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

Hui Wen\textsuperscript{a}, Xiaohui Gong\textsuperscript{a}, Pei Han\textsuperscript{a}, Baoping Lin\textsuperscript{a,*}, Lei Zhang\textsuperscript{b}, Shanghui Ye\textsuperscript{b,*}, Ying Sun\textsuperscript{a}, Xueqin Zhang\textsuperscript{a} and Hong Yang\textsuperscript{a}

a. School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China. E-mail: lbp@seu.edu.cn

b. Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, PR China. E-mail: iamshye@njupt.edu.cn

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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 a supporting electrolyte with a scan rate of 100 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 °C/min. Conventional X-ray diffraction (XRD) on two compounds was carried out on X Pert Powder equipment ($d = \frac{\lambda}{2\sin\theta}$, $\lambda = 0.15418$ nm). Grazing incident X-ray diffraction (GIXRD) experiments of thin films spin-coated on octadecyltrichlorosilane (OTS)-modified SiO₂/Si substrate were performed on Anton Paar SAXSess mc² equipment ($q = \frac{4\pi\sin\theta}{\lambda}$) using point X-ray source (Cu Kα, 40 kv; $\lambda = 0.15418$ nm) with an incident angle of 0.2°. 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

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\begin{align*}
\text{K-region} & \quad \text{a} \quad \text{b} \\
& \quad \text{c} \quad \text{d} \\
& \quad \text{e} \quad \text{f}
\end{align*}
\]

**Compound 1.** This compound was prepared following a published procedure¹. To a solution of pyrene (4.0 g, 20 mmol), NaIO₄ (35 g, 163.6 mmol) and RuCl₃·xH₂O (0.50 g, 2.4 mmol) in CH₂Cl₂ (80 mL) and CH₃CN (80 mL) was added H₂O at 0 °C. The mixture was stirred at 0 °C for 20 min, then warmed up to 30 °C-40 °C for 12 h. After cooling, CHCl₃ (50 mL) was added followed by filtration, the solution was then poured into water (200 mL). The mixture was extracted with CHCl₃ (3×40 mL) and the organic layers combined, dried over MgSO₄, and
concentrated under reduced pressure. The resulting crude orange product was purified via silica column chromatography using CH$_2$Cl$_2$ as eluent. The title compound was isolated as yellow crystals (0.36 g, 6.8%). $^1$H-NMR (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 NH$_4$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$_1$-Br and R$_2$-Br. To a solution of PPh$_3$ (25 g, 0.096 mol) in CH$_2$Cl$_2$ (200 mL), 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 CH$_2$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$_1$-Br and R$_2$-Br were isolated as colorless oil (R$_1$-Br: 33 g, 91%; R$_2$-Br: 31 g, 90%). $^1$H-NMR for R$_1$-Br (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).

$^1$H-NMR for R$_2$-Br (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 K$_2$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 CHCl$_3$ as eluent. The title compound was isolated as pale yellow powder (0.68 g, 67%). $^1$H-NMR (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 K$_2$CO$_3$ (0.91 g, 6.6 mmol) in DMF was added 1-Bromo-2-octyldodecane (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 CH$_2$Cl$_2$ as eluent. The title compound was isolated as pale green powder (0.40 g, 41%). $^1$H-NMR (CD$_2$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 K$_2$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 CHCl$_3$ as eluent. The title compound was isolated as pale green powder (0.40 g, 41%). $^1$H-NMR (CD$_2$Cl$_2$, 300 MHz, ppm): 9.19 (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). MS (MALDI-TOF, m/z): Calc. for C$_{90}$H$_{114}$N$_4$S$_2$: 1314.85; Found: 1314.776 [M$^+$]. Elemental analysis: Calc. for C$_{90}$H$_{114}$N$_4$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 K₂CO₃ 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 CH₂Cl₂ as eluent. ¹H-NMR (CDCl₃, 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 C₈₆H₁₀₈N₄S₂: 1259.79; Found: 1259.842 [M⁺]. Elemental analysis: Calc. for C₈₆H₁₀₈N₄S₂: 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 SiO₂ dielectric (capacitance (Cᵢ) of 18 nF cm⁻²). The SiO₂/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 3 min 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/SiO₂ 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 μm and 80 μm, respectively. OFET devices were characterized under an ambient environment using a Keithley 4200 parameter analyzer. The field effect mobility (μₑₐ₅) was calculated from the saturation regime of the transfer characteristics from the following equation: Iₙₛ = μ (W Cᵢ/2L) (Vₛ₋V₉)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$_2$/Si substrate annealed at different temperatures for 10 min in nitrogen.
Fig. S6 The 300 MHz $^1$H NMR spectrum measured in CDCl$_3$ and matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum of PBI-L-Na.
Fig. S7. The 300 MHz $^1$H NMR spectrum measured in CDCl$_3$ and matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum of PBI-B-Na.

5. References