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Introduction of Two Anthracene Moieties into Perylenebis(dicarboximide) Core by Suzuki–Miyaura Coupling toward Construction of Donor–Acceptor–Donor Arrays

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To create new π-conjugated compounds having a donor–acceptor–donor array, two 4-(9-anthrylethynyl)phenyl groups were introduced into a perylenebis(dicarboximide) structure at 1,6- or 1,7-positions by the Suzuki–Miyaura coupling of corresponding dibromoperylenebis(dicarboximide) and boronic acid ester derivatives. The UV–vis and fluorescence spectra and the electrochemical data of these donor–acceptor–donor type compounds suggested weak electronic interactions between the anthracene units and the perylenebis(dicarboximide) unit.

Perylenebis(dicarboximide) (PBI) units have been extensively utilized in the molecular design of various functional molecules because of their abilities as π-acceptor as well as effective chromophores and fluorophores (Figure 1).[1] It is noted that the properties of PBI derivatives are readily tunable by the introduction of substituents at aromatic moieties and imide-nitrogen atoms. Substituents at the bay positions (1,6,7,12-C) are known to greatly influence the electronic properties of the perylene moiety. In particular, the attachment of donor moieties to form a donor–acceptor (D–A) array[2] is a fascinating motif for organic dyes,[3] FETs,[1b,1c,4] and solar cell devices.[5] In order to synthesize such molecules, brominated PBIs are convenient starting materials that can be used for various cross-coupling reactions. For example, phthalocyanine and porphyrin units have been successfully introduced via acetylene linkers by the Sonogashira coupling.[6] In order to create new types of PBI derivatives as candidates for functional molecules, we introduced two rod-like donor units involving electron-rich anthracene moieties into a PBI center to construct a rigid D–A–D array that tends to form segregated tabular assemblies in the solid state. Therefore, we synthesized compounds **1a** and **2a** having two 4-(9-anthrylethynyl)phenyl (AEP) groups at 1,6- and 1,7-positions, respectively, by the Suzuki–Miyaura coupling. As far as we surveyed, anthracene units have not been adopted at the bay positions in functional PBI materials.[7] We expected that the rod-like units should not only extend the π-conjugation but also result in strong absorption and photoinduced electron transfer. We herein report the synthesis and spectroscopic data of the new D–A–D type PBI derivatives. Features in their electronic spectra and electrochemical data were compared with those of phenyl analogs **1b** and **2b** to evaluate the role of the anthracene units.

Target compounds **1a** and **2a** were synthesized by the Suzuki–Miyaura coupling (Figure 1).[8] A mixture of dibromo-PBI derivatives **3** and **4** in a 1:4 ratio, which were difficult to separate, was prepared by bromination followed by imidation of perylenetetracarboxylic dianhydride by a known method.[9] Boronic acid ester **5a** was prepared by the Sonogashira coupling of 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[10] and 9-ethynylanthracene.[11] The Suzuki–Miyaura coupling of **3** and **4** with **5a** was carried out in a conventional manner with [Pd(PPh$_3$)$_4$] and K$_2$CO$_3$ (aq) in THF. From the reaction products, **1a** and **2a** could be separated by chromatography on silica gel in 24 and 52% yields, respectively. Compounds **1a** and **2a** were obtained as a dark green solid and a purple solid, respectively, and were stable under ambient conditions. Phenyl analogs **1b** and **2b** were similarly synthesized from **3**, **4**, and **5b** in 12 and 50% yields, respectively. These compounds were reasonably characterized by NMR and mass spectrometry.[12]

The regioisomers were readily identified from the signal patterns of the ^{1}H NMR spectra based on the differences in molecular symmetry. Compound **1a** of C_{2v} symmetry gave two sets of signals due to N-CH$_2$ protons at δ 4.14 and 4.23, whereas **2a** of C_{2h} symmetry gave one set of signals at δ 4.11. Signals

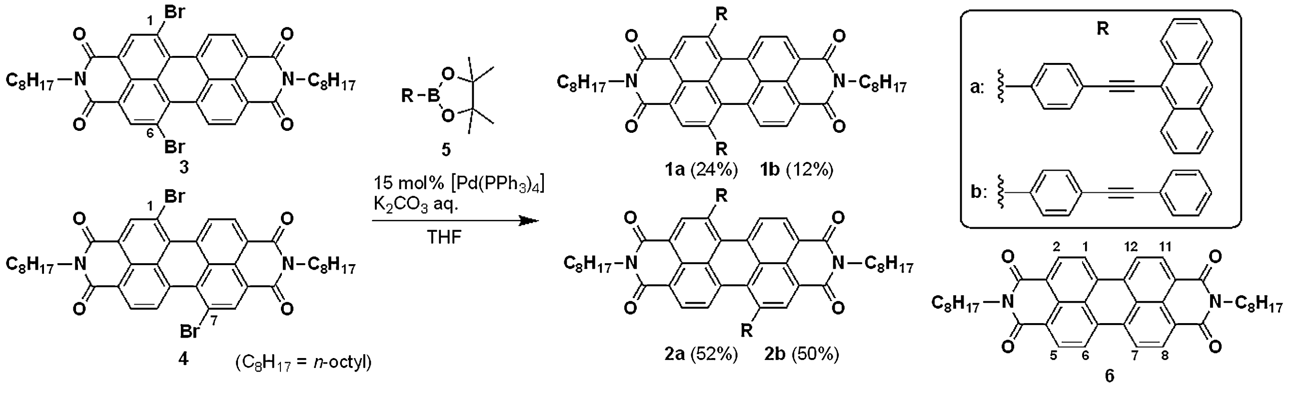

Figure 1. Synthesis of donor–acceptor–donor type PBI derivatives **1** and **2**.

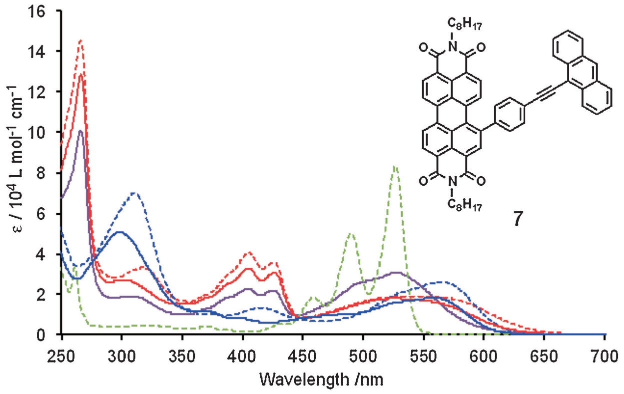

Figure 2. Absorption spectra of PBI derivatives and reference compounds in $CHCl_3$ at 1.2–2.5 × 10^{-5} M. —— **1a**, ---- **2a**, —— **1b**, ---- **2b**, —— **7**, and ---- **6**.

assignable the perylene protons were observed as one singlet and two doublets for both compounds. Those signals were shifted upfield by 0.3–1.0 ppm upon the introduction of AEP units, because the protons are located in the shielding region of the attaching phenylene groups. This structural requirement is supported by the DFT calculation of **1a′** and **2a′**, where the *N*-alkyl groups are methyl groups instead of alkyl groups. The structural optimization at the B3LYP/6-31G* level suggested that dihedral angles between the central PBI unit and the attaching phenylene units were 50–55° for both model compounds.[12]

The absorption spectra of **1a**, **2a**, and related compounds were measured in $CHCl_3$ (Figure 2). In the longest wavelength region, the absorption spectra of **1a** and **2a** gave broad bands with a shoulder extending to 600 nm. Meanwhile, the absorption spectrum of parent PBI **6** gave structured bands with a maximum at 523 nm, whereas the corresponding bands were shifted to the long-wavelength region in the order of monosubstituted analog **7**,[12] **1a** and **2a**, accompanied with broadened bands. This means that the π system is extended as more AEP units are introduced,[13] even though the perylene and phenyl moieties are nonplanar, as mentioned above. As for the disubstituted compounds, the bathochromic effect was slightly larger in the absorption spectrum of 1,7-substitution than in that of 1,6-substitution. In the absorption spectrum of **2a**, the intensity of the broad band at 500–600 nm was significantly decreased in aromatic solvents, such as benzene and toluene (see Supporting Information; SI[12]). We could not elucidate the cause of this characteristic solvent effect from available data.

Fluorescence spectra were measured in $CHCl_3$ (Table 1). The fluorescence quantum yields of **1a** and **2a** ($\Phi_f \leqq 0.03$) are much lower than those of phenyl analogs **1b** and **2b** and the reference compound **6**. The fluorescence lifetimes of **1a** and **2a** are shorter than those of the other compounds. These findings are attributed to the efficient photoinduced electron transfer from AEP units to PBI unit. The presence of 9-anthryl groups rather than phenyl groups at the tips of the rod-like units plays an important role in the quenching process. We also measured cyclic voltammograms in CH_2Cl_2 to evaluate the redox properties in solution (see SI[12]). All PBI derivatives gave two reversible reduction waves and irreversible oxidation waves. The reduction potentials listed in Table 1 indicate that the values are comparable for **1** and **2**, the absolute values of which are slightly smaller than those of **4**. This trend is consistent with the weak electronic coupling due to the twisting structure between the PBI unit and the attaching phenylene unit.

Table 1. Fluorescence and electrochemical data of PBI derivatives and reference compounds

Compound	λ_{em}/nm (Φ_f)[a]	τ_f/ns[b]	$E^{1/2}_{red}$/V[c]
1a	594 (0.03)	2.99	−1.03, −1.21
2a	600 (0.02)	2.60	−1.04, −1.18
1b	612 (0.76)	7.98	−1.01, −1.18
2b	617 (0.78)	5.30	−1.05, −1.20
7	571 (0.02)	4.64	−1.05, −1.20
6	527 (0.91)	3.65	−0.97, −1.11[d]

[a]Absolute fluorescence quantum yields. [b]Fluorescence lifetimes. [c]Measured in CH_2Cl_2 (1.0 mmol L^{-1}) with *n*-Bu_4NBF_4 (0.10 mol L^{-1}) as supporting electrolyte, Ag/Ag^+ as reference electrode. [d]Values for compound **4** instead of the parent PBI **6**.

In conclusion, we synthesized new PBI derivatives with two AEP groups by the Suzuki–Miyaura coupling. The photophysical properties were influenced by the rod-like donor units for several factors involving electron-transfer interactions. These properties can be further tuned by the introduction of various substituents, and cross-coupling reactions are powerful tools for the functionalization of PBI derivatives. Further studies of the synthesis of other PBI derivatives and the assembly of the D–A–D type molecules for use in organic devices are in progress.

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