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Exceptional Coupling of Tetrachloroperylene Bisimide: Combination of Ullmann Reaction and C−H Transformation

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In the recent years, great advances have been achieved on the modification of Ullmann-type coupling reactions,[1] which are mostly attributed to the utilization of some special bidentate ligands such as aliphatic diamines,[2] ethylene glycol,[3] and amino acids.[4] Their purpose is to soften the reaction conditions, extend the scope toward unactivated substrates, and increase the tolerance to sensitive groups. Especially, amino acids promoted CuI-catalyzed reactions have been widely employed in the formation of C−N, C−S, and C−C bonds.[4]

Perylene-3,4:9,10-tetracarboxylic acid bisimides **1** (PBIs), as the most intensively investigated chromophores, have found use in a wide range of applications including electron-transfer systems,[5] energy transfer cascades,[6] photovoltaic devices,[7] organic field effect transistors,[8] light emitting diodes,[9] and other organic electronic devices. Interest in these compounds is due to their exceptional optical and electronic properties and high fluorescence quantum yields.[10] A variety of perylene bisimides has been prepared by conventional imidization as well as the introduction of different groups in the bay-regions. Approaches have been reported to synthesize rylene bisimides **2**, such as terrylene and quaterrylene bisimides,[11] and their derivatives, whose optical properties can be dramatically altered by the enlargement of the π system. Bi− and trichromophoric perylene dyes **3** have also been prepared,[12] which can be considered as "intense dyes" owing to their extremely high extinction coefficients (Figure 1).

Recently, we reported the palladium-catalyzed cross-coupling reaction of tetrachloro-PBI with $Bu_3SnSSnBu_3$.[13b] Stimulated by this result, we envisaged that tetrahalogen-PBIs might conduct homocoupling to construct more extended conjugated π-systems under proper condition. Herein we present the facile one-pot synthesis of novel triply linked[14] diperylene bisimide (diPBI) and tetrachlorinated diperylene bisimide (4CldiPBI) by L-proline promoted CuI-involved coupling of tetrachloro-PBI, which represents the first step toward the completely bay-region fused oligo-PBIs **4**. In the view of structures, the triply linked oligo-PBIs **4** can be regarded as the activated graphene ribbon modulated by arrays of electron-withdrawing imide groups, providing an ideal model compound for rarely investigated graphenes with electron-transporting (n-type) ability.

Using stoichiometric amount of CuI as the reagent, L-proline as the ligand and K_2CO_3 as the base, the homocoupling of **5**[13] proceeded in DMSO to give **7** at 75 °C and **6** at 110 °C (Scheme 1) in moderate yields, while no desired product was observed in the present of catalytic amount of copper salt. The structures of **6** and **7** were unambiguously verified by ^1H NMR, ^{13}C NMR spectroscopy, and HRMS. It is surprising that with this highly efficient and simple CuI-mediated reaction, the enlargement of π system was easily and successfully achieved along the bay-region of PBIs. Moreover, triPBI and/or its derivatives have been observed in the mixtures, which are hard to separate probably because of the existence of several isomers. It should be noted that using the same system, **6** was obtained from **7** at 110 °C by dehalogenation, which provides useful clues to further investigation of the reaction mechanism.

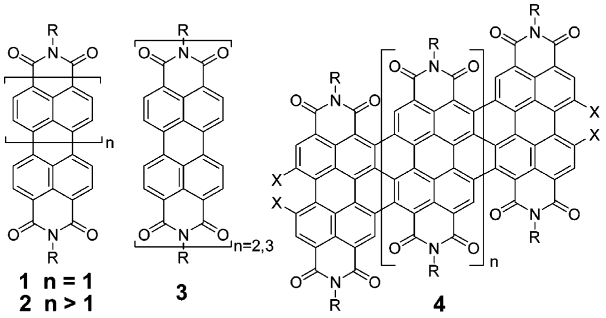
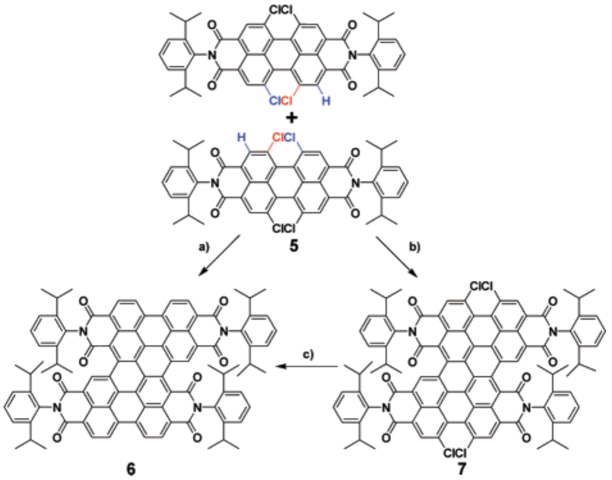


Figure 1. PBIs and their derivatives.

Scheme 1. Synthesis of diPBI **6** and 4CldiPBI **7**[a]



[a] Conditions: CuI, L-proline, K_2CO_3, DMSO, 15 h: (a) 110 °C, 30%; (b) 75 °C, 16%; (c) 110 °C, 40%.

Although the system of CuI and L-proline has been proved to be powerful in Ullmann-type coupling reactions, there are only a few examples of the more accessible but less active chlorides. The probable reason for succeeding in tetrachloro-PBI is the release of strain in the severely twisted tetrachloride **5**. Moreover, the ortho sp^2 C−H bond (Scheme **1**) maybe functionalized to construct C−C bonds via Cu-catalyzation.[15] As a one-pot domino process, the formation of three new C−C bonds induced by the corporation of Ullmann-type coupling and C−H transformation (for **7**) together with cleavage of four C−Cl bonds (for **6**) is truly remarkable. Moreover, diPBIs can be easily modulated in imide groups and the bay-regions to achieve good process ability and tunable optical and electronic properties.

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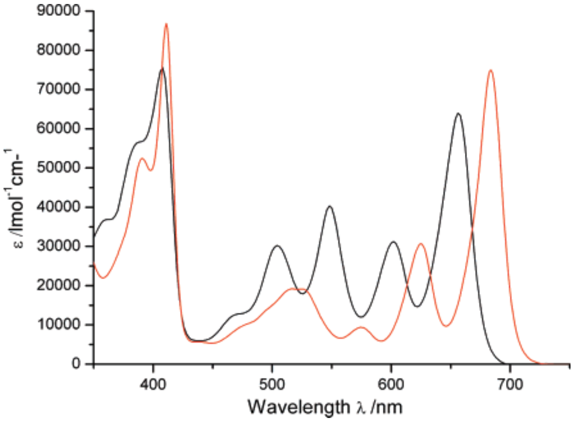

Figure 2. UV−vis absorption spectra of **6** (red) and **7** (black) in $CHCl_3$.

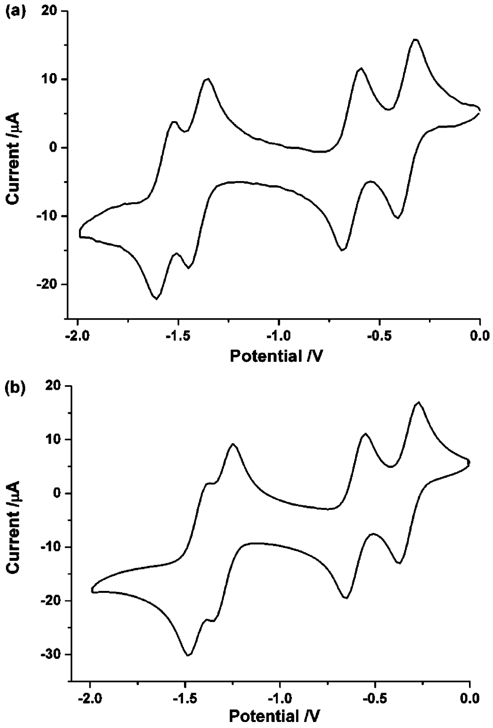

Figure 3. Reductive cyclic voltammogram of 0.5 mM **6** (a) and **7** (b) in CH_2Cl_2. Scan rate = 0.2 V/s (electrolyte, 0.1 M $TBAPF_6$).

Both diPBI **6** and 4CldiPBI **7** are black solids and soluble in common organic solvents such as dichloromethane, chloroform, and toluene. Room-temperature absorption spectra of **6** and **7** in $CHCl_3$ are shown in Figure 2. In contrast with PBIs **1**, triply linked diPBI **6** and 4CldiPBI **7** display broad and red-shifted spectra, probably as a reflection of largely extensive conjugation over the π-electronic system. The spectrum of **6** and **7** show major bands at 411, 517, 625, 684 nm (ϵ_{max} = 87 000 M^{-1} cm^{-1}) and 408, 504, 548, 602, 656 nm (ϵ_{max} = 76 000 M^{-1} cm^{-1}), respectively, which suggests the decreased optical HOMO−LUMO gaps compared to that of **1**. In comparison with **6**, the UV−vis spectrum of **7** is hypsochromic shifted because of the electron-withdrawing effect of chlorine substituents. As revealed by absorption spectra, diPBI **6** and 4CldiPBI **7** have broad absorption with high extinction coefficients which covers almost the whole visible region, rendering them as “full-absorption dyes” and therefore potential objects in solar cells.

Cyclic voltammetry (Figure 3) on **6** and **7** in CH_2Cl_2, using a silver wire as quasi-reference electrode and ferrocene as an internal potential marker have been investigated. The cyclic voltammograms of **6** and **7** exhibit well-defined, single-electron, two reversible and two quasireversible reduction waves, while only two reduction waves are found in that of **1**.[16] The half-wave reduction potentials vs Fc/Fc^+ are −0.46, −0.73, −1.49, and −1.66 V for **6** and −0.41, −0.69, −1.39, and −1.52 V for **7**. Because of the electron affinity of chlorine atoms, the reduction potentials of **7** are less negative than those of **6**, respectively. Furthermore, the first reduction potentials of **6** and **7** are much less negative than that of PBI,[16] thus revealing the extremely strong electron-accepting ability of triply linked diPBIs.

In summary, we report a highly efficient synthetic methodology toward bay-region fused diPBIs from easily available tetrachloro-PBI, which is conducted by the combination of copper involved traditional Ullmann-type coupling and C−H transformation. In light of the broad absorption with high extinction coefficients in the region of visible light and the extremely strong electron-accepting ability, which are evidenced from the low reduction potentials, triply linked fused diPBIs must be very promising for use as functional components of photovoltaic devices. Extension of this synthetic strategy to higher oligomeric perylene bisimides as well as further investigation to clearly understand the reaction mechanism is a fascinating next project that is currently underway.

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Supporting Information Available: Experimental details and characterization of compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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