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Highly Regiospecific Synthetic Approach to Monobay-Functionalized Perylene Bisimide and Di(perylene bisimide)

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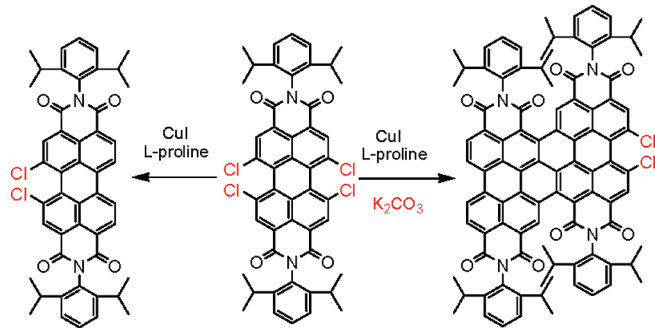
ABSTRACT



Monobay-dichlorinated perylene bisimide and diperylene bisimide have been regiospecifically synthesized from tetrachlorinated perylene bisimide in different copper-mediated reaction conditions, thus opening a new avenue to their monobay-functionalization.

Due to good chemical and physical stabilities, intense photoluminescence, high electron affinity, and carrier mobility,[1] perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs) have received a great deal of attention as promising organic n-type semiconducting materials which have found widespread applications as light-harvesting arrays,[2] field effect transistors,[3] light-emitting diodes,[4] and photovoltaics[5] in the past decades. Chemical modifications both at the imide groups and in the bay regions are two different successful synthetic strategies for perylene bisimide derivatives. However, the dramatic change of optical and electronic properties can only be achieved by the bay-functionalization because of nodes in the HOMO and LUMO orbitals at the imide nitrogen atoms.[1b] Therefore, the functionalization of a perylene aromatic core is a current research topic to develop the applications of these chromophores in electronic devices. Tetrachloro- and dibromo-substituted PBIs have taken important parts in the synthesis of functional perylene dyes such as phenoxy,[6] aryl,[7] cyano,[3a] pyrrolidino,[8] sulfur,[9] fluorine,[10]

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and perfluoroalkyl[11] substitution in bay regions by nucleophilic halogen-exchange reactions.

To the best of our knowledge, functionaliztion in the monobay region of PBI is mostly originated from unselective and irreproducible monobay-nitration and monobay-bromination. Until now, there has been no precedent on the synthesis of monobay-dichlorinated PBIs, which are key intermediates for monobay-functionalized PBIs. (Figure 1).

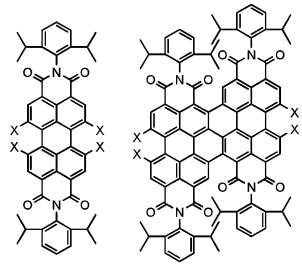


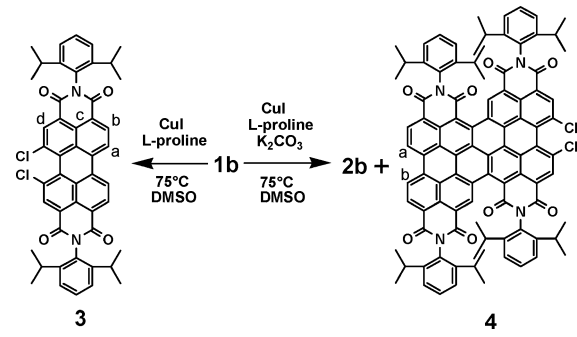
Figure 1. PBI (**1a**), 4Cl-PBI (**1b**), diPBI (**2a**), and 4Cl-diPBI (**2b**).

Utilization of soluble copper complexes or salts with mono- or bidentate chelating ligands such as amino acids, diamines, and phosphines has made a great contribution to the development of Ullmann-like coupling reactions in the formation of C−N, C−O, C−S, and C−C bonds in recent years.[12] Recently, we reported the facile synthesis of triply linked di(perylene bisimides) (diPBIs) and tri(perylene bisimides) (triPBIs) using the system of CuI, L-proline, and K_2CO_3.[13]

Herein, we present the copper-mediated synthesis for monobay-dichlorinated perylene bisimide (2Cl-PBI) and di(perylene bisimides) (2Cl-diPBI), providing a new efficient avenue to construct monobay-functionalized PBIs and diPBIs which are expected to possess extraordinary optoelectronic features.

Starting from tetrachloro-PBI (**1b**) (4Cl-PBI), 2Cl-PBI (**3**) was prepared at 75 °C in 48% yield (98% based on the recovered 4Cl-PBI) under the system of CuI and L-proline without K_2CO_3, while 2Cl-diPBI (**4**) as well as 4Cl-diPBI (**2b**) was obtained in 15% yield using amounts of CuI, L-proline, and K_2CO_3 (Scheme 1). Compounds **3** and **4** show

Scheme 1



good solubility in common organic solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran. Their structures are unambiguously identified by ^{1}H NMR and ^{13}C NMR spectroscopy and MALDI-TOF.

Surprisingly, there were no other isomers of 2Cl-PBI (**3**) obtained in the above reaction as evidenced by HMBC experiments. The $^3J_{CH}$ correlations between protons H_b (δ 8.83) and H_d (δ 8.80) and carbonyl carbons (δ 162, δ 163) determined the assignments of H_a (δ 8.67), H_b, and H_d. The presence of $^3J_{CH}$ coupling from protons both H_b and H_d to C_c (δ 127.3) and the absence of $^3J_{CH}$ coupling from protons H_a and H_d to the same carbon was consistent with the structure of 2Cl-PBI **3** rather than other isomers (see the Supporting Information).

Furthermore, to determine the molecular structure of 2Cl-PBI (**3**), crystals suitable for single-crystal X-ray structure analysis were obtained by slow evaporation of a solution of **3** in methol at room temperature. Owing to the big difference of electrostatic repulsion and steric encumbrance in chlorine and hydrogen substituents, the twisting of central six-membered ring is unsymmetrical with dihedral angle of 34.6° and 9.9°, respectively, while the tetrachloroperylene bisimide has a torsional angle of 36.7°[14] (Figure 2).

Notably, we also found that only monobay-dichlorinated diPBI (2Cl-diPBI, **4**) was produced in the reaction, although

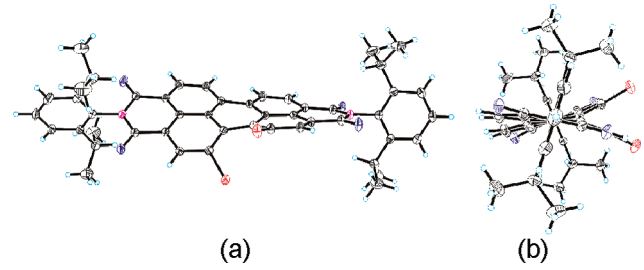


Figure 2. ORTEP drawing of the molecular structure of 2Cl-PBI (**3**): (a) top view; (b) side view. The solvent molecules are omitted for clarity.

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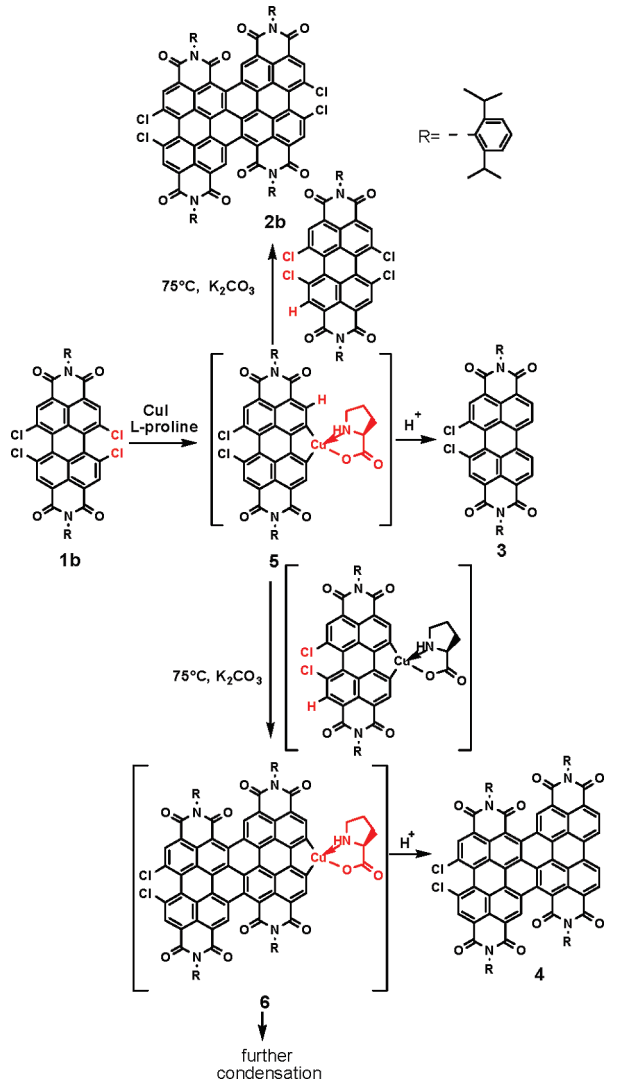
Scheme 2

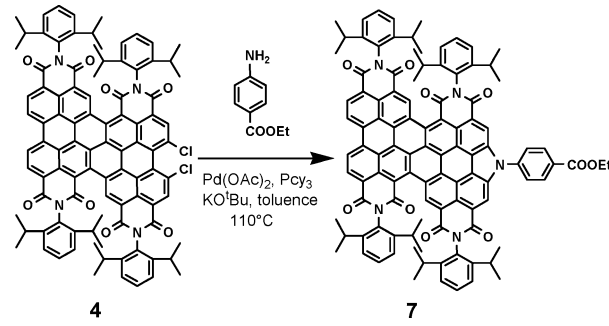


there are three isomers according to the different sites of two chlorine atoms in the bay regions. From the ROESY spetrum, an obvious cross-peak was observed between two protons H_a and H_b (δ 9.45, δ 9.35) of bay regions which have been assigned on the basis of $^1H-^1H$ COSY and HMBC, suggesting that the two protons are in the same bay region. The result was definitely in accord with the structure of 2Cl-diPBI (**4**) providing reliable evidence to exclusion of other isomers (see the Supporting Information).

The regiospecific synthesis of monobay-chlorinated PBI and diPBI provided important clues to comprehension of this copper-mediated reaction mechanism. Thus, we proposed the monobay copper(III)-substituted PBI complex **5** as a key intermediate in the reaction pathway. First, CuI and L-proline formed copper chelate, which is more reactive toward the oxidation addition at one bay position, and then an intramolecular substitution involving the adjacent carbon atom at bay positon affords the intermediate **5**. Under basic conditions, it reacted with 4Cl-PBI to afford 4Cl-diPBI (**2b**) or self-coupled to give another intermediate monobay copper(III)-substituted diPBI complex **6** and then changed to 2Cl-diPBI (**4**) when the reaction was quenched with aqueous acid, whereas without K_2CO_3 the five-membered organocopper ring **5** decomposed to 2Cl-PBI after treatment with aqueous acid (Scheme 2).

Due to broad and red-shifted absorption spectra and extremely strong eletron-accepting ability in contrast with PBIs,[13a] we are particularly interested in chemical modication of diPBI to develop novel electronic materials. Therefore, we decided to introduce functional units such as a nitrogen group into the monobay region of diPBI selectively to explore the subtle changes of optical and electronic properties. Buchwald−Hartwig couping reaction between aryl halides and amines is a successful synthetic strategy for C−N formation;[15] accordingly, we present the synthesis of monobay-functionalized diPBI derivative **7** in 92% yields by cross-coupling of 2Cl-diPBI with ethyl 4-aminobenzoate (Scheme 3).

Scheme 3



The absorption spectra of 2Cl-PBI (**3**), 2Cl-diPBI (**4**), and its derivative **7** in $CHCl_3$ show a well-defined vibronic fine structure of the S_0-S_1 transition (Figure 3). The orange

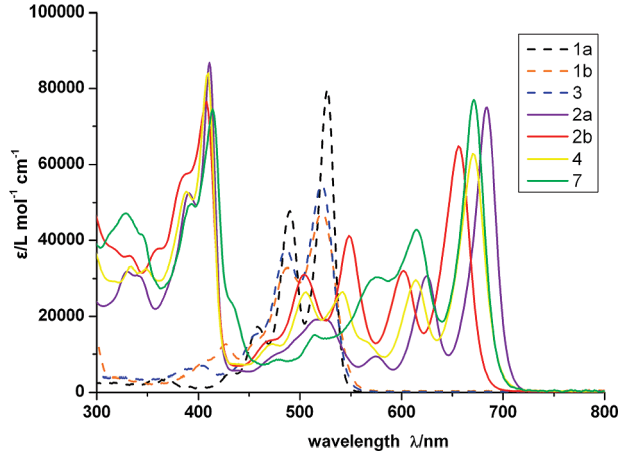


Figure 3. UV−vis absorption spectra of PBI (**1a**) (black dash line), 4Cl-PBI (**1b**) (orange dash line), 2Cl-PBI (**3**) (blue dash line), diPBI (**2a**) (purple solid line), 4Cl-diPBI (**2b**) (red solid line), 2Cl-diPBI (**4**) (yellow solid line), and **7** (green solid line) in $CHCl_3$ at room temperature.

solution of 2Cl-PBI (**3**) shows two major bands at 486 and 521 nm ($\varepsilon_{max} = 54600\ M^{-1}\ cm^{-1}$) with a slight hypsochromic shift relative to PBI (**1a**), probably due to the electron-withdrawing effect of chlorine substituents. The blue solution of 2Cl-diPBI (**4**) exhibits five major bands at 410, 506, 542, 614, and 670 nm ($\varepsilon_{max} = 84050\ M^{-1}\ cm^{-1}$). Similarly, the maximum absorption of 2Cl-diPBI (**4**) is blue-shifted by 14 nm in comparison with diPBI **2a**.

The absorption spectrum of **7** shows major bands at 671, 615, 578, and 414 nm ($\varepsilon_{max} = 76980\ M^{-1}\ cm^{-1}$). Given that there is relatively weak absorption in region of 500−550 nm for **7**, its solution is green rather than violet relative to 2Cl-diPBI (**4**).

Cyclic voltammetry of 2Cl-PBI (**3**) in CH_2Cl_2 shows one reversible reduction wave and one quasireversible reduction wave. The half-wave reduction potentials vs Fc/Fc^+ are −0.85 and −1.10 V for **3** (table 1). Obviously, the first reduction potentials of PBI (**1a**), 2Cl-PBI (**3**), and 4Cl-PBI (**1b**) is proportional to the number of electron-withdrawing chlorine atoms in bay regions. Cyclic voltammetry of 2Cl-diPBI (**4**) in CH_2Cl_2 exhibits two reversible reduction waves and two quasireversible reduction waves. The half-wave reduction potentials vs Fc/Fc^+ are −0.45, −0.75, −1.47, and −1.64 V for **4**. Similar to 2Cl-PBI (**3**), the first reduction potential of **4** is between that of diPBI (**2a**) and 4Cl-diPBI (**2b**).

Table 1. Half-Wave Redox Potential (in V vs Fc/Fc^+)[a]

	E_{1r}	E_{2r}	E_{3r}	E_{4r}
4Cl-PBI (**1b**)	−0.74	−1.06		
2Cl-PBI (**3**)	−0.85	−1.10		
PBI (**1a**)	−0.96	−1.22		
4Cl-diPBI (**2b**)	−0.41	−0.69	−1.39	−1.52
2Cl-diPBI (**4**)	−0.45	−0.75	−1.47	−1.64
diPBI (**2a**)	−0.46	−0.73	−1.49	−1.66
7	−0.57	−0.85	−1.60	−1.77

[a] Measured in 0.1 M solution of Bu_4NPF_6 in dichloromethane with a scan rate of 100 mV/s.

Cyclic voltammogram of **7** exhibits two reversible reduction waves and two quasireversible reduction waves. Its half-wave potentials vs Fc/Fc^+ are −0.57, −0.85, −1.60, and −1.77 V, more negative in comparison with 2ClDiPBI (**4**) probably due to the incorporation of the electron-donating nitrogen group.

In summary, we report a highly regiospecific synthesis of monobay-dichloronated PBI and diPBI from tetrachloro-PBI by an amino acid promoted CuI-mediated reaction, establishing a new synthetic protocol to monobay-functionalized PBIs and diPBIs. A monobay copper-substituted PBI complex was also proposed as an important intermediate. The introduction of a nitrogen group directly on the core has a drastic influence on the optical and electronic properties of diPBIs, as expected. Further studies on monobay-functionalization of PBIs and diPBIs and their applications in electronic devices such as photovoltaic cells are 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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