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Copper-Mediated Domino Process for the Synthesis of Tetraiodinated Di(perylene bisimide)

Yubai Shi,[†,‡] Hualei Qian,[†,‡] Yan Li,[†,‡] Wan Yue,[†,‡] and Zhaohui Wang*[,†]

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School of the Chinese Academy of Sciences, Beijing 100080, China

wangzhaohui@iccas.ac.cn

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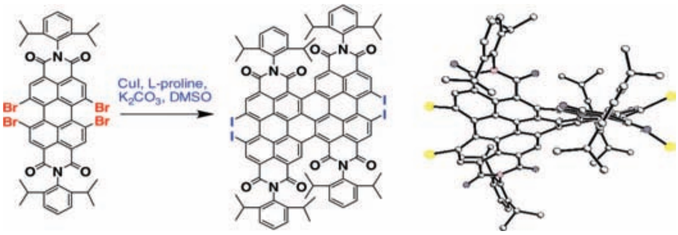
ABSTRACT



Tetraiodinated di(perylene bisimide) has been prepared from tetrabrominated perylene bisimide by the combination of Ullmann-type coupling, C−H transformation, and halogen-exchange. The crystal structure analysis confirmed that the aromatic core is quite distorted because of the electrostatic repulsion and steric encumbrance of iodine substituents in the bay regions.

Perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs) have attracted extensive interest in the past decade as excellent n-type semiconductors with good chemical and physical stabilities, high electron affinity, and carrier mobility.[1] Various synthetic protocols have been established to prepare PBIs and their derivatives. A diverse library of perylene bisimides has been obtained from commercially available dianhydride and a wide array of amines via conventional imidization.[2] Approaches have also been reported for attaching electron-donating or electron-withdrawing groups directly to the perylene core, which dramatically alter the optical and electronic properties.[3]

In the PBIs family, 1,7-dibromo- and tetrachloro-substituted PBIs have played important roles in the synthesis of bay-functionalized perylene dyes, which are attractive for application in fields such as light-harvesting arrays,[4] solar cells,[5] field effect transistors,[6] light-emitting diodes,[7] etc. Very recently, a series of core-fluorinated PBIs have also been synthesized by nucleophilic halogen-exchange reactions of the corresponding dibromo- and tetrachloro-substituted PBIs, which achieved promising n-type semiconducting

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[‡] Institute of Chemistry, Chinese Academy of Sciences.

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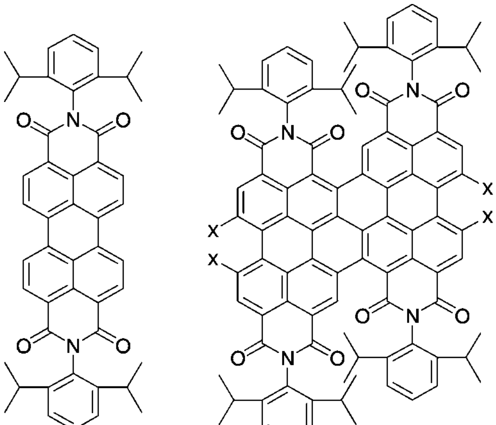
properties.[8] Iodide was usually selected among halides due to its higher reactivity in transition-metal-catalyzed processes such as the Stille-, Heck-, Suzuki-, and Ullmann-type coupling reactions[9] and was expected to have the advantage with many more synthetic possibilities of structural modifications. The copper-catalyzed halogen exchange at sp^2-carbons under Ullmann-type reaction conditions[10] has been regarded as one of useful methods for the incorporation of iodine substituents into PBIs. However, to the best of our knowledge, there have been no precedents of such a successful iodine exchange employing in halogenated PBIs. The difficulties may be due to steric congestion of bulky atoms and strong strain energies in conjugated aromatic cores.

Amino acid promoted CuI-catalyzed Ullmann-type coupling reactions have been widely employed in the formation of C−N, C−S, C−O, and C−C bonds.[11] Recently, we report the facile synthesis of triply linked[12] di(perylene bisimide) (diPBI) **2a** and tetrachloronated di(perylene bisimide) (4Cl-diPBI) **2b** (Figure 1) by coupling of tetrachloro-PBI under system of CuI and L-proline in different temperature.[13] In diPBI **2a**, the steric encumbrance of neighboring imide rings are expected to result in a distorted molecular structure, which may lead to the release of strain energies. Herein, we present the first example of one-pot synthesis of tetraiodinated di(perylene bisimide) (4I-diPBI) **5** by the combination of modified Ullmann coupling, C−H transformation and halogen-exchange reactions.



1

2a X = H

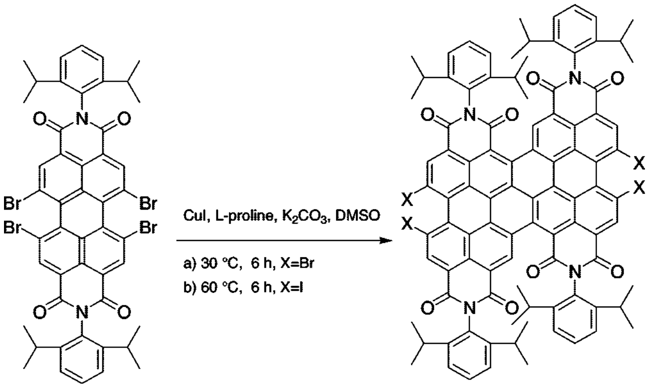
2b X = Cl

Figure 1. PBI **1**, triply linked diPBI **2a**, and 4Cl-diPBI **2b**.

First, we extended the established synthetic protocol to tetrabromo-PBIs.[14] Using CuI as the reagent, L-proline as the ligand, and K_2CO_3 as the base, the expected tetrabrominated diPBI (4Br-diPBI) **4** was obtained as a purple-black solid by homocoupling of tetrabromo-PBI **3** at 30 °C in 20% yield.

Generally, bromine−iodine exchange is observed at high temperatures under modified-Ullmann conditions. Thus, it will be feasible to incorporate four bulky iodine atoms into the diPBI backbone by raising the reaction temperature (Scheme 1). However, the reaction temperature should not be too high, as it may lead to the cleavage of C−halogen bonds. Accordingly, we raised the temperature to 60 °C and obtained the desired tetraiodinated diPBI (4I-diPBI) **5** as a navy-blue solid in 15% yield. Using CuBr as the reagent instead of CuI, only 4Br-diPBI was obtained by homocoupling of **3** at 30 and 60 °C. These results suggest that copper iodide played multiple roles in these reactions. In particular, excess CuI is the iodine source in halogen-exchange reactions. Four bromo−iodine exchanges as well as the formation of three new carbon−carbon bonds have been successfully achieved in this *domino*-type process.[15] The structures of 4Br-diPBI **4** and 4I-diPBI **5** were clearly characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and MALDI-TOF.

Scheme 1



3

4 X = Br
5 X = I

To determine the molecular structure of 4I-diPBI, crystals of **5** suitable for single-crystal X-ray structure analysis were obtained. The crystal structures revealed that **5** has crystallographically imposed inversion symmetry.[16] In 4I-diPBI **5**, owing to the electrostatic repulsion and steric encumbrance of the iodine substituents at the bay regions and the steric

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congestion between O4 (O4A) and adjacent H21 (H21A), the two perylene rings are fused to adopt a distorted conformation as expected with a mean plane deviation of 0.762 Å for the 40 core carbon atoms above and below the mean plane, and with C22−C24A and C22A−C24 bonds of 1.48 Å and a C23−C23A bond of 1.43 Å (Figure 2). The lengths of three newly formed C−C bonds are quite similar, as a reflection of effective conjugation over the diperylene core. The twist angle between the two benzene rings (C2−C3−C4−C5−C17−C18 and C6−C7−C8−C9−C13−C14) was determined to be 35.8°, thus indicating the extremely distorted molecular structure of **5**. Notably, the atropo-enantiomers which result from the distorted π system are contained in the crystal of **5**, separation of which is a difficult but interesting project.[17] Additionally, the neighboring imide rings are forced to adopt an up and down conformation with a dihedral angle of 24.8° and 28.2° relative to that mean plane, respectively. The distance between O4 (O4A) and the adjacent H21 (H21A) is as short as 2.32 Å indicating the existence of intramolecular hydrogen bonding. Interestingly, the self-assembly ribbons consisting of the ruffled nanographenes are observed in the crystal of **5** (Figure 3). The inversion-related pairs of 4I-diPBI molecules in the crystal of **5** are linked by weak intermolecular interactions of I1···O3 3.40 Å and I1···H8 3.05 Å (see the Supporting Information).

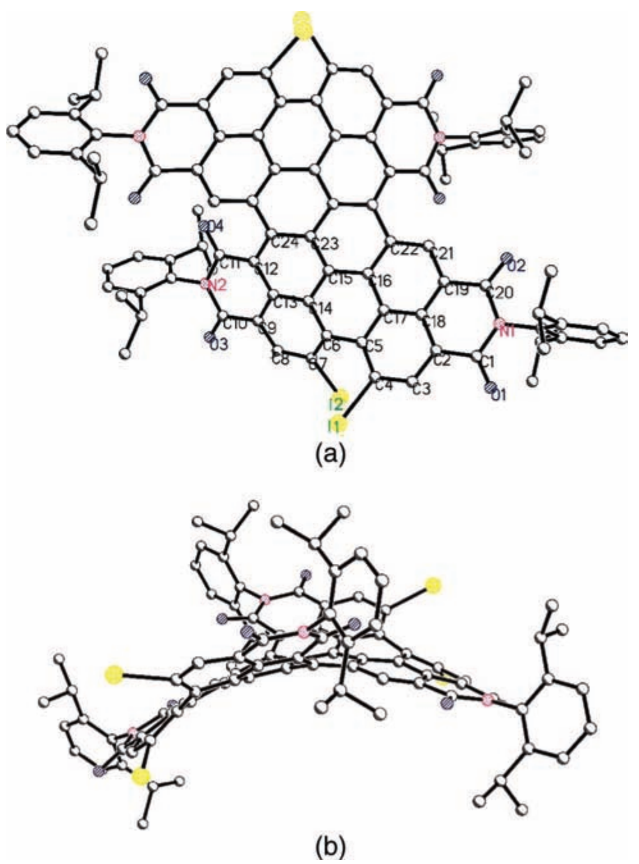

Figure 2. Molecular structure of 4I-diPBI **5**: (a) top view; (b) side view. The solvent molecules and hydrogen atoms are omitted for clarity.

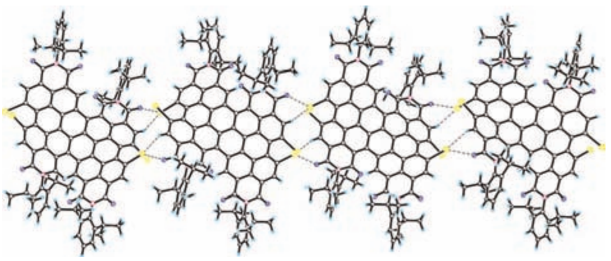

Figure 3. Intermolecular interactions in the ruffled ribbons of 4I-diPBI **5**.

Due to the combination of the twisted molecular structures and the bulky diisopropylphenyl groups, 4Br-diPBI **4** and 4I-diPBI **5** are soluble in common solvents such as toluene, dichloromethane, and THF. 4Br-diPBI **4** and 4I-diPBI **5** display broad absorption spectra in the region of visible light (Figure 4). In comparison with diPBI **2a**, the spectra of **4** and **5** are hypsochromically shifted resulting from the introduction of the electron-withdrawing halogen atoms. The blue solution of **5** exhibits five major

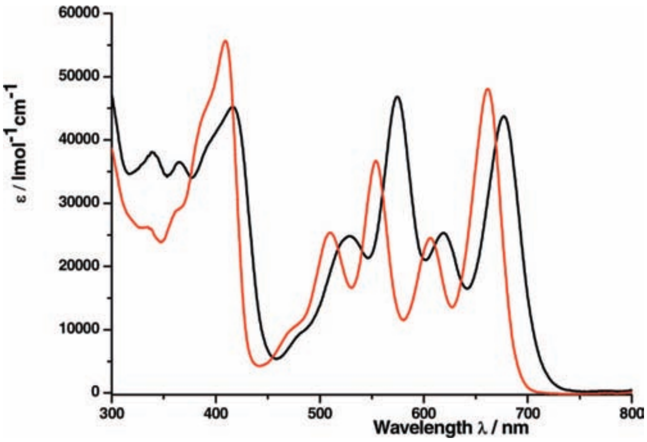

Figure 4. UV−vis absorption spectra of 4Br-diPBI **4** (red line) and 4I-diPBI **5** (black line) in $CHCl_3$ at room temperature.

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(16) **Crystal Data of $5\cdot 2C_6H_{12}$.** The measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation (λ 0.71073 Å) at 113 K. All calculations were performed using the CrystalStructure crystallographic software package and SHELXL-97. $C_{108}H_{98}I_4N_4O_8$, $M = 2087.50$, blue prisms, crystal dimension $0.24 \times 0.20 \times 0.10$ mm, monoclinic, space group $C12/c1$, $a = 35.341(5)$ Å, $b = 14.3173(14)$ Å, $c = 29.323(3)$ Å, $\alpha = 90.00°$, $\beta = 120.923(3)°$, $\gamma = 90.00°$, $V = 12729(3)$ Å^3, $Z = 4$, $D_c = 1.089$ g/cm^3, $\mu = 1.023$ mm^{-1}, θ range 1.60−25.00°. Of the 11193 reflections that were collected, 8518 were unique ($R_{int} = 0.0549$), GOF = 1.097.

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bands at 417, 528, 574, 618, and 677 nm, bathochromically shifted relative to **4** which exhibits five major bands at 409, 510, 554, 606, and 661 nm.

According to the previous studies, PBIs are fairly electron-deficient dyes and are easily reduced to anions and dianions, corresponding to the two imide groups in their structure.[1a,18] Thus, fully conjugated diPBIs are expected to display stronger electron-accepting ability and obtain four electrons. Cyclic voltammetry on **4** and **5** in CH_2Cl_2 has been investigated, which exhibits two reversible and two irreversible reduction waves (Table 1). The half-wave reduction potentials vs Fc/Fc$^+$ are −0.43, −0.71, −1.38, and −1.51 V for **4** and −0.42, −0.69, −1.32, and −1.47 V for **5**. Compared with diPBI **2a**, the reduction potentials of **4** and **5** are less negative, originating from the incorporation of the electron-withdrawing bromine and iodine atoms, respectively.

Table 1. Redox Potential (in V vs Fc/Fc$^+$)

	E_{1r}[a]	E_{2r}[a]	E_{3r}[a]	E_{4r}[a]
diPBI **2a**[c]	−0.46	−0.73	−1.49	−1.66
4Cl-diPBI **2b**[c]	−0.41	−0.69	−1.39	−1.52
4Br-diPBI **4**	−0.43	−0.71	−1.38[b]	−1.51[b]
4I- diPBI **5**	−0.42	−0.69	−1.32[b]	−1.47[b]

[a] Half-wave potential. [b] Determined by differential pulse voltammetry (DPV). [c] Data from ref 13.

In summary, we report the facile synthesis of 4I-diPBI **5** via the copper-mediated *domino* process which combines modified Ullmann coupling, C−H transformation, and halo-exchange reactions. X-Ray single-crystal analysis reveals that the extremely distorted molecular structure is dominated by the electrostatic repulsion and steric encumbrance of the iodine substituents at the bay regions and the steric congestion between the neighboring imide rings. The synthesis of 4I-diPBI opens the door to easy structural modifications on diPBI molecular skeletons in the bay regions. Further functionalization and investigation of bay-functionalized triply linked diPBIs are in progress.

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Supporting Information Available: General experimental methods, the synthesis and characterizations of compounds **4** and **5**, CIF file of **5**, and ^1H and ^{13}C NMR spectra and cyclovoltammograms for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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