Hierarchical Assembly of L-Phenylalanine-Terminated Bolaamphiphile with Porphyrin Show Tunable Nanostructures and Photocatalytic Properties

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ABSTRACT: Demands related to clean energy and environmental protection promote the development of novel supramolecular assemblies for photocatalysis. Because of the distinctive aggregation behaviors, bolaamphiphiles with two hydrophilic end groups could be theoretically the right candidates for the fabrication of high-performance photocatalysis. However, photocatalytic applications based on bolaamphiphilic assemblies were still rarely investigated. Especially, the relationship between diverse assembled nanostructures and the properties for different applications is urgently needed to be studied. Herein, we demonstrate that using the hierarchical assembly of bolaamphiphiles could correctly induce the porphyrin supramolecular architectures with much better photocatalytic performances than the aggregations containing 450 times of the porphyrin molecules, even though both molecular structures as well as the J-aggregations of porphyrin building blocks are same in two different systems. Thus, the co-assembly of L-phenylalanine terminated bolaamphiphile (Bola-F) and the porphyrin containing four hydroxyl groups (tetakis-5,10,15,20-(4-hydroxyphenyl)porphyrin) can form microtube in methanol and forms fibers/spheres in methanol/water mixture. For catalyzing the photodegradation of rhodamine B, the small amount of J-aggregated porphyrin within Bola-F microtubes show much better photocatalytic performance comparing with that of huge porphyrin J-aggregations in fibers/spheres. The supramolecular assemblies as well as the photocatalysis were thoroughly characterized by different spectroscopies and electron microscopy. It is demonstrated that the co-assembly with bolaamphiphiles could inhibit the energy transfer of porphyrin aggregation and subsequently benefit the electron transfer and corresponding photocatalysis under photo-irradiation. This work is not only useful for further understanding the hierarchically supramolecular assembly but also provides a new strategy for making novel functional supramolecular architectures based on the assembly of bolaamphiphiles and porphyrins.

INTRODUCTION

The existence and evolution of life is considered to be dependent on the nanostructures and functions of biological membranes, which are the assemblies of phospholipids, a type of amphiphilic molecule containing one chiral hydrophilic end group.1−4 As a type of special amphiphilic molecules, bolaamphiphiles with two hydrophilic end groups connected by hydrophobic linkers, show distinctive aggregation behaviors.5−19 For example, natural bolaamphiphiles with special molecular structures can form extremely robust membrane, which can help the archaeabacteria survive in highly acidic environments.11 Indeed, phospholipids with one hydrophilic end group and double hydrophobic alkyl chains are widespread in the life systems, whereas bolaamphiphiles are only applied by nature under special circumstances. Considering the very good mobility and flexibility of phospholipid assemblies, only the life systems have the complex regulatory mechanism, which can take advantage of these supramolecular architectures well.1,2 Nevertheless, for the fabrication of functional supramolecular assemblies in laboratory, bolaamphiphiles could be more appropriate building blocks.11,17−21 The strong non-covalent interactions between bolaamphiphilic molecules could induce the formation of various nanostructures with very good controllability and stability.22−25 However, although the self-assembled nanostructures of bolaamphiphiles have been thoroughly investigated, the relationships between these diverse nanostructures and some important applications, such as photocatalysis, were still rarely investigated.

With the growth of research related to new energy and environmental protection, the photocatalytic systems based on supramolecular assemblies are attracting increased interests recently.26−33 Theoretically, bolaamphiphiles should be very good building blocks for the fabrication of functional supramolecular architectures. However, the only known
bolaamphiphilic assembly for photocatalytic applications was developed by Lee, et al., wherein the bolaamphiphiles containing odd number alkyl chains can form nanoparticles upon co-assembly with porphyrins. In addition, the mimicking of photosynthesis systems of these bolaamphiphile–porphyrin hybrids was investigated. On the other hand, the performance of natural photosynthetic reaction center is highly depended on its subtle nanostructures. Because the self-assembly of bolaamphiphiles can form complex nanostructures, understanding how morphology changes affect the functions of these supramolecular architectures could be very useful for improving the corresponding photocatalytic properties. In this context, the bolaamphiphile (Bola-F) with medium length and even numbered alkyl chain was synthesized (Figure 1). Considering that the phenylalanine dipeptide has significant advantages for making functional supramolecular assemblies, the phenylalanine was selected as the hydrophilic head groups of Bola-F. For the photodegradation of RhB under visible-light irradiation, microtubes with small amount of THPP show much better photocatalytic efficiency comparing with that of fibers/spheres mixtures. In methanol, it is demonstrated that the self-assembly of Bola-F can form monolayer lipid membranes (MLM). In addition, the porphyrins form dispersedly small J-aggregates, which are located on different Bola-F MLM layers. Including porphyrins aggregates changes the twists into microtubes. In water/methanol, THPP and Bola-F cannot form good co-assemblies because of their different solubility. The phase separation renders the formation of both fibers and spheres, wherein porphyrins form very huge J-aggregates. These large porphyrin assemblies have energy transfer between different porphyrin molecules under the photo-irradiation, as demonstrated by strong fluorescence quenching. Therefore, although the fibers/spheres mixtures contain very large amount of porphyrin with strong J-aggregation, they show poor photocatalytic performance. These results open a new perspective for the fabrication of functional soft matters based on the assembly of bolaamphiphilic molecules.

![Schematic illustration](image)

Figure 1. Schematic illustration shows that the bolaamphiphile containing even numbered alkyl chain and L-phenylalanine head groups (Bola-F) self-assemble into twists in methanol, while forming fibers in methanol/water mixture. The co-assembly of Bola-F with THPP in methanol forms microtubes. In methanol/water mixture, the nanostructures of Bola-F/THPP assemblies are mixed fibers and spheres. For the photodegradation of RhB under visible-light irradiation, microtubes with small amount of THPP show much better photocatalytic efficiency comparing with that of fibers/spheres containing large amount of THPP.

that the phenylalanine dipeptide has significant advantages for making functional supramolecular assemblies, the phenylalanine was selected as the hydrophilic head groups of Bola-F. In addition, the aromatic ring of L-phenylalanine is expected to improve the solubility of Bola-F in organic solvents, which may expand the possible application of the bolaamphiphilic systems.

The assemblies of Bola-F with tetrakis-5,10,15,20-(-4-hydroxyphenyl)porphyrin (THPP) were investigated (Figure 1). The results show that the co-assembly with bolaamphiphiles could help porphyrin form different supramolecular architectures with subtle distinction. In methanol, Bola-F molecules self-assemble into microscale twists. While inter-

**RESULTS AND DISCUSSION**

Supramolecular Assembly of Bolaamphiphiles with Porphyrin. Bola-F is the bolaamphiphile containing medium length, even numbered alkyl chain, and L-phenylalanine head groups. The self-assembly was first performed by dissolving Bola-F into the methanol upon heating. In addition, the gels can be obtained when the 15.0 mM Bola-F methanol solution was cooled to room temperature. The scanning electron microscopy (SEM) measurements show that Bola-F self-assembled into twists larger than micrometer scale (Figure 2A). In addition, the X-ray diffraction (XRD) pattern of Bola-F assemblies formed in methanol clearly suggests the layered molecular packing mode with the d-spacing of 1.86 nm (Figure 2B). The molecular packing mode and noncovalent interactions were further investigated by Fourier transform infrared (FT-IR) spectra of Bola-F assemblies formed in methanol (Figure S1A), wherein the amide I and amide II bands appearing at 1647 and 1537 cm⁻¹, respectively, suggest the hydrogen bonding between the amide groups. In addition, the stretching vibrations of CH₃ (2917 and 2851 cm⁻¹) proved the ordered packing of alkyl chains (Figure S1A). These results indicate that the self-assembly of Bola-F forms MLM depending on the hydrogen bonding and hydrophobic interactions. Because of the molecular chirality of the head groups, the multilayer MLM assemblies form twist. Moreover, when same volume of pure water was added into the methanol solution of Bola-F, white precipitates could form. SEM measurements show that the Bola-F assemblies formed in methanol/water mixture are large threads with the diameter of 1−2 μm (Figure 2C). The XRD pattern of Bola-F assemblies formed in water/methanol show strong scattering at the low 2θ.
value, wherein no clear diffraction peaks corresponding to layered molecular packing of bolaamphiphiles can be detected (Figure 2D). The two diffraction peaks at $2\theta = 19.08^\circ$ and $21.12^\circ$ could be attributed to the $\pi-\pi$ interactions between the phenyl rings of L-phenylalanine. Presumably, because of the fast assembly procedure with the formation of precipitates, some of the molecular building blocks cannot be organized well within the assemblies. No helical nanostructures can be detected from the assemblies obtained from methanol/water mixture.

For preparing the Bola-F/porphyrin co-assemblies, $10 \mu$L of methanol solution of THPP (1.0 mM) and $500 \mu$L Bola-F (5.0 mM) were mixed together. When the corresponding methanol solution was stored at $-10^\circ$ C for 30 min, green color gels would form. For the Bola-F/porphyrin co-assemblies in methanol, the stoichiometry ratio between Bola-F and THPP was kept as 250/1. The SEM images show that the twists formed by Bola-F have changed into tubular structures upon interaction with small amount of porphyrin (Figure 3A). The length of these microtubes can be tens of micrometers with the diameter about several micrometers. Although the walls of these microtubes are relatively thick, the opening of these microtubes can still be clearly observed (red circle in Figure 3A). In addition, the SEM images of dilacerated wall of microtubes suggest that the formation of tubular structures should be attributed to the rolling up of multilayer films. Notably, these tubular structures are relatively stable, which cannot be changed after keeping for a long time.

The micrometer level thickness of Bola-F/THPP microtubes was analyzed by the atomic force microscopy (AFM) height images (Figure 3C), which further demonstrates the multilayer assemblies. However, presumably because of the very thick of microtube walls, the hollow structures cannot be identified by transmission electron microscopy (TEM) measurements. The UV−vis spectra of the Bola-F/THPP co-assemblies formed in methanol were also studied (Figure 3D). Comparing with the UV−vis spectra of THPP in chloroform solution, the porphyrin Soret band shifts from 419 to 478 nm. The very strong red shifts suggest that porphyrin molecules form strong J-aggregations upon the co-assembly with Bola-F.48−51 The diffraction peaks corresponding to the layered nanostructures of bolaamphiphilic assemblies are remaining constant in the XRD pattern of Bola-F/THPP supramolecular systems, even though the d-spacing is slightly decreased to 1.84 nm (Figure 3E). These results suggest that the MLM formed by Bola-F were not changed largely upon interaction with porphyrin. Actually, this feature can be further demonstrated by the FT-IR spectra of Bola-F/THPP co-assemblies, which is similar to the FT-IR spectra of Bola-F twists (Figure S1B). Moreover, two new diffraction peaks at $2\theta = 10.32^\circ$ and $11.24^\circ$ were also detected from the XRD pattern of Bola-F/THPP co-assemblies. These peaks are presumably owing to the aggregation of porphyrins but cannot be simply assigned as the features of some layered nanostructures.

For further understanding the supramolecular systems in methanol, the circular dichroism (CD) spectra of bolaamphiphiles and porphyrin assemblies were measured (Figure 4). In the case of Bola-F methanol solution, the CD spectra show positive Cotton effect (Figure 4A). However, the corresponding CD signals changed into negative Cotton effect when Bola-F assembled into twists (Figure 4A). The chiral inversion could be dependent on delicate balance between different noncovalent interactions during the self-assembly.52,53 For Bola-F/THPP microtubes, the CD signals derived from Bola-F assemblies still show strong negative Cotton effect, whereas only weak negative Cotton effect can be detected from the Soret band of porphyrin (Figure 4B). These results further
leads the formation of methanol/water mixture is a fast, kinetic control pathway and which forms tubular structures. In contrast, the aggregation in relatively a slow, thermodynamic control assembly pathway, structures. It is notable that the self-assembly in methanol is μ solution was obtained. Then, 10 μL of Bola-F methanol solution (5.0 mM) was slowly added into the methanol/water mixture, a green turbid suspension would appear. The systems were allowed to rest for 30 min, and the precipitates were separated and collected by centrifugation at 5000 rpm for 10 min. For the Bola-F/THPP systems prepared in methanol/water mixture, the molar ratio between Bola-F and THPP is about 5/9. Thus, for the same weight of Bola-F/THPP assemblies formed in different solvents, fiber and sphere mixture contains much more porphyrin molecules compared with that of the microtubes. Because of the solubility limit of Bola-F in water, increasing the quantity of Bola-F will induce that of the microtubes. Because of the solubility limit of Bola-F in water, increasing the quantity of Bola-F will induce assemblies after inducing porphyrin into the systems. In addition, the porphyrins aggregates, which could be dispersed on different Bola-F MLM layers, do not show strong supramolecular chirality induced by the assembly of bolaamphiphiles.

Although the co-assembly of Bola-F/THPP in methanol forms microtubes, mixing Bola-F and THPP in methanol/water mixture can lead the formation of both fibers and spheres. For preparing the assemblies in methanol/water mixture, the typical bolaamphiphile—porphyrin systems can be obtained as follows: when 100 μL of pure water was slowly added to 90 μL THPP methanol solution (1.0 mM), a clear solution was obtained. Then, 10 μL of Bola-F methanol solution (5.0 mM) was slowly added into the methanol/water mixture, a green turbid suspension would appear. The systems were allowed to rest for 30 min, and the precipitates were separated and collected by centrifugation at 5000 rpm for 10 min. For the Bola-F/THPP systems prepared in methanol/water mixture, the molar ratio between Bola-F and THPP is about 5/9. Thus, for the same weight of Bola-F/THPP assemblies formed in different solvents, fiber and sphere mixture contains much more porphyrin molecules compared with that of the microtubes. Because of the solubility limit of Bola-F in water, increasing the quantity of Bola-F will induce the faster precipitation with the formation of more fibrous structures. It is notable that the self-assembly in methanol is relatively a slow, thermodynamic control assembly pathway, which forms tubular structures. In contrast, the aggregation in methanol/water mixture is a fast, kinetic control pathway and leads the formation of fibers and spheres.54

The SEM images of Bola-F/THPP systems formed in the methanol/water mixture show both huge fibrous structures and small nanoparticles (Figure 5A). The enlarged the SEM images (Figure 5C) and TEM images (Figure 5D) of the aggregations of nanoparticles disclose the discrete spherical structures with diameter of ca. 150−300 nm (Figure 5C). The AFM measurement also demonstrates that the height of typical nanospheres is about 150 nm. The supramolecular aggregations were further investigated by UV−vis spectral measurements, as shown in Figure 5E. Comparing with the UV−vis spectra of THPP in chloroform solution, the Soret band of the UV−vis spectra of THPP porphyrin in methanol/water = 1/1 mixture only show slight red shifts. However, the UV−vis spectra of Bola-F/THPP in methanol/water = 1/1 mixture show very strong red shifts of Soret band, suggesting that the bolaamphiphiles induce the J-aggregation of porphyrin in methanol/water = 1/1 mixture. The XRD patterns of Bola-F/THPP systems in methanol/water = 1/1 mixture were also investigated (Figure 5F), wherein no clear diffraction peaks showing MLM assembly of bolaamphiphiles can be detected. Two diffraction peaks at 2θ = 10.12° and 20.68° could be attributed to the aggregation of porphyrin as well as the π−π interactions, respectively. The FT-IR spectra of fibers/spheres mixtures show strong characteristic peaks of porphyrin, demonstrate that very large amount of porphyrin molecules have been included into Bola-F/THPP assemblies. These results suggest that the aggregation of Bola-F/THPP in methanol/water = 1/1 mixture forms phase separation. Although molecular-level mixing cannot be totally ruled out, most of the porphyrin molecules might aggregate into nanoparticles in methanol/water = 1/1 mixture.

Photocatalytic Properties of Bolaamphiphiles−Porphyrin Coassemblies. The porphyrin containing four hydroxyl groups (THPP) can form different co-assemblies with bolaamphiphiles. In addition, the nanostructures and properties of these supramolecular systems can be modulated simply by changing the solvents. Thus, taking advantage of the characteristics of bolaamphiphilic assembly, the aggregations of porphyrin photosensitizers with delicate difference of molecular packing modes can be achieved. Interestingly, although THPP forms similar J-aggregations, the small porphyrin assemblies within Bola-F microtubes show much better photocatalytic performance comparing with that of the huge porphyrin J-aggregations.

The photocatalytic performance of different Bola-F/THPP systems were investigated in terms of photodegradation of RhB under visible light irradiation.55 By measuring the real-time UV−vis absorption spectra of RhB at 554 nm, the effects of photo-degradation were evaluated. As shown in Figures 6 and S2, for the systems without THPP (blank), the absorption of RhB show negligible changes upon photo-irradiation. These results suggest that the photodegradation of RhB cannot be self-sensitized. In addition, Bola-F itself also cannot catalyze the photodegradation of RhB molecules. However, when Bola-F/THPP supramolecular assemblies were added into the photocatalytic systems, the degradation of RhB could be clearly observed (Figures 6 and S2). These results suggest that the bolaamphiphile−porphyrin assemblies can catalyze the photodegradation of RhB molecules. Notably, more than 90% RhB molecules have been photodegraded catalyzed by Bola-F/
the reactions based on Bola-F/THPP microtubes, the rate constants \( C \) of diverse bolaamphiphilic molecules were photodegraded when THPP microtubes within 5 h. In contrast, only about 60% RhB molecules were photodegraded when fibers/nanospheres systems is 450 times higher than that of the same weight of the microtubes. Most interestingly, the microtubes containing very small amount of J-aggregated porphyrin molecules show much better photocatalytic performance than that of fibers/spheres, in which very large amount of THPP molecules also form strong J-aggregation.

The rate constant of the photodegradation reaction catalyzed by fibers/nanospheres is calculated as about \( 1.90 \times 10^{-1} \) h\(^{-1}\). In contrast, in the case of the reactions based on Bola-F/THPP microtubes, the rate constant is about \( 3.49 \times 10^{-1} \) h\(^{-1}\).

These results indicate that the Bola-F/THPP microtubes perform better photocatalytic activity than fibers/nanospheres in terms of photodegradation of RhB molecules. Considering that the porphyrin content in the fibers/nanospheres systems is 450 times higher than that of the same weight of the microtubes, as well as porphyrins in different supramolecular systems form similar J-aggregation, the photocatalytic performance of different Bola-F/THPP assemblies is not simply dependent on their morphologies. The subtle molecular packing mode should be evaluated.

**Possible Mechanism for Different Photocatalytic Performance.** As mentioned previously, the co-assembly with porphyrin in methanol could change the twists, which are the aggregation of bolaamphiphiles, into microtubes. In this case, the packing mode of bolaamphiphilic molecules (Bola-F), which should be the typical MLM, is not changed. In addition, the porphyrins form J-aggregates, which could be dispersed on different Bola-F MLM layers. For Bola-F/THPP in methanol/water mixture forming fibers/spheres, however, the packing mode of Bola-F cannot show layered nanostructures; while porphyrin also form clear J-aggregation.

It is known that photodegradation of RhB by photosensitizers under light irradiation is based on the generation of some reactive oxygen species, such as superoxide anion radical \( (O_2^-) \) and hydroxyl radical \( (*OH) \).\(^{56-59}\) While singlet oxygen was found to lead limited photodegradation of RhB in many different systems.\(^{56,59}\) It is worth mentioning that the generation of superoxide anion radical \( (O_2^-) \) and hydroxyl radical \( (*OH) \) is dependent on the electron transfer as well as the supramolecular assembly of photosensitizers.

For Bola-F/THPP systems, however, even though the morphologies of Bola-F/THPP aggregations formed in two solvents are totally different, the porphyrin J-aggregation within all the assemblies are nearly same. Certainly, the amount of porphyrin molecules in difference supramolecular assemblies are also worth mentioning. The porphyrin content in the fibers/nanospheres systems is 450 times higher than that of the same weight of the microtubes. Most interestingly, the microtubes containing very small amount of J-aggregated porphyrin molecules show much better photocatalytic performance than that of fibers/spheres, in which very large amount of THPP molecules also form strong J-aggregation.

The reasonable explanation about this unexpected result can be that the very large porphyrin aggregations within fibers/spheres systems could have serious energy transfer, which inhibits the electron transfer within porphyrin J-aggregations and further reduces the production of reactive oxygen species. As shown in Figure 7A, porphyrin J-aggregations supported by Bola-F MLM layered assemblies could perform good electron transfer upon photo-irradiation. In contrast, too much closely

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**Figure 6.** Photo-degradation of RhB under visible light irradiation illustrates the photocatalytic performances of different Bola-F/THPP systems (A), which were also analyzed by the first-order kinetic linear relation curves (B) and the corresponding histograms of the reaction rate constants (C) of diverse bolaamphiphile–porphyrin catalysts. The blank experiment is also presented for comparison in which no porphyrin is involved.

**Figure 7.** Schematic illustrations show porphyrin J-aggregations supported by Bola-F MLM layered assemblies, which could perform good electron transfer upon photo-irradiation within Bola-F/THPP microtubes (A). In the case of porphyrin spheres, too much closely J-aggregated porphyrin molecules should induce strong energy transfer (B).
J-aggregated porphyrin molecules should induce strong energy transfer. This mechanism can be simply proved by fluorescence-quenching experiment, as shown in Figure 8. The methanol solution of THPP has strong fluorescence. When Bola-F was added into the solution, the fluorescence of porphyrin was only slightly quenched. Even when the concentration of Bola-F was increased into 4 mM, more than 65% of the fluorescence intensity of porphyrin can still be kept (Figure 8A). These results demonstrate that the energy transfer between Bola-F and porphyrins is relatively weak. On the other hand, when the solvent was changed into methanol/water mixture, the aggregation of porphyrin molecules leads very strong fluorescence quenching, suggesting the serious energy transfer within porphyrin aggregations.

**CONCLUSION**

In summary, the co-assembly of L-phenylalanine terminated bolaamphiphile (Bola-F) with porphyrin (THPP) can form microtubes in methanol, and forms fibers/spheres in methanol/water mixture. Microtubes show much better photocatalytic performances comparing with that of fibers/spheres, even though fibers/spheres have 450 times of same porphyrin molecular building blocks with similar J-aggregation. These results demonstrated that the hierarchically assembly of bolaamphiphiles can play very important roles for the fabrication of novel functional supramolecular architectures.

**EXPERIMENTAL SECTION**

**Materials.** THPP was prepared by following the method previously reported. Tetradecanedioic acid, 1-(3-dimethylamino-propyl)-3-ethylcarbodiimide hydrochloride (EDAC) and 1-hydroxybenzotriazole monohydrate (HOBT) were purchased from Acros Organics. Ltd. and used without further purification. L-Phenylalanine methyl ester hydrochloride was purchased from J&K. Ltd. RhB was obtained from Aladdin Ltd. Other chemicals and solvents were purchased from Sinopharm Chemical Reagent C., Ltd. Milli-Q water (18.2 MΩ cm) was used in all processes.

**Synthesis of Bola-F.** Tetradecanedioic acid (0.56 g, 2.17 mmol) and HOBT (0.64 g, 4.77 mmol) were dissolved in 100 mL dimethylformamide (DMF) under stirring. To this mixture, 0.91 g EDAC (4.77 mmol) dissolved in 10 mL chloroform was added. The system was then stirred under −5 °C for about 1 h. After that, 1.03 g L-phenylalanine methyl ester hydrochloride (4.77 mmol) dissolved in 10 mL methanol and 0.67 mL triethylamine were added. The corresponding mixture was again stirred at 0 °C for 2 days. And the reaction was checked by thin-layer chromatography. When the reaction was finished, 1000 mL water was added into the mixture. The crude products can be obtained as white solid, which was filtered, washed with citric acid solution (0.1 M), sodium hydrogen carbonate solution (0.1 M), and pure water, respectively. The resulting products were dried at 30 °C under vacuum. For changing the esters into corresponding acids, the previously mentioned dried products were re-dissolved in 100 mL DMF, and then, 50 mL NaOH (0.1 M) aqueous solution was added. The mixture was stirred upon heating at 90 °C for 4 h. Then, the reaction was quenched by slowly adding 60 mL 0.1 M HCl, and the products (Bola-F) will precipitate. The Bola-F was collected by filtration, which was further purified by washing with the 1/1 mixture of acetone and ice-cold water. And pure Bola-F can be obtained as a white powder after vacuum drying (yield, 68.5%).

Bis(N-alpha-amido-phenylalanine)-1,12-dodecane dicarboxylic acid (Bola-F): 1H NMR (DMSO-d$_6$): 1.1 (m, 16H), 1.4 (m, 4H), 2.0 (t, 4H), 3.0 (d, 4H), 4.4 (m, 2H), 7.2 (s, 10H), 8.1 (d, 2H). Elemental analysis calcd (%) for C$_{12}$H$_{23}$N$_2$O$_2$: C, 69.54; H, 7.68; N, 5.07. Found: C, 68.92; H, 7.68; N, 5.01.

**Instruments.** A JASCO UV-550 spectrophotometer was used for the measurements of UV–vis spectra. 1H NMR spectra (400 MHz) were recorded on a Bruker DPX 400 spectrometer. Elemental analyses were carried out with an Elemental Vario El IR spectra were recorded using a Bruker Tensor 37 spectrometer. The TEM measurements were achieved by using a JEOL TEM-2010 electron microscope (Japan) equipped with a charge-coupled device camera, operated at 200 kV. SEM images were obtained using a JEOL JEM-6510A scanning electron microscope at 10 kV. The AFM images were recorded from a Bruker Multimode 8 system with a silicon cantilever by using tapping mode. XRD was measured on a Rigaku TTRIII X-ray diffractometer (Japan) with Cu Kα radiation (λ = 1.54 Å), which was operated at 45 kV, 100 mA. F-4500 FL spectrophotometer and JASCO J-815 CD spectropolarimeter were used for fluorescence spectral measurements and CD spectral measurements, respectively. For photodegradation measurements, a 500 W xenon arc lamp (CEL-LAX-500 W, Beijing Aulighttech Co. Ltd, China) served as the light source. In addition, the photodegradation experiment was performed on a photocatalytic reactor which came from Beijing Aulighttech Co. Ltd, China.

**Procedures.** For UV–vis, CD and fluorescence spectral measurements of the assemblies, quartz cuvettes (light path 0.1 mm) were used. The sample for TEM imaging was prepared by dropping dispersions onto a copper-coated grid. For SEM imaging, a drop of freshly prepared sample was cast onto a silicon slice, and then Au (1–2 nm) was sputtered onto the grids to prevent charging effects and to improve the image.
clarity. The samples for AFM measurements were prepared by casting assemblies on the mica surface.

For photodegradation measurements, an aqueous solution of RhB dye (100 mL, 10 mg/L) was first prepared and stored in the dark for about 24 h. In addition, 10 mg bolaamphiphile–porphyrin assemblies were dispersed in 5 mL of the RhB aqueous solution. The dispersion was kept in the dark place again and stirred for 30 min to achieve an adsorption–desorption equilibrium. For checking photodegradation properties, the dispersion was then irradiated with visible light which passed through a 10 cm water filter and a 420 nm cutoff filter. The reaction was lasted for 5 h and during this procedure, 0.5 mL of the dispersion was taken out from the photocatalytic reactor every hour for real-time sampling. The sample taken out was centrifuged (10,000 rpm, 10 min), the supernatant was pipetted into a quartz cuvette (1 mm path), and the variation of the absorption intensity of RhB (554 nm) was measured by UV–vis spectroscopy. For evaluating the photocatalytic character, C represented the concentration of RhB which was measured at different time, and C0 was used as that of RhB before the dark treatment. The rate constant of the photocatalytic performances, in terms of the correlation that of RhB before the dark treatment. The rate constant of the photocatalytic performances, in terms of the correlation that of RhB before the dark treatment.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01822.

FT-IR spectra of different assemblies, and changes of the UV–vis absorption spectra of RhB upon photodegradation (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The financial support from Natural Science Foundation of China (nos. 21631003, 21471015, 21671017, 21474118, and 21773006), Major Science and Technology Program for Water Pollution Control and Treatment (2017ZX07402001), Beijing Municipal Commission of Education, and University of Science and Technology Beijing (no. FRF-BR-16-008A) is gratefully acknowledged.

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