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One-Pot Facile Synthesis of Pyridyl Annelated Perylene Bisimides

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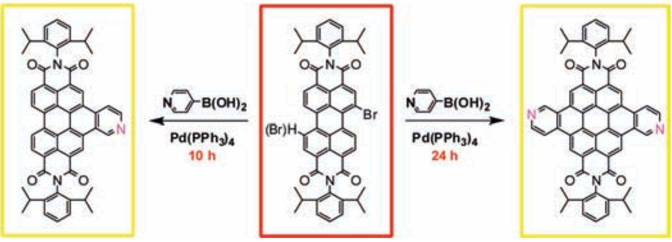
ABSTRACT



Two regiospecifically pyridyl annelated perylene bisimides have been prepared in one pot by the combination of the Suzuki cross-coupling reaction and subsequent light-promoted cyclization in high yields.

Perylene bisimides (PBIs) as chromophores are the subjects of current research interest largely due to their exceptional optical and electronic properties, photochemical stabilities, high quantum yields, and ability to self-assemble into ordered supramolecular structures.[1] In particular, they have found wide applications as electron transfer cascades,[2] photovoltaic devices,[3] organic field effect transistors,[4] liquid crystalline materials,[5] and NIR absorbing systems.[6]

The extension of the aromatic core of perylene is a currently active topic, the goal being to modulate their structure and properties to improve their performance as functional materials in devices. Arguably, extension along the long molecular axis from perylene to hexarylene bisimides (**1**) induces a significant bathochromic shift to the near-infrared (NIR),[6c] and enlargement along the short axis such as coronene derivatives (**2**) causes a hypsochromic shift, leading to yellow chromophores with high stability,[5a,7] or results in almost full absorption in the visible region with high extinction coefficient for the triply linked fully conjugated oligomeric perylene bisimides.[8] Annelation of PBIs with diverse heterocycles in bay-regions have also been

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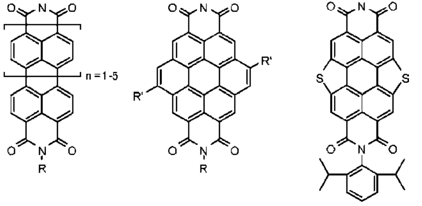
investigated.[9] Recently, we have developed a facile synthetic methodology to produce bay-annelation of *S*-heterocyclic PBI (**3**), which displays extraordinary supramolecular self-assembly behavior by the inclusion of different guest molecules.[10]



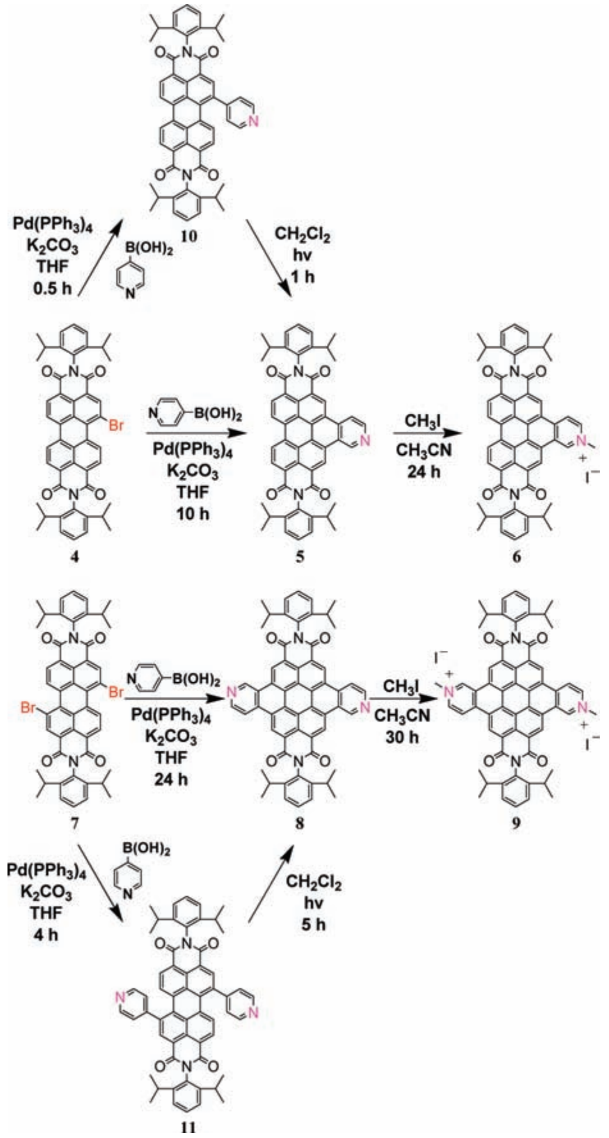
1 **2** **3**

Figure 1. PBIs and core-extended PBIs.

Pyridine is one of the most widely used motifs for providing versatile reactivity for the synthesis of biologically active compounds and has been observed to act as a good ligand that can afford diverse linking sites to transition metal ions with tunable binding strength and directionality. In recent years, pyridine complexes[11] have also been used as building blocks to form various supramolecular structures such as macrocycles, nanotubes, and coordination polymers. It is well-known that conventional imidization with pyridyl amines,[12] as well as the substitution with pyridin-ol or thiol in the bay-regions[13] of PBIs, has often been employed to prepare PBI derivatives that bearing pyridine groups; however, transition-metal-catalyzed direct PBIs-pyridine cross-coupling has not yet been reported.

Herein, we present the first example of a one-pot synthesis of two regiospecifically pyridyl annelated PBIs in the bay-regions by the combination of the Suzuki cross-coupling reaction and subsequent light-promoted cyclization. Furthermore, the ionic derivatives by quaternization have also been synthesized, of which the optical properties are significantly changed.

Scheme 1. Synthesis of Regiospecifically Pyridyl Annelated PBIs and Subsequent Quaternization



The synthesis of monobrominated PBIs and the separation of dibrominated PBIs are always intriguing targets.[14] We have found the synthesis of monobromo- and dibromoperylene bisanhydride in one pot with 1.0 equiv of Br_2 in a shorter reaction time (see Supporting Information). After imidization, the mixture was separated by column chromatography to produce 1,7(6)-dibromo-PBI (first fraction, yield

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25%) and 1-bromo-PBI (second fraction, yield 37%). The 1,6-isomer could be removed by recrystallization from toluene according to the literature[15] to assign unequivocally the regioisomerically pure 1,7-isomer (total yield 15%), which is a prerequisite for the synthesis of pure disubstituted perylene bisimides derivatives and further investigation of their electro-optical properties.

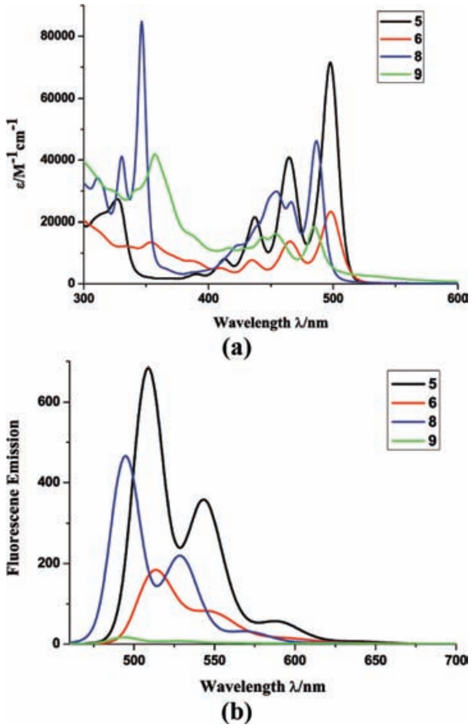

Figure 2. (a) UV−vis absorption and (b) fluorescence emission spectra of **5** (black line), **6** (red line), **8** (blue line), and **9** (green line) in THF at room temperature.

We chose 4-pyridylboronic acid as organoboron reagent for two reasons: it is more stable than 2-pyridylboronic acid,[16] and the desired pyridyl annelated product has higher symmetry. The reaction of bromo-PBIs with pyridin-4-ylboronic acid under Suzuki conditions using $Pd(PPh_3)_4$ as the catalyst, K_2CO_3 (aqueous 2 M) as the base, and THF as the solvent, successfully affords pyridyl substituted PBIs in high yield (82% yield, 30 min for **10**, and 69% yield, 4 h for **11**); subsequently exposing to sunlight produces the pyridyl annelated PBIs (**5** and **8**) quantitatively (Scheme 1). Remarkably, when brominated PBIs are treated with pyridin-4-ylboronic acid under the same Suzuki conditions with prolonged reaction time (10 h for **5**, and 24 h for **8**), they directly afford the desired heterocyclic annelated PBIs in yields of 70% for **5** and 62% for **8.** Compared to other aryl substituted PBIs reported in the literature,[7] the pyridyl substitued PBIs are highly inclined to cyclization, probably by light.

Differring from $\pi-\pi$ interaction, various noncovalent intermolecular interactions such as ionic self-assembly from oppositely charged systems are of paramount importance for creating new columnar superstructures and allowing one to tune liquid crystal (LC) properties.[17] Accordingly, to prove the reactivities of the pyridine units annelated on the highly electron-deficient PBI core, quaternization is carried out by treatment with an excess of methyl iodide in boiling acetonitrile to afford the positively charged heterocyclic annelated PBIs (**6** and **9**) readily.

All of the compounds are unambiguously characterized by mass spectrometry, NMR spectroscopy, and elemental analyses. Compound **5** is highly soluble in various organic solvents, such as CH_2Cl_2, acetone, and toluene, except in the case of the doubly cyclized product **8**, which dissolved reasonably only in $CHCl_3$ and toluene. The positively charged PBIs **6** and **9** only dissolve readily in CH_3CN and DMSO.

Table 1. Photophysical Properties of the Heterocyclic Annelated PBIs

	Abs $_{max}^{a}$ [nm]	ε^{a} [M^{-1} cm^{-1}]	Fluor$_{max}^{b}$ [nm]	Φ_{fl}^{c}
5	498	71 500	509	1.00
6	498	23 300	514	0.59
8	486	46 200	495	0.80
9	485	18 600	494	0.02

[a] Measured in dilute THF solution (1.0 × 10^{-5} M). [b] Measured in dilute THF solution (1.0 × 10^{-6} M). [c] In THF, PBI (*N,N′*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide, $\Phi_{fl} = 1.00$ in $CHCl_3$) as the standard.

Room-temperature absorption and emission spectra of these compounds are shown in Figure 2. The UV−vis absorption spectra showed that they all exhibit well-defined vibronic $\pi-\pi^*$ transition absorption bands with high extinction coefficients ($\varepsilon_{max} = 71\,500$ M^{-1} cm^{-1} for **5**, and $\varepsilon_{max} = 46\,200$ M^{-1} cm^{-1} for **8**). Compounds **5** and **8** are blue-shifted relative to the corresponding parent compound (PBI)[18] as a reflection of the extended perylene core along the short molecular axis. The spectra of **8** shows a sharp band with a defined structure at 346 nm, whereas after quaternization, the band with a maximum absorbance of 357 nm in the spectra of **9** is broad. The longest absorbance maximum of **8** at 486 nm is slightly hypsochromically shifted compared to dibenzocoronene bisimide (494 nm, $\varepsilon_{max} = 66\,000$ M^{-1} cm^{-1} in $CHCl_3$).[7] The solution of **5** and **8** is brilliant greenish-yellow, and the fluorescence quantum yield of **5** is the same as that of PBI. The absorption intensity of compounds **6** and **9** is largely decreased and the fluorescence is highly quenched, while the absorbance maxima do not show a significant shift after quaternization (Figure 2b).

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Cyclic voltammetry of heterocyclic annelated PBIs **5** and **8** in CH_2Cl_2 has been investigated, and each shows one reversible reduction wave and one quasireversible reduction wave. Compared with PBI,[19] the half-wave reduction potentials vs Fc/Fc^+ are −0.99, −1.27 V for **5**, and −1.01, −1.30 V for **8**, indicating that the incorporation of pyridine moieties does not induce a significant shift on electrochemical behavior.

In conclusion, we report the one-pot synthesis of regiospecifically pyridyl annelated PBIs by combination of the Suzuki reaction and subsequent light-promoted cyclization. Quaternization on the highly electron-deficient PBI system has been successfully achieved, and the optical properties of these positively charged PBIs can be largely tuned. Future work on the use of more elaborate counterions and metal coordination to tune their supramolecular organization is currently underway.

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Supporting Information Available: Experimental procedure and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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