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# Integration of nitrogen into coronene bisimides

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### ABSTRACT

*N*-Decorated PBIs and CBIs have been synthesized by the combination of Pictet–Spengler condensation and subsequent oxidative aromatization based on highly electron-deficient amino-PBIs. A detailed analysis of their photophysical properties and molecular crystals has shown that the lateral aryl groups appended on the *N*-heterocycle have a negligible effect on their optical absorptions and electrochemical potentials, but the subtle modification leads to significant variations on arrangement in the solid state. © 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Derivatives of perylene-3,4:9,10-tetracarboxylic acid bisimides (PBIs) have received considerable attention as functional materials because of their outstanding optical and electronic properties, chemical and thermal stabilities, easily modified which have found their great potential in the field of photovoltaic devices,<sup>1</sup> organic field effect transistors,<sup>2</sup> light emitting diodes,<sup>3</sup> near-infrared dyes,<sup>4</sup> and constructing of graphene nanoribbons.<sup>5</sup>

Core-extended PBIs have been sought with the aim of creating various novel chromophores to improve their performance in molecular (opto)electronic devices.<sup>6</sup> Annulation of PBIs with a variety of cyclic units in the bay regions including diverse heterocycles such as sulfur-, thiophene-, and *N*-heterocycles has been actively investigated.<sup>7</sup> An *S*-heterocyclic annulated PBI with tunable self-assembly behavior by the inclusion of different guest molecules has been reported recently by our group.<sup>8</sup> Furthermore, bay-regions annulated *S*-diPBIs or *N*-diPBIs that bears two chromophores coupled by triply linkage displays extraordinary doubly bowl-shaped structures.<sup>9</sup>

Recently, we have presented regiospecifically pyridyl annulated PBIs by a facile synthesis, which realized the light-promoted cyclization in high yields.<sup>10</sup> The incorporation of electron-rich or electron-deficient heterocycles directly into the framework of PBIs can offer the means by which properties of them can be modulated

and also provide access to various new potentially useful molecular scaffold by affording a reaction site for further transformation.

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The Pictet–Spengler condensation of aromatic amines with aldehydes and ketones has been explored extensively for the preparation of tetrahydroisoquinolines and  $\beta$ -cabolines.<sup>11</sup> In general, the electron-rich aromatic amines used to undergo Pictet–Spengler reaction to achieve *N*-heterocycles can improve the reaction effectively.<sup>12</sup> In this contribution, we describe our endeavors to develop *N*-decorated coronene bisimides, a new family of coreextended PBIs, from the highly electron-deficient PBI amines and corresponding aldehydes by the combination of Pictet–Spengler reaction and subsequent oxidative aromatization. Accordingly, we elucidate the crystal structures with different substituents appended on the *N*-heterocylces, as well as their influence on photophysical properties (Fig. 1).



Fig. 1. The molecular structures of PBIs, CBIs, and N-decorated CBIs.



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#### 2. Results and discussion

#### 2.1. Synthesis

The key starting materials are nitrated PBIs (Scheme 1). Previous synthetic reports of regiospecific nitration of PBI utilizing  $N_2O_4$  or



Scheme 1. Nitration of perylene bisanhydride and subsequent imidization.

HNO<sub>3</sub> were unsatisfactory because of the harsh conditions needed and low yield of both mono- and dinitro-PBI products.<sup>7a,13</sup> We have found the practical and reproducible synthesis of mono- and dinitroperylene bisanhydride in one pot through dropping fuming nitric acid to a solution of perylene bisanhydride (**1**) in chloroform



Scheme 2. The synthetic route toward N-decorated PBIs.

at room temperature. After imidization, the dark red mixture was separated by column chromatograph to produce well-soluble dinitro-PBI (first fraction, yield 46.3%) and mononitro-PBI as the second fraction (yield 25.2%) easily. There was no 1,6-substituted isomer obtained in the dinitration product as evidenced by <sup>1</sup>H NMR and HMBC spectroscopy. The <sup>3</sup>*I*<sub>CH</sub> correlations between protons H<sub>b</sub>

 $(\delta = 8.84)$  and H<sub>d</sub> ( $\delta = 8.96$ ) and carbonyl carbons ( $\delta = 161.96$ , 162.86) determined the assignments of H<sub>a</sub> ( $\delta = 8.44$ ), H<sub>b</sub>, and H<sub>d</sub>. The presence of  ${}^{3}J_{CH}$  coupling from protons both H<sub>b</sub> and H<sub>d</sub> to the same carbon ( $C_c$ ,  $\delta = 129.74$ ) could be observed for 1,7-isomer but not in the case of 1,6-isomer because of their different symmetry (see Supplementary data).

Recent research results show that many protocols have been employed for the reducing nitroarenes to arylamines,<sup>14</sup> the catalytic hydrogenation of hydrazine and Pd/C in 1,2-dimethoxyethane (DME) was found to be the most effective for achieving both monoamino-PBI (**4**) and diamino-PBI (**7**) quantitatively. Subsequently, we applied a Pictet–Spengler reaction of **4** with benzaldehyde or 2-pyridinecarboxaldehyde using triflic acid as the catalyst, and DMF as the solvent to directly afford the corresponding *N*-decorated PBIs, accompanied by oxidative aromatization in one pot (Scheme 2).

We then envisaged that the reaction of regioisomerically 1,7diamino-PBIs with aldehyde under the same conditions could produce the definite N-decorated coronene bisimides (CBIs). Unexpectedly, when we use benzaldehyde as the reactant, there were two isomers of N-decorated CBIs produced in the reaction simultaneously, and the molar ratio of 8 to 8' was 2:1, which was demonstrated by <sup>1</sup>H NMR and HMBC spectroscopy (see Supplementary data). However, when 2-pyridinecarboxaldehyde was selected to prove the presence of the isomers is not a case. We just find the trace amount of the normal N-decorated CBIs (9), but its isomerization compound  $\mathbf{9}'$  existed in the resulting mixture as a main product, which was proved by <sup>1</sup>H NMR and HMBC spectroscopy and X-ray single-crystal analysis as a definite structure (Scheme 3). This phenomenon may be explained by the occurrence of C-N transformation in the process of the reaction with highly electrondeficient PBI amines that leads to the presence of isomers in the resulting mixture. The mixture of *N*-decorated products (8 and 8') could not be separated by column chromatography. Regioisomerically pure N-decorated CBI 8 was obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and hexane, which structure is unambiguously characterized by mass spectrometry, NMR spectroscopy, and X-ray singlecrystal analysis. A full assignment of the signals of compound 8 and 9' has been achieved using a HMBC experiment (see Supplementary data).

#### 2.2. X-ray single-crystal structure analysis

X-ray structures of **8** and **9**' have been performed for single crystals grown by slow evaporation of a solution of *N*-decorated CBIs. They both show almost planar conformation of the perylene core, and the lateral aryl groups appended on the *N*-heterocycles have a significant effect on the crystal structure in the solid state. As shown in Fig. 2, the molecules of **8** regularly stack along the b-axis of the unit cell that form a unique columnar structure without



Scheme 3. The synthetic route toward N-decorated CBIs.



**Fig. 2.** Space-filling diagram of *N*-decorated CBI **8** sandwiched by two toluene molecules (carbon in dark green, oxygen in red, nitrogen in blue, and hydrogen in white color).

strong  $\pi - \pi$  interactions. In the structure, each molecule is sandwiched by two toluene molecules which from the solvent. The pervlene core and additive toluene molecule packed through weak C–C interactions (3.31 Å) and C–H interactions (2.66–2.86 Å). The weak hydrogen bonds are observed between the molecules of neighboring stacks, and the lateral phenyl groups are twisted by 49.3° in relative to the perylene backbone. In contrast, the lateral pyridyl groups are less twisted by just 23.4° in compound 9', and the molecules pack along the *a*-axis. The repeated unit in crystal 9'contains six molecules (Fig. 3), in which the main contacts are C-H···O contacts (2.44–2.69 Å) between the lateral pyridyl hydrogen and the oxygen atoms of carbonyl. Together with short distances between the phenyl group on the imide position and lateral pyridyl hydrogen with C···H distances in the range of 2.84–2.89 Å that is indicative of the C–H $\cdots$  $\pi$  interactions, and close C-H···O contacts (2.51 Å) between phenyl hydrogen and the oxygen atoms of carbonyl, this network structure for promising absorbing materials can be expected.



Fig. 3. Crystal structure of N-decorated CBI 9'.

#### 2.3. Optical and electrochemical properties

Room temperature absorption spectra of these compounds are shown in Fig. 4, and optical data are listed in Table 1. The UV–vis absorption spectra showed that they all exhibit well-defined vibronic  $\pi$ – $\pi$ \* transition absorption bands with high extinction coefficients. As a result of the extended perylene core along the short molecular axis, the *N*-decorated PBIs and CBIs are blueshifted relative to the corresponding parent compound (PBI).<sup>15</sup> In the spectra of *N*-decorated PBIs (**5** and **6**), the typical perylene vibronic structure can be seen at a shorter wavelength with an absorbance maximum at 476 nm, 474 nm, respectively, that give



Fig. 4. UV-vis absorption spectra: N-decorated PBIs 5 (black) and 6 (green), N-decorated CBIs 8 (blue) and 9' (red) in chloroform.

rise to the yellow color. The longest absorbance maxima of *N*-decorated CBIs (**8** and **9**') are hypsochromically shifted compared to all-carbon parent CBI (511 nm,  $\varepsilon_{max}=71,500 \text{ M}^{-1} \text{ cm}^{-1}$  in CHCl<sub>3</sub>)<sup>16</sup> as a result of incorporation of electronegative nitrogen atoms. In the region of shorter wavelengths, up to 400 nm, the spectra of **8** and **9**' disclose a small red-shift and sharp band with a defined structure at 352 nm, 354 nm to that of parent CBI (338 nm). Furthermore, the longest absorbance maxima of phenyl substituted products both for PBIs and CBIs are just slightly bathochromically shifted to their pyridyl counterpart. The fluorescence quantum yields of these *N*-decorated PBIs and CBIs are largely decreased, and they all possess small Stokes shifts of about 8–17 nm.

Cyclic voltammentry of compounds **5**, **6**, **8**, and **9**' in  $CH_2Cl_2$  has been investigated, and electrochemical data are summarized in Table 1. They all show two reversible reduction waves (Fig. 5). Compared with PBI,<sup>17</sup> the first half-wave reduction potentials versus Fc/Fc<sup>+</sup> are -1.00, -1.01, -1.04, and -1.05 V for **5**, **6**, **8**, and **9**', respectively, indicating that the incorporation of nitrogen as well as their substituents does not induce a significant shift on electrochemical behavior. LUMO levels estimated by the onset of reduction peaks are -3.88 eV for **5**, -3.86 eV for **6**, -3.87 eV for **8**, and -3.82 eV for **9**', respectively. According to the optical gap that were determined from the onset absorption of UV–vis spectra, HOMO levels of these *N*-decorated PBIs and CBIs are deeper than that of parent PBI, indicating effective tunability of energy levels for promising electronic applications.

#### 3. Conclusion

In conclusion, we have presented the facile synthesis of novel *N*-decorated perylene bisimides (PBI) and coronene bisimides (CBI) derivatives by the combination of Pictet–Spengler condensation and subsequent oxidative aromatization from highly electron-deficient amino-PBIs with different aldehydes. A detailed analysis of their photophysical properties and molecular crystals has shown that the lateral aryl groups appended on the *N*-heterocycle have a negligible effect on their optical absorptions and electrochemical potentials, but the subtle modification leads to significant variations on the packing arrangement. Extension of this synthetic strategy to highly ordered heterocoronene bisimides as well as detailed investigation to clearly understand the reaction mechanism for the occurrence of different isomers is currently underway.

#### Table 1

Compound	Abs <sub>max</sub> <sup>a</sup> [nm]	$\varepsilon_{\max}^{a}$ [M <sup>-1</sup> cm <sup>-1</sup> ]	Fluo <sub>max</sub> <sup>b</sup> [nm]	$\Phi_{\rm fl}{}^{\rm c}$	$E_{1r}^{d}$ [V]	$E_{2r}^{d}$ [V]	$E_{\text{onset}}^{d}$ [V]	$E_{\rm LUMO}^{\rm e} [\rm eV]$	$E_{\rm g}^{\rm f}$ [eV]	$E_{\rm HOMO}^{\rm g}$ [eV]
PBI	527	80,900	534	1.00	-0.96	-1.22	-0.89	-3.91	2.30	-6.21
5	476	68,662	493	0.74	-1.00	-1.30	-0.92	-3.88	2.52	-6.40
6	474	68,376	485	0.36	-1.01	-1.29	-0.94	-3.86	2.55	-6.41
8	488	27,092	502	0.25	-1.04	-1.36	-0.93	-3.87	2.47	-6.34
<b>9</b> ′	480	8326	488	0.10	-1.05	-1.34	-0.98	-3.82	2.49	-6.31

 $^{a}\,$  Measured in dilute CHCl\_3 solution (1.0 $\times 10^{-5}$  M).

<sup>b</sup> Measured in dilute CHCl<sub>3</sub> solution ( $1.0 \times 10^{-6}$  M).

 $^{c}$  Average deviation for  $\Phi_{\rm fl}$ ,  $\pm 0.04$ , determined with PBI (*N*,*N*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide,  $\Phi_{\rm fl}$ =1.00 in CHCl<sub>3</sub>) as the standard.

 $^{\rm d}$  Half-wave potential in CH\_2Cl\_2 solution versus Fc/Fc<sup>+</sup>

<sup>e</sup> Estimated by the onset of reduction peaks and calculated according to  $E_{LUMO} = -(4.8 + E_{onset}) \text{ eV}$ .

<sup>f</sup> Calculated by the onset of absorption according to  $E_g=1240/\lambda_{onset}$ .

 $^{\rm g}\,$  Calculated according to  $E_{\rm HOMO}{=}(E_{\rm LUMO}{-}E_{\rm g})$  eV.



Fig. 5. Reductive cyclic voltammograms of 5, 6, 8, and 9' in  $CH_2Cl_2$  (electrolyte, 0.1 M  $Bu_4NPF_6$ ) with a scan rate of 100 mV/s versus  $Fc/Fc^+$ .

#### 4. Experimental section

#### 4.1. General materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. N,N'-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI) was synthesized according to the literature.<sup>18</sup> <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. *J* values are expressed in hertz and quoted chemical shifts are in parts per million downfield from tetrame-thylsilane (TMS) reference using the residual protonated solvent as an internal standard. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplets). Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer.

UV—vis spectra were measured with Hitachi (Model U-3010) UV—vis spectrophotometer in a 1-cm quartz cell. Fluorescence excitation and emission spectra were recorded with a Hitachi FP-6600 FL fluorimeter at room temperature. And fluorescence quantum yields were determined by optical dilute method with *N*,*N*'-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI) in CHCl<sub>3</sub> as reference ( $\Phi_{\rm fl}$ =1.0).<sup>15</sup> Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation at a scan rate of 50 mV s<sup>-1</sup>, with using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker for the calibration of potential. 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (HPLC grade) was employed as the supporting electrolyte.

# **4.2.** Nitration of perylene bisanhydride and subsequent imidization (2 and 3)

A mixture of perylene-3,4:9,10-tetracarboxylic acid bisanhydride **1** (5.0 g, 12.74 mmol) in CHCl<sub>3</sub> (150 mL) was stirred at room temperature, and then fuming nitric acid (50 mL) was added dropwise over a time period of 2 h and the mixture was stirred for an additional 3 h at room temperature. Then the dark red mixture was poured into water (500 mL) slowly. The resultant precipitate was filtered through a funnel, washed with a large amount of water until the filtrate became neutral. The residue was dried at 110 °C for 5 h to give crude dark red powder (5.8 g). The crude product was used directly for the next step without further purification.

Next, A suspension of nitrated perylene bisanhydrides (5.8 g) obtained in the above reaction, and excess 2,6-diisopropylaniline (7.05 g, 39.76 mmol) in 100 mL of *n*-propionic acid under N<sub>2</sub> atmosphere, the reaction mixture was stirred and heated at 140 °C for 12 h. After being cooled to room temperature, the resulting solution was poured into 500 mL of water. The red solid was collected, washed with water and brine until neutral and dried in a vacuum. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/PE=1:3 to 1:1 in v/v) to afford 1,7-dinitro-PBI (**3**, first fraction: 4.73 g, 46.3%) and 1-nitro-PBI (**2**, second fraction: 2.43 g, 25.2%) as dark red solids.

4.2.1. N,N'-Di(2,6-diisopropylphenyl)-1-nitroperylene-3,4:9,10-tetracarboxylic acid bisimide (**2**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =8.92 (d, J=8.0 Hz, 1H), 8.80–8.87 (m, 4H), 8.73 (d, J=8.0 Hz, 1H), 8.36 (d, J=8.0 Hz, 1H), 7.50–7.55 (m, 2H), 7.35–7.38 (m, 4H), 2.68–2.78 (m, 4H), 1.18–1.20 (m, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm)  $\delta$ =163.51, 163.19, 163.12, 162.30, 148.27, 145.95, 145.88, 136.36, 133.88, 133.81, 132.40, 132.13, 130.50, 130.38, 130.27, 130.20, 129.99, 128.58, 128.27, 127.64, 127.22, 127.17, 125.25, 125.17, 124.69, 124.63, 124.53, 124.27, 123.79, 123.44, 29.67, 29.61, 24.35. MS (MALDI-TOF): calcd for M<sup>-</sup>, 755.3; found, 755.1.

4.2.2. N,N'-Di(2,6-diisopropylphenyl)-1,7-dinitroperylene-3,4:9,10tetracarboxylic acid bisimide (**3**). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =8.96 (s, 2H), 8.84 (dd, 2H), 8.40–8.44 (m, 2H), 7.51–7.58 (m, 2H), 7.36–7.40 (m, 4H), 2.65–2.77 (m, 4H), 1.19–1.20 (m, 24H). <sup>13</sup>C NMR  $({\rm CDCl}_3, 100$  MHz, ppm)  $\delta{=}162.86, 162.47, 161.96, 161.59, 149.25, 148.88, 145.90, 145.82, 145.75, 133.58, 132.05, 131.11, 130.69, 130.52, 130.34, 130.16, 130.07, 129.84, 129.74, 129.54, 129.48, 129.38, 128.60, 128.36, 128.24, 127.22, 127.07, 126.33, 125.85, 124.95, 124.76, 124.67, 124.58, 123.96, 29.75, 29.68, 29.61, 24.36. MS (MALDI-TOF): calcd for M<sup>-</sup>, 800.3; found, 800.4.$ 

#### 4.3. Synthesis of amino-PBIs (4 or 7)

To a solution of 1-nitro-PBI **2** or 1,7-dinitro-PBI **3** (0.25 mmol) in 1,2-dimethoxyethane (10 mL) was added about 10% palladium on charcoal (20 mg), then 0.2 mL of 85% hydrazine wad added into the reaction. The mixture was stirred at 83 °C for 15 min, and then cooled to room temperature. The catalyst was removed and the solvent was distilled to leave a blue solid. The crude product either monoamino-PBI **4** or diamino-PBI **7** was used directly for the next step without further purification because of the instability of the amino in the air.

#### 4.4. Synthesis of N-decorated PBIs and CBIs

4.4.1. Compound (5). A mixture of monoamino-PBI 4 (200 mg) and benzaldehyde (175 mg, 1.65 mmol) in DMF (10 mL) containing triflic acid (0.1 mL) was stirred at 110 °C until the starting material could not be detected by TLC. Then the reaction mixture was cooled to room temperature and diluted with water, alkalized with 15% aqueous NaOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic phase was washed with brine and water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography ( $CH_2Cl_2/PE=1:1$  in v/v) to afford 5 (94 mg, 42.1%) as an orange-yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =9.81 (s, 1H), 9.75 (s, 1H), 9.51 (d, *J*=8.0 Hz, 2H), 9.31 (d, *J*=8.0 Hz, 1H), 9.26 (d, J=8.0 Hz, 1H), 8.05 (d, J=8.0 Hz, 2H), 7.66-7.75 (m, 3H), 7.51-7.56 (m, 2H), 7.37-7.41 (m, 4H), 2.79-2.91 (m, 4H), 1.20-1.24 (m, 24H). <sup>13</sup>C NMR (THF- $d_8$ , 100 MHz, ppm)  $\delta$ =164.42, 164.12, 164.00, 162.01, 146.91, 146.83, 145.41, 139.58, 135.63, 135.54, 134.20, 133.13, 132.20, 132.11, 132.03, 131.65, 130.49, 130.33, 130.05, 129.61, 129.49, 127.96, 127.21, 125.82, 125.02, 124.93, 124.58, 124.53, 124.36, 124.30, 124.20, 123.30, 122.69, 119.56, 30.16, 30.09, 24.50, 24.40. MS (MALDI-TOF): calcd for M<sup>-</sup>, 811.3; found, 811.3. HRMS calcd for C<sub>55</sub>H<sub>46</sub>N<sub>3</sub>O<sup>+</sup><sub>4</sub> [MH<sup>+</sup>], 812.34828; found, 812.34618.

4.4.2. Compound (6). A mixture of monoamino-PBI 4 (200 mg) and 2-pyridinecarboxaldehyde (180 mg, 1.68 mmol) in DMF (10 mL) containing triflic acid (0.15 mL) was stirred at 110 °C until the starting material could not be detected by TLC. Then the reaction mixture was cooled to room temperature and diluted with water, alkalized with 15% aqueous NaOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic phase was washed with brine and water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography ( $CH_2Cl_2/PE=1:1$  in v/v) to afford 6 (83 mg, 37.4%) as an orange-yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =10.47 (s, 1H), 9.79 (s, 1H), 9.51 (dd, 2H), 9.31 (dd, 2H), 8.99 (d, J=8.0 Hz, 1H), 8.58 (d, J=8.0 Hz, 1H), 8.12-8.16 (m, 1H), 7.57-7.62 (m, 1H), 7.51-7.55 (m, 2H), 7.38-7.42 (m, 4H), 2.81-2.92 (m, 4H), 1.20–1.24 (m, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm)  $\delta = 164.13, 164.04, 164.01, 163.95, 157.89, 157.44, 149.48, 146.04,$ 144.52, 138.23, 136.03, 135.13, 134.95, 133.93, 131.86, 130.88, 130.62, 130.51, 130.21, 130.09, 129.17, 127.76, 126.61, 126.32, 124.72, 124.59, 124.50, 124.30, 124.13, 123.97, 123.66, 123.49, 122.82, 122.72, 120.21, 29.70, 29.63, 24.49, 24.41. MS (MALDI-TOF): calcd for M<sup>-</sup>, 812.3; found, 812.4. HRMS calcd for C<sub>54</sub>H<sub>45</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>], 813.34353; found, 813.34306.

4.4.3. Compound (8 and 8'). A mixture of diamino-PBI 7 (400 mg) and benzaldehyde (696 mg, 6.56 mmol) in DMF (20 mL) containing

triflic acid (0.25 mL) was stirred at 110 °C until the starting material could not be detected by TLC. Then the reaction mixture was cooled to room temperature and diluted with water, alkalized with 15% aqueous NaOH solution and extracted with  $CH_2Cl_2$  (20 mL). The organic phase was washed with brine and water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/PE=1:1 in v/v) to afford **8** and **8**' (150 mg, 30%, the ratio of **8** to **8**' is 2:1) as yellow solids. Then the mixture isomers were recrystallized with  $CH_2Cl_2$  and hexane and the regioisomerically pure **8** was obtained.

Compound **8**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =10.41 (s, 2H), 10.30 (s, 2H), 8.27 (d, *J*=8.0 Hz, 4H), 7.75–7.85 (m, 6H), 7.56–7.59 (m, 2H), 7.43–7.45 (m, 4H), 2.95–2.97 (m, 4H), 1.24–1.26 (m, 24H). <sup>13</sup>C NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 MHz, ppm)  $\delta$ =163.90, 163.75, 162.72, 145.43, 143.14, 138.13, 134.36, 131.13, 130.88, 130.58, 130.30, 129.68, 129.25, 127.51, 125.15, 124.47, 124.22, 123.23, 122.47, 120.09, 118.37, 31.48, 29.26, 24.14, 22.60. MS (MALDI-TOF): calcd for M<sup>-</sup>, 912.4; found, 912.7. HRMS calcd for C<sub>62</sub>H<sub>49</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup> [MH<sup>+</sup>], 913.37483; found, 913.37329.

Compound **8**': <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =10.39 (s, 2H), 10.35 (s, 2H), 8.25 (s, 2H), 8.26 (s, 2H), 7.75–7.85 (m, 6H), 7.54–7.60 (m, 2H), 7.41–7.46 (m, 4H), 2.87–3.04 (m, 4H), 1.21–1.27 (m, 24H). MS (MALDI-TOF): calcd for M<sup>-</sup>, 912.4; found, 912.7.

4.4.4. Compound (9'). A mixture of diamino-PBI 7 (300 mg) and 2pyridinecarboxaldehyde (520 mg, 4.86 mmol) in DMF (15 mL) containing triflic acid (0.15 mL) was stirred at 110 °C until the starting material could not be detected by TLC. Then the reaction mixture was cooled to room temperature and diluted with water. alkalized with 15% aqueous NaOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic phase was washed with brine and water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel column chromatography ( $CH_2Cl_2/THF=150:1$  in v/v) to afford **9**' (102 mg, 27.7%) as yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ =11.12 (s, 2H), 10.36 (s, 2H), 9.11–9.12 (m, 2H), 8.79–8.81 (d, J=8.0 Hz, 2H), 8.25–8.29 (m, 2H), 7.71–7.74 (m, 2H), 7.55–7.62 (m, 2H), 7.42–7.48 (m, 4H), 2.92–3.06 (m, 4H), 1.23–1.28 (m, 24H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm)  $\delta$ =164.12, 164.02, 163.93, 157.95, 157.49, 149.52, 146.03, 144.49, 138.17, 136.01, 135.10, 134.98, 133.90, 131.83, 130.88, 130.85, 130.60, 130.48, 130.21, 130.09, 129.36, 129.15, 128.55, 127.73, 126.59, 126.30, 125.62, 124.69, 124.59, 124.50, 124.27, 124.10, 123.94, 123.63, 123.47, 122.80, 122.70, 120.17, 29.70, 29.62, 24.50, 24.41. MS (MALDI-TOF): calcd for M<sup>-</sup>, 914.4; found, 914.2. HRMS calcd for  $C_{60}H_{47}N_6O_4^+$  [MH<sup>+</sup>], 915.36533; found, 915.36287.

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#### Supplementary data

<sup>1</sup>H and <sup>13</sup>C spectra for all the new compounds. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/ j.tet.2012.08.084.

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