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Suzuki Coupling Reaction of 1,6,7,12-Tetrabromoperylene Bisimide

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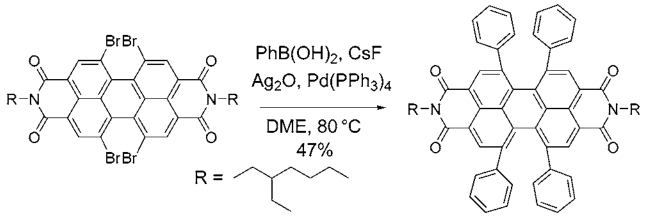
ABSTRACT



1,6,7,12-Tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride and the corresponding tetrabrominated perylene bisimide were first synthesized with high yields. The Suzuki coupling reaction of novel tetrabromoperylene bisimide with phenylbonoric acid was studied. The four bromines in the bay position of the perylene core were substituted successfully to yield 1,6,7,12-teraphenylperylene bisimide. The photochemical properties of the novel perylene bisimides were studied and presented.

Perylene-3,4,9,10-tetracarboxylic acid bisimides (Perylene bisimides, PBIs) are excellent n-type semiconductors with good chemical and physical stabilities, high electron affinity, and carrier mobility.[1] The properties of PBI derivatives may be modulated by proper functionalization of perylene bisimides. Usually, two different methods were adopted to achieve the chemical modification of PBIs. One is to introduce substituents at N atoms of imide groups, which does not significantly affect the optical and electronic properties. Another way is to introduce the substituents to the perylene core of PBI, i.e., the bay position; with electron-donor or electron-acceptor groups, such modification will greatly change the properties of PBIs.[2] Usually, the synthesis of the latter method starts from the corresponding halogenated perylene-3,4,9,10-tetracarboxylic acid bisanhydride with dibrominated product for difunctionalized PBI derivatives or tetrachlorinated product for tetrafunctionalized PBI derivatives.[2−4] The subsequent imidization of halogenated bisanhydride product as well as exchange of halogen atoms in perylene bisimides by various substituents was effective to develop numerous novel PBIs derivatives with novel photoelectronic properties.[2,5]

The bay position functionalized PBI materials have been widely used in the field of light-harvesting arrays,[6] photovoltaic cells,[7] organic field effect transistors,[8] organic light emitting diodes,[9] etc. They also have been proven to be good building blocks for constructing supramolecular or giant-molecular systems.[2,10] The exchange of the bromines of dibrominated PBIs is straightforward. Therefore, aryl, cyano, phenoxy, and nitrogen nucleophiles could be easily coupled to the perylene core leading to novel difunctionalized PBI derivatives.[2] In the case of tetrachlorinated PBIs, four phenoxy-like substituents could be easily incorporated into the bay positions by nucleophilic displacement of chlorines to give tetrafunctionalized PBI compounds. However, incorporation of four other nucleophiles or substituents, such as aryl groups, was known to be difficult and challenging.[2]

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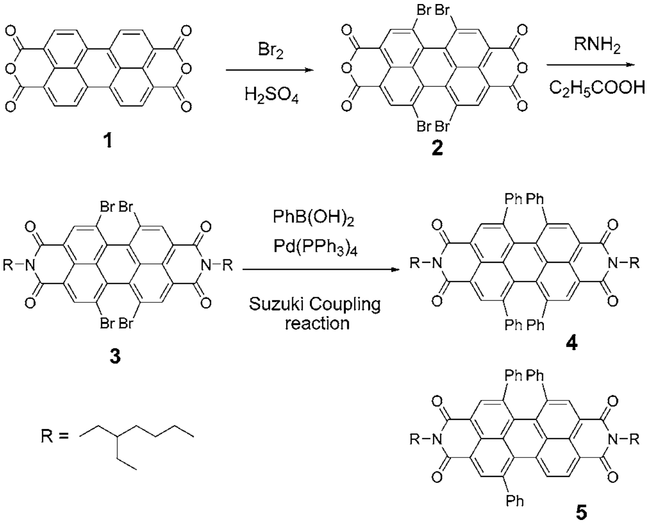
Here we report the first synthesis of 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride, as well as the corresponding tetrabrominated perylene bisimide, with high yields. Thus, it will be feasible to incorporate four substituents into the bay position of PBIs besides the phenoxy-like groups. We tried the Suzuki coupling reaction of tetrabrominated PBI with phenylboronic acid, and as a result, four phenyl groups were successfully introduced to the 1-, 6-, 7-, and 12-positions of the PBI backbone. The bromination of perylene bisanhydride **1** was carried out by treatment of **1** and 4.2 equiv of Br_2 in the mixture of sulfuric acid and fuming sulfuric acid at 100 °C for 5 days. The crude yield is as good as 96%. The tetrabrominated perylene bisanhydride **2** is insoluble in organic solvents, the common characterizations are difficult to perform except for the mass spectrum measurement. Subsequently, 2-ethylhexylamine was heated with **2** in propionic acid, leading to tetrabrominated PBI **3** with a high yield of 95%; this was also the indirect evidence for the high-yield synthesis of **2** in the reaction of the last step. Due to the existence of two 2-ethylhexyl groups, compound **3** exhibits good solubility in organic solvents, which provide convenience for purification and full characterizations. Column chromatography is effective in affording pure bisimide product. In the ^{1}H NMR spectrum of **3**, only one singlet appears at 8.83 ppm in the aromatic region, corresponding to the chemical shifts of protons at the 2-, 5-, 8-, and 11-positions of the perylene backbone. The result is consistent with the highly symmetric structure of **3**. Further evidence for structural assignment also could be found in the ^{13}C NMR spectrum—only six carbon signals appear in the aromatic region. The mass spectrum and elemental analysis also are in good agreement with the chemical structure. Thus, we successfully synthesized tetrabrominated PBI by a relatively easy procedure for the common synthetic laboratory.

Scheme 1. Synthesis of Tetrasubstituted PBI Derivatives



The tetrabrominated PBI derivative has the advantage over tetrachloroperylene bisimides with many more synthetic possibilities of structural modifications. The palladium-catalyzed coupling reaction of aryl halides with aryl boronic acids is a powerful method to construct the C−C bond for multi-aryl compounds. We investigated the Suzuki coupling reaction of **3** with commercially available phenylboronic acid. To the best of our knowledge, this is the first report on the 1,6,7,12-tetraphenylperylene bisimide derivative.

First, we tried the reaction of **3** with phenylboronic acid using the most common conditions: K_2CO_3 as the base and toluene or DME as the solvent (Table 1: condition A, entries 1 and 2). The strong base conditions resulted in so many byproducts that no tetraphenyl product **4** was obtained, possibly due to the high steric hindrance at 6, 7 (or 1, 12) bay position of tetrabromoperylene bisimide **3** and the strong electron-withdrawing effect of the perylene bisimide core. Therefore, the base was changed to $NaHCO_3$, a weaker base (condition B: entry 3). In condition B, the target compound tetraphenylperylene bisimide was successfully obtained, but the yield was very low (11%) and the purification was very difficult due to the existence of many byproducts, including debrominated products (such as diphenyl, triphenylperylene bisimides)[8a] and the byproducts still containing unsubstituted

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Table 1. $Pd(PPh_3)_4$-Catalyzed Coupling Reaction of **3** with $PhB(OH)_2$[a]

entry	base	solvent	*T* (°C)	yield[b] (%)
1	K_2CO_3	DME	80	0
2	K_2CO_3	toluene	115	0
3	$NaHCO_3$	DME	80	11
4	KF/Ag_2O	DME	80	33[c]
5	CsF/Ag_2O	DME	80	47[c]
6	CsF	DME	80	23[c]
7	CsF/Ag_2O	DMF	80	21[c]
8	CsF/Ag_2O	THF	80	41[c]

[a] All reactions were performed with 10 mol % of $Pd(PPh_3)_4$ under N_2 atmosphere. [b] Isolated yield. [c] 1,6,7-Triphenylperylene bisimide **5** was obtained as the main byproduct.

bromine (deduced from the results of MALDI-TOF-MS measurements). The results demonstrate that the weaker base should be used and the higher reactivity should be achieved for such coupling reactions.

Recently, fluoride ion-mediated and Ag_2O-promoted coupling reactions were reported and found to greatly increase the reactivity of the Pd-catalyzed coupling reaction.[11] Thus, we investigated Ag_2O-promoted coupling reactions of **3** with phenylboronic acid using KF or CsF as a mild base (Table 1, entries 4−8). In a typical synthetic procedure, a mixture of **3**, phenylboronic acid (6 equiv, excess), $Pd(PPh_3)_4$ (10 mol %), Ag_2O (4.4 equiv), and KF or CsF (8 equiv, 2 equiv for each bromine) in solvents was stirred at 80 °C for 24 h under N_2 atmosphere. The reaction with KF and Ag_2O (condition C, entry 4) in DME afforded a yield of 33%, much higher than the yield with condition B, while the use of CsF could further increase the yield to near 50% (condition D, entry 5). Without Ag_2O, the yield was found to be low (23%, entry 6). Furthermore, the solvent also was found to be important. The use of DMF decreased the yield to 21% (entry 7). Besides DME, THF was also a good solvent with a yield of 41% (entry 8). During the column separation of crude products under mild base conditions, mainly two colorful bands were exhibited: the first band was target compound **4** and the second band was characterized to be 1,6,7-triphenylperylene bisimide **5** (with the yield of about 30% as the main byproduct). The effect of using mild bases is obvious, which will not produce large amounts of various byproducts such as with the use of K_2CO_3 or $NaHCO_3$. Due to the great steric hindrance and crowding in the bay positions of **3** and **4**, the mild bases could still result in the debromination product. In our case, as much as four bromines needed to be displaced—47% was a relatively high yield.

The chemical structure of **4** was fully characterized by IR, NMR spectra, MS, elemental analysis, etc. The highly symmetric structure was confirmed by simple ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of **4**, only one singlet, corresponding to the protons of the perylene backbone at the 2-, 5-, 8-, and 11-positions, appears at 8.32 ppm in the aromatic region. This proton signal undergos upfield shifting relative to that of compound **3** (8.83 ppm). Comparatively, both ^1H and ^{13}C NMR spectra of compound **5** exhibit complicated spectra due to its unsymmetrical structure.

Figure 1 shows the UV−vis absorption spectra of compounds **3**, **4**, and **5** in CH_2Cl_2. Over 400 nm, compound **3** shows two PBI core absorption bands with maximum absorption at 529 and 439 nm, respectively, along with one shoulder absorption at 499 nm. Comparatively, the spectrum of **4** exhibits a similar trend of band shape and distribution with maximum absorption at 603 and 449 nm as well as the shoulder absorption at 568 nm. In the case of compound **5**, the maximum absorptions appear at 579, 549 nm (shoulder absorption), and 428 nm, respectively. The longest absorption bands can be assigned to the electronic S_0−S_1 transition (a transition dipole moment along the long molecular axis) and the lower absorption bands assigned to the electronic S_0−S_2 transition (a transition dipole moment perpendicular to the long molecular axis).[2,12] Although the characteristic absorption behaviors of perylene bisimide compounds could be found in compounds **4** and **5**, their absorption bands undergo a significant bathochromic shift along with considerable band broadening, especially for the longest absorptions. These results could be attributed to the electron-donating effect of four phenyl groups and the steric twisting of the perylene core.[5a,h,13,14] Furthermore, the absorption bands below 400 nm in **4** and **5** could be attributed to the phenyl groups.

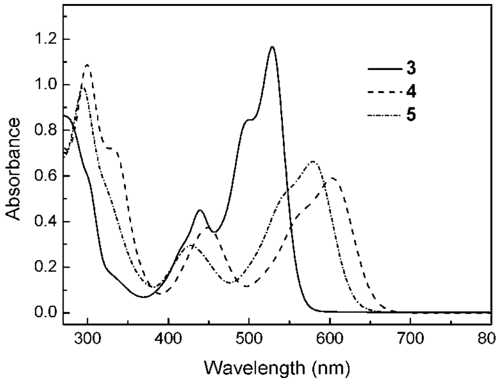

Figure 1. UV−vis spectra of **3**, **4**, and **5** in CH_2Cl_2 with concentrations of 3.5×10^{-5}, 2.6×10^{-5}, and 2.7×10^{-5} M, respectively.

Figure 2 shows the normalized emission spectra of comounds **3**, **4**, and **5** in CH_2Cl_2 with the maximum emission located at 566, 665, and 642 nm, respectively. As compared with tetrabromoperylene bisimide compound **3**, displacement of bromines by phenyl groups causes the significant batho-

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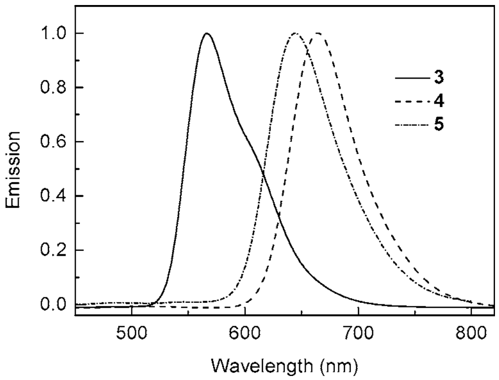

Figure 2. Normalized emission spectra of **3**, **4**, and **5** in CH_2Cl_2, excited at 420 nm.

chromic shift of the emission band. In comparison to compound **5**, the increase in the number of phenyl groups in **4** results in 23 nm of bathochromic shifts of the emission band. The fluorescence quantum yields of **3**, **4**, and **5** were measured with use of Rhodamine B in ethanol solution as a reference (excitation wavelength of 510 nm for all the samples).[15] The Φ_f values are determined to be 0.62, 0.29, and 0.39, respectively. The presence of steric-crowding phenyl groups decreases the fluorescence of perylene core in a way.

In summary, 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride and the corresponding tetrabrominated perylene bisimide were successfully synthesized in high yields. The fluoride ion-mediated and Ag_2O-promoted Suzuki coupling reaction of tetrabromoperylene bisimide and phenylboronic acid was proved to be effective for synthesizing tetraphenylperylene bisimide with acceptable yield. The novel tetraphenylperylene bisimide possesses the basic photochemical characteristics of the PBI parent core with modulated absorption and fluorescent properties. Thus, novel PBI derivatives can be developed by displacement of four bromines in the bay position of tetrabromoperylene bisimides. All these will provide more synthetic possibilities than tetrachloroperylene bisimides and will significantly broaden and facilitate the research of PBI chemistry. Other synthetic modifications of tetrabromoperylene bisimides are underway.

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Supporting Information Available: General experimental methods, the synthesis and characterizations of compounds **2**−**5**, and ^{1}H and ^{13}C NMR spectra of **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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