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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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

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To explore the potential of pyrene-fused biimidazole as a building block for soluble small molecule semiconductors, we designed and synthesized **PBI-L-Na** and **PBI-B-Na**. Imidazole rings provided substitution positions for the solubilising groups at K-region, however, DFT calculations revealed that the repulsive steric hindrance from the neighboring hydrogen atoms on pyrene forced alkyl side chains into a twisted conformation. Thus, side chains on this type of molecules exerted a prominent influence on the molecular packing and affected their optoelectronic properties intensively in the solid state. **PBI-L-Na** exhibited a more ordered packing of the large conjugated plane with a π - π stacking distance of 0.36 nm and showed a hole mobility up to 0.12 cm² V¹ s⁻¹. Bulkier branched chains provided better solubility but impeded molecular packing of **PBI-B-Na**, thus giving a hole mobility of 4.6 × 10⁻³ cm² V¹ s⁻¹.

Introduction

Conjugated semiconducting materials for the next-generation flexible and printed electronics have attracted great attentions due to their solution processability, superior mechanical and tunable optoelectronic properties.¹ Optimal molecular design of organic semiconductors for improving the device performance generally contains two parts: synthesis of new π conjugated systems and side chain engineering. Most efforts have been focused on the design and synthesis of new π conjugated systems because the optoelectronic properties can be easily tuned by the modulation of conjugated moieties.² In particular, π-conjugated systems constructed bv diketopyrrolopyrole (DPP),³ isoindigo⁴ and fused thiophene derivatives⁵ have been extensively investigated. Alkyl chains are commonly attached to the π -conjugated systems as solubilising groups to provide solution processability. However, it has been demonstrated that side chains also play important roles in the molecular packing and hence affect device performance.⁶ Compared to linear chains, the commonly used branched side chains (2-octyldodecyl, 2-decyltetradecyl) provide better solubility, but π - π intermolecular interaction is affected by the bulky chains due to the branch point is so close to conjugated systems. To reduce such steric hindrance while maintaining solubility, Pei et al. moved branch point away from the conjugated backbones and the polymers exhibited promoted π - π interaction with moving branch positions, which was consistent with the improved charge mobility.⁷

Pyrene, a potential building block with the large conjugated plane, has been widely investigated to develop new π -conjugated systems.⁸ Electrophilic substitution of pyrene preferentially takes place at the active sites (1-, 3-, 6-, and 8-positions). Thus, the most efforts to explore its potential in organic semiconductors often start from 1-substituted pyrenes due to the difficulties in synthesis of diverse substitution patterns.⁹ An Ir-catalysed aromatic borylation at 2, 7 positions to produce pyrene-2,7-bis(boronate)ester was developed by Marder et al. which can be easily used in Suzuki coupling to synthesize new π -conjugated systems.¹⁰ Expansion of π -system by fusing at pyrene core opens up a new way for the more efficient utilization of pyrene conjugation. Recently, a few of polycyclic aromatics fused at K-region and non-Kregion of pyrene were synthesized and they exhibited interesting properties.¹¹ Rigid structure, large π -system and strong stacking ability make this type of polycyclic aromatic hydrocarbons received increasing attentions.

Herein, we developed a type of polycyclic building block (**PBI-L** and **PBI-B**, scheme 1) by fusing two imidazole rings onto pyrene core at K-region. Fusion of five-membered imidazole rings with a symmetrical pattern by Debus-Radziszewski condensation offered several advantages: extended π -systems, large conjugated plane can be easily used in metal-catalyzed cross-coupling reactions for synthesis of new semiconductors and alkyl chains can be readily introduced on N atoms to afford satisfactory solubility for the purification and solution processing. Considering that the soluble small molecules

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⁺ Electronic Supplementary Information (ESI) available: ¹H spectra, electrochemical and OFET data. See DOI: 10.1039/x0xx00000x

display advantages of simple purification and well-defined structures, we synthesized two compounds (**PBI-L-Na** and **PBI-B-Na**, scheme 1) based on the pyrene-fused biimidazole to explore the potential of this large conjugated system in small molecule semiconductors. Linear and branched chains were used to reveal side chain effects on the physical properties. **PBI-L-Na** showed a more ordered structure with a hole mobility of 0.12 cm² V⁻¹ s⁻¹, which is almost 30 times larger than that of **PBI-B-Na** (4.6 × 10⁻³ cm² V⁻¹ s⁻¹).

Results and discussion

Synthesis and characterizations

The synthesis of PBI-L-Na and PBI-B-Na, consisting of pyrene-fused biimidazole, is shown in scheme 1. Pyrene-4,5,9,10-teraketone (1) was prepared by RuCl₃•xH₂O catalysed oxidation at K-region. Debus-Radziszewski condensation in the presence of ammonium salt and 5-Bromothiophene-2carboxaldehyde was successfully applied on 1 to construct compound 2. This compound only has solubility in the strong polar solvents such as DMF and DMSO, which originates from the active hydrogen atoms on the imidazole rings. Therefore, the crude compound 2 was directly employed in the next reaction without any further purification. In order to get the satisfactory solubility and study influence of side chain on physical properties, the long linear and branched alkyl chains were attached on the nitrogen atoms, thus giving PBI-L and PBI-B. Finally, the target compounds PBI-L-Na and PBI-B-Na can be easily prepared using a palladium-catalyzed Suzuki coupling reaction between the building blocks and naphthalene-2-ylboronic acid.

The decomposition temperatures were determined by thermal gravimetric analysis (TGA). The 5% weight loss temperatures were 392 °C and 387 °C for **PBI-L-Na** and **PBI-B-Na** (Fig. S1), respectively, indicating their high thermal stability which can be attributed to the robust conjugated system of pyrene-fused biimidazole.

Density functional theory (DFT) calculations

To further understand structural and electronic characteristics of pyrene-fused biimidazole based small molecules, density functional theory (DFT) calculations were performed at the B3LYP 6-31G* level using Gaussian 09 program. Note that calculations were performed in the single molecular state. Alkyl chains were kept with a short length in the calculations to figure out their architecture that can exert an important influence on the molecular packing. As shown in Fig. 1, pyrene-fused biimidazole unit, which is expected to facilitate strong π -stacking, displayed a rigid and planar π skeleton in both molecules. PBI-L-Na and PBI-B-Na exhibited almost identical geometry of aromatic core suggesting that side chains do not affect conjugated systems. It is also should be noted that alkyl chains extended out of the conjugated plane. Especially for PBI-B-Na, the bulkier branched chains may strongly impede intermolecular π - π interactions by extending out of the conjugated plane with two directions.



Scheme 1: synthetic route for **PBI-L-Na** and **PBI-B-Na**: (a) NaIO₄, RuCl₃•xH₂O, acetonitrile/dichloromethane/H₂O, 30 °C-40 °C, 12 h, 6.8%; (b) NH₄OAc, glacial acetic acid, reflux, 10 h, 75%; (c) Br₂, triphenylphosphine, dichloromethane, 25 °C, 12 h, 90%; (d) K₂CO₃, DMF, 100 °C, 12 h, 67-41%; (e) Palladiumtetrakis(triphenylphosphine), K₂CO₃, H₂O/THF, 65 °C, 12 h, 65%.

Imidazole rings fused at K-region of pyrene provide substitution positions for the side chains, thus, the steric interaction between alkyl chains and the neighboring hydrogen atoms on pyrene (indicated by red cycle in Fig. 1) may exist to cause the twisted structure. Calculation on the molecule based on naphthalene-fused bisimidazole (without the neighboring hydrogen atoms) substantiated this kind of steric hindrance (Fig. S2). **PBI-L-Na** and **PBI-B-Na** presented almost the same LUMO/HOMO orbitals, indicating that influence of alkyl chains on the electronic properties was negligible in the single molecular state. Imidazole ring is usually treated as an electron-deficient unit, however DFT



Fig. 1 Optimized geometry and calculated molecular orbitals for the **PBI-L-Na** and **PBI-B-Na**. DFT calculations were performed at the B3LYP/6-31G(d,p) level on Gaussian 09.



Fig. 2 Normalized UV-Vis absorption spectra of **PBI-L-Na** and **PBI-B-Na** in chloroform solution and thin films.

calculations showed that LUMO orbitals were mainly delocalized over thiophene and naphthalene units and partially located on pyrene-fused bisimidazole. Additionally, the HOMO orbitals were predominantly located on pyrene-fused bisimidazole. This distribution of molecular orbitals was different from the typical D-A organic semiconductors constructed with strong donor and acceptor. We suggested that imidazole ring is a weak electron-withdrawing unit due to the electron-donating ability of the sp³ N in the five-membered ring.

Optical and electrochemical properties

The UV-vis absorption spectra of **PBI-L-Na** and **PBI-B-Na** were measured in CHCl₃ solution and thin films (Fig. 2). Solution of two compounds presented similar absorption spectra, indicating that alkyl chains had no effect on the photophysical properties in the single molecular state which is consistent with the result from the DFT calculations. Considering a small overlap between HOMO and LUMO orbitals, the peak at around 400 nm in solution was attributed to the intramolecular charge transfer (ICT) transition. The other two characteristic bands located at ca. 349 nm and 293 nm can be assigned to the π - π * transition and imidazolecentered n- π * transition, respectively. In solid state, **PBI-L-Na** spectra showed a notable bathochromic shift and a pronounced peak at 423 nm with a small shoulder, which were



Fig. 3 Cyclic voltammograms (CV) and schematic energy diagrams of **PBI-L-Na** and **PBI-B-Na** films drop-casted onto platinum working electrode.

Table 1 Electrochemical properties of PBI-L-Na and PBI-B-Na

DOI: 10.1039/C6RA13864K

ARTICLE

Compound	LUMO (eV)	HOMO (eV)	Eg ^{ec} (eV)	E ^{opt} (eV)
PBI-L-Na	-3.15	-5.64	2.49	2.58
PBI-B-Na	-3.0	-5.72	2.72	2.93

commonly observed for conjugated materials due to the stacking of π -systems. Furthermore, the shoulder at 455 nm turned to an obvious peak after annealing at 125 °C, implying that **PBI-L-Na** had an enhanced π - π interaction after thermal treatment. In contrast, spectra of **PBI-B-Na** films only exhibited more vibronic fine structures and a tiny red shift compared to that of solution, suggesting that the bulkier branched chains disrupted the π -stacking in the solid state. As a result, the optical energy gap (E_g^{opt}) of **PBI-L-Na** (2.58 eV) measured from the onset of its absorption in the film was much narrower than that of **PBI-B-Na** (2.93 eV).

These results suggested that side chains on pyrene-fused biimidazole based molecules can exert a prominent influence on the molecular packing, thus affected optoelectronic properties in the solid state. However, in the single molecular state, the effect of side chains on π -conjugated system can be neglected.

Electrochemical properties of PBI-L-Na and PBI-B-Na were investigated using cyclic voltammetry measurements from their drop-cast thin films on the platinum working electrode and the data are summarized in Table 1. Both compounds presented oxidation and reduction waves in their voltammograms (Fig. 3). From the onset of reduction, the LUMO energy level of PBI-L-Na was estimated to be -3.15 eV, which is 0.15 eV lower than that of PBI-B-Na. On the other hand, the HOMO energy levels were estimated to be -5.64 eV and -5.72 eV for PBI-L-Na and PBI-B-Na, respectively. The extremely deep HOMO energy levels of two molecules were likely due to the pyrene unit consisting of four fused benzene rings. Energy levels in solid state changed with different side chains and similar tendency were observed in Jian Pei's work.⁷ The electrochemical band gaps (E_g^{ec}) were found to be 2.49 eV for PBI-L-Na and 2.72 eV for PBI-B-Na, respectively, within 0.4 eV of the optical energy gaps.

Characteristics of organic field-effect transistors

Large and coplanar conjugated plane may facilitate the charge transport and it is believed that side chains also have a great influence on the device performance. To investigate the charge transport properties of **PBI-L-Na** and **PBI-B-Na**, top-contact-bottom-gate OFET devices were fabricated by spin-coating of their solutions on heavily doped n-type silicon wafers with the 300 nm thermally grown SiO₂. The field-effect mobilities were extracted from transfer curves in saturation region tested in the ambient air conditions, and the performance data are listed in Table 2. Two compounds are typical P-type semiconductors according to their transfer and

Table 2 Summary of performance of OFET devices based on	
PBI-L-Na and PBI-B-Na	

Compound	T (°C)	μ (cm ² V ⁻¹ S ⁻¹)	V _T (V)	I _{on} /I _{off}
PBI-L-Na		0.032	-10.3	3.2×10^{4}
	100	0.069	-25.1	5.9×10^{4}
	125	0.12	-21.5	1.0×10^{5}
	150	0.080	-15.6	5.3×10^{5}
PBI-B-Na		1.5×10^{-3}	-45.6	5.1×10^{3}
	100	2.6×10^{-3}	-46.1	8.1×10^{3}
	125	4.6×10^{-3}	-30.3	1.9×10^4
	150	3.3 × 10 ⁻³	-48.1	4.2×10^{3}

output curves (Fig. 4, Fig. S3 and Fig. S4). Devices based on pristine films showed hole mobilities of 0.032 and 1.5 × 10^{-3} cm² V⁻¹ s⁻¹ for **PBI-L-Na** and **PBI-B-Na**, respectively. Thermal annealing improved device performance significantly for **PBI-L-Na** and it was found to exhibit the maximum hole mobility of 0.12 cm² V⁻¹ s⁻¹ with an on/off ratio of 1.0 × 10^{5} after annealing at 125 °C. In contrast, the maximum hole mobility of 4.6 × 10^{-3} cm² V⁻¹ s⁻¹ for **PBI-B-Na** was dramatically lower than that of **PBI-L-Na**.

Results from the OFET devices revealed that pyrene-fused biimidazole is a potential core for the design of new small molecule semiconductors. It is also interesting to note that selection of side chains for this type of molecules is very important as they can dramatically affect the charge transport properties.

Microstructures and film morphology

To gain insight into above results, conventional X-ray diffraction (XRD) measurements were performed to investigate molecular aggregation of **PBI-L-Na** and **PBI-B-Na**. As shown in Fig. 5, an intense diffraction peak at $2\theta = 1.9^{\circ}$,



Fig. 4 Output (left) and transfer (right) characteristics for **PBI-L-Na** annealed at 125 °C. The hole mobility value calculated in the saturation region is $0.12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.



Fig. 5 XRD data obtained from **PBI-L-Na** and **PBI-B-Na** before and after thermal annealing (125 °C).

corresponding to the lamellar structure with a d-spacing of 4.64 nm. was observed in pristine **PBI-L-Na**. Two weak peaks at $2\theta = 2.8^{\circ}$ and 4.0° also indicated a small number of more closed lamellar structures. The π - π stacking resulted in a series of peaks after $2\theta = 20^{\circ}$ in the pristine **PBI-L-Na**, suggested the coexistence of different packing motifs of conjugated plane. After thermal annealing, PBI-L-Na exhibited a stronger primary peak and the peak red-shifted slightly to $2\theta = 2.2^{\circ}$ (d-spacing of 4.01 nm), due to the drastically improved crystallinity. Most importantly, thermal treatment also decreased distance of π - π stacking to 0.36 nm as evidenced by the diffraction peak redshifted to the 2θ = 24.25°. On the other hand, Bulkier branched chains on PBI-B-Na impeded aggregation of the molecules, thus the effect of thermal annealing was limited. A less intensive primary peak at $2\theta = 5.7^{\circ}$ was observed for **PBI**-B-Na, indicating the reduced crystallinity compared to PBI-L-Na. The much smaller lamellar d-spacing (1.55 nm) corresponding to this diffraction was originated from the interdigitation of the shorter branched chains. However, the broad peak at $2\theta = 22.80^\circ$ showed a larger π - π stacking distance of 0.39 nm.

To further elucidate molecular packing in OFET devices and correlate this important property with device performance, 2-



Fig. 6 2-D GIXRD images (top) and out-of-plane GIXRD profiles (bottom) for **PBI-L-Na** and **PBI-B-Na** films annealed at 125 °C.



Fig. 7 AFM height images for **PBI-L-Na** films before and after thermal annealing at different temperatures

D grazing-incident X-ray diffraction (GIXRD) was used to examine spin-coated films on OTS modified Si/SiO₂ substrates annealed at 125 °C. The bright diffraction spot at around $q_7 =$ 0.5 nm⁻¹ which was partially blocked by the beam stop originated from the intense diffuse reflectivity. As shown in Fig. 6, **PBI-L-Na** exhibited an intensive peak at $q_z = 1.53 \text{ nm}^{-1}$ along with a weak diffraction at $q_7 = 3.18 \text{ nm}^{-1}$, which were consistent with the data obtained from the conventional XRD. The clarity of diffraction peak indicated a high degree of crystallinity in PBI-L-Na, whereas the arc shape suggested that the crystalline regions were somewhat misaligned with respect to the substrate. In contrast to PBI-B-Na, an arc diffraction pattern with a drastically decreased intensity was observed at $q_z = 3.75 \text{ nm}^{-1}$. All the above results revealed that side chains on pyrene-fused biimidazole exhibited a significant impact on conjugated plane packing, which was correlated well with the device performance. The GIXRD signal for the π - π interactions at q₇ direction was too weak to detect using our equipment. According to the conventional XRD, a characteristic peak of π - π stacking might be found at $q_{xy} \approx \pm 16-17 \text{ nm}^{-1}$, However, this detection was restricted by the limited measurement range at q_{xy} direction (-5-5 nm⁻¹) of GIXRD instrument.

Surface morphology of two compounds spun onto OTS treated Si/SiO₂ substrates was analyzed using Atomic force microscopy (AFM) (Fig. 7 and Fig. S5). The as-spun thin film of **PBI-L-Na** was uniform and featured with fine grains. Upon thermal annealing, the grain size and surface roughness increased obviously, suggestive of enhanced crystallinity organized by the strong intermolecular packing force. Surface morphology of **PBI-B-Na** looked quite different and no apparent grains were found in the films thus giving the smoother surface. This result was consistent with the lower crystallinity nature of **PBI-B-Na** revealed by the conventional XRD and GIXRD analysis.

Conclusions

Two small molecule semiconductors, PBI-L-Na and PBI-B-Na, were designed and synthesized based on pyrene-fused biimidazole. According to the DFT calculations, steric hindrance of neighboring hydrogen atoms on pyrene caused a twisted structure of side chains. Thus, it was found that side chains on this type of molecules had a prominent influence on the molecular packing and intensively affected optoelectronic properties in the solid state. Linear chains facilitated a more ordered packing of the large conjugated plane with a $\pi\text{-}\pi$ stacking distance of 0.36 nm, thereby PBI-L-Na exhibited a hole mobility up to 0.12 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. While bulkier branched chains impeded molecular packing thus giving a much lower hole mobility of $4.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This work showed the potential of pyrene-fused biimidazole as a building block for small molecule semiconductors and emphasized the importance of side chain selection for this type of molecules.

DOI: 10.1039/C6RA13864K

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Acknowledgements

We gratefully acknowledge the financial support from National Natural Science Foundation of China (21304018 21374016 61106017) and Jiangsu Provincial Natural Science Foundation of China (BK20130619 BK20130617).

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Highlights:

Soluble small molecule semiconductors based on pyrene-fused biimidazole and side-chain effects on the semiconducting properties.