Preparation of Few-Layer Two-Dimensional Polymers By Self-Assembly of Bola-Amphiphilic Small Molecules

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ABSTRACT: Two bola-amphiphilic small molecules, based on the diphenylanthracene skeleton structure, namely, **BASM-1** and its functionalized small molecule **BASM-2**, were designed and synthesized. The self-assembly behavior and mechanism of these two molecules in aqueous solution were studied. The supramolecular two-dimensional (2D) layer and the covalent 2D polymers were, respectively, prepared by these two molecules. What is more, the transverse size of the covalent 2D polymer laminates increased with the extension of the polymerization time. Atomic force microscopy results showed that both free-

standing single-layer 2D polymers and few layer laminates with two to three molecular layers were obtained. So our work provides a simple and efficient method for directly preparing independent both supramolecular 2D polymers and covalent 2D polymers in liquid phase which is of great significance. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: bola-amphiphilic; covalent two-dimensional polymer; diphenylanthracene; self-assembly; supramolecular two-dimensional layer

INTRODUCTION In recent years, two-dimensional (2D) materials have attracted extensive attention and their emergence emphasizes the important influence of atomic-scale molecular structure and dimension on material properties.¹⁻⁹ Among them, organic 2D materials (organic supramolecular 2D layer and organic covalent 2D polymer) have attracted people's attention recently, because they have more special properties, such as light weight, good flexibility, structural tunability, and high adaptability.¹⁰⁻¹⁷ Distinct from graphene, a 2D polymer prepared by organic synthesis offers more flexibility in structural tailoring and opportunity for atomic level structure-property investigations. Due to its structure peculiarities, 2D polymers might serve as optoelectronic device, molecular electronics, sensor and drug release platforms, and so on. Recently, more and more people are engaged in the synthesis of organic 2D materials and some achievements have been made.^{18,19} There are two main methods for synthesis of 2D polymers: "top-down" synthesis and "bottom-up" synthesis. Compared with the top-down method, molecular selfassembly is a bottom-up method which is simpler and more efficient to prepare 2D planar structures, especially for organic 2D structures.13,20,21

Bola-amphiphilic small molecules (BASMs) are amphiphilic small molecules with hydrophobic parts in the middle and hydrophilic parts at both ends. It has been reported in literature that such amphiphilic small molecules have rich self-assembly behaviors and can obtain various unique assembly structures.^{22–28} Due to the bipolar nature of BASM, planar assembly structures are expected to be formed. However, of all the papers that reported the self-assembly of these amphiphilic molecules, only a few BASM accidentally formed 2D structures.^{29–31} In most cases, the resulting assemblies were zero-dimensional or one-dimensional structures, such as spherical micelles and fibers.^{32–41} In general, when the packing parameters (which represent the ability to aggregate between adjacent molecules) of amphiphilic molecules were small, it was easy to obtain zero-dimensional or onedimensional structures. When the stacking parameters were large, it was easy to form a 2D plane structure.⁴² Therefore, if the packing parameters of BASM could be designed properly, these molecules would greatly broaden the range of organic 2D structures.

In this article, we aim to develop a simple solution self-assembly method for the direct preparation of independent organic 2D polymers. Inspired by the above research, we first designed and synthesized two new ionic BASMs, named **BASM-1** and **BASM-2**, respectively (Fig. 1), in which the hydrophobic part was a large conjugated structure. We suggested that the molecular stacking parameters could be increased by increasing the area and rigidity of the hydrophobic part. In addition, due to the presence of ionic groups in the hydrophilic parts at both ends of the molecules, electrostatic repulsion could weaken the interlayer interaction.

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FIGURE 1 The structures of **BASM-1** and **BASM-2**. [Color figure can be viewed at wileyonlinelibrary.com]

Therefore, we expected to obtain the thin layer 2D structures. **BASM-2** with the reactive functional groups in the middle part was synthesized in order to further obtain covalent-linked 2D polymers, in which the obtained 2D supramolecular structure could be polymerized in layers through the Suzuki coupling reaction.

EXPERIMENTAL

Synthesis of 9,10-Diphenyl -2,3,6,7-Tetramethoxy Anthracene (1)

The mixture of veratrole (3.98 g, 28.8 mmol), benzaldehyde (1.02 g, 9.6 mmol), and phosphotungstic acid (PWA, $H_3PW_{12}O_{40}$) (7 mol %) (1.935 g, 67.2 mmol) was first added into a 100 mL flask. The mixture was stirred at 75 °C for 30 min. The reaction process was monitored by thin-layer chromatography (TLC) (eluent: petroleum ether/ethyl acetate = 1/4). Then benzaldehyde (2.04 g, 19.2 mmol), PWA (2 mol %) (0.553 g, 19.2 mmol), acetic anhydride (3.92 g, 38.4 mmol), and 20 mL glacial acetic acid were added to the reaction system, and then stirred for 90 min at 75 °C. After the reaction mixture was cooled to room temperature, 20 mL of dichloromethane was added to the system. Filter away the phosphotungstate hydrate and collect the filtrate. The organic phase was washed with saturated sodium bicarbonate solution, and the solvent was removed by rotatory evaporation after drying with anhydrous sodium sulfate. The residue was separated and purified by column chromatography (eluent: petroleum ether/ethyl acetate = 1/4) to obtain solid products with a yield of 73%. Proton nuclear magnetic resonance (¹H NMR; 400 MHz, $CDCl_3$): δ = 7.69 (m, 10 H), 6.82 (s, 4 H, 1, 4, 5, 8 - H anthracene), 3.73 (s, 12 H, OCH₃).

Synthesis of 9,10-Diphenyl-2,3,6,7-Tetrahydroxy Anthracene (2)

Compound **1** (0.45 g, 1 mmol), 47% hydrobromic acid aqueous solution (60 mL), and glacial acetic acid (60 mL) were mixed and added into a 250 mL flask. The mixture was stirred with nitrogen for 10 min, and then slowly heated to $105 \,^{\circ}C$ under nitrogen protection. Under the above conditions, the mixture refluxed overnight for 24 h and then slowly cooled to room temperature in the atmosphere of nitrogen. Filtration,

precipitation collection, and washing with ether. The raw product could be recrystallized with water/glacial acetic acid (3/2) solution to obtain colorless acicular crystals with a yield of 70%. Alternatively, the crude product could be dissolved in ethanol, filtered to remove insoluble impurities, collected in filtrate, and rotated to evaporate to obtain brown solids, with a yield of 85%. ¹H NMR [400 MHz, d_6 - dimethyl sulfoxide (DMSO)]: δ 9.34 (s, 4H), δ 7.63 (t, 4H), δ 7.53 (t, 2H), 7.38 (d, 4H), 6.65 (s, 4H).

Synthesis of 9,10-Diphenyl-2,3,6,7-Tetraphenyl(ethyl oxybutyrate) Anthracene (3)

Compound 2 (0.28 g, 0.72 mmol) and 20 mL acetone were added to a 100 mL three-necked flask and stirred with nitrogen gas, followed by ethyl 4-bromobutyrate (0.702 g, 3.6 mmol) and potassium carbonate (0.9 g, 6.48 mmol). The mixture was refluxed at 60 °C for 48 h, and the reaction was monitored by TLC (eluent: methylene chloride/ethyl acetate = 20/1). After the reaction was finished, the insoluble potassium carbonate was filtered out and filtrate was collected. Added 50 mL of dichloromethane to the filtrate, washed it three times with water, collected the organic phase, dried the anhydrous sodium sulfate, removed the solvent by rotary evaporation, purified the residue by column chromatography (eluent: dichloromethane/ethyl acetate = 20/1), and finally got the solid product, the yield was 61.3%. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m, 10H), 6.79 (s, 4H), 4.12 (q, / = 5.4 Hz, 8H), 3.86 (t, / = 4.5 Hz, 8H), 2.47 (t, / = 5.4 Hz, 8H), 2.07 (m, 8H), 1.24 (t, / = 5.4 Hz, 12H).

Synthesis of 9,10-Diphenyl-2,3,6,7-Tetra(oxybutyric acid) Anthracene (4)

Compound **3** (0.2 g, 0.235 mmol), sodium hydroxide (0.15 g, 3.76 mmol), 5 mL water, and 10 mL ethanol were added into a 25 mL flask. The mixture was reflux stirred at 60 °C for 12 h until completely dissolved. After the reaction was complete, the mixture solution was directly dried, and then 10 mL of water was added. The mixture was acidified with dilute hydrochloric acid, and the solid products were separated out, filtered, and collected. The yield was 99%. ¹H NMR (400 MHz, *d*₆ - DMSO): δ 7.61 (m, 6H), 7.42 (d, 4H), 6.71 (s, 4H), 3.74 (t, 8H), 2.32 (t, 8H), 1.89 (m, 8H).

Synthesis of 9,10-Diphenyl-2,3,6,7-Tetra(sodium oxybutyrate) Anthracene (BASM-1)

First, Compound **4** (0.113 g, 0.134 mmol), sodium hydroxide (0.022 g, 0.536 mmol), and 10 mL water were added to the round-bottom flask. Then, the mixture was stirred until completely dissolved under room temperature (or stirring 3 h at 60 °C). Filter, collect filtrate, directly spin dry, and then obtain solid product **BASM-1**. The yield was 100%. ¹H NMR (400 MHz, D₂O): δ 7.45 (m, 6H), 6.88 (d, 4H), 6.58 (s, 4H), 3.73 (t, 8H), 2.13 (t, 8H), 1.86 (m, 8H).

Synthesis of 9,10-Bis(4-bromophenyl)-2,3,6,7-Tetramethoxy Anthracene (5)

The mixture of veratrole (3.98 g, 28.8 mmol), 4-bromobenzaldehyde (1.78 g, 9.6 mmol), and PWA (7 mol %) (1.935 g, 67.2 mmol) was first added into a 100 mL flask. The mixture was stirred at 75 °C for 30 min. The reaction process was monitored by TLC (eluent: petroleum ether/ethyl acetate = 1/4). Then, 4-bromobenzaldehyde (3.55 g, 19.2 mmol), PWA (2 mol %) (0.553 g, 19.2 mmol), acetic anhydride (3.92 g, 38.4 mmol), and 20 mL glacial acetic acid were added to the reaction system, and then stirred for 90 min at 75 °C. After the reaction mixture was cooled to room temperature, 20 mL of dichloromethane was added to the system. Filter away the phosphotungstate hydrate and collect the filtrate. The organic phase was washed with saturated sodium bicarbonate solution, and the solvent was removed by rotatory evaporation after drying with anhydrous sodium sulfate. The residue was separated and purified by column chromatography (eluent: petroleum ether/ethyl acetate = 1/4) to obtain solid products with a yield of 65%. ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.2 Hz, 4 H, 2, 6 - H phenyl), 7.37 (d, *J* = 8.25 Hz, 4 H, 3, 5 - H phenyl), 6.76 (s, 4 H, 1, 4, 5, 8 - H anthracene), 3.76 (s, 12 H, OCH₃).

Synthesis of 9,10-Bis(4-bromophenyl)-2,3,6,7-Tetrahydroxy Anthracene (6)

Compound **5** (0.15 g, 0.025 mmol), 47% hydrobromic acid aqueous solution (20 mL), and glacial acetic acid (20 mL) were mixed and added into a 250 mL flask. The mixture was stirred with nitrogen for 10 min, and then slowly heated to 105 °C under nitrogen protection. Under the above conditions, the mixture refluxed overnight for 24 h and then slowly cooled to room temperature in the atmosphere of nitrogen. Filtration, precipitation collection, and washing with ether. The raw product could be recrystallized with water/glacial acetic acid (3/2) solution to obtain colorless acicular crystals with a yield of 65%. Alternatively, the crude product could be dissolved in ethanol, filtered to remove insoluble impurities, collected in filtrate, and rotated to evaporate to obtain brown solids, with a yield of 83.3%. ¹H NMR (400 MHz, d_6 - DMSO): δ 7.80 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 6.62 (s, 4H).

Synthesis of 9,10-Bis(4-bromophenyl)-2,3,6,7-Tetraphenyl (ethyl oxybutyrate) Anthracene (7)

Compound 6 (0.4 g, 0.72 mmol) and 20 mL acetone were added to a 100 mL three-necked flask and stirred with nitrogen gas, followed by ethyl 4-bromobutyrate (0.702 g, 3.6 mmol) and potassium carbonate (0.9 g, 6.48 mmol). The mixture was refluxed at 60 °C for 48 h, and the reaction was monitored by TLC (eluent: methylene chloride/ethyl acetate = 20/1). After the reaction was finished, the insoluble potassium carbonate was filtered out and filtrate was collected. Added 50 mL of dichloromethane to the filtrate, washed it three times with water, collected the organic phase, dried the anhydrous sodium sulfate, removed the solvent by rotary evaporation, purified the residue by column chromatography (eluent: dichloromethane/ethyl acetate = 20/1), and finally got the solid product, the yield was 51%. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: δ 7.72 (d, J = 6.0 Hz, 4H), 7.32 (d, J = 6.0 Hz, 4H), 6.73 (s, 4H), 4.13 (q, J = 5.4 Hz, 8H), 3.88 (t, J = 4.5 Hz, 8H), 2.49 (t, J = 5.4 Hz, 8H), 2.09 (m, 8H), 1.24 (t, J = 5.4 Hz, 12 H).

Synthesis of 9,10-Bis(4-bromophenyl)-2,3,6,7-Tetra (oxybutyric acid) Anthracene (8)

Compound **7** (0.2 g, 0.198 mmol), sodium hydroxide (0.13 g, 3.16 mmol), 5 mL water, and 10 mL ethanol were added into a 25 mL flask. The mixture was reflux stirred at 60 °C for 12 h until completely dissolved. After the reaction was complete, the mixture solution was directly dried, and then 10 mL of water was added. The mixture was acidified with dilute hydrochloric acid, and the solid products were separated out, filtered, and collected. The yield was 98%. ¹H NMR (400 MHz, *d*₆ - DMSO): δ 12.1 (s, 4H), δ 7.83 (d, *J* = 6.0 Hz, 4H), 7.38 (d, *J* = 6.0 Hz, 4H), 6.68 (s, 4H), 3.79 (t, *J* = 5.4 Hz, 8H), 2.35 (t, *J* = 5.4 Hz, 8H), 1.90 (m, 8H).

Synthesis of 9,10-Bis(4-bromophenyl)-2,3,6,7-Tetra (sodium oxybutyrate) Anthracene (*BASM-2*)

First, Compound **8** (0.161 g, 0.177 mmol), sodium hydroxide (0.028 g, 0.708 mmol), and 10 mL water were added to the round-bottom flask. Then, the mixture was stirred until completely dissolved under room temperature (or stirring 3 h at 60 °C). Filter, collect filtrate, directly spin dry, and then obtain solid product **BASM-2**. The yield was 100%. ¹H NMR (400 MHz, D₂O): δ 7.56 (t, 4H), 6.66 (d, 4H), 6.53 (s, 4H), 3.76 (t, 8H), 2.23 (t, 8H), 1.96 (m, 8H).

Synthesis of 1,3,5-Triborate Ester Benzene (9)

First, 1,3,5-tribromobenzene (0.5 g, 1.6 mmol), bis(pinacolato) diboron (1.46 g, 5.76 mmol), potassium acetate (0.95 g, 9.6 mmol), Tetrakis(triphenylphosphine)palladium(0) (39.2 mg, 0.048 mmol) and 10 mL refined dimethylformamide (DMF) were added to 20 mL stoker reactor. After three times of freezing-vacuum-nitrogen-thawing operation, the reaction mixture was stirred under 90 °C for 24 h. After the reaction, the mixture was poured into the beaker, and 100 mL dichloromethane was added. Then, the oil was washed with water (3 × 50 mL), the organic layer was dried with Na₂SO₄ and concentrated in vacuum. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10/1), and the solid product was obtained with a yield of 51.5%. ¹H NMR (400 MHz, CDCl₃): δ 8.36 (s, 3H), 1.34 (s, 36H).

Self-Assembly of BASM-1 and BASM-2 in Pure Water

First, 1 mg **BASM-1** and 1 mg **BASM-2** were weighed and placed in bottle, and 1 mL distilled water was added, respectively. The solution was fully dissolved by ultrasound for 5 min, and then allowed to stand for 24 h to obtain the assembly solution with a concentration of 1 mg mL⁻¹. The above assembly solutions were numbered nos. 1 and 2, respectively.

Self-Assembly of *BASM-2* in a Mixture of Organic Solvent/Water

First, six samples of **BASM-2** with a mass of 1 mg were weighed and placed in six bottles, and then 3 mL distilled water was added, respectively. After being completely dissolved, six aqueous solutions were added to 3 mL dioxane, 3 mL tetrahydrofuran (THF), 3 mL acetone, 3 mL DMF, 6 mL DMF, and 1.5 mL DMF, drop by drop, respectively. Then, the above solutions were dialysed 2 h with corresponding mixed solvent for assembly, and



finally obtained six different assembly solutions, which were numbered nos. 3, 4, 5, 6, 7, and 8, respectively.

Synthesis of Few-Layer Covalent 2D Polymers

1,3,5-Triborate ester benzene (1 mol), Tetrakis(triphenylphosphine)palladium(0) (0.05 mol) and potassium carbonate (6 mol) were added to no. 6 assembly solution containing 1.5 mole **BASM-2**, in turn. After three times of freezing-vacuumnitrogen-thawing operation, the reaction mixture was standing under 90 °C for 72 h. When the reaction was finished, the reaction mixture was directly filtered to remove the insoluble solids. The filtrate was dialyzed for 3 days with DMF/H₂O = 1/1 mixed solvent (molecular weight cutoff = 3500), to remove the unreacted raw materials. The polymer solution was precipitated with acetone to obtain a solid polymer.

RESULTS AND DISCUSSION

The synthetic procedures of **BASM-1** and **BASM-2** are shown in Scheme 1. The structures were characterized by 1 H, 13 C NMR spectroscopy, and mass spectroscopy. The results were shown in Figures S1–S20.

Self-Assembly Mechanism of *BASM-1* and *BASM-2* in Aqueous Solution

The molecular structure of **BASM-1** and **BASM-2** that we designed and synthesized both have three characteristics:

(a) The intermediate hydrophobic part is a rigid large conjugate structure, with a strong π - π accumulation interaction; (b) Molecules have bipolar properties, so the hydrophobic interactions will be observed in aqueous solutions, which will further increase the degree of molecular aggregation; and (c) The hydrophilic parts at both ends of the molecules also have ionic groups and the highly polar aqueous solution has a strong solvation effect on the ions, so the negative ions can be dissociated, which eventually leads to the electrostatic repulsion between the negative ions, weakens the layer-layer accumulation, and obtains the oligolayer 2D plane structure. Therefore, we chose aqueous solution as the self-assembled solvent system.

The self-assembly of **BASM** was in two directions in aqueous solution. The inducing force of lamellar growth along the *x* axis includes π - π accumulation and hydrophobic interaction. Among them, π - π accumulation played a dominant role because of the large conjugate area of the molecule itself. And the induced force along the *y* axis was only hydrophobic interaction. So the main driving force along the *x* axis was π - π stacking interaction, and the main driving force along the *y* axis was the hydrophobic interaction. The relative magnitude of dominant forces in the two directions was mainly regulated by the variation of hydrophobic effect, while the strength of hydrophobic effect was affected by the water content in the solvent. The higher the water content was, the stronger the



SCHEME 1 Synthetic procedures of bola-amphiphilic BASM-1 and BASM-2.

hydrophobic effect and the greater the inducing force of growth along the y axis.

To claim the π - π interaction, X-ray diffraction (XRD) (Figs. S23 and S24) and ultraviolet-visible spectroscopy (UV-vis) (Fig. S25) of **BASM-1** and **BASM-2** were measured. The XRD results turned out that both **BASM-1** and **BASM-2** showed strong intermolecular accumulation in solid state, and the accumulation of **BASM-1** was more compact and orderly. UV-vis results also proved that both the two compounds had wide absorption peaks near 398–399 nm in aqueous solution due to intermolecular π - π accumulation.

Self-Assembly of BASM-1 and BASM-2 in Pure Water

We first studied the self-assembly behavior of two BASM in pure water, as shown in Figure 2. The results showed that BASM-1 could directly self-assemble in pure water to obtain 2D nanosheet structure, and the surface of the sheet was smooth, with the transverse size ranging from hundreds of nanometers to dozens of micrometers. However, the self-assembly of BASM-2 in pure water resulted in nanoribbon structure, and the width of the nanoribbon was about hundreds of nanometers, the length was about ten of micrometers. This was due to, in pure water, the hydrophobic effect was very strong, which was much larger than the intermolecular π - π stacking interaction, so the induced growth force of **BASM-1** along the *x* axis (the hydrophobic effect) and *y* axis (π - π stacking interaction and the hydrophobic effect) was close, and easy to form a uniform-sized slice structure. However, due to the steric hindrance of larger bromine atoms, which limited the horizontal growth of the lamellar along the *x* axis, BASM-2 could only form nanoribbon structures.

Self-Assembly of *BASM-2* in a Mixture of Organic Solvent/Water

Although **BASM-1** was self-assembled in pure water to obtain 2D lamellar structure, it further proved that our method based on solution self-assembly to prepare 2D layer was reasonable.

However, instead of forming a 2D structure, the small molecule **BASM-2** assembled into a nanoribbon-like structure (a few hundreds of nanometers wide and a few tens of micrometers long). Therefore, in order to prepare covalently bonded 2D polymers, we studied the solution assembly conditions of **BASM-2** in detail.

The previous research results showed that the reason why **BASM-2** could not obtain a 2D plane structure in pure water was that its hydrophilic–hydrophobic effect was very strong, resulting in a large steric effect between bromine atoms, and the induced force of molecules growing along the x axis was less than that growing along the y axis. In order to balance the growth rate of molecules in all directions, we reduced the inducing force of molecules growing along the y axis by adjusting the solvent. When using the mixed solution of organic solvent and water, the hydrophobic effects were weakened, the steric hindrance between bromine atoms was reduced, and **BASM-2** grew uniformly along all directions to form regular nanosheet.

We selected the mixed solution of different organic solvents (dioxane, THF, acetone, N,N-DMF) and water as the self-assembly solvent, with the proportion of 1/1 (v/v). The transmission electron microscope (TEM) results are shown in Figure 3. The results showed that BASM-2 self-assembled into one-dimensional nanobelts and nanorods structure in dioxane/H2O mixture and in THF/H₂O mixture, respectively. However, in acetone/H₂O and DMF/H₂O mixture, 2D planar structure with low contrast and uniform smooth surface were obtained, and their lateral sizes were about tens of more micrometers. Because of the different polarities of the organic solvents we used (The order of polarity of solvent is THF < dioxane < acetone < DMF.), different morphologies were obtained in various mixed solvents. The main driving force along the *x* axis was π - π stacking interaction, and the main driving force along the y axis was the hydrophobic interaction. The relative magnitude of dominant forces in the two directions was mainly regulated by the variation of hydrophobic effect. The greater the polarity of solvent, the stronger the



FIGURE 2 TEM images of $\ensuremath{\text{BASM-1}}$ (a,b) and $\ensuremath{\text{BASM-2}}$ (c,d) in water.



FIGURE 3 TEM images of BASM-2 in organic solvent/water.



hydrophobic effect, and the closer the growth force of molecules along the x and y axes, which was conducive to the formation of laminates. Considering that higher temperature was required for the preparation of covalent 2D polymers in the later stage, we chose DMF/water mixed solution as the solvent system for self-assembly polymerization next.

Self-Assembly of BASM-2 in a Mixture of DMF/H₂O with Different Water Contents

In order to obtain the 2D laminates with the best morphology and the largest size, we further studied the influence of water content in the DMF/H₂O mixed solvent on the self-assembly behavior of **BASM-2**. DMF/H₂O = 2/1, DMF/H₂O = 1/1, DMF/H₂O = 1/2, and $DMF/H_2O = O/1$ were selected as solvents (water content was 33, 50, 67, and 100%, respectively) for assembly and the results are shown in Figure 4. The results showed that low water content or high water content was not conducive to the formation of 2D lamellar. When the water content was 50%, the obtained lamellar morphology was the best. This was because, when the water content was too low (33%), the hydrophobic effect was weak and intermolecular π - π stacking interaction dominated, which led to the induced force of **BASM-2** along the *x* axis (the hydrophobic effect) less than the induced force along y axis (π - π stacking interaction and the hydrophobic effect), eventually forming nanoribbon structures; when the water content was high (67 and 100%), the hydrophobic interaction was dominant, but the steric effect of bromine atoms along the x axis was so large that the induced force of **BASM-2** along the *x* axis (the hydrophobic interaction) was still less than the induced force along the *y* axis (π - π stacking interaction and the hydrophobic interaction). Only when the water content was moderate, the π - π stacking interaction and the hydrophobic effect were close to each other, leading to the uniform growth of BASM-2 along all directions, and finally 2D plane structures were obtained. So we chose $DMF/H_2O = 1/1$ of the mixed solution as the solvent system of self-assembly polymerization.

Synthesis and Characteristic of Few-Layer Covalent 2D Polymers

In order to prepare covalent 2D polymers, trifunctional monomer 1,3,5-triborate ester benzene (9) was added into the selfassembly solution, and the Suzuki coupling of borate and bromobenzene was used for the polymerization reaction. Since 1,3,5-triborate ester benzene was an oil-soluble monomer, it diffused to the hydrophobic part in the middle of the 2D layer, resulting that the polymerization reaction could not occur among the layers, but only in the 2D layers. Therefore, in the XY plane, bromobenzene coupled with Compound 9 to form covalent bonds in the initial stage, and covalent 2D polymer was obtained. In the later stage, bromobenzene at the edge of 2D polymer layer coupled with Compound 9 to make the polymer layer grow continuously with the extension of time. In the z axis (i.e., perpendicular to the XY plane), the electrostatic repulsion of ions prevented the accumulation among the layers, resulting in thin layers or even single-layer 2D polymers.

The polymerization conditions were as follows: $DMF/H_2O = 1/1$ as the solvent, Tetrakis(triphenylphosphine)palladium(0) as the catalyst, potassium carbonate as the base, the concentration of **BASM-2** was 0.1 mg mL⁻¹, the temperature was 90 °C, the polymerization was standing in the atmosphere of nitrogen, and the polymerization time was 12, 24, 36, and 72 h, respectively. The TEMs of the polymers are shown in Figure 5. The results showed that with the extension of the polymerization time, the polymer sheet grew gradually. When the polymerization time was 72 h, the sheet size could reach 10 or even dozens of micrometers, and the sheet surface was smooth and flat. The structure of the polymer was characterized by infrared spectroscopy, as shown in Figure S21. After polymerization, the stretching vibration peak (C-Br bond 595 cm^{-1}) of **BASM-2** and the characteristic peaks $(B-0 \text{ bond } 1337 \text{ cm}^{-1} \text{ and } C-0 \text{ bond } 1273 \text{ cm}^{-1})$ of 1,3,5-triborate ester benzene disappeared, indicating the occurrence of Suzuki coupling reaction and the formation of covalent 2D polymers.



FIGURE 4 TEM images of BASM-2 in a mixture of DMF/H₂O with different water contents.



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FIGURE 6 AFM image and height profile of 2D polymers (simulated monomer conformation giving $h_{calc} \approx 2.26$ nm). [Color figure can be viewed at wileyonlinelibrary.com]

Next, we used atomic force microscopy (AFM) to characterize the thickness of the polymers, as shown in Figure 6. The results showed that theoretically simulated monolayer thickness was 2.26 nm, and the measured experimentally thickness of polymer sheet was about 2.65 nm. Considering the water layer on the surface of the sample, the roughness of the substrate surface, the repulsion between the substrate and the probe, and so forth, we judged that the synthesized 2D polymer was single layer structure. Theoretically, electrostatic repulsion existed among polymer layers, and 2D polymers with a single molecular thickness could be obtained in aqueous solutions,^{43,44} which was consistent with the results. What is more, due to the large transverse size (large specific surface area) of the polymer sheet layer, partial accumulation was likely to occur during the sample



FIGURE 7 Schematic illustration of the formation pathway of few-layer 2D polymers. [Color figure can be viewed at wileyonlinelibrary.com]

preparation process, so we also got the 2D polymer with few layers eventually (Fig. S22).

The synthesis mechanism of 2D polymers is shown in Figure 7. First of all, the **BASM-2** self-assembled in mixed solvent $(DMF/H_2O = 1/1)$ to form a supramolecular 2D layer. Then, the oil-soluble trifunctional monomer (9) was added to the above assembly solution. Due to the hydrophobic interaction, the oil-soluble monomer diffused to the middle hydrophobic part and polymerized with **BASM-2** in the 2D layer to obtain the covalent 2D polymers with small size. Finally, with the extension of the polymerization time, the small polymer laminates were further crosslinked to make the laminates grew up gradually and obtained the 2D polymers with the transverse size of tens of micrometers.

CONCLUSIONS

Two ionic BASMs, BASM-1 and BASM-2, were successfully designed and synthesized, and supramolecular 2D planar structures were obtained in pure water and organic solvent/water, respectively, based on solution self-assembly. Then, the self-assembly behavior and mechanism of two small molecules in different solvents were studied in detail. The results showed that BASM-1 directly self-assembled into lamellar structure in pure water, while BASM-2 could only self-assembled into regular supramolecular nanolayer in $DMF/H_2O = 1/1$ and acetone/ $H_2O = 1/1$ mixed solution. Finally, the 2D polymers were obtained by the within-layer crosslinking polymerization of BASM-2 nanosheets via Suzuki coupling reaction. The formation of the polymerization reaction was demonstrated by infrared spectroscopy, and the morphology and thickness of the polymer sheets were characterized by TEM and AFM. So our work provides a simple and efficient method for directly preparing independent both supramolecular 2D polymers and covalent 2D polymers in liquid phase which is of great significance.

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