion of naphthalene diimide in the nanosheets, we have employed UV/Vis and fluorescence spectroscopy to provide more information. In methanol, the BNDIV shows a typical monomer absorption and fluorescence emission (Figure 2), indicating a monomeric state.[10] When going from methanol to water, the main absorption band of naphthalene diimide are redshifted by 8 nm with a decrease of the intensity (Figure 2 a). This is characteristic of "J-type" aggregation of naphthalene diimide chromophores in solution, in which the naphthalene diimide may adopt a tilted and slipped "head-to-tail" conformation with respect to each other.[10] Moreover, upon assembly, the fluorescence intensity of BNDIV is strongly increased (Figure 2 b), as a result of the high fluorescence quantum yield upon forming the "J-aggregates" of naphthalene diimide in the assemblies.

To confirm that viologen moieties in BNDIV molecules can form a charge-transfer complex with PYR, different characterization methods were employed.[7–9,11] BNDIV and PYR were mixed in pH 9 buffer at a 1:2 molar ratio. Firstly, as shown in Figure 3 a, the resulting solution exhibits a green color, which is characteristic for the charge-transfer complex of viologen derivative with PYR. Secondly, it can be imagined that, the 1:2 complexation of BNDIV and PYR will turn the overall charge of the assemblies from positive to negative. In zeta potential measurement, BNDIV assemblies exhibit a potential of 16 mV, which should be attributed to the positively charged viologen derivative head-group. In contrast, upon complexation with PYR, the zeta potential of the assemblies changed to −31 mV, thus confirming the formation of the supra-amphiphiles. Thirdly, a new and broad charge-transfer band appears between 540 and 700 nm after complexation, confirming the formation of charge-transfer complex (Figure 3 b). Fourth, the fluorescence of PYR is strongly quenched upon complexation with BNDIV (Figure 3 c), which is caused by the charge-transfer interaction. Moreover, the complex formed by BNDIV and

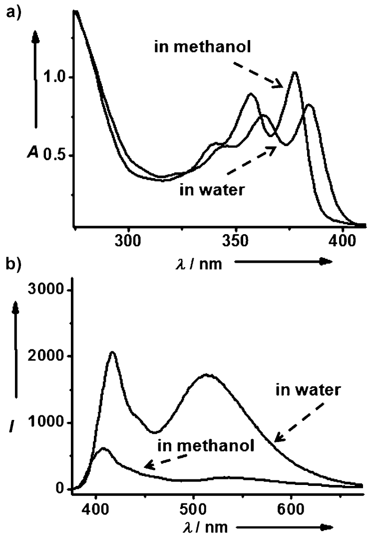

Figure 2. a) UV/Vis absorption and b) fluorescence spectra of BNDIV in methanol and water. The concentration of BNDIV is fixed at 5.0×10^{-4} M.

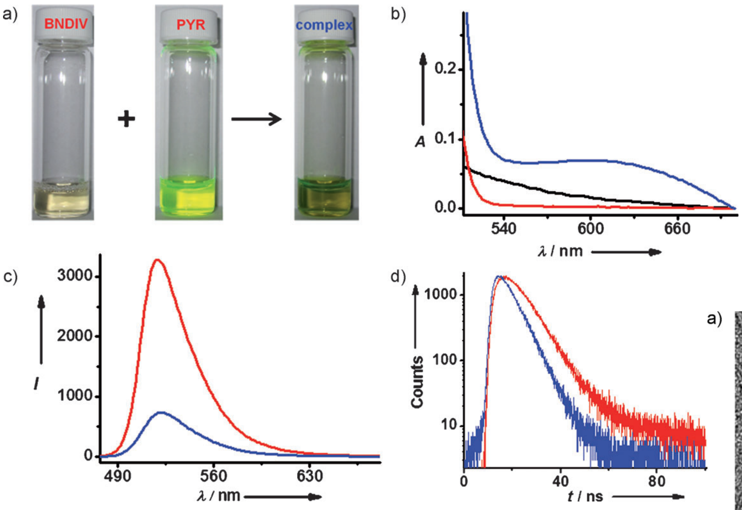

Figure 3. a) Photographs of the BNDIV, PYR, and BNDIV/(PYR)$_2$ complex solutions showing their colours. b) UV/Vis absorption and c) fluorescence emission. d) Time-resolved fluorescence spectra of the BNDIV, PYR, and BNDIV/(PYR)$_2$ complex solutions (BNDIV: black, PYR: red, complex: blue). The concentration of BNDIV is 5.0×10^{-4} and PYR is 1.0×10^{-3} M, respectively.

PYR was studied by time-resolved fluorescence analysis. As shown in Figure 3d, the lifetime of the PYR emission is shortened after the complexation with BNDIV. It should be noted that the exciplex of charge-transfer complex is non-emissive, since no new emission peak has been observed in the BNDIV–PYR complex compared with that of PYR. Thus, the decreased emission lifetime should be ascribed to charge-transfer process. This result confirms the formation of charge-transfer complex of BNDIV and PYR. In addition, mass spectroscopy supports the formation of charge-transfer complex between BNDIV and PYR. A strong peak at $m/z=898.49$ is observed, which should correspond to the charge-transfer complex of BNDIV^{4+}/(PYR)$_2^{6-}$ (see the Supporting Information, Figure S1). All these data indicate that BNDIV and PYR can form supramolecular complex with a 1:2 stoichiometry because of the charge-transfer interaction between viologen derivatives with PYR, which is responsible for the formation of the supra-amphiphiles.

Interestingly, upon formation of the supra-amphiphiles, the two-dimensional nanosheets transform into one-dimensional nanofibers, as indicated by TEM (Figure 4a) and confirmed by cryo-TEM (Figure 4b). There is no clear contrast between the edge and the central part, thus indicating that the one-dimensional structures are solid nanofibers. It should be noted that the nanofibers have a high length/diameter ratio. As shown in Figure 4c, the nanofibers are quite uniform with a diameter of 4.7 nm. Moreover, their length reaches several micrometers. The formation of nanofibers is also supported by AFM images (see the Supporting Information, Figure S2), and the diameter of the nanofibers is about 4.2 nm as indicated by Figure S2b in the Supporting Information. It should be pointed out that the diameter of the nanofibers measured by AFM is lower than that obtained in cryo-TEM, which should be attributed to compression effect by the AFM tip. The angular dependent scattering intensities were obtained using static light-scattering (SLS) measurements, as shown in Figure 4d, which allowed us to characterize the nanostructures in situ. Typically, for cylindrical one-dimensional nanostructures, the scattering intensity, *I,* follows a q^{-1} power law, in which q represents the scattering vectors, $q=4\pi sin\theta/\lambda$.[12] As shown in Figure 4d, the napierian logarithm of I shows a linear dependence on

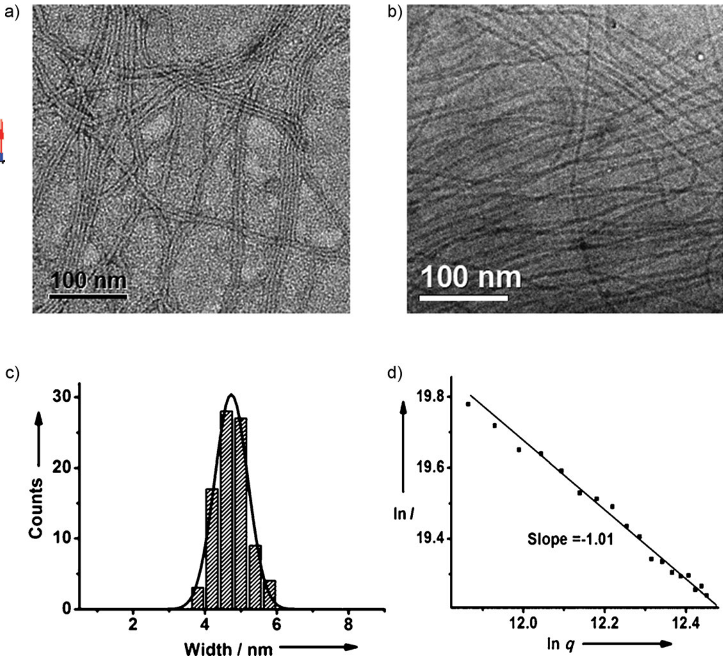

Figure 4. a) TEM and b) cryo-TEM images of the BNDIV/(PYR)$_2$ assemblies in buffer solution (pH 9). c) Statistical analysis of the width of the BNDIV/(PYR)$_2$ nanofibers. d) The vector-dependent scattering intensities of the BNDIV/(PYR)$_2$ assemblies. The concentration of PYR is 1.0×10^{-3} and 5.0×10^{-4} M for BNDIV.

the napierian logarithm of q. The slope was measured to be -1.01, which is consistent with the value predicted for one-dimensional nanostructures (-1.0). Generally, the fabrication of one-dimensional nanostructures relies on highly directional intermolecular interactions.[13] Thus, the strong and highly directional charge-transfer interactions between the viologen head of BNDIV and PYR (Scheme 1) is attributed as the main driving force to transform the two-dimensional nanosheets into one-dimensional nanofibers.

As PYR is pH-responsive, we wondered if the nanofibers formed by the supra-amphiphiles have the same responsiveness. It is interesting to find that, the straight nanofibers in pH 9 buffer as shown in Figure 4a become curled in pH 8 buffer (see the Supporting Information, Figure S3). However, the diameter and length of the nanofibers at pH 8 are the same with that in pH 9, indicating the molecular arrangement in the nanofibers remain unchanged. The "non-covalent-synthesized" nature of the supra-amphiphiles is advantageous in that the pH-responsive functional moiety, PYR, can be incorporated into the supra-amphiphiles just by simply mixing with the other building block in water, thus avoiding the time-consuming covalent organic syntheses. It is a facile and efficient way to fabricate pH-responsive one-dimensional nanofibers.

We envisage that the dramatic changes of the nanostructures upon the formation of the supra-amphiphile will lead to a different packing fashion of naphthalene diimide in the assemblies. Different characterization methods were used to provide evidence. First, as shown in Figure 5a, the circular dichroism (CD) is quite different after the formation of the supra-amphiphiles, indicating a different packing arrangement of naphthalene diimide.[14] Second, the close-packing state of naphthalene diimide is suggested by the UV/Vis absorption, as shown in Figure 5b. The absorbance of naphthalene diimide is decreased after the formation of the supra-amphiphiles. Hypochromism, that is, the decrease in the extinction coefficient of chromophores, can be widely observed in dye aggregates. It has been well studied that hypochromism of chromophores is strongly dependent on r, the distance between chromophores by a function of $1/r^3$: the shorter of the distance, the more of the hypochromism.[15–16] The hypochromism of naphthalene diimide indicates a closed packing state of naphthalene diimide in the nanofibers.

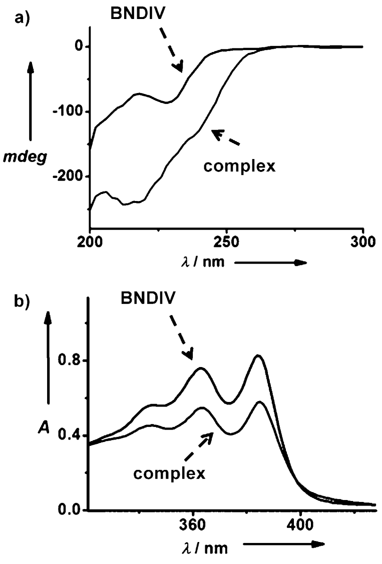

Figure 5. a) CD and b) UV/Vis spectra of BNDIV and BNDIV/(PYR)$_2$ complex. The concentration of PYR and BNDIV is 1.0×10^{-3} and 5.0×10^{-4} M, respectively.

With all these data in mind, the transformation mechanism is proposed as follows: the BNDIV molecules self-assemble into "J-aggregates", in which the naphthalene diimide may adopt a tilted and slipped conformation with respect to each other, as shown in Scheme 1. However, the strong and highly directional charge-transfer interaction of viologen derivatives with PYR in the head-group of the supra-amphiphiles facilitates the growth of the assembly along one dimension, finally leading to the formation of nanofibers, in which the naphthalene diimide group in the middle part of the supra-amphiphiles may adopt a rotated and close-packing fashion. In addition, the increase of pH value of the solution can lead to an increased ionization extent of the hydroxy group on PYR. As a result, the charge-repulsion force on the surface of the nanofibers increases accordingly, leading to the transformation of curled nanofibers into straight ones.

Conclusion

We have demonstrated the feasibility of using supra-amphiphiles to fabricate dimension-controlled well-defined nanostructures with a tunable-packing-fashioned naphthalene diimide, a typical organic n-type semiconducting chromophore, in aqueous solution. The nanosheets, in which naphthalene diimide is "J-aggregated", transform into ultralong nanofibers with a close packing of naphthalene diimide. The nanofibers formed by the supra-amphiphile exhibit a tunable straightness upon the change of the pH value: the increase of pH value of the solution can lead to an increased ionization extent of the hydroxy group on PYR, leading to the transformation of curled nanofibers into straight ones. The close packing and one-dimensional arrangement of the n-type semiconducting naphthalene diimide in the nanofibers is crucial for organic optoelectronic materials. Notably, just by mixing the two building blocks of the supra-amphiphiles in aqueous solution can lead to a dimension-controlled evolution of the nanostructures as well as the packing fashion of the functional chromophores, which is facile and environmental friendly. We hope such a strategy can be extended to the design of other functional materials with different optical and electronic properties.

Experimental Section

General procedures: ^{1}H NMR spectra were obtained by using a JOEL JNM-ECA300 apparatus; ESI MS spectra were recorded using a PE Sciex API 3000 apparatus. UV/Vis spectra were measured using a HITACHI U-3010 spectrophotometer (path length is 10.0 mm for Figure 2b, whereas 1.0 mm for Figure 4b); fluorescence spectra were measured using a HITACHI F-7000 apparatus; CD spectra were obtained by using Applied Photophysics-Pistar π-180 spectrophotometer.

SLS measurements were carried out on a commercial LS spectrometer (ALV5000) equipped with a single avalanche photo diode detector and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632.8$ nm). The LS cell was held in a thermostat refractive index matching vat filled with purified and dust-free toluene.

TEM measurements were carried out on a JEMO 2010 electron microscope operating at an acceleration voltage of 120 kV. The samples were prepared by drop-casting the aqueous solution on the carbon-coated copper grid and were then negatively stained with a phosphotungstic acid solution. Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) at 28 °C. The vitrified samples were stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined by a JEM2200FS TEM (200 kV) at about −174 °C.

AFM was performed using tapping-mode in air on a commercial multimode Nanoscope IVAFM. For sample preparation, a few drops of the solution were placed on a mica surface and were incubated for 10 min under moist conditions; excess solution was removed by absorption onto filter paper, then the substrate was washed slightly with water and air-dried.

XRD measurements: For sample preparation, a few drops of the solution were placed on a glass surface, and then the solvent was evaporated at room temperature. The sample was then directly used for XRD measurements. The Bragg peak θ was extracted from the XRD data and the layer thickness d could be obtained according to the Bragg equation $d = \lambda/2\sin\theta$, in which $\lambda = 0.15405$ nm.

Zeta potential measurements were measured on Malvern ZS 90 Zetasizer instrument.

Time-resolved fluorescence measurements were performed on a single-photon-counting spectrofluorimeter from Edinburgh Analytical Instruments (FLSP 920).

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