ARTICLE

# Polybenzobisimidazole-Derived Two-Dimensional Supramolecular Polymer

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**ABSTRACT**: We report a novel crystalline supramolecular polybenzobisimidazole (SP-PBBI) capable of providing a twodimensional polymer (2DSP-PBBI) by liquid-phase exfoliation. A regular arrangement of rigid rod-like polybenzobisimidazole (PBBI) chains is achieved by interchain hydrogen bonding. Titration of 2DSP-PBBI with cobalt chloride (CoCl<sub>2</sub>) using UV-Vis spectroscopy demonstrates the presence of bidentate NO ligands on the PBBI backbone and NO–Co(II) complexation. Imaging analysis using atomic force microscopy (AFM) reveals the planar surface morphology of exfoliated 2DSP-PBBI sheets with lateral

**INTRODUCTION** An increasing number of two-dimensional polymers (2DPs) have been developed and found applications in catalysts,<sup>1</sup> photovoltaic cells,<sup>2</sup> and colorimetric sensing.<sup>3</sup> The importance of 2DPs as substrates for hierarchically ordered heterostructures with novel properties is rapidly being recognized.<sup>4</sup> 2DPs are constructed by connecting building units covalently (e.g., covalent organic frameworks) or noncovalently (e.g., supramolecular polymers).<sup>5</sup> Envisioning realization of a 2D semiconducting and chemical sensing material for field-effect transistor (FET) devices, we designed a novel covalent organic framework COF-Salophen consisting of multiple salophen macrocycles (Scheme 1). This covalent organic framework (COF) can be synthesized by condensation of aromatic monomers bearing aldehyde and amine functional groups,<sup>6</sup> which provides an imine linker connecting salophen units and pores with two different sizes. The salophen ligands can serve as a sensing moiety for the detection of Co(II) ions,<sup>7</sup> and the extended  $\pi$ -conjugated system imparts planarity and rigidity, thereby providing semiconducting properties to the polymer.<sup>8</sup> The high surface-tovolume ratio of 2D COFs allows for facile electron transfer due to the excellent surface contact within FET devices.<sup>5(a)</sup> However, an initial effort for direct condensation of 1 and commercially available 1,2,4,5-benzenetetramine tetrahydrochloride, the precursor of 2, in the presence of N,N-diisopropylethylamine

dimensions of <1  $\mu$ m and thickness of <30 nm. The size of the polymer crystal growth is tuned by employing condensation/ precipitation polymerization under nonisothermal conditions. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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failed to provide COF-Salophen. We also attempted to neutralize 1,2,4,5-benzenetetramine tetrahydrochloride before polymerization, but found that spontaneous air-oxidation of an unstable **2** provided **3** (3,6-diimino-1,4-cyclohexadiene-1,4-diamine) under atmospheric conditions. Despite the conversion into **3**, we have utilized it as a monomer for polycondensation with **1** to investigate whether the product forms a conjugated linear polymer that may possess distinct electrical properties. Interestingly, we have found that a novel supramolecular polymer (SP-PBBI) is formed by self-assembly of linear polybenzobisimidazole (PBBI) chains in a one-step reaction. SP-PBBI features a regular arrangement of rigid linear PBBI chains stabilized by intramolecular hydrogen bonding within a planar sheet. The size of SP-PBBI crystal growth is controlled by gradually raising the temperature during the precipitation polymerization process.

The rigid rod structure of crystalline polybenzimidazoles (PBI) and their derivatives were previously reported,<sup>9</sup> some of which possess interchain hydrogen bonds and are able to form spun fibers.<sup>10</sup> PBI can be synthesized with condensation of an amine and a carbonyl group (e.g., carboxylic acid,<sup>11</sup> ester,<sup>12</sup> or aldehyde<sup>13</sup>) at high temperatures of 100 to 350 °C. However, neither two-dimensional morphology nor supramolecular polymerization of PBI has been investigated.<sup>14</sup> Herein, we report the one-step synthesis of supramolecular polymer

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**SCHEME 1** Attempted synthesis of COF-Salophen yields a supramolecular polybenzobisimidazole (SP-PBBI) consisting of multiple polycrystalline domains, and exfoliation of bulk SP-PBBI affords a two-dimensional supramolecular polymer (2DSP-PBBI). [Color figure can be viewed at wileyonlinelibrary.com]

polybenzobisimidazole (SP-PBBI) by nonisothermally controlled condensation/precipitation polymerization. The surface morphology of 2DSP-PBBI isolated by liquid-exfoliation of as-synthesized, bulk SP-PBBI is analyzed with atomic force microscopy (AFM) and transmission electron microscopy (TEM). The bidentate NO ligands of PBBI chains are further investigated by UV-Vis spectroscopic titration with Co(II).

# EXPERIMENTAL

#### General

All chemicals were obtained from Sigma Aldrich and used without further purification. All reaction solvents were anhydrous reagent graded. Detailed synthetic procedures, materials characterization, and instrumentation details can be found in the Supporting Information.

#### Synthesis of SP-PBBI

Monomers **1** and **3** were synthesized as described in the Supporting Information. A solution of **1** (6.0 mg, 0.04 mmol) and **3** 

(3.3 mg, 0.02 mmol) in N,N-dimethylformamide (1 mL) was prepared in a 25 mL round bottom flask. The solution of the monomers was degassed by two freeze-pump-thaw cycles and was sealed with a septum and PTFE tape. After sonication for 5 min, the reaction mixture was kept at 95 °C (for 2 days) in an oil bath without stirring and then at 100 °C for 1 day. After gradually raising the temperature to 145 °C, the reaction was left undisturbed for 3 days. After total 6 days, the reaction flask was cooled to room temperature for 2 h, and the crude polymer was washed with dichloromethane (4  $\times$  15 mL) and methanol  $(4 \times 15 \text{ mL})$  over a Millipore filter and a 200 nm fluoropore filter membrane. After drying in vacuo for 48 h over 100 °C, 2DSP-PBBI was obtained as a dark brown solid (89%). <sup>13</sup>C CP MAS solid-state NMR (15 kHz)  $\delta$  ppm, 198.6, 150.0, 147.0, 138.2, 129.9, 121.3, 119.0, 116.5, 99.0. IR (KBr, ATR) 3327, 1641, 1580, 1557, 1483, 1440, 1394, 1302, 1152, 839 cm $^{-1}$ .

# **Preparation of 2DSP-PBBI**

Exfoliation was performed in a 100 mL round bottom flask containing dry 2DSP-PBBI (2.0 mg) and anhydrous DMF

(12 mL) with gentle stirring for >24 h at 60 °C. Supernatants contained relatively well-suspended polymer sheets and exhibited varying degrees of orange hues, depending on the exfoliation time.

#### **Characterization of SP-PBBI and 2DSP-PBBI**

Fourier transform infrared spectroscopy (FTIR) was performed using an IR-Prestige spectrophotometer (Shimadzu Scientific) outfitted with an EasiDiff accessory (Pike Technologies). Solid samples were ground with KBr to prepare a homogenous mixture. <sup>13</sup>C cross-polarization magic-angle spinning (CP MAS) spectroscopy was performed on a Bruker Avance spectrometer (500 MHz). Powder X-ray diffraction (PXRD) was recorded on a Bruker X8 Prospector Ultra equipped with a Bruker Smart Apex CCD diffractometer and a copper micro-focus X-ray source employing Cu Ka radiation at 40 kV, 40 mA. A ground sample was loaded in a capillary tube (D: 1 mm) for analysis. The size and the morphology of materials were analyzed with transmission electron microscope (FEI-Morgani, 80 keV). TEM samples were prepared by dropcasting 3.5  $\mu$ L of a sample onto a lacey carbon films/ 400 mesh copper grid and dried under ambient conditions over 24 h. An Asylum MFP-3D atomic force microscope (AFM) was utilized with high resolution probes (Hi'Res-C14/ Cr-Au) purchased from MikroMasch. AFM samples were prepared by deposition of 10 µL of an exfoliated solution onto freshly cleaved mica. The sample was spin-coated and then allowed to dry under ambient conditions over 24 h. UV-Vis-NIR spectra were acquired using a Lambda 900 spectrophotometer (PerkinElmer). Scanning Electron Microscopy (SEM) was performed with FEI XL-30 (20 keV).

#### Co(II) Titration of 2DSP-PBBI

A 5.3 mM CoCl<sub>2</sub> solution was prepared in DMF, and 5  $\mu$ L was delivered to an exfoliated polymer solution (600  $\mu$ L) for each titration at ambient conditions. The polymer solution contained about 32  $\mu$ g of 2DSP-PBBI. The sample for weight measurement was prepared by depositing an exfoliated polymer solution on a glass slide and was dried on a hot plate for 24 h. The optical change of 2DSP-PBBI solution was measured by UV-Vis absorption spectroscopy immediately after each addition of CoCl<sub>2</sub>.

#### **RESULTS AND DISCUSSION**

#### Synthesis of SP-PBBI

In an attempt to perform imine condensation under neutral conditions, 1,2,4,5-benzenetetramine tetrahydrochloride was treated with cesium carbonate ( $Cs_2CO_3$ ) in air prior to polymerization. Upon exposure to air, **2** was rapidly oxidized to **3**, and polycondensation of the isolated 3,6-diimino-1,4-cyclohexadiene-1,4-diamine **3** and 2,3-dihydroxybenzene-1,4-dicarbaldehyde **1** in *N*,*N*-dimethylformamide (DMF) proceeded at 95 to 145 °C. An aprotic polar solvent DMF was employed to completely solubilize both compounds **1** and **3**, thereby initiating precipitate polymerization in a homogenous solution. DMF may also have facilitated  $\pi$ - $\pi$  stacking due to the enhanced solvophobic effect and the self-assembled

macromolecular structure.<sup>15</sup> Condensation of **1** and **3** allowed formation of two imine bonds and subsequent cyclization to a benzobisimidazole moiety. To confirm the formation of benzobisimidazole from **3**, a model compound **4** was prepared with salicylaldehyde and **3** under the same nonisothermal conditions [Supporting Information, <sup>1</sup>H and <sup>13</sup>C NMR spectra in Fig. S2(c–e)]. The reaction afforded a brown powder of as-synthesized 2DSP-PBBI in 89% yield, exhibiting insolubility in water and most common organic solvents at room temperature. The sufficiently long reaction time (total 6 days) was crucial to achieving high polymer conversions, whereas reactions performed for less than 3 days formed the precipitated product in much lower conversions.

The FTIR spectrum [Fig. 1(a)] confirms the formation of an imine (C=N) stretch at a very intense peak of 1641  $cm^{-1}$  in the polymer sample while peaks characteristic to the monomers such as the aldehyde C-H stretch (2866 and 2769 cm<sup>-1</sup>) of **1** and primary amine N–H stretch (3444 and 3417  $\text{cm}^{-1}$ ) of **3** are clearly absent [Supporting Information Fig. S1(b,c)]. The relatively high frequency of an imine stretch can be observed due to the highly rigid conformation arising from the cyclic imine of benzobisimidazole and a strong intramolecular hydrogen bond occurring between the hydroxyl hydrogen and the imino nitrogen (OH...N=C)<sup>16</sup> although a different hydrogen bonding motif (HO···H-N) was proposed by X-ray crystal structure analysis of PIPD.<sup>14(c),17</sup> The distinct O-H stretch at 3321  $\text{cm}^{-1}$  can be used as a marker for predicting the crystallinity of the polymer. Also, the shift in O–H stretch by about 40  $\text{cm}^{-1}$  from the monomer 1 and a higher intensity of the peak suggest that a strong intramolecular hydrogen bond is present.<sup>18</sup> When a less crystalline polymer sample was obtained, only a broad O-H stretch was observed in the region between 3100 and 3400 cm<sup>-1</sup> [Supporting Information Fig. S1(d)]. The structure of the polymer was further confirmed by <sup>13</sup>C CP MAS solid-state nuclear magnetic resonance (NMR) spectrum [Fig. 1(b)]. The characteristic phenolic  $(C_1)$  and cyclic imino  $(C_2)$ carbons resonate at  $\delta = 150.0$  and 147.0 ppm, respectively, and the resonance at  $\delta = 129.2$  ppm was attributed to C<sub>3</sub> connecting the benzobisimidazole moiety.<sup>19</sup> In the case of a less crystalline sample, a weak resonance of downfield carbon was present at  $\delta = 175.6$  ppm, most likely a carbonyl carbon (C=O) resulting from the keto-enamine tautomerization [Supporting Information Fig. S2(a)].

To support the evidence of a periodic structure with welldefined crystalline parameters, powder X-ray diffraction (PXRD) was implemented. As shown in the experimental PXRD spectrum [Fig. 1(c)], *d* spacing values corresponding to the well-defined peaks were found (16.67, 8.43, 6.33, 5.86, and 3.31 Å), based on which a two-dimensional unit cell model (*a* and *b* axes) was proposed [Fig. 1(d)]. To construct a periodic alignment of PBBI, we referred to the structural analyses of poly(pyridobisimidazole) that is very similar to PBBI except for the position of one hydroxyl group and the pyridine moiety.<sup>14(c),17,20</sup> Based on the information of bond lengths and unit cell (either monoclinic or triclinic)





**FIGURE 1** Characterization of as-synthesized SP-PBBI. (a) FTIR, (b) <sup>13</sup>C CP MAS solid state NMR, and (c) experimental PXRD spectra of SP-PBBI. (d) Proposed two-dimensional (*ab* plane) structure and optimization of the unit cell parameters calculated by B3LYP/6-31g(d) level (a = 16.13 Å) for SP-PBBI, which is close to 16.67 Å of an experimental PXRD *d* spacing value, and (a = 23.55 Å, b = 25.69 Å) for (e) COF-Salophen. [Color figure can be viewed at wileyonlinelibrary.com]

of poly(pyridobisimidazole),<sup>14(c)</sup> we indexed a = 16.67 Å and b = 6.63 Å for SP-PBBI parameters [Fig. 1(d)]. These lattice parameters are very different from those of the COF-Salophen estimated at the B3LYP/6-31g(d) level [Fig. 1(e)]. We reason that the interlayer spacing (*c* axis) is 3.31 Å, which is within van der Waals contact distances arising from the  $\pi$ - $\pi$  stacking of aromatic rings and comparable to previously synthesized arene-based polymers.<sup>21</sup> Due to limited structural information gleaned from the powder diffraction data, the analysis of angles between unit cell parameters was not proposed.<sup>14(c)</sup> Thermogravimetric analysis (TGA) showed a weight loss of 10% around 330 °C and a slow decomposition of 20% up to approximately 400 °C (Supporting Information Fig. S4).

### Morphology of 2DSP-PBBI

The morphology and the size of 2DSP-PBBI were investigated using TEM and noncontact-mode AFM shown in Figure 2(a-d). Both bulk SP-PBBI and exfoliated 2DSP-PBBI samples exhibit a planar morphology consisting of largely stacked platelets [Fig. 2(a)]. We confirmed the supramolecular polymerization process with 2DSP-PBBI samples that were sonicated or manually ground from 5 to 30 min. It appears that large planar sheets were disintegrated into small rods under the mechanical forces, probably due to weakened intermolecular bonds [Supporting Information Fig. S5(a)]. The planar configuration and rigidity arise from the individual PBBI chain capable of arranging in a quasi-aromatic six-membered chelate ring induced by intramolecular hydrogen bonding between the imino nitrogen and the o-hydroxyhydrogen (OH. N=C).<sup>14(a),16(a),17</sup> Once linear PBBI backbones are formed and ready for self-preorganization, secondary amines (NH), imines (N=C), and 1,2-dihydroxyphenyl (OH) groups of PBBI provide intermolecular hydrogen bonding motifs for promoting self-assembly and the resulting formation of 2DSP. Each layer of 2DSP-PBBI consists of multiple crystallites aligned in various orientations, as indicated in the presence of moiré fringes shown in two different directions [inset, Fig. 2(a)].<sup>22</sup> A 100 nm lateral resolution AFM image also confirms the polycrystalline grain boundaries [Fig. 2(d)]. 2DSP-PBBI also vertically grows into a 3D bulk, mainly driven by  $\pi$ - $\pi$  stacking that exists between the aromatic PBBI backbones. Thus as-synthesized samples were multiple stacks strongly held by each 2DSP-PBBI layer and poorly soluble in most organic solvents at room temperature. However, we were successfully able to exfoliate bulk SP-PBBI in DMF at 60 °C. After 2 h-exfoliation, mostly small molecular weight and amorphous-like flakes were visible under TEM, but larger flakes were slowly delaminated into thin layers (<30 layers) within 4 to 6 days [Fig. 2(b) and Supporting Information Fig. S5(c)]. The height distribution of exfoliated layers analyzed by AFM ranges from 0.4 to 8.6 nm, equivalent to about 1 to 25 layers of 2DSP-PBBI in the sample [Fig. 2(c,d)].

Large polymer sheets with lateral dimensions of 0.1–10  $\mu$ m were observed under TEM [Fig. 2(a) and Supporting Information Fig. S5(b)]. Given that cooperative supramolecular



**FIGURE 2** TEM (a, b) and AFM (c, d) micrographs of 2DSP-PBBI. (a) A large flake 2DSP-PBBI showing the stacked edges seen through multiple layers (1 d-exfoliation). Inset: Moiré fringes marked in the red circle is indicative of high crystallinity. (b) 4 d-exfoliation. (c) A height of 2.5 nm of exfoliated 2DSP-PBBI on mica and its height profile (below). (d) Grain boundaries of a polycrystalline sample show the height profile range of 6 to 12 nm (below) in a 100 nm lateral dimension. [Color figure can be viewed at wileyonlinelibrary.com]

polymerization is based on the two-step mechanism of (1) nucleation and (2) elongation,<sup>23</sup> the formation of the large SP-PBBI seems reasonable. The size of as-synthesized SP-PBBI was dependent on temperature control during polymerization. We tested it by initiating the reaction at 95 °C and completing it at 145 °C. The PBBI crystals grew in larger sheets if the temperature was gradually raised in multiple

stages. Precipitation polymerization involves monomers that are initially soluble in the reaction solvent, and the locus of polymerization remains in a homogeneous solution until the growing macromolecular network reaches the critical molecular weight for precipitation.<sup>24</sup> We reason that slow diffusion of building blocks and formation of dynamic intermolecular bonds under the gradual increments of temperature (95–145

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**FIGURE 3** Titration of 2DSP-PBBI with Co(II). (a) Complexation between Co(II) ions and the bidentate ligands (NO) on the PBBI backbone. M: divalent metal ions. (b) UV-Vis absorption spectra of an exfoliated 2DSP-PBBI solution in DMF upon addition of a 5.2 mM of CoCl<sub>2</sub> prepared in DMF. The arrows indicate the direction of absorbance change with increasing concentration of Co(II). Inset: Absorbance at 381 nm. Instrumental artifacts at 319 and 378 nm. (c) A titrated sample of 2DSP-PBBI was deposited on a copper foil and dried at room temperature for SEM analysis. [Color figure can be viewed at wileyonlinelibrary. com]

°C) result in a slow nucleation and growth process of structurally well-defined, large polymer crystallites (ca. >1  $\mu$ m) over an extended period of time. Notably, the growth rate of polymer layer postulated from the morphology of 2DSP-PBBI suggests that cooperative interchain hydrogen bonding was more effective in the elongation of polymer sheet than the interlayer  $\pi$ - $\pi$  stacking under the given reaction conditions (i.e., rate<sub>*ab*-axis</sub>  $\gg$  rate<sub>*c*-axis</sub>). To further verify the temperature effect, a different reaction batch (PBBI-2) was stored at a constant temperature of 145 °C throughout the entire

polymerization. Interestingly, the isothermal condition resulted in the same PXRD pattern as that of the nonisothermally treated sample, but yielded much smaller and more monodisperse polymer flakes [Supporting Information Fig. S5(d)]. To further investigate the effects of temperature and solvent in supramolecular polymerization, we attempted a higher temperature increment ( $T_1 = 95$  °C,  $T_2 = 170$  °C) in a mixture of dimethylsulfoxide/mesitylene (10:1) for 6 days. The reaction yielded a significantly different crystalline polymer PBBI-170 [see FTIR, <sup>13</sup>C CP MAS solid-state NMR, and PXRD in Supporting Information Fig. S1(e), S2(b), and S3, respectively]. PBBI-170 was hardly exfoliated in most organic solvents even after 7 days, and only small rod fragments were isolated, probably delaminated at the early stage of exfoliation [Supporting Information Fig. S5(e)].

# **Optical Properties of 2DSP-PBBI**

We investigated the optical properties of the exfoliated 2DSP-PBBI using UV-Vis absorption spectroscopy. The absorption spectrum of 2DSP-PBBI exhibits a broad band with a maximum at 381 nm and minor peaks at 274 nm and 461 nm (Supporting Information Fig. S7). Each PBBI chain possesses bidentate NO ligands, capable of complexation with divalent metal ions such as Co(II), Cu(II), and Zn(II) ions [Fig. 3(a)].<sup>25</sup> To confirm the complexation of NO-Co(II), titration of exfoliated 2DSP-PBBI in DMF was performed with cobalt(II) chloride (CoCl<sub>2</sub>). Upon serial addition of a 5.2 mM CoCl<sub>2</sub> aliquot to the polymer solution, the absorbance at 381 nm progressively decreases, indicative of the metal-ligand complexation [Fig. 3(b)]. The titration spectra also show a successively increasing absorption band at 609 and 674 nm with the addition of Co(II). The inset of Figure 3(b) shows the saturation point of NO-Co(II) complexation, based on which about a 1.2:1 binding stoichiometry of Co(II) to the NO ligand was estimated. The CoCl<sub>2</sub> solution in DMF showed absorption bands at 609 and 674 nm, typical of pseudotetrahedral complexes of Co(II),<sup>26</sup> and the wavelength of these bands did not change during the titration of 2DSP-PBBI. This result indicates that ligand exchange between the NO and Cl<sup>-</sup>/DMF occurred while maintaining the pseudotetrahedral geometry in the CoCl<sub>2</sub> solution.<sup>27</sup> After titration of 2DSP-PBBI with Co(II), the polymer sample was analyzed by SEM imaging, showing that the planar sheet-like shape remained intact [Fig. 3(c)].

To test the realization of conjugated 2DSP-PBBI as a semiconducting material, the energy band gap was estimated from emission/excitation spectroscopic data (Supporting Information Fig. S8).<sup>28</sup> From the excitation (at 382 nm) and emission (at 512 nm) spectra, an energy band gap of 1.08 eV was calculated, indicating that exfoliated 2DSP-PBBI can be potentially semiconducting. We performed dropcasting of an exfoliated 2DSP-PBBI sample on a glass slide and measured the polymer film conductivity using manual probe station, and no significant electrical current was observed in IV measurements in the temperature range of 25 to 200 °C. Additionally, the polymer conductivity was tested by dropcasting polymer films on Si wafers with gold interdigitated electrodes (10  $\mu$ m electrode spacing). Although no significant electrical current was measured for undoped polymer and polymer doped with LiClO<sub>4</sub>, doping with NaBF<sub>4</sub> dramatically increased the polymer conductivity (Supporting Information Fig. S9c).

## CONCLUSIONS

We were able to develop a strategy for the one-step synthesis of SP-PBBI by condensation/precipitation polymerization. The slow crystallite growth and precipitation under nonisothermally controlled conditions allowed formation of well-defined bulk SP-PBBI with the lateral dimension of  $<10 \ \mu m$ . Each PBBI building block were laterally grown into large self-assembled planar 2DSP sheets primarily by interchain hydrogen bonding bearing multiple hydrogen bonding motifs, and  $\pi$ - $\pi$  stacking facilitated formation of an orderly stacked architecture from individual 2DSP sheets. Liquid-exfoliation of as-synthesized SP-PBBI provided multiple planar sheets composed of polycrystalline domains, and distinct optical absorption and emission characteristics of 2DSP-PBBI suspended in DMF were observed. Despite some concerns regarding the susceptibility to mechanical forces of supramolecular polymers, we anticipate that exfoliated 2DSP-PBBI can provide convenient means for utilization into various 2D heterostructures and nanodevices.

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