

# Perylene Bisimide-Based Donor–Acceptor Materials Incorporating Oligothiophenes: Synthesis, Characterization, Thin-Film Properties, and Nanomorphology

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Kazuhiro Nakabayashi was born in Mie, Japan, and received his B.S. degree in Nagoya Institute of Technology (2006). Then he received his M.S. (2008) and Ph.D. (2011) degrees in Tokyo Institute of Technology under the supervision of Prof. Mitsuru Ueda. He joined Yamagata University in 2011 as an assistant professor. He also joined Massachusetts Institute of Technology during 2014–2015 under the supervision of Prof. Timothy M. Swager. His current research interests are the development of new synthetic method for  $\pi$ -conjugated polymers and their opto-electronic applications, functional nanoparticles based on living/controlled polymerization, high refractive index polymers.

#### Abstract

We developed a series of perylene bisimide (PBI)-based small molecules with donor-acceptor (D–A) architecture (**PBI1**, **PBI2**, and **PBI3**). By tuning the D–A architecture, intramolecular charge transfer (ICT) could be controlled; as a result, optical band gaps and HOMO levels of **PBI1–3** were widely tunable from 1.83 to 1.44 eV and from -5.85 to -5.55 eV, respectively. Furthermore, extremely wide light absorption over 900 nm was observed in the thermal annealed **PBI1–3** blend film. The grazing incidence wide angle X-ray scattering (GIWAXS) analysis demonstrated that the as-spun **PBI2** thin film had the highest ordered nanostructure among **PBI1–3**, in which diffraction corresponding to  $\pi$ – $\pi$  stacking was clearly observed in isotropic orientations.

## 1. Introduction

Semiconducting materials with donor–acceptor (D–A) architecture have received much attention for optoelectronic applications, such as organic photovoltaics (OPVs),<sup>1–5</sup> organic field-effect transistors (OFETs),<sup>6–8</sup> and organic light-emitting diodes.<sup>9,10</sup> Intramolecular charge transfer (ICT) derived from the D–A architecture is quite effective for the tuning of various properties in semiconducting materials, such as HOMO/LUMO levels, light absorption, charge carrier mobilities, and nanomorphology; the careful design and selection of each donor and acceptor structure can allow the precise tuning of the properties.<sup>1–10</sup> For the design of D–A semiconducting materials, the selection of the acceptor structure is particularly important because it affects the key properties of D–A semiconducting materials (e.g., electron mobility, LUMO levels, and

light-absorption properties). To date, semiconducting materials with various acceptor structures, such as quinoline, <sup>11,12</sup> 2,1,3benzothiadiazole,<sup>13,14</sup> arylene bisimide,<sup>15–21</sup> isoindigo,<sup>22–24</sup> thienoisoindigo,<sup>25-29</sup> and diketopyrrolepyrrole,<sup>30-32</sup> have been widely developed and applied for OPVs and OFETs. The precise tuning of semiconducting properties by the proper combination of acceptor and donor structure in D-A semiconducting materials contributed to high performance in those devices. Yet, it should be noted that semiconducting materials with the aforementioned acceptor structures generally functioned as donor materials in devices. In contrast to donor materials, acceptor materials based on the D-A architecture are less developed. Incorporation of a strong acceptor structure is necessary to exhibit the acceptor properties in preference to the donor properties in D-A semiconducting materials. However, such strong acceptor structures are limited.

Arylene bisimides, e.g., naphthalene bisimide (NBI) and perylene bisimide (PBI), are promising acceptor structures because of their high electron affinity, high electron mobility, and excellent chemical and thermal stability.15-21 Arylene bisimide-based materials containing donor units (i.e., arylene bisimide-based D-A materials) are well-known as potential acceptor materials for OFETs and OPVs. For example, the OFET using poly(NBI-alt-dithiophene) achieved the excellent electron mobility of  $1.2 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>33</sup> The OPVs using poly(PBI-alt-carbazole)<sup>34</sup> and poly(NBI-alt-selenophene)<sup>35</sup> as acceptor materials exhibited a PCE of 1.2 and 3.3%, respectively. Recently, PBI-based small molecules have been considered as promising acceptor materials for optoelectronic applications.<sup>36–43</sup> Yao and co-workers developed a PBI-based small molecule with thiophene donor units as an acceptor material;<sup>39</sup> the undesirable aggregation that was one of drawbacks on traditional PBI-based materials was successfully suppressed using a precise molecular design.<sup>34,40</sup> Furthermore, the OPV using the PBI-based small molecule as a non-fullerene acceptor material achieved an excellent PCE over 4% in a non-fullerene OPV, indicating the huge potential of PBI-based small molecules as acceptor materials. Other researchers also reported the potential results of PBI-based small molecules as non-fullerene acceptor materials in OPVs.<sup>41–43</sup>

Herein, we present a series of PBI-based small molecules with the D–A architecture (**PBI1**, **PBI2**, and **PBI3**). **PBI1–3** were synthesized systematically by typical Stille coupling reactions between traditional dibromo PBI monomer and thiophene derivatives with tributylstannyl functionalities. The tuning of optical, electrochemical, and thermal properties, and nanomorphology of **PBI1–3** derived from the D–A architecture was also investigated in detail.

## 2. Experimental

**Materials.** All reagents and solvents were used as received unless otherwise stated. *N*,*N*-Bis(2-decyl-1-tetradecyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide (1),<sup>15,44</sup> and 5-(tributylstannyl)-2,2'-bithiophene (**T2**)<sup>45</sup> were synthesized according to the previous literature. 5-Tributylstannyl-terthiophene (**T3**) was synthesized by reference to the synthesis of **T2**.

The <sup>1</sup>H and <sup>13</sup>CNMR spectra were Characterization. recorded with a JEOL JNM-ECX400. The UV-vis spectra were recorded on a JASCO V-630BIO UV-vis spectrophotometer. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer. Cyclic voltammetry (CV) experiments were performed on a BAS electrochemical analyzer (model 660C) in benzene/acetnitrile (10/3, vol/vol) solutions with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. A three-electrode cell was used with platinum electrodes as both the counter and working electrodes. Silver/ silver ion (Ag in 0.1 M AgNO<sub>3</sub> solution) was used as the reference electrode. Ferrocene/Ferrocenium (Fc/Fc<sup>+</sup>) was used as an internal standard. The potential values obtained in reference to Ag/Ag<sup>+</sup> were converted to the values relative to the saturated calomel electrode (SCE). Thermal gravimetric (TG) analysis was performed on a SEIKO SSC6200 at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Grazing incidence wide angle X-ray scattering (GIWAXS) experiments were conducted at the Spring-8 on beamline BL19B2. The sample was irradiated at a fixed incident angle on the order of 0.12° through a Hubber diffractometer with an X-ray energy of 12.39 keV ( $\lambda = 1$  Å), and the GIXD patterns were recorded with a 2-D image detector (Pilatus 300K).

Synthesis of PBI1. A dry toluene solution (5 mL) of 1 (244 mg, 0.2 mmol), 2-(tributylstannyl)thiophene (T1) (224 mg, 0.6 mmol), and [Pd(PPh\_3)\_4] (11.6 mg, 0.01 mmol) was refluxed at 120 °C for 16 h under a nitrogen atmosphere. After the reaction, the solvents were removed. The residue was purified with column chromatography (chloroform/hexane = 3/2) to yield a purple viscous solid (155 mg, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 8.65 (s, 2H), 8.24 (d, 2H, J = 8.4 Hz), 8.05 (d, 2H, J = 8.0 Hz),

7.50 (dd, 2H, J = 5.2, 0.8 Hz), 7.32 (dd, 2H, J = 4.8, 1.2 Hz), 7.19 (t, 2H, J = 5.6 Hz), 4.11 (d, 4H, J = 7.2 Hz), 1.94 (m, 2H), 1.45–1.15, (m, 80H), 0.88 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 163.7, 163.6, 143.6, 135.7, 134.4, 133.2, 133.1, 129.7, 129.0, 128.4, 127.8, 127.5, 122.2, 122.1, 44.8, 36.7, 32.0, 31.8, 30.1, 29.8, 29.5, 26.6, 22.8, 14.2. Anal. Calcd for C<sub>80</sub>H<sub>110</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C, 78.25; H, 9.03; N, 2.28. Found: C, 78.01; H, 9.15; N, 2.20.

**Synthesis of PBI2.** A dry toluene solution (5 mL) of **1** (244 mg, 0.2 mmol), **T2** (273 mg, 0.6 mmol), and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (11.6 mg, 0.01 mmol) was refluxed at 120 °C for 16 h under a nitrogen atmosphere. After the reaction, the solvents were removed. The residue was purified with column chromatography (chloroform/hexane = 3/2) to yield a purple solid (75.0 mg, 27%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 8.68 (s, 2H), 8.31 (m, 4H), 7.29 (d, 2H, J = 4.8 Hz), 7.23 (m, 4H), 7.20 (d, 2H, J = 4.4 Hz), 7.05 (m, 2H), 4.11 (d, 4H, J = 7.2 Hz), 1.97 (m, 2H), 1.45–1.13 (m, 80H), 0.90 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 163.5, 163.4, 142.0, 140.6, 136.6, 135.4, 134.0, 132.7, 132.6, 129.7, 128.9, 128.6, 128.1, 127.6, 125.4, 125.2, 124.6, 122.2, 122.1, 44.9, 36.7, 32.0, 31.8, 30.2, 29.8, 29.5, 26.6, 22.8, 14.2. Anal. Calcd for C<sub>88</sub>H<sub>114</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>: C, 75.92; H, 8.25; N, 2.01. Found: C, 75.70; H, 8.26; N, 2.10.

Synthesis of PBI3. A dry toluene solution (5 mL) of 1  $(244 \text{ mg}, 0.2 \text{ mmol}), T3 (322 \text{ mg}, 0.6 \text{ mmol}), and [Pd(PPh_3)_4]$ (11.6 mg, 0.01 mmol) was refluxed at 120 °C for 16 h under a nitrogen atmosphere. After the reaction, the solvents were removed. The residue was purified with column chromatography (chloroform/hexane = 2/3) to yield a green solid (93.4 mg, 30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 8.69 (s, 2H), 8.33 (m, 4H), 7.27 (m, 2H), 7.23 (m, 2H), 7.20 (d, 2H, J = 3.6 Hz), 7.11 (m, 6H), 7.04 (m, 2H), 4.12 (d, 4H, J = 6.8 Hz), 1.99 (m, 2H), 1.45–1.10 (m, 80H), 0.90 (m, 12H).  $^{13}$ C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 163.4, 163.3, 142.6, 142.2, 140.3, 139.9, 137.3, 136.8, 135.3, 135.1, 133.9, 132.6, 132.4, 129.7, 128.9, 128.7, 128.0, 127.6, 125.2, 125.0, 124.9, 124.5, 124.1, 122.2, 44.9, 36.8, 32.0, 31.8, 30.2, 29.8, 29.5, 26.6, 22.8, 14.2. Anal. Calcd for C<sub>96</sub>H<sub>118</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: C, 74.08; H, 7.64; N, 1.80. Found: C, 74.30; H, 7.47; N, 1.90.

#### 3. Results and Discussion

N,N-Bis(2-decyl-1-tetradecyl)-1,7-dibromoperylene-3,4,9,10tetracarboxylic acid bisimide (1) was synthesized by the Nalkylation between 1,7-dibromoperylene-3,4,9,10-tetracarboxvlic acid bisanhydride and 2-decyl-1-tetradecylamine in acetic acid as described in previous literature.<sup>15,44</sup> Two thiophene derivatives with tributylstannyl functionality (T2 and T3) were synthesized from the corresponding bromothiophene derivatives (5-bromo-2,2'-bithiophene and 5-bromo-2,2':5',2"-terthiophene, respectively) by treatment with *n*-BuLi and Bu<sub>3</sub>SnCl.<sup>45</sup> The structures of 1, T2, and T3 were characterized by <sup>1</sup>H NMR measurements. Stille coupling was then carried out at 120 °C for 16h between 1 and 2-(tributylstannyl)thiophene (T1) in the presence of [Pd(PPh<sub>3</sub>)<sub>4</sub>] (Scheme 1). After the reaction, the obtained products were purified with column chromatography (chloroform/hexane = 3/2) to yield a purple viscous solid (PBI1). The structure of PBI1 was characterized by <sup>1</sup>H and <sup>13</sup>C NMR measurements to determine the synthesis of desired PBI1 (Figure 1). PBI2 and PBI3 were also synthesized by



Scheme 1. Synthesis of PBI1-3.



**Figure 1.** <sup>1</sup>H (a) and <sup>13</sup>C (b) NMR spectra of **PBI1** in CDCl<sub>3</sub>. The residual CHCl<sub>3</sub> peak is marked.

Stille coupling reaction using **T2** and **T3**, respectively. The same reaction conditions and purification used for **PBI1** were applied for those of **PBI2** and **PBI3**. The structures of **PBI2** and **PBI3** were also characterized by <sup>1</sup>H and <sup>13</sup>C NMR measurements (Figures S1 and S2). **PBI1–3** exhibited good solubility in common organic solvents, such as dichloromethane, chloroform, toluene, THF, diethyl ether, and ethyl acetate, due to the long and branched alkyl chains in the PBI units.

The thermal properties of **PBI1–3** were investigated by TG and DSC measurements. In TG profiles (Figure 2), the temperature of 5 wt % decomposition was observed over 250 °C in all samples, demonstrating that **PBI1–3** had high thermal stability. In DSC profiles (Figure S3), **PBI2** exhibited a melting temperature of 178 °C whereas **PBI1** and **PBI3** did not exhibit any transition or melting temperature, which might result in the difference in each nanomorphology.

The optical properties of **PBI1–3** were investigated by UV– vis absorption measurement (Figure 3). In the chloroform diluted solutions (Figure 3a), **PBI1–3** exhibited two absorption bands; the former absorption band can be assigned to  $\pi$ – $\pi$ \*



Figure 2. TG curves of PBI1-3 under nitrogen atmosphere.

transition in the PBI units, whereas the lower energy band is due to intramolecular charge transfer (ICT) between the donor units and the PBI units.<sup>17</sup> The ICT was gradually enhanced with an increase in the number of thiophene rings, which resulted in the absorption band at longer wavelength.<sup>46,47</sup> The optical band gaps  $(E_g^{opt}s)$  were estimated to be 1.83, 1.77, and 1.51 eV in the PBI1-3 solutions, respectively. As for the thin-film state (Figure 3b), the absorption bands were red-shifted in comparison to the solution state due to the enhancement in intermolecular stacking; **PBI1**, **PBI2**, and **PBI3** had  $E_{\sigma}^{\text{opt}}$ s of 1.79, 1.63, and 1.44 eV in the thin-film state, respectively. The optical behavior of PBI1-3 blend film was also investigated (Figure 3c). The PBI1-3 blend film exhibited wide light absorption at 800 nm due to overlapping of the absorption corresponding to ICT of PBI1-3. Furthermore, the wider absorption over 900 nm was achieved by thermal annealing. Another PBIbased D-A system was reported by Balaji and co-workers,<sup>38</sup> which is a PBI-based D-A molecule with linear pentathiophene units attached to the bay position of the PBI unit via the central thiophene unit through a  $\beta$ -linkage. The absorption of that molecule in the range of 500-900 nm was really weak. This result demonstrated that the  $\beta$ -linkage system prevented the effective conjugation between the donor and acceptor units to result in poor ICT compared to PBI1-3. Considering this fact, **PBI1–3** with the excellent light-absorption properties have potential for usage in light-harvesting applications, such as OPVs.

The electrochemical properties of **PBI1–3** were investigated in the solution states by the CV measurements (Figure 4). To determine the HOMO/LUMO levels, each measurement was calibrated with a saturated calomel electrode (SCE). **PBI1–3** exhibited clear oxidation and reduction waves, which corresponded to those of the thiophene derivatives and PBI units, respectively. LUMO levels of **PBI1**, **PBI2**, and **PBI3** were estimated to be -4.00, -4.05, and -4.08 eV, respectively, using the onset reduction potentials ( $E_{\text{red}}^{\text{onset}}$ ) of -0.40, -0.35, and -0.32 V, respectively. In D–A semiconducting materials, LUMO levels of acceptor units are generally dominant in those of materials; the obtained LUMO levels were in agreement with those of PBI units previously reported.<sup>17,36–39</sup> On the other hand, HOMO levels of D–A semiconducting materials result from those of donor units. HOMO levels of **PBI1**, **PBI2**,



Figure 3. UV-vis absorption spectra; (a) PBI1-3 chloroform solutions, (b) PBI1-3 thin films, and (c) PBI1-3 blend film. The annealing was carried out at 200 °C for 5 min under a nitrogen atmosphere.

<b>Table 1.</b> UV-VIS and UV profiles of <b>PBI</b> .
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and **PBI3** were estimated to be -5.85, -5.72, and -5.55 eV, respectively, from the onset oxidative potentials ( $E_{ox}^{onset}$ ) of 1.45, 1.33, and 1.15 V, respectively. Energy band gaps of **PBI1–3**, which were estimated from the offset between HOMO and LUMO levels, were 1.85, 1.67, and 1.47 eV, respectively; these values are in agreement with  $E_g^{opt}$ s of **PBI1–3**. In this way, the optical and electrochemical properties of **PBI1–3** were tunable by the structure of the donor units in PBI-based small molecules with the D–A architecture (Table 1).

Thin film nanostructure of **PB11–3** was investigated by GIWAXS analysis (Figure 5). All samples had isotropic diffractions at  $q \approx 0.25$  Å<sup>-1</sup>, corresponding to the distances between alkyl side chains in the PBI units. As can be seen in Figure 5b, the diffraction was observed at  $q_{xy} = 1.44$  and  $q_z = 1.45$  Å<sup>-1</sup> in the as-spun **PB12** film, which corresponds to the  $\pi$ - $\pi$  spacing of 4.36 Å in isotropic orientations. On the other hand, much weaker diffraction was observed in the annealed **PB12** film and **PB13** films exhibited diffractions corresponding to amorphous halo at  $q \approx 1.4$  Å<sup>-1</sup> in both the as-spun **PB12** film had the



Figure 4. CV profiles of PBI1–3 solutions under the nitrogen atmosphere.

	UV–vis			CV <sup>a)</sup>	
	$\lambda_{ m max}/ m nm$	$\lambda_{\rm onset}/{\rm nm}$	$E_{\rm g}^{\rm opt}/{\rm eV^{b)}}$	HOMO-LUMO/eV <sup>c),d)</sup>	$E_{\rm g}^{\rm el}/{\rm eV}^{\rm e)}$
PBI1 (solution)	412, 553	678	1.83	-5.85/-4.00	1.85
PBI1 (thin film)	422, 541	693	1.79		
PBI2 (solution)	465, 609	699	1.77	-5.72/-4.05	1.67
PBI2 (thin film)	463, 607	760	1.63		
PBI3 (solution)	495, 628	820	1.51	-5.55/-4.08	1.47
PBI3 (thin film)	503, 646	861	1.44		

a) vs. SCE. b) Calculated from  $E_g^{opt} = 1240/\lambda_{onset}$  (eV). c) Calculated from HOMO =  $-(E_{ox}^{onset} + 4.4)$  (eV). d) Calculated from LUMO =  $-(E_{red}^{onset} + 4.4)$  (eV). e) Calculated from  $E_g^{el} = (LUMO - HOMO)$  (eV).



**Figure 5.** GIWAXS images of **PBI1–3** films. The thermal annealing was conducted at 170 °C for 15 min under a nitrogen atmosphere.

highest ordered nanostructure in an isotropic manner among **PBI1–3**. The observed nanomorphology was consistent with their DSC analysis (i.e., the melting temperature was observed only in **PBI2**). The solubilized alkyl chains of the PBI units were mainly attributed to the lower crystallinity of **PBI1**, whereas the solubilized alkyl chains and twisted structure due to the terthiophene units might result in the lower crystallinity of **PBI3**. The nanomorphology of **PBI1–3** was tunable by the number of thiophene rings as well as optical, electrochemical, and thermal properties. The OPV performance is dominated by the nanomorphology of **PBI1–3** can be an advantage assuming OPV applications.

#### 4. Conclusion

A series of PBI-based small molecules with the D-A architecture PBI1-3 was synthesized systematically by a typical Stille coupling reaction. Optical, electrochemical, and thermal properties of PBI1-3 were successfully tuned by the simple modification of molecular structure (i.e., by changing the number of thiophene rings). Optical band gaps and HOMO levels were widely tunable from 1.83 to 1.44 eV, and from -5.85 to -5.55 eV, respectively. Furthermore, extremely wide light absorption over 900 nm was observed in thermal annealed PBI1-3 blend film. As for the thermal properties, only PBI2 exhibited a melting temperature (178 °C) among PBI1-3. The GIWAXS analysis demonstrated that the as-spun PBI2 film possessed the highest  $\pi$ - $\pi$  stacking nanostructure with isotropic orientations. Judging from these results, PBI1-3 achieved the tuning of various material properties and nanomorphology by the simple modification of molecular structure; this fact demonstrated that PBI-based small molecules with the D–A architecture could be a utility material for optoelectronic applications such as non-fullerene acceptor materials for OPV, and a device study is currently underway.

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## **Supporting Information**

<sup>1</sup>H and <sup>13</sup>C NMR spectra of **PBI2** and **PBI3**, and thermal analysis of **PBI1–3**. This material is available on http://dx.doi.org/10.1246/bcsj.20160178.

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