

Iridium-Catalyzed Direct Tetraborylation of Perylene Bisimides

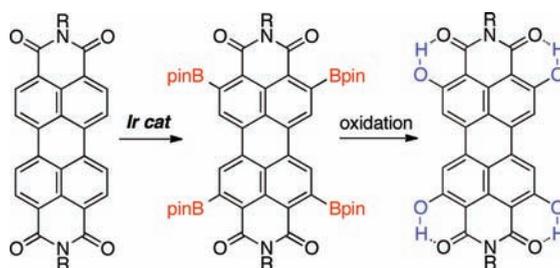
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ABSTRACT



Treatment of perylene bisimides (PBIs) with bis(pinacolato)diboron in the presence of an iridium catalyst provides tetraborylated PBIs at 2,5,8,11-positions in good yields with perfect regioselectivity. The planar structure of the perylene core has been confirmed by X-ray diffraction analysis. Oxidation of tetraborylated PBI with hydroxylamine hydrochloride affords tetrahydroxy PBI in excellent yield, which exhibits a substantially blue-shifted absorption spectrum due to an intramolecular hydrogenbonding interaction between carbonyl and hydroxy groups.

Perylene tetracarboxylic acid bisimide (PBI) is an important class of dyes for widespread use. This molecule has received much attention for wide areas of applications toward organic material devices such as organic solar cells, organic light-emitting diodes, single molecule spectroscopy, field effect transistors, and biomedical sensors.¹ The synthesis of novel PBI derivatives often utilizes modification of the perylene core by halogenation at the bay area, namely, 1,6,7,12-positions. This is due to the high reactivity of the bay area toward electrophilic substitutions. On the other hand, functionalization at 2,5,8,11-positions of PBIs has been unavailable until our recent

reports on direct alkylation and arylation of PBIs at 2,5,8,11-positions through Ru-catalyzed C–H bond cleavage.^{2,3} We have demonstrated that the substitutions at 2,5,8,11-positions maintain planar geometry of the perylene π -plane, while the substitutions at the bay area often induced significant distortion. We have also demonstrated that alkylation of PBIs at 2,5,8,11-positions substantially enhances solid state emission and arylation at these positions has a significant impact on their optical and electrochemical properties in solution. However, introduction of heteroatoms and other functionalities at these positions of PBIs has not been achieved so far.

Direct C–H borylation has proven to be a powerful tool in organic synthesis.⁴ Recently, Miyaura, Ishiyama, and co-workers have reported iridium-catalyzed ortho-borylation of benzoate esters.⁵ Encouraged by this pioneering

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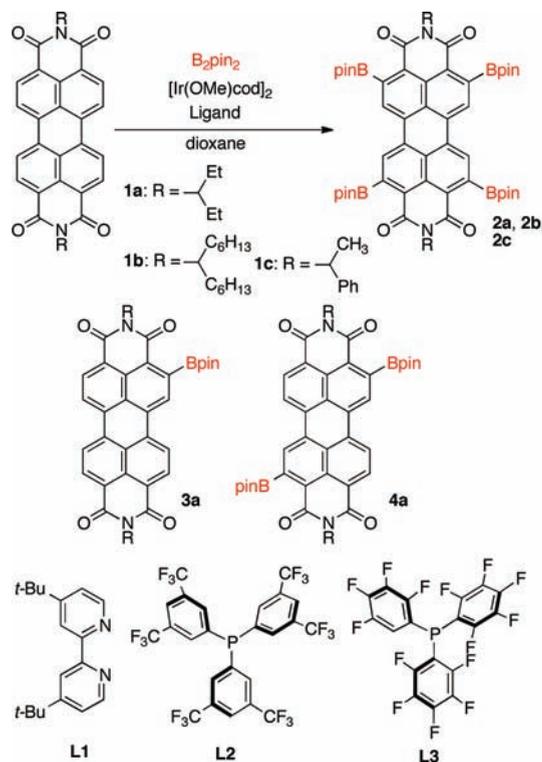
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work, we decided to explore borylation of PBIs at 2,5,8,11-positions under iridium-catalysis.

Table 1. ^aIr-Catalyzed Direct Borylation of PBI 1



entry	ligand	R	yield (%)		
			2	3	4
1	L1	2-ethylpropyl (1a)		13	
2	L2	2-ethylpropyl (1a)		37	12
3	L3	2-ethylpropyl (1a)	59		
4	L3	2-hexylheptyl (1b)	78		
5	L3	2-phenethyl (1c)	64		

^a Reaction conditions: PBI **1** (0.25 mmol), bis(pinacolato)diboron, (2.0 mmol), [Ir(OMe)cod]₂ (0.0075 mmol), 1,4-dioxane (5 mL), ligand (0.003 mmol), 110 °C, 48–96 h.

Table 1 illustrates Ir-catalyzed direct borylation of PBI. In the presence of 3.0 mol % of [Ir(OMe)cod]₂ and di-*tert*-butylbipyridyl (**L1**) as a ligand, a mixture of bis(*N*-ethylpropyl)PBI **1a** and bis(pinacolato)diboron was heated in refluxing 1,4-dioxane. Purification of the reaction mixture by silica gel chromatography afforded only monoborylated PBI **3a** in 13% yield (entry 1). Miyaura et al. have reported that tris(3,5-bis(trifluoromethyl)phenyl)phosphine (**L2**) is effective for borylation of benzoates. In fact, the use of **L2** significantly improved the yield of **3a** to 37% and also provided diborylated PBI **4a** in 12% yield but without formation of tetraborylated PBI **2a** (entry 2). Eventually, we found that the use of tris(pentafluorophenyl)phosphine (**L3**) is quite effective to furnish **2a** and **2b** in 59 and 78% yields, respectively (entries 3 and 4). Interestingly, this

catalyst system effected exclusive borylation on the 2,5,8,11-positions of the perylene core: no borylation occurred on the phenyl groups of the imide substituents of **1c** to furnish tetraborylated PBI **2c** (entry 5). In sharp contrast, borylation with **L1** took place only on the phenyl groups but afforded a mixture of several products due to formation of regioisomers.

Single crystals of **2a** suitable for X-ray diffraction analysis were obtained by vapor diffusion of acetone into a chloroform solution of **2a**. The solid-state structure of **2a** was unambiguously determined to elucidate the highly planar structure of the perylene core, of which mean plane deviation is calculated to be only 0.015 Å (Figure 1).⁶ This characteristic is in sharp contrast to the functionalized PBIs at the bay areas, of which perylene backbone are considerably twisted. The boryl groups are tilted to the perylene core by 86.0 or 97.3° and the C–B bond lengths between the perylene core and the boryl groups range from 1.569 to 1.585 Å. These structural features imply weak electronic communication between the boryl substituents and the perylene moiety. The crystal packing of **2a** does not show any π – π interaction because of steric hindrance of bulky 2,2,3,3-tetramethyldioxaborolanyl substituents (Supporting Information, SI).

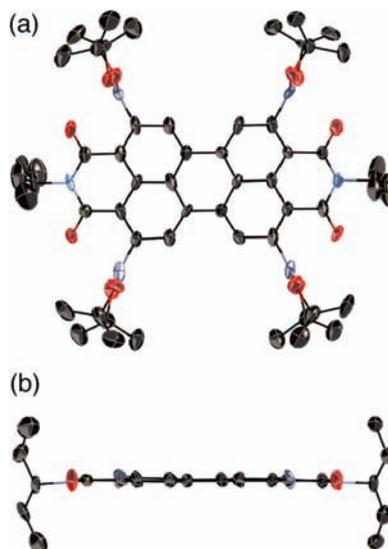
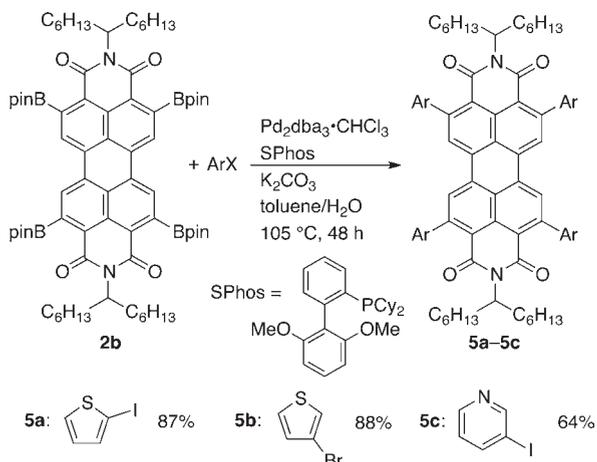


Figure 1. X-ray crystal structure of (a) top view and (b) side view of tetraborylated PBI **2a**. The thermal ellipsoids were scaled to the 50% probability level. Hydrogen atoms, solvents, and boryl substituents in the side view were omitted for clarity.

Suzuki–Miyaura cross-coupling of **2b** was then examined. After several trials, the use of SPhos as a phosphine ligand was found to be optimal to afford heteroarylated

(6) Crystal data for **2a**: C₆₇H₉₂B₄N₂O₁₅, *M_w* = 1208.67, orthorhombic, space group *P*2₁2₁2₁ (No. 19), *a* = 11.010(5) Å, *b* = 18.968(8) Å, *c* = 33.023(15) Å, *V* = 6896(5) Å³, *Z* = 4, *D_{calc}* = 1.164 g/cm³, *T* = 153(2) K, *R* = 0.0918 (*I* > 2.0σ(*I*)), *R_w* = 0.3186 (all data), GOF = 0.934 (*I* > 2.0σ(*I*)).

Scheme 1. Suzuki–Miyaura Coupling of **2b**

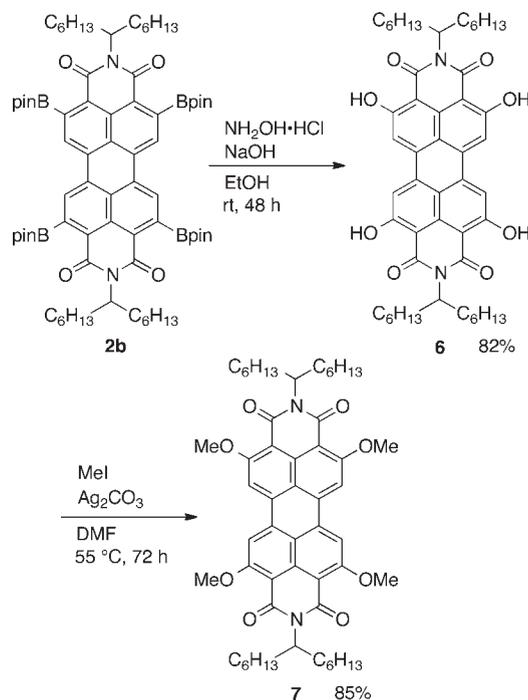


PBIs in good yields (Scheme 1). Although arylation of PBIs at 2,5,8,11-positions can be achieved by Ru-catalyzed direct arylation with arylboronic esters,^{3b} introduction of heteroaryl groups was difficult. The borylation–cross-coupling sequence would be useful for the synthesis of this type of heteroarylated PBIs.

We also attempted the oxidation of tetraborylated PBI **2b** to tetrahydroxy PBI **6**, since the effect of heteroatoms at the 2,5,8,11-positions has not been investigated. Oxidation of arylboronic acid pinacol esters often employs Oxone⁷ or basic hydrogen peroxide,⁸ but these protocols afforded only a trace amount of the desired tetrahydroxy PBI **6**. After several trials, we found that the use of hydroxylamine hydrochloride as an oxidant in the presence of NaOH successfully provided **6** in 82% yield (Scheme 2).⁹ Conversion of **6** to **7** by methylation of OH group was carried out with an excess amount of iodomethane in the presence of Ag_2CO_3 as bases. In the ^1H NMR spectrum of **6**, the hydroxyl protons were observed in a substantially downfield region at $\delta = 13.2$ ppm, suggesting intramolecular hydrogen bonding interaction between carbonyl and hydroxy moieties.

Figure 2 shows UV/vis absorption spectra of **1b**, **2b**, **6**, and **7** in dichloromethane. Notably, introduction of OH groups induced a significant blue-shift of the lowest energy band from 525 to 512 nm, despite that the electron-donating substituents often cause a red-shift by lifting the HOMO energy. This spectral change can be explained by intramolecular hydrogen bonding between carbonyl and hydroxy groups in tetrahydroxy PBI **6**. The hydrogen bonding interaction enhances the electron-withdrawing nature of imide carbonyl groups and stabilizes the HOMO level to increase the HOMO–LUMO gap of **6**. The role of hydrogen bonding can be suggested from the red-shifted feature in the absorption spectrum of methoxy derivative **7**. The existence of the intramolecular hydrogen bondings

Scheme 2. Introduction of Hydroxy and Methoxy Groups



in **6** was confirmed by the IR spectrum, in which imide carbonyl stretching bands shifted down to lower wavenumbers than that of **7** (SI). Theoretical calculations at the B3LYP/6-31G(d) level revealed considerable stabilization of HOMO in the case of **6**, while destabilization was observed for **7** (Figure 3). Lowering of the HOMO energy was also confirmed by the cyclic voltammetry (SI). The first oxidation potentials (E_{ox}^1) of **1b**, **6**, and **7** are 1.23, 1.56, and 1.10 V (vs Fc/Fc^+), respectively. Accordingly, the potential differences between the first oxidation potentials and the first reduction potentials are 2.33, 2.68, and 2.28 V, respectively. This trend in electrochemical HOMO–LUMO gaps are well matched with the optical HOMO–LUMO gaps as well as theoretical calculations.

Interestingly, tetraborylated PBI **2b** was found to be emissive even in the solid state. A powder sample of **2b** emits at 609 nm with a relatively high quantum yield of 0.18, which was determined by a calibrated integrating sphere system. The enhancement of photoluminescence efficiency in the solid state is probably due to the bulky pinacolboranyl substituents, which reduce intermolecular interaction in the excited state of PBI.

In summary, we have accomplished regioselective 4-fold direct borylation of PBI at the 2,5,8,11-positions of the perylene core under Ir-catalysis. The boron substituents can be oxidized to hydroxy groups with hydroxylamine. Interestingly, introduction of the

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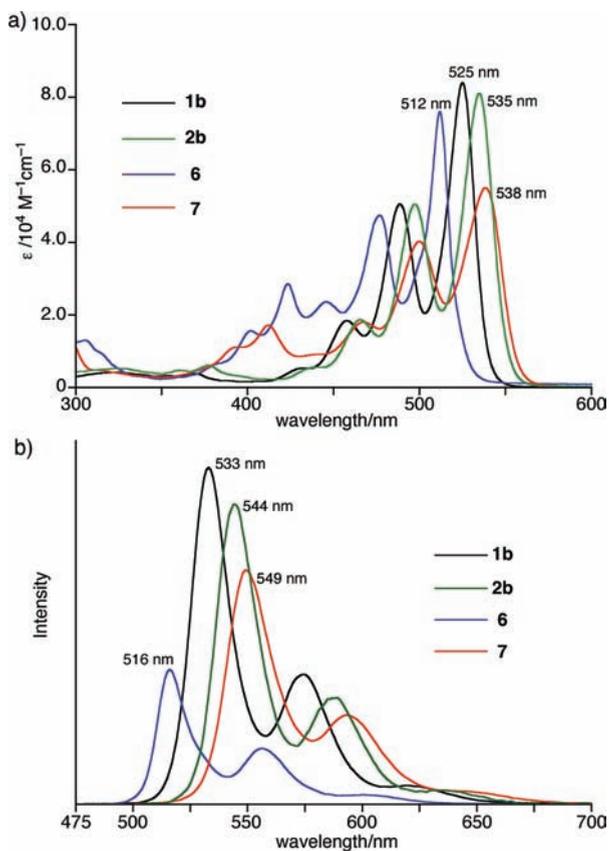


Figure 2. (a) UV/vis absorption spectra of **1b** (black), **2b**, **6**, and **7** measured in CH_2Cl_2 . (b) Emission spectra of **1b**, **2b**, **6**, and **7** measured in CH_2Cl_2 . Excitation wavelength is at 450 nm.

hydroxy group induced a substantial blue-shift in the UV/vis absorption spectrum due to an intramolecular hydrogen bonding interaction, which stabilizes the

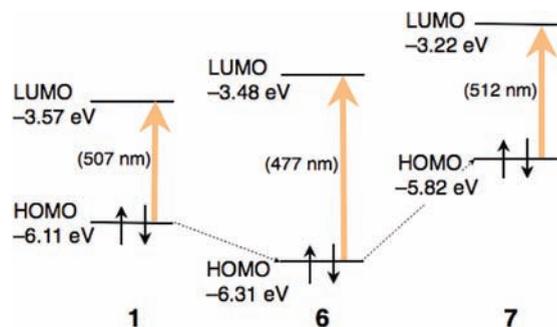


Figure 3. Calculated HOMO and LUMO levels of **1**, **6**, and **7** at the B3LYP/6–31G(d) level. Calculated absorption wavelengths by the TD-DFT method are shown in the parentheses.

HOMO level. This feature is specific to hydroxylation at the 2,5,8,11-positions of PBI, which enables intramolecular hydrogen bonding with imide carbonyl groups. In addition, boronated PBIs would serve as a nice building block for molecular assemblies on the basis of PBI through transition metal-catalyzed transformations. Further direct functionalization of PBIs is currently underway in our group.

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Supporting Information Available. General procedures, spectral data for compounds, and CIF file for the X-ray analysis of **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.