

**Solution-processable small molecule semiconductors based on pyrene-fused  
bisimidazole and influence of alkyl side-chain on the charge transport**

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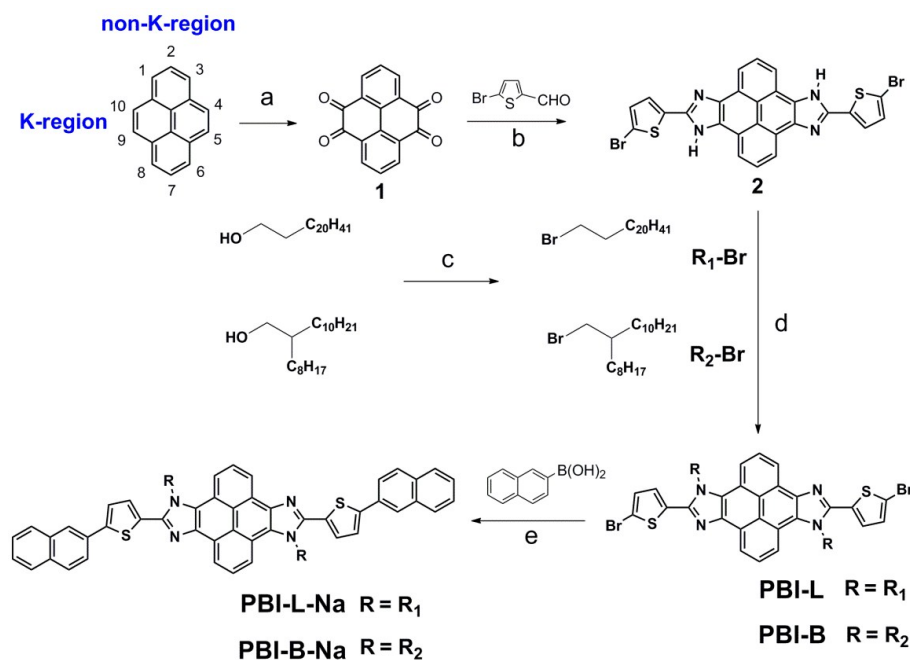
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## 1. Materials and General Experimental Methods

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise noted. Bruker AV-300 MHz spectrometer was used to collect NMR spectra with tetramethylsilane (TMS) as an internal reference. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum was obtained using dithranol as a matrix on Bruker Autoflex TOF/TOF instrument. UV-Vis absorption spectra in chloroform solution and solid states were recorded on Shimadzu UV-2450 spectrophotometer. Cyclic voltammetry measurements were performed in dry acetonitrile with 0.1 M TBAPC as supporting electrolyte with a scan rate of  $100 \text{ mV s}^{-1}$  using a computer-controlled CHI660E (Shanghai Chenhua, China) electrochemical workstation. A platinum (Pt) disk, a Pt wire and an Ag/AgCl in 1 M KCl electrode served as working electrode, counter electrode and reference electrode, respectively. TA Instruments SDT-Q600 was used to perform thermogravimetric analysis (TGA) under nitrogen atmosphere with a heating rate of  $10 \text{ }^\circ\text{C/min}$ . Conventional X-ray diffraction (XRD) on two compounds was carried out on X Pert Powder equipment ( $d = \lambda / 2\sin\theta$ ,  $\lambda = 0.15418 \text{ nm}$ ). Grazing incident X-ray diffraction (GIXRD) experiments of thin films spin-coated on octadecyltrichlorosilane (OTS)-modified  $\text{SiO}_2/\text{Si}$  substrate were performed on Anton Paar SAXSess  $\text{mc}^2$  equipment ( $q = 4\pi\sin\theta / \lambda$ ) using point X-ray source (Cu  $K\alpha$ , 40 kv;  $\lambda = 0.15418 \text{ nm}$ ) with an incident angle of  $0.2^\circ$ . The images were recorded by a 2D-Imaging plate detector. Atomic force microscopic (AFM) images of the thin films on OFETs were obtained by using an SII Nanonavi SPA-400 scanning probe microscope with an SII SI-DF40 cantilever. In order to explore molecular architecture, the geometries were optimized with density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level on Gaussian 09.

## 2. Synthetic Procedures



**Compound 1.** This compound was prepared following a published procedure<sup>1</sup>. To a solution of pyrene (4.0 g, 20 mmol),  $\text{NaIO}_4$  (35 g, 163.6 mmol) and  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (0.50 g, 2.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (80 mL) and  $\text{CH}_3\text{CN}$  (80 mL) was added  $\text{H}_2\text{O}$  at  $0 \text{ }^\circ\text{C}$ . The mixture was stirred at  $0 \text{ }^\circ\text{C}$  for 20 min, then warmed up to  $30 \text{ }^\circ\text{C}$ - $40 \text{ }^\circ\text{C}$  for 12 h. After cooling,  $\text{CHCl}_3$  (50 mL) was added followed by filtration, the solution was then poured into water (200 mL). The mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 40 \text{ mL}$ ) and the organic layers combined, dried over  $\text{MgSO}_4$ , and

concentrated under reduced pressure. The resulting crude orange product was purified via silica column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent. The title compound was isolated as yellow crystals (0.36 g, 6.8%).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , 300 MHz, ppm): 8.33 (d, 4H,  $J = 7.7$  Hz), 7.74 (t, 2H,  $J = 7.7$  Hz).

**Compound 2.** To a solution of **1** (0.30 g, 1.1 mmol) and  $\text{NH}_4\text{OAc}$  (0.68 g, 8.8 mmol) in glacial acetic acid (50 mL) was added 5-Bromo-2-thiophenecarbaldehyde (0.84 g, 4.4 mmol). The mixture was stirred at 110 °C for 10 h. After cooling to room temperature, the dark green precipitate was separated, washed with water, and dried *in vacuo*. This compound is insoluble in the most common solvents except for DMF and DMSO and was used for the next step without further purification (0.51 g, 75%).

**R<sub>1</sub>-Br** and **R<sub>2</sub>-Br.** To a solution of  $\text{PPh}_3$  (25 g, 0.096 mol) in  $\text{CH}_2\text{Cl}_2$  (200 mL),  $\text{Br}_2$  (15.26 g, 0.096 mol) was added dropwise at 0 °C. After stirring 20 min, 1-Docosanol (31.35 g, 0.096 mol) or 2-Octyl-1-dodecanol (28.66 g, 0.096 mol) was added dropwise into the solution. The mixture was stirred at room temperature for 12 h. After removal of  $\text{CH}_2\text{Cl}_2$  under reduced pressure, the residue was washed with n-hexane and filtrated. The filtrate was concentrated via rotary evaporation and the crude oil was washed by the methanol. The compound **R<sub>1</sub>-Br** and **R<sub>2</sub>-Br** were isolated as colorless oil (**R<sub>1</sub>-Br**: 33 g, 91 %; **R<sub>2</sub>-Br**: 31 g, 90 %).  $^1\text{H-NMR}$  for **R<sub>1</sub>-Br** ( $\text{CDCl}_3$ , 300 MHz, ppm): 3.40 (t, 2H,  $J = 7.0$  Hz), 1.87 (m, 2H), 1.48 - 1.20 (m, 38H), 0.90 (t, 3H,  $J = 6.5$  Hz).  $^1\text{H-NMR}$  for **R<sub>2</sub>-Br** ( $\text{CDCl}_3$ , 300 MHz, ppm): 3.47 (d, 2H,  $J = 6.0$  Hz), 1.60 (m, 1H), 1.35 (m, 32H), 0.91 (m, 6H).

**PBI-L.** To a solution of **2** (0.50 g, 0.827 mmol) and  $\text{K}_2\text{CO}_3$  (0.91 g, 6.6 mmol) in DMF was added 1-Bromodocosane (3.22 g, 8.27 mmol). The mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with chloroform three times. The combined organic phase was concentrated under reduced pressure. The resulting crude yellow product was washed with n-hexane and dichloromethane, and then purified via column chromatography using  $\text{CHCl}_3$  as eluent. The title compound was isolated as pale yellow powder (0.68 g, 67%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, ppm): 8.94 (2H), 8.41 (2H), 8.07 (2H), 7.38 (2H), 7.24 (2H), 4.83 (m, 4H), 2.16 (m, 4H), 1.61-1.11 (m, 76H), 0.86 (6H).

**PBI-B.** To a solution of **2** (0.50 g, 0.827 mmol) and  $\text{K}_2\text{CO}_3$  (0.91 g, 6.6 mmol) in DMF was added 1-Bromo-2-octyl-dodecane (2.99 g, 8.27 mmol). The mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the mixture was poured into water and extracted with chloroform three times. The combined organic phase was concentrated under reduced pressure. The resulting crude brown oil was purified via column chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent. The title compound was isolated as pale green powder (0.40 g, 41%).  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, ppm): 9.02 (d, 2H,  $J = 7.4$  Hz), 8.53 (d, 2H,  $J = 7.8$  Hz), 8.14 (t, 2H,  $J = 7.7$  Hz), 7.37 (2H), 7.27 (d, 2H,  $J = 3.6$  Hz), 4.89 (m, 4H), 2.32 (2H), 1.77 - 0.72 (m, 64H), 0.89 (m, 6H).

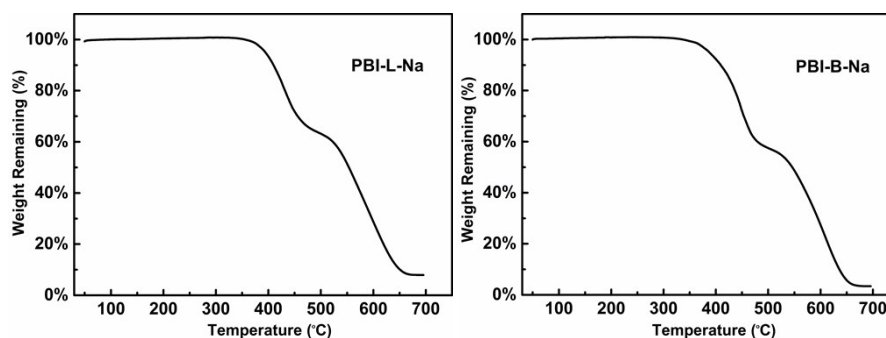
**PBI-L-Na.** To a 100 mL dry flask was added a solution of **PBI-L** (0.1 g, 0.082 mmol), 2-naphthyl boronic acid (0.06 g, 0.328 mmol), aqueous  $\text{K}_2\text{CO}_3$  solution (2 M, 1 mL) and tetrakis(triphenylphosphine)palladium(0) (0.01 g, 0.009 mmol) in THF (50 mL). The mixture was degassed and refilled argon for 10 times, then stirred for 12 h at 65 °C. After cooling to room temperature, the reaction mixture was poured into methanol (100 mL). The precipitate was collected by filtration, and then purified via column chromatography using  $\text{CHCl}_3$  as eluent.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, ppm): 9.19 (2H), 8.40 (2H), 8.25 - 7.46 (20H), 5.04 (4H), 2.24 (4H), 1.87 - 1.04 (76H), 0.92 (6H). MS (MALDI-TOF, m/z): Calc. for  $\text{C}_{90}\text{H}_{114}\text{N}_4\text{S}_2$ : 1314.85; Found: 1314.776 [ $\text{M}^+$ ]. Elemental analysis: Calc. for  $\text{C}_{90}\text{H}_{114}\text{N}_4\text{S}_2$ : C, 82.14; H, 8.73; N, 4.26%; Found: C, 82.03; H, 8.90; N, 4.15%.

**PBI-B-Na.** To a 100 mL dry flask was added a solution of **PBI-B** (0.095 g, 0.082 mmol), 2-naphthyl boronic acid (0.06 g, 0.328 mmol), aqueous  $K_2CO_3$  solution (2 M, 1 mL) and tetrakis(triphenylphosphine)palladium(0) (0.01 g, 0.009 mmol) in THF (30 mL). The mixture was degassed and refilled argon for 10 times, then stirred for 12 h at 65 °C. After cooling to room temperature, the reaction mixture was poured into methanol (100 ml). The precipitate was collected by filtration, and then purified via column chromatography using  $CH_2Cl_2$  as eluent.  $^1H$ -NMR ( $CDCl_3$ , 300 MHz, ppm): 9.15 (2H), 8.47 (2H), 8.26 - 7.45 (20H), 5.00 (4H), 2.73 (2H), 1.41 – 0.90 (64H), 0.88 - 0.59 (12H). MS (MALDI-TOF, m/z): Calc. for  $C_{86}H_{108}N_4S_2$ : 1259.79; Found: 1259.842 [ $M^+$ ]. Elemental analysis: Calc. for  $C_{86}H_{108}N_4S_2$ : C, 81.98; H, 8.48; N, 4.45%; Found: C, 81.83; H, 8.69; N, 4.23%.

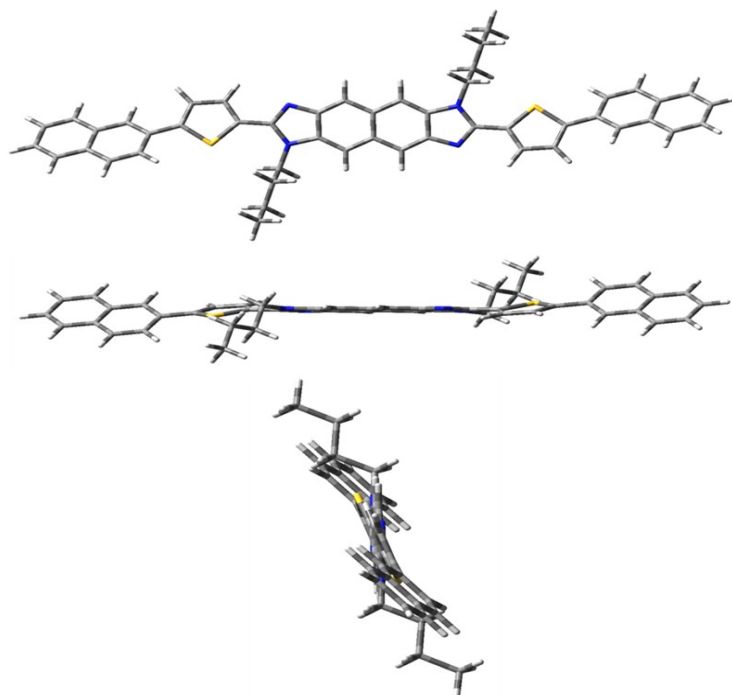
### 3. Fabrication and Characterization of OFET Devices

Top-contact-bottom-gate OFET devices were fabricated on heavily p-doped silicon wafer (the gate) with a 200 nm layer of thermally grown  $SiO_2$  dielectric (capacitance ( $C_i$ ) of 18 nF  $cm^{-2}$ ). The  $SiO_2/Si$  wafer substrates were cleaned by ultrasonication in acetone and methanol and dried under nitrogen flow then subjected to UV-ozone cleaning for 20 min. The cleaned substrates were kept in desiccators with a few drops of OTS. The desiccators were evacuated for 3min and placed in an oven at 120 °C for 3 hours and then the substrates were rinsed thoroughly with toluene, acetone and isopropanol. The **PBI-L-Na** and **PBI-B-Na** were dissolved in anhydrous chloroform (5 mg  $mL^{-1}$ ) and stirred at 50 °C for 1 h. The solution was spin-coated on the OTS treated  $Si/SiO_2$  substrates and annealed at various temperatures (ranging from 100, 125 and 150 °C) for 10 min. Finally, the gold (Au) source and drain electrodes (ca. 100 nm) were thermal evaporated through a shadow mask. The channel width (W) and length (L) were 8800  $\mu m$  and 80  $\mu m$ , respectively. OFET devices were characterized under an ambient environment using a Keithley 4200 parameter analyzer. The field effect mobility ( $\mu_{sat}$ ) was calculated from the saturation regime of the transfer characteristics from the following equation:  $I_{DS} = \mu (W C_i/2L) (V_G - V_T)^2$ .

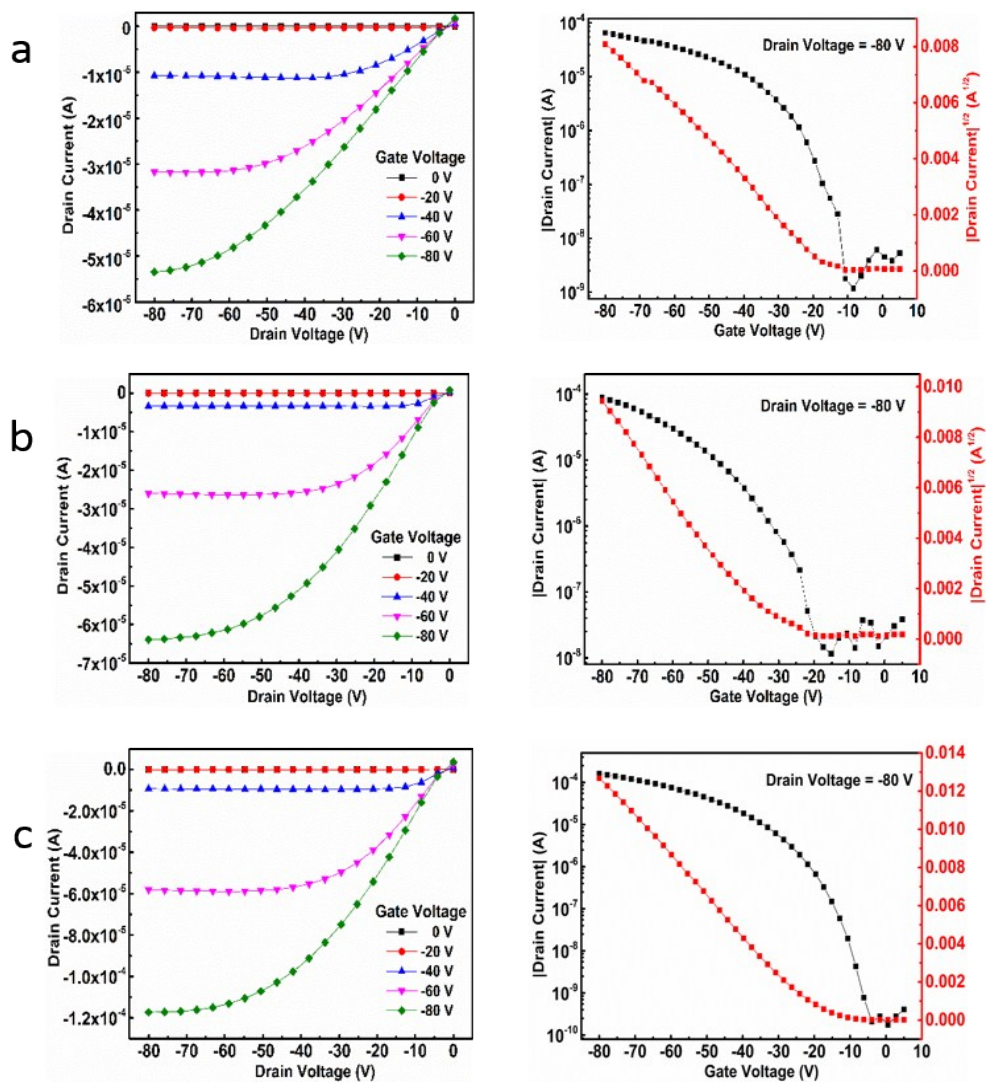
### 4. Supplementary Data



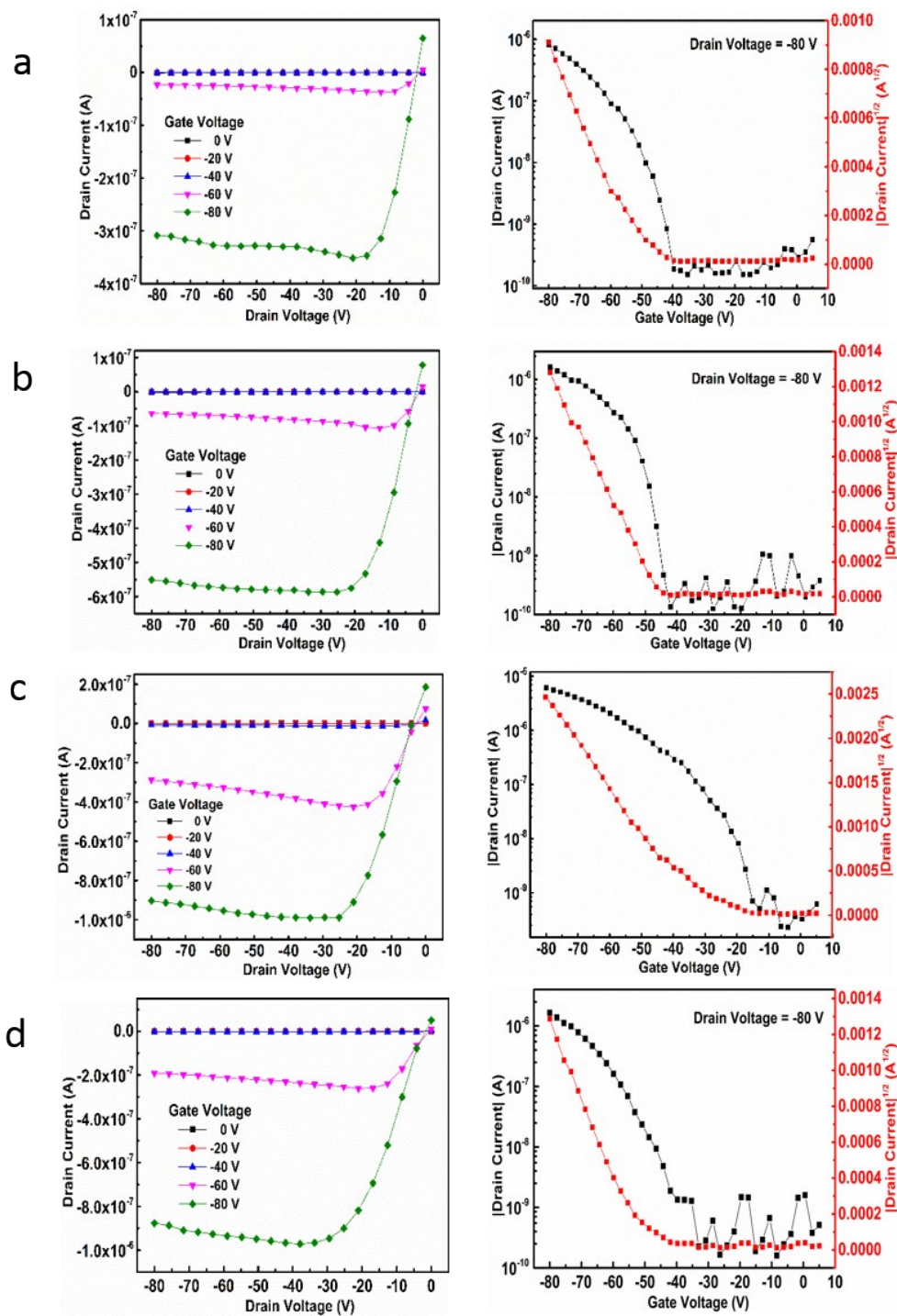
**Fig. S1** TGA curves of **PBI-L-Na** and **PBI-B-Na** with a heating rate of 10 °C  $min^{-1}$  under nitrogen.



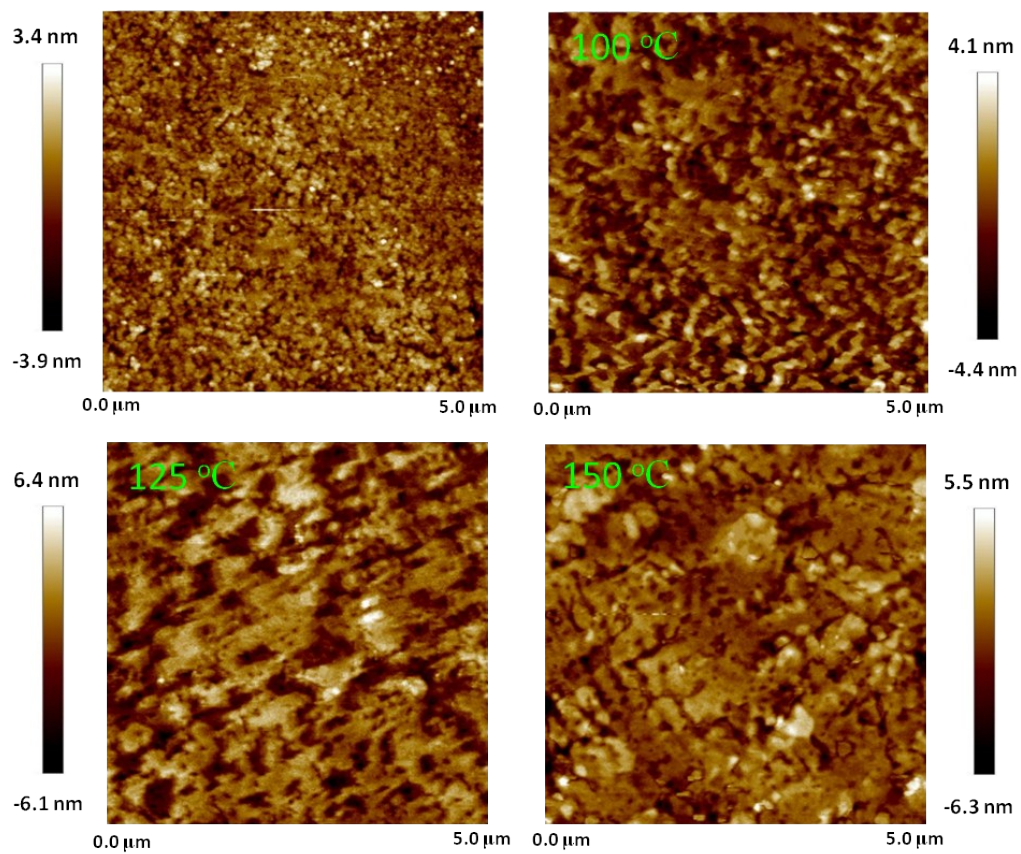
**Fig. S2** Optimized geometry for the molecule based on naphthalene-fused bisimidazole. DFT calculations were performed at the B3LYP/6-31G(d,p) level on Gaussian 09.



**Fig. S3** Output (left) and transfer (right) characteristics for **PBI-L-Na** films: as-spun (a), annealed at 100 °C (b), 150 °C (c).

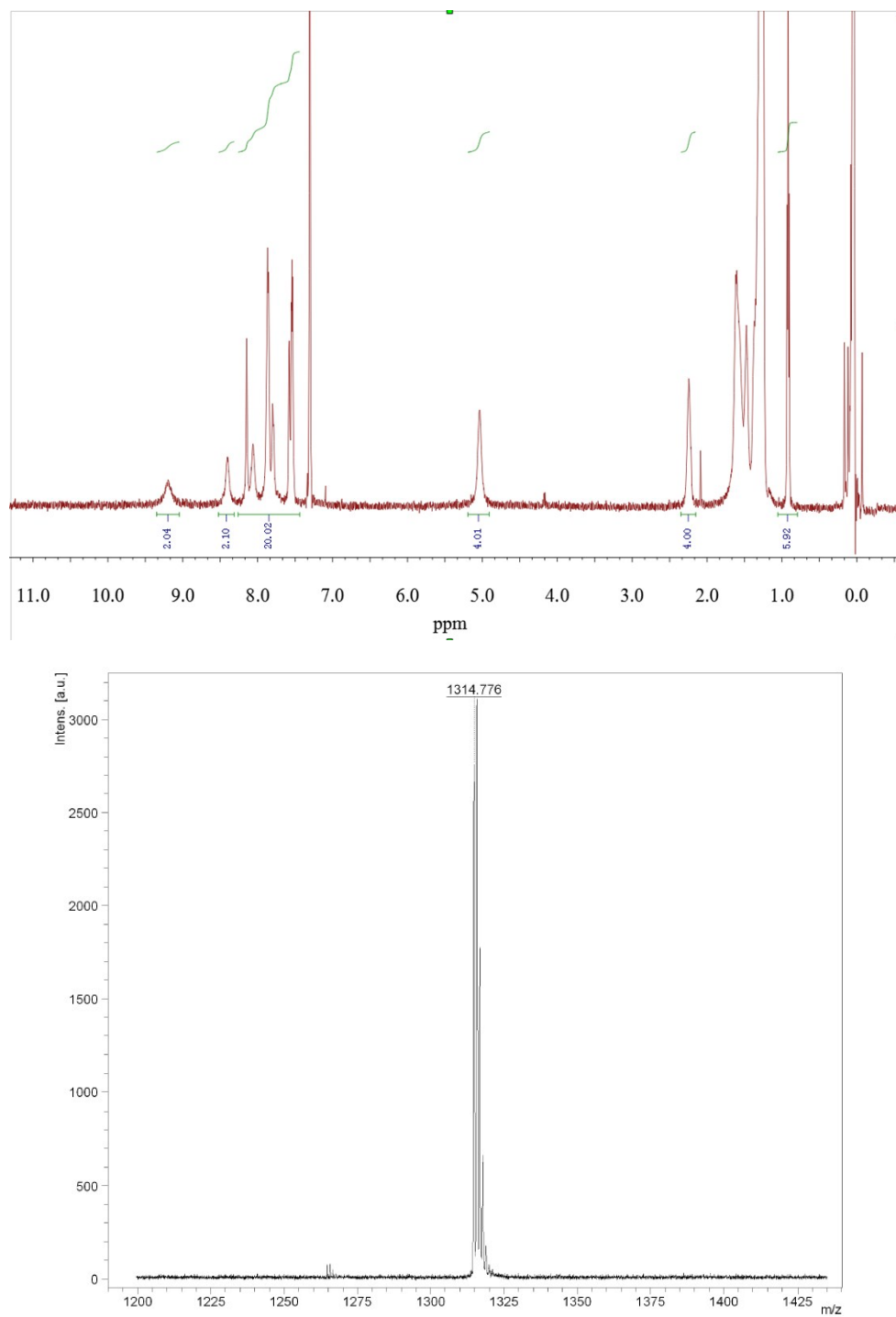


**Fig. S4** Output (left) and transfer (right) characteristics for PBI-B-Na films: as-spun (a), annealed at 100 °C (b), 125 °C (c), 150 °C (d).

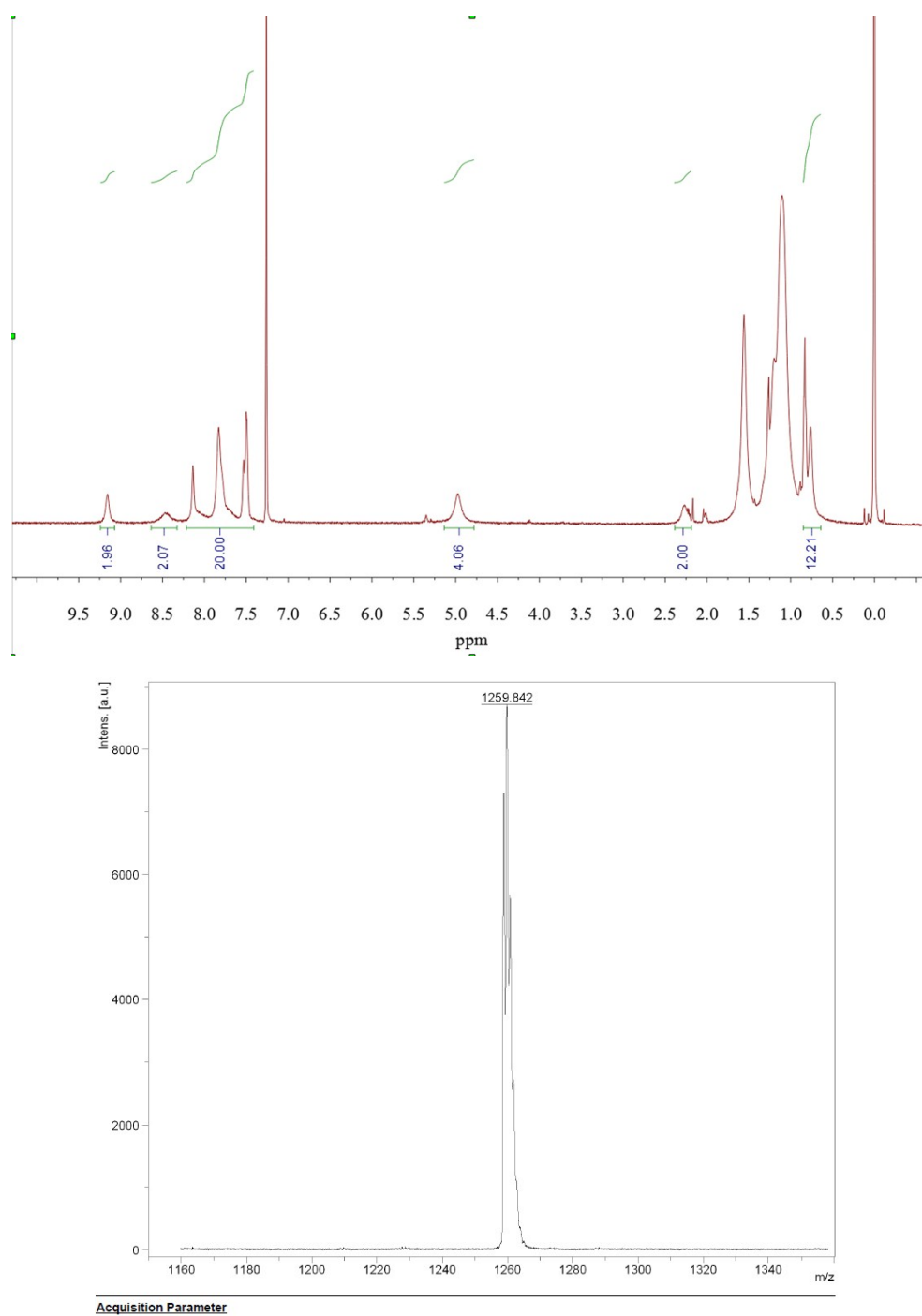


**Fig. S5** AFM height images of PBI-B-Na thin films spin-coated on the OTS-modified SiO<sub>2</sub>/Si substrate annealed at different temperatures for 10 min in nitrogen





**Fig. S6** The 300 MHz  $^1\text{H}$  NMR spectrum measured in  $\text{CDCl}_3$  and matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum of **PBI-L-Na**.



**Fig. S7** The 300 MHz <sup>1</sup>H NMR spectrum measured in CDCl<sub>3</sub> and matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum of **PBI-B-Na**.

## 5. References

1 J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, 70, 707-708.