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# **Highly Conductive Organosilica Hybrid Films Prepared** from a Liquid-Crystal Perylene Bisimide Precursor

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Significant anisotropic electrical conduction in organosilica films is achieved by long-range orientation of electroactive perylene bisimide (PBI) moieties in the silica scaffold. A new PBI-based organosilane precursor is designed with lyotropic liquid-crystalline properties. The PBI precursor with triethoxysilylphenyl groups exhibits a hexagonal columnar phase in the presence of organic solvents. The lyotropic liquid-crystalline behavior of the precursor enables the preparation of dip-coated films consisting of uniaxially aligned columnar aggregates of the PBI precursor on the centimeter scale. The oriented structure is successfully fixed by in situ polycondensation, which yields insoluble, thermally stable PBI-silica hybrid films. The oriented organosilica films doped with hydrazine exhibit high electrical conductivities on the order of 10<sup>-2</sup> S cm<sup>-1</sup>, which are at the highest level for organosilica materials, and are comparable to those of all-organic PBI assemblies. Definite anisotropy of conductivities is also found for these films. The present results suggest that the induction of significant electrical properties in organic molecular assemblies is compatible with the structural stabilization by inorganic-organic hybridization.

# 1. Introduction

Electronic devices based on organic semiconductors have attracted much attention due to numerous advantages such as molecular-level tunability of structure-property relationships, solution processability, light weight, and low-cost device fabrication.<sup>[1-3]</sup> Excellent electrical properties have been observed for well-ordered assemblies of low-molecular-weight organic compounds, such as vapor-deposited crystalline films,<sup>[4]</sup> selforganized mesomorphic materials,<sup>[5]</sup> and large single crystals.<sup>[6]</sup> However, their low chemical and mechanical stability is problematic for current applications. On the other hand, electroactive polymers are chemically and mechanically stable and solution processable, but they do not exhibit high electronic conduction because of their less-ordered or amorphous structures.<sup>[2]</sup>

Organosilica hybrid materials, prepared by polycondensation of bridged organosilane precursors  $(R[Si(OR')_3]_n; n \ge 2)$ , have significant potential applications in optical and electrical

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devices because of the flexible design of

their functionalities by appropriate selection of the bridging organic group (R), and also their high thermal and chemical stability, which results from the formation of covalent Si-O-Si bonds.<sup>[7-9]</sup> However, in general it has been difficult to achieve significant electrical conduction in organosilica materials because of the insulating properties of the silica moieties and the disorder in the organic moieties,<sup>[10]</sup> except for an oligothiophene-based polysilsesquioxane film that exhibits electrical conductivity on the order of  $10^{-3}$  to  $10^{-2}$  S cm<sup>-1</sup> by doping with FeCl<sub>3</sub>.<sup>[11]</sup> Recently, highly organized organosilicas with molecularscale periodicity in the organic groups have been prepared by solid-state polycondensation or by the use of organosilane precursors with R groups that exhibit strong intermolecular interactions.[12-15] Molecular-scale ordering of electroac-

tive organic groups through strong interactions could lead to high electrical conductivity in organosilica materials, despite the presence of the insulating silica moiety. Lu and co-workers reported the synthesis of organosilica microtubes and -flakes with lamellar orientation of the organic groups from bridged organosilane precursors containing  $\pi$ -conjugated perylene bisimide (PBI) and porphyrin, respectively.<sup>[15]</sup> However, the organosilica hybrids exhibited relatively low electrical conductivities (on the order of  $10^{-7}$  to  $10^{-4}$  S cm<sup>-1</sup>), probably because the orientation of organic groups is limited within the micrometersized tubes and flakes, and the conducting path is likely intercepted at the grain boundary. Long-range orientation over the entire centimeter-scale sample area responsible for the current-voltage (I-V) properties is important for achieving higher conductivity in organosilica hybrids.

Here we report the preparation of highly conductive PBI-silica hybrid thin films with long-range orientation on the centimeter scale. The PBI unit has been used as a key component in the construction of electron-transport materials and self-assembled nano-objects.<sup>[16]</sup> However, conventional PBI molecules tend to form polycrystalline phases with small single-crystal domains due to strong intermolecular interactions. Our strategy is to prepare a liquid-crystal (LC) film from a PBI-based organosilane precursor (PBI-Si, Figure 1) with long-range orientation, and to subsequently fix the LC structure through polycondensation of the precursors. In order to develop solution-processable LC PBI precursors, we designed PBI-Si with bulky and flexible triethoxysilylphenyl substituents. As shown in Figure 1, PBI-Si

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Figure 1. Molecular structure of PBI-Si and space-filling models of the monomer and dimers.

has a dumbbell-like (rather than rod-like) molecular shape; therefore the  $\pi$ -stacking of the PBI planes is expected to occur with rotational displacement, leading to suppression of crystallization and formation of mesomorphic structures. After hydrolytic treatment, the  $\pi$ - $\pi$  stacking of PBI planes can be enhanced by the elimination of ethoxy groups (Figure 1). A PBI precursor with mesomorphic and self-assembling properties would thus be applicable to the preparation of electroconductive organosilica films that maintain long-range homogeneous orientation of the PBI units after in situ polycondensation.

#### 2. Results and Discussion

#### 2.1. Lyotropic Liquid-Crystalline Behavior of PBI-Si

The **PBI-Si** precursor was successfully synthesized from perylene-3,4:9,10-tetracarboxylic dianhydride in 84% overall yield (two step, **Scheme 1**). In the first step, 4-iodophenyl-substituted PBI was obtained in 96% yield by imidation using 4-iodoaniline. Rh-catalyzed silylation of the iodide gave **PBI-Si** in 88% yield.

The lyotropic behavior of **PBI-Si** was examined in organic solvents (**Figure 2**a and 2b). Polarizing optical microscopy observations show that concentrated solutions of **PBI-Si** in tetrahydrofuran (THF) and dimethyl formamide (DMF) exhibit fan-like

optical textures, which are characteristic of ordered mesophases (Figure 2a and S1 in the Supporting Information). The X-ray diffraction (XRD) pattern of a 60 wt% solution of **PBI-Si** in DMF shows an intense peak at d = 2.83 nm and small peaks at d = 1.58, 1.42, 1.20, and 0.71 nm (Figure 2c). These peaks are assignable to a hexagonal columnar (Col) phase due to the *d*-spacing ratio of ca. 1:1/ $\sqrt{3}$ :1/2:1/ $\sqrt{7}$ :1/4. The phase-transition temperatures of the **PBI-Si**/DMF mixtures were plotted as a function of the concentration of **PBI-Si** (Figure 2b). The **PBI-Si**/DMF mixtures with more than 60 wt% **PBI-Si** 



exhibit the Col phase at room temperature. UV–vis spectra of the LC mixtures showed an absorption maximum ( $\lambda_{max}$ ) at 498 nm, whereas the  $\lambda_{max}$  of a dilute solution of **PBI-Si** in DMF (2 × 10<sup>-6</sup> M) was 526 nm (**Figure 3**). The blueshift in  $\lambda_{max}$  is due to face-to-face aggregate formation of the PBI moieties in the LC state, which indicates that the LC structure is formed by a hexagonal arrangement of columnar aggregates of **PBI-Si**.

# 2.2. Preparation of Oriented Organosilane and Organosilica Films

Oriented films of **PBI-Si** were successfully obtained by dip-coating quartz substrates with **PBI-Si**/DMF solutions under optimal

conditions (concentration: 5 wt%, lift-off rate: 10 mm min<sup>-1</sup>). The triethoxysilyl groups of PBI-Si were intact without condensation in the dip-coated film (PBI-Si-F), because no water or catalyst (acid or base) was added to the PBI-Si/DMF solutions. Polarizing optical microscopy observations of PBI-Si-F indicate long-range orientation of the optical axis over the entire film (1.5 cm  $\times$  2.0 cm). Dark images were observed when the polarization direction of the light was parallel or perpendicular to the dip-coating direction, while the brightest images were obtained when the polarization direction was 45° with respect to the coating direction (Figure 4a). The molecular alignment of PBI-Si in the film was shown by polarized UV-vis spectroscopy. The maximum absorption intensity was obtained when the polarization direction of the incident light was perpendicular to the coating direction (Figure 4b), which indicates that the transition dipole moment of PBI-Si is distributed perpendicularly to the coating direction. These results show that columnar aggregates of  $\pi$ -stacked **PBI-Si** formed during evaporation of DMF at the air-solution interface (Figure 2b) are laid onto the substrate along the lift-off motion, as schematically illustrated in Figure 4c. The  $\lambda_{max}$  of **PBI-Si-F** was 497 nm (Figure 3), which is almost the same as that of the lyotropic LC mixtures (498 nm). The XRD pattern of PBI-Si-F showed an intense peak at d = 2.70 nm, but very weak peaks at higher angles (Figure 2c), which suggests that the hexagonal structure was distorted, but that the columnar structure was preserved during solvent evaporation.[17]



Scheme 1. Synthesis of PBI-Si.

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Figure 2. a) Polarized photomicrograph of the optical texture developed in a 60 wt% solution of **PBI-Si** in DMF upon cooling; b) phase-transition behavior of the **PBI-Si**/DMF mixture as a function of **PBI-Si** concentration upon heating; c) XRD patterns of organosilane and organosilica films. XRD patterns were obtained for organosilica film samples peeled off substrates. The arrow in (b) indicates the change in the composition of the mixture during the dip-coating process.

The triethoxysilyl groups of **PBI-Si** were polycondensed by exposure of **PBI-Si-F** to vapor from aqueous NH<sub>3</sub> or acetic acid solution. <sup>29</sup>Si magic-angle spinning (MAS) NMR spectra showed the disappearance of the T<sup>0</sup> signal (R–*Si*(OEt)<sub>3</sub>) and the appearance of new T<sup>1</sup> and T<sup>2</sup> signals (R–*Si*(OSi)<sub>*n*</sub>(OH)<sub>3–*n*</sub>; *n* = 1 and 2, respectively) after NH<sub>3</sub> and AcOH treatment, which indicated that the polycondensation had proceeded (see Figure S2 in the Supporting Information). The polycondensed organosilica films were insoluble in common organic solvents and were thermally



Figure 3. UV-vis spectra of (A) PBI-Si in a dilute DMF solution (2  $\times$  10<sup>-6</sup> M), (B) lyotropic mixture of PBI-Si/DMF (60/40, w/w), (C) PBI-Si-F, (D) PBI-Si-F-NH<sub>3</sub>, and (E) PBI-Si-F-ACOH.

stable up to at least 350 °C.<sup>[18]</sup> The NH3- and AcOH-treated films, denoted as PBI-Si-F-NH3 and PBI-Si-F-AcOH, respectively, preserved the oriented optical textures of the original noncondensed PBI-Si-F. The dichroism of the polarized UV-vis spectra was maintained (PBI-Si-F-AcOH) or slightly enhanced (PBI-Si-F-NH<sub>3</sub>) during polycondensation (Figure S3 in the Supporting Information). On the other hand, the intense XRD peak at d = 2.70 nm due to the columnar structure in **PBI-Si-F** disappeared, and a new peak at d = 0.34 nm—typical of a  $\pi$ -stacking structure-appeared after polycondensation (Figure 2c). New peaks also appeared at d = 1.36 and 0.83 nm for **PBI-Si-F-NH**<sub>3</sub> and at 2.41 and 0.80 nm for PBI-Si-F-AcOH, which are due to the packing structure of PBI units in the lateral direction. The large blueshift of  $\lambda_{\rm max}$  from 497 to 473 nm ( $\Delta$  = –24 nm) implied the promotion of strong  $\pi$ - $\pi$  interactions between the PBI units during polycondensation (Figure 3).

The nanostructure of the organosilica films was examined by transmission electron microscopy (TEM). **Figure 5**a and 5b show the TEM images of **PBI-Si-F-NH**<sub>3</sub> and **PBI-Si-F-AcOH**, respectively. Nanometer-scale periodic structures can be partially observed in the organosilica films. For **PBI-Si-F-AcOH**, a striped structure with ca. 2 nm periodicity can be seen (Figure 5b), which is in agreement with the size of the columnar aggregates of PBI and the appearance of the weak XRD peak at d = 2.41 nm. On the other hand, the periodicity of the striped structure in **PBI-Si-F-NH**<sub>3</sub> was ca. 1 nm (Figure 5a), which is consistent with the XRD peak at d = 1.34 nm. The 1 nm periodic structure presumably corresponds to packing structure of the PBI-silica hybrid in the short-axis direction of PBI units, considering the

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**Figure 4.** a) Polarized optical photomicrographs of **PBI-Si-F** (P: polarizer, A: analyzer); b) polarized UV–vis spectra of **PBI-Si-F**; c) schematic illustration of the molecular arrangement in the dip-coated film.

molecular size of the precursor (Figure 1). Based on these observations, polycondensation under acidic condi-

tions seems to preserve the original columnar structures with 2 nm periodicity, while polycondensation under basic conditions likely results in rearrangement of the PBI columns into a more closely packed structure with edge-to-edge packing of PBIs in their short axis direction.

A schematic illustration for the structural change in the dip-coated film before and after polycondensation is presented in Figure 5c. The columnar structure in **PBI-Si-F** is disturbed by the anisotropic condensation of **PBI-Si**, mainly in the lateral direction of the columns. However, condensation promotes the close packing of PBI moieties through the elimination of bulky ethoxy groups, which results in the formation of strong  $\pi$ - $\pi$  interactions between PBI units with dense lateral packing of the columnar aggregates.

#### 2.3. Measurements of Electrical Conductivity

The I-V characteristics of the thin films before and after polycondensation were measured using a two-probe method. The PBI-based films were doped with hydrazine



vapor according to a previously published method.<sup>[19]</sup> The formation of PBI anionic radicals through hydrazine doping was confirmed by UV–vis spectroscopy.<sup>[20]</sup> Electrodes were placed onto the films, as shown in **Figure 6**a, in order to compare the conductivities parallel ( $\sigma_{\parallel}$ ) and perpendicular ( $\sigma_{\perp}$ ) to the dip-coating direction. In air (without hydrazine doping), none of the films showed obvious electric currents upon application of voltages up to 50 V. However, linear *I–V* profiles were obtained for the films doped with hydrazine (Figure 6b).

The highest electric current was obtained for PBI-Si-F in the coating direction, which is parallel to the stacking direction of the PBI moieties in the columnar aggregates. After polycondensation, the slopes of the I-V profiles decreased to less than half. For these oriented films, the electric currents along the coating direction are larger than those in the perpendicular direction; i.e., electrical conduction is anisotropic in the films. Table 1 gives the electrical conductivities ( $\sigma_{\parallel}$  and  $\sigma_{\perp}$ ) and the anisotropy ( $\sigma_{\parallel}/\sigma_{\perp}$ ) of conductivities. **PBI-Si-F** exhibits high  $\sigma_{\parallel}$ , on the order of  $10^{-1}$  S cm<sup>-1</sup>, whereas  $\sigma_{\perp}$  is on the order of  $10^{-3}$  S cm<sup>-1</sup>. The anisotropy is greater than 40. After polycondensation, the conductivities ( $\sigma_{\parallel}$ ) of **PBI**-Si-F-NH3 and PBI-Si-F-AcOH were still on the order of  $10^{-2}$  S cm<sup>-1</sup>, which is the highest

level for organosilica materials.<sup>[10,11,15]</sup> These values are also



**Figure 5.** TEM images of (a) **PBI-Si-F-NH**<sub>3</sub> and (b) **PBI-Si-F-ACOH**. c) Schematic illustration of arrangement of PBI columns before and after polycondensation. Black arrows indicate plausible charge conduction.



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**Figure 6.** a) Polarized optical photomicrographs of **PBI-Si-F-NH**<sub>3</sub> equipped with copper-foil electrodes and b) *I–V* properties of the oriented organosilane and organosilica films measured in saturated hydrazine vapor.

comparable to those reported for all-organic PBI assemblies.<sup>[19,21]</sup> The high conductivities of the present organosilica materials are due to the long-range homogeneous orientation of the PBI moieties between the electrodes, which had not been reported for previous conductive organosilica hybrids.<sup>[10,11,15]</sup> On the other hand, the values of  $\sigma_{\perp}$  increased after polycondensation and the anisotropy decreased from 40–50 to 2–8.

The conducting behavior of the films can be explained by the change in the molecular arrangement (Figure 5c). Before polycondensation, electron hopping occurs easily along the conducting path consisting of the  $\pi$ -stacked columns of **PBI-Si**. In the perpendicular direction, electron hopping is strongly suppressed due to the weak interactions between PBI moieties and the presence of insulating layers consisting of triethoxysilyl groups. After polycondensation, although the columnar order of the PBI aggregates is disturbed, the PBI moieties are anisotropically aligned with enhanced  $\pi$ -stacking in the silica scaffold, which leads to the suppression of a large decrease in  $\sigma_{\parallel}$ . On the other hand,  $\sigma_{\perp}$  increases because charge hopping is allowed, following the elimination of the ethoxy groups and the partial overlap of PBI moieties. Considering the different packing structure of the PBIsilica hybrids (Figure 2c, 5a, and 5b), it is reasonable that the anisotropy of conductivities of PBI-Si-F-NH<sub>3</sub> with denser lateral packing of PBIs is lower than that of PBI-Si-F-AcOH.

### 3. Conclusions

PBI-based organosilica hybrid thin films with long-range homogeneous orientation were successfully prepared by a dip-coating method utilizing the lyotropic LC behavior of the **PBI-Si** precursor, followed by in situ polycondensation. The oriented precursor and organosilica thin films doped with hydrazine exhibited high electrical conductivities on the order of  $10^{-1}$ and  $10^{-2}$  S cm<sup>-1</sup>, respectively, and definite anisotropy of the ADVANCED FUNCTIONAL MATERIALS www.afm-journal.de

conductivities. The conductivity of the present organosilica film is at the highest level for organosilica materials, and is comparable to those reported for all-organic PBI assemblies. The present results suggest that the induction of significant electrical properties in selfassembled organic materials is compatible with the structural stabilization by inorganicorganic hybridization. The robustness and chemical stability of organosilica hybrid films are advantageous for the preparation of patterned semiconductors and the lamination of thin films using solution processes. The concept for the construction of highly conductive inorganic-organic hybrids is preferentially applied in the design of various architectures, including monolithic particles and mesostructured materials.

#### 4. Experimental Section

*General*: All reagents and solvents were purchased from Aldrich and Tokyo Chemical Industry and used without further purification.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Jeol JNM-ECX400P spectrometer. Mass spectra were recorded on a MICROMASS Q-TOF. IR spectroscopy (Thermo Nicolet Avatar 360 FT-IR) was conducted using an attenuated total reflection (ATR) attachment. XRD measurements were performed using Cu K $\alpha$  radiation (Rigaku RINT-TTR, 50 kV, 300 mA). UV-vis absorption spectra were measured using a Jasco V-670 spectrometer. <sup>29</sup>Si MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer at 79.49 MHz using 7 mm zirconia rotors and a sample-spinning frequency of 4 kHz. The chemical shifts for all spectra were referenced to tetramethylsilane at 0 ppm. Polarizing microscopy was conducted with an Olympus BX51 equipped with a hot stage (Mettler Toledo FP82HT). TEM was performed on a Jeol JEM-2010FEF with an accelerating voltage of 200 kV. Thermogravimetric analysis was performed using a Rigaku Thermo Plus TG 8120 at the heating rate of 10 °C min<sup>-1</sup> under nitrogen gas flow (0.5 L min<sup>-1</sup>).

Synthesis of N, N'-Bis(4-iodophenyl)-3, 4:9, 10-tetracarboxylic acid bisimide: A mixture of perylene-3, 4:9, 10-tetracarboxylic dianhydride (2.35 g, 6.0 mmol), Zn(OAc)<sub>2</sub> (0.85 g), and quinoline (45 mL) was stirred at 100 °C for 0.5 h under an argon atmosphere. Then, 4-iodoaniline (6.57 g, 30.0 mmol) was added and the reaction mixture was stirred at 200 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into ethanol (350 mL) and the precipitate was collected by suction filtration. The residue was stirred in a 5% K<sub>2</sub>CO<sub>3</sub> aqueous solution (500 mL) at 70 °C for 10 min then collected by suction filtration. This procedure was repeated twice. The residue was then dispersed in methanol (100 mL) and stirred at 70 °C for 30 min. The precipitate was collected by suction filtration and dried under reduced pressure to

 Table 1. Electrical properties of dip-coated PBI films measured in saturated hydrazine vapor.

Sample <sup>a)</sup>	$\sigma_{\parallel}$ [S cm <sup>-1</sup> ]	$\sigma_{\!\perp}$ [S cm <sup>-1</sup> ]	$\sigma_{\scriptscriptstyle \parallel}/\sigma_{\! \perp}$
PBI-Si-F	$(1.1 \pm 0.6) \times 10^{-1}$	$(2.7 \pm 1.3) \times 10^{-3}$	40–50
PBI-Si-F-NH <sub>3</sub>	$(4.4 \pm 2.2) \times 10^{-2}$	$(2.2 \pm 1.1) \times 10^{-2}$	2–3
PBI-Si-F-AcOH	$(3.3 \pm 1.6) \times 10^{-2}$	$(6.3 \pm 3.1) \times 10^{-3}$	5—8

<sup>a)</sup>Film thickness: 7–15 nm; channel width: 4–5 mm; channel length: 150–210  $\mu$ m. Measurements at nine points were averaged for each sample.

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afford an insolut (Ar–H), 1703 (C 1254, 1194, 1175 Synthesis of

afford an insoluble dark red solid (4.56 g, 96%). IR (ATR): v = 3090-3030 (Ar–H), 1703 (C=O st), 1661, 1591, 1576, 1483, 1429, 1404, 1356, 1342, 1254, 1194, 1175, 1136, 1121, 1057 (Ar–I), 1009, 970, 955 cm<sup>-1</sup>.

Synthesis of N, N'-Bis[4-(triethoxysilyl)phenyl]-3, 4:9, 10-tetracarboxylic acid bisimide (PBI-Si): DMF (anhydrous; 40 mL) and dry trimethylamine (anhydrous: 1.67 mL) were added to a mixture of N.N'-bis(4-iodophenyl)-3,4:9,10-tetracarboxylic acid bisimide (1.59 g, 2.00 mmol) and Rh[(cod) (CH<sub>3</sub>CN)<sub>2</sub>]BF<sub>4</sub> (38.0 mg, 0.10 mmol) under argon atmosphere. Triethoxysilane (1.48 mL, 1.31 g, 8.00 mmol) was added at 0 °C and the mixture was stirred at 80 °C for 4 h. After removal of the solvents by a rotary evaporator, chloroform (150 mL) was added to the residue. The mixture was filtered using Celite and activated carbon, and the filtrate was washed quickly with water. The organic phase was dried with MgSO<sub>4</sub> and concentrated under reduced pressure. After adding hexane (300 mL), the resulting precipitate was collected by centrifugation (3500 rpm, 5 min) to afford the product as a dark red solid (1.53 g, 88%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 1.30 (t, J = 7.0 Hz, 18H), 3.95 (q, J = 7.0 Hz, 12H), 7.39 (d, J = 8.4 Hz, 4H), 7.89 (d, J = 8.4 Hz, 4H), 8.67 (d, J = 8.5 Hz, 4H), 8.75 ppm(d, J = 8.5 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 18.2, 58.8, 123.0, 123.2, 125.7, 128.0, 129.0, 131.1, 132.0, 134.0, 135.8, 136.6, 162.9 ppm; IR (ATR): v = 3090-3030 (Ar-H), 2974, 2926, 2889, 1705 (C=O st), 1662, 1591, 1578, 1506, 1483, 1431, 1404, 1356, 1344, 1254, 1165, 1149, 1065, 955 cm<sup>-1</sup>; MS (APCI) m/z: [M]<sup>+</sup> calcd for C48H46N2O10Si2, 866.27; found: 866.29.

Preparation and Polycondensation of Dip-Coated Films: Thin films of **PBI-Si** were prepared by dipping quartz substrates (1.5 cm  $\times$  2.5 cm) in DMF solutions of **PBI-Si** (0.1–10 wt%) at a lift-off rate of 1–40 mm min<sup>-1</sup> under constant temperature and humidity of 20–22 °C and 55–58%, respectively. In situ polycondensation of the dip-coated films was conducted by exposure to the vapor from a 50% aqueous solution of AcOH at 75 °C for 12 h or a 10% aqueous solution of NH<sub>3</sub> at 60 °C for 6 h in a sealed vessel.

Conductivity Measurement: Current–voltage (*I–V*) properties of dipcoated films were measured using a two-probe method with a Keithley 2636A System SourceMeter. The sample cells were prepared by placing two copper foil electrodes (3M CU-35C, width: 4–5 mm, gap: 150–210  $\mu$ m) onto the films as shown in Figure 6a. In order to obtain *I–V* properties of doped films, the sample cells were fixed onto sealed glass vessels containing a small amount of hydrazine (monohydrate) and exposed to the saturated hydrazine vapor. Conductivity measurements were carried out after standing for more than 3 min to stabilize the *I–V* properties in the hydrazine vapor. The conductivity ( $\sigma$ ) extracted from the linear region of *I–V* profiles was calculated using the equation  $\sigma = I d/(V S)$ , where d is the distance between electrodes, and S is the cross section of the samples.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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