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journal homepage: [www.elsevier.com/locate/dyepig](http://www.elsevier.com/locate/dyepig)

## Balancing intermolecular interactions by variation of pendent alkyl chains for high performance organic photovoltaics

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## ARTICLE INFO

## Article history:

Received 31 August 2016

Received in revised form

21 October 2016

Accepted 21 October 2016

Available online xxx

## Keywords:

Donor-acceptor-type small molecules

Crystallinity

Morphology

Organic solar cells

Power conversion efficiency

## ABSTRACT

Understanding the role of appended alkyl side chains is a key issue to enhance photovoltaic performance because the side chains control molecular solubility, film crystallinity, and morphology. For this purpose, we synthesized three new planar aromatic backbone molecules (**Eh-Hex**, **Eh-Eh** and **Oct-Eh**), where the appended alkyl side chains on the aromatic core unit were either 2-ethylhexyl (Eh) or n-octyl (Oct) and those on the side ends were either Eh or hexyl (Hex). Characterization of the molecular films revealed that all of the molecules were crystalline with mainly edge-on orientation, while the **Eh-Hex** and **Eh-Eh** molecules having Eh groups on the core units manifested higher crystallinity than the molecule (**Oct-Eh**) having Oct groups on the core units. Of the small molecule:PC<sub>71</sub>BM blend films, only the **Eh-Hex** case exhibited both good intermolecular packing and uniformly distributed nanoscopic networks of molecular channels, maintaining extensive interfacial contacts between the **Eh-Hex** and PC<sub>71</sub>BM domains. On the other hand, the **Eh-Eh** molecules showed poor miscibility with PC<sub>71</sub>BM, and the **Oct-Eh** molecules displayed excessive miscibility with PC<sub>71</sub>BM. These morphological differences resulted in significant differences in the photovoltaic performance of the devices using small molecule:PC<sub>71</sub>BM blend films. Inverted-type photovoltaic devices fabricated using the **Eh-Hex**:PC<sub>71</sub>BM blend had the highest power conversion efficiency among the three molecule-based devices. Overall, this work demonstrated that both the type of alkyl side chain and its position are crucial factors controlling the balance of interactions between small molecules and PC<sub>71</sub>BM molecules, which can significantly alter blend morphology and photovoltaic performance.

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### 1. Introduction

Organic semiconductors are an important class of materials in optoelectronic applications, especially for bulk heterojunction (BHJ)-type organic solar cells (OSCs) [1–5]. Photoactive layers in BHJ-type OSCs consist of a pair of electron-donor molecules and electron-acceptor molecules. [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) are the most common electron-acceptor molecules due to

their good solubility in organic solvents, reversible electrochemical reductions, and low-lying energy levels [6–8]. Good electron-donor molecules must possess a broad range of light absorption to capture solar energy and possess optimal energy level alignment with respect to the electron-acceptor molecules for efficient charge separation [9]. Excitons, generated in the electron-donor molecules under sunlight illumination, diffuse to the electron-donor/electron-acceptor interfaces where they split into holes and electrons. Then, holes travel through the electron-donor phase to an anode and electrons migrate through the electron-acceptor phase toward a cathode. High crystallinity of molecular domains is important for highly efficient carrier transport.

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Recently, the performance of single OSCs exceeded 10% power conversion efficiency (PCE) [10–12]. Much of this success has come with well-defined small molecule (SM)-based OSCs in addition to the electron-donors of conjugated polymers. Chemists have focused on the development of electron-donor SMs due to their unique advantages compared with their polymeric counterparts, including simple synthesis and purification, easily tunable molecular structures and molecular energy levels, very low batch-to-batch variability, and perceived promising molecular properties of high carrier mobility and PCEs [13–15]. Small electron-donor molecules are typically designed to use electron-donating (D) units and electron-withdrawing (A) units in a D–A–D or A–D–A form. These molecular designs have been a promising strategy as the symmetric D–A–D or A–D–A structures in semiconducting molecules tend to induce high intermolecular interactions through self-assembly of aromatic planar molecular backbones and alkyl side chains, leading to increased long-range molecular ordering [16–19]. In this design concept, planar molecular backbones in SMs and polymers for OSCs are known to be beneficial [12,20–23]. However, it is not well understood how the alkyl side chains play a role in forming intermolecular organizations within electron-donor molecules and also intermolecular interactions between electron-donor molecules with electron-acceptor molecules in the BHJ-type blend films.

In this work, we synthesized and characterized the three solution-processable SMs of 4,7-bis(5'-alkyl-[2,2'-bithiophen]-5-yl)-6-(4,4-bis(2-alkyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (**Eh-Hex**, **Eh-Eh** and **Oct-Eh**), where the alkyl chains on the core were either 2-ethylhexyl (Eh) or n-octyl (Oct), and those on the side arms were either Eh or n-hexyl (Hex). The synthetic routes and molecular structures are shown in Scheme 1. The aromatic backbones consisted of difluorobenzothiadiazole (DFBT), dithienosilole (DTS), and bithiophene (BiT). DFBT moieties are good electron acceptors, and DTS moieties are good electron donors; the combination of these moieties form highly planar, well-conjugated aromatic backbones through F...S and N...S interactions [24,25]. These moieties constituted the D–A–D core part of the molecules and BiT constituted the side-arm part. Density functional theory (DFT) calculations proved that these molecules contain low (<13°) dihedral angles between aromatic moieties. These characteristics lead to the promotion of intramolecular  $\pi$ -electron delocalization and intermolecular interactions. Crystallinity decreased in the order of **Eh-Hex** > **Eh-Eh** > **Oct-Eh** in the molecular films. In the SM:PC<sub>71</sub>BM blend films, crystallinity was generally reduced with incorporating PC<sub>71</sub>BM molecules between SM domains. **Eh-Hex** having linear alkyl chains on the side arms displayed an optimal degree of crystallinity reduction with retaining ca. 20-nm-wide interconnected domains. In contrast, **Eh-Eh** showed too much phase separation with PC<sub>71</sub>BM and **Oct-Eh** had too high miscibility with PC<sub>71</sub>BM. These features resulted in photovoltaic devices incorporating the **Eh-Hex**:PC<sub>71</sub>BM blend having the highest PCE. This work demonstrated the critical role of alkyl side chains in forming intermolecular stacking between semiconducting planar SMs and also in generating optimal domain sizes of electron donors and electron acceptors for high-performance OSCs.

## 2. Experimental

### 2.1. Materials

N-bromosuccinimide (NBS), 1.6 M *n*-butyllithium (BuLi) solution in hexanes, 1.0 M trimethyltin chloride solution in tetrahydrofuran (THF), tetrakis(triphenylphosphine)palladium(0), tris(dibenzylideneacetone)dipalladium(0), tri(*o*-tolyl)phosphine, and cesium

fluoride were purchased from Aldrich. 5-bromo-5'-hexyl-2,2'-bithiophene (**1**) and 5-bromo-5'-(2-ethylhexyl)-2,2'-bithiophene (**2**) were purchased from Aldrich. 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (**5**) was purchased from TCI. 4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene and 4,4-bis(2-octyl)-4H-silolo[3,2-b:4,5-b']dithiophene were purchased from SunaTech. Synthesis of compounds (**3**, **4**, **6–11**) are provided in Supplementary Data. Common organic solvents were purchased from Daejung and J. T. Baker. Tetrahydrofuran (THF) was dried over sodium and benzophenone prior to use. All other solvents (dichloromethane (DCM), chlorobenzene (CB), toluene, *N,N*-dimethylformamide (DMF), CH<sub>3</sub>OH, and CHCl<sub>3</sub>) were used as received without further purification.

#### 2.1.1. 4,7-bis((5'-hexyl-[2,2'-bithiophen]-5-yl)-6-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (Eh-Hex)

To a 50 mL flame-dried reaction tube with a magnetic bar, compound **8** (0.31 g, 0.27 mmol) compound **3** (0.32 g, 0.75 mmol) was added. Anhydrous chlorobenzene (9 mL) and anhydrous DMF (3 mL) were degassed by three freeze-pump-thaw cycling and added to the reaction tube. Pd<sub>2</sub>(dba)<sub>3</sub> (0.007 g, 0.0133 mmol), P(*o*-tolyl)<sub>3</sub> (0.03 g, 0.11 mmol), and cesium fluoride (0.10 g, 0.67 mmol) were then added to the reaction mixture. This reaction mixture was warmed up to 105 °C and stirred for 5 h. After reaction completion, H<sub>2</sub>O (15 mL) was added to the reaction mixture. The solution was extracted with CHCl<sub>3</sub> (60 mL) three times. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing MgSO<sub>4</sub> by filtration, the solvent was evaporated. The crude product was purified by column chromatography using an eluent of CH<sub>2</sub>Cl<sub>2</sub>:hexane (1:30 v/v) to yield **Eh-Hex**. Yield: 0.21 g, 51% <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31–8.29 (t, 2H, *J* = 4.8 Hz), 7.16 (s, 2H), 7.08–7.07 (d, 2H, *J* = 4.0 Hz), 7.02–7.01 (d, 2H, *J* = 4.0 Hz), 7.00–6.99 (d, 2H, *J* = 3.6 Hz), 6.70–6.69 (d, 2H, *J* = 3.6 Hz), 2.82–2.79 (t, 4H, *J* = 7.8 Hz), 1.75–1.64 (m, 4H), 1.63–1.58 (m, 2H), 1.53–1.45 (m, 4H), 1.45–1.13 (m, 46H), 1.08–1.00 (m, 8H), 0.93–0.76 (m, 30H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.08, 155.95, 153.90, 152.44, 148.85, 147.16, 145.66, 143.25, 139.09, 136.60, 135.65, 134.50, 133.97, 132.80, 126.40, 124.84, 124.01, 123.61, 123.32, 35.95, 35.71, 31.56, 30.20, 29.72, 28.91, 28.76, 26.65, 23.00, 22.57, 17.66, 14.14, 14.08, 10.82; MS (MALDI-TOF), *m/z*, 1500.44; Anal. Calcd. for C<sub>82</sub>H<sub>106</sub>F<sub>2</sub>N<sub>2</sub>S<sub>9</sub>Si<sub>2</sub>: C, 65.6; H, 7.1; N, 1.9; S, 19.2; Found: C, 65.5; H, 7.3; N, 1.6; S, 19.5.

#### 2.1.2. 4,7-bis((5'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-6-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (Eh-Eh)

To a 100 mL flame-dried reaction tube with a magnetic bar, compound **8** (1.13 g, 0.97 mmol) compound **4** (1.15 g, 2.60 mmol) was added. Anhydrous chlorobenzene (27 mL) and anhydrous DMF (9 mL) were degassed by three freeze-pump-thaw cycling and added to the reaction tube. Pd<sub>2</sub>(dba)<sub>3</sub> (0.02 g, 0.05 mmol), P(*o*-tolyl)<sub>3</sub> (0.12 g, 0.39 mmol), and cesium fluoride (0.37 g, 2.42 mmol) were then added to the reaction mixture. This reaction mixture was warmed up to 105 °C and stirred for 5 h. After reaction completion, H<sub>2</sub>O (30 mL) was added to the reaction mixture. The solution was extracted with CHCl<sub>3</sub> (100 mL) three times. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was evaporated. The crude product was purified by column chromatography using hexane as an eluent to yield **Eh-Eh**. Yield: 1.05 g, 71%

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.31–8.29 (t, 2H, *J* = 4.6 Hz), 7.16 (s, 2H), 7.08–7.07 (d, 2H, *J* = 3.6 Hz), 7.03–7.02 (d, 2H, *J* = 3.6 Hz), 7.01–7.00 (d, 2H, *J* = 4.0 Hz), 6.68–6.67 (d, 2H, *J* = 3.2 Hz) 2.75–2.74 (d, 4H, *J* = 6.4 Hz), 1.68–1.57 (m, 2H), 1.54–1.46 (m, 4H), 1.45–1.15

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