

Anthraceno-Perylene Bisimides: The Precursor of a New Acene

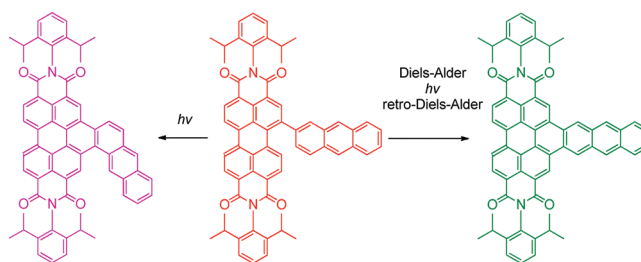
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Received September 6, 2011

ABSTRACT



A controlled synthesis strategy for a anthracene-fused perylene bisimide was developed from the cyclization of an anthracene unit pendant to a perylene diimide scaffold. The direct cyclization led to a zigzag molecule, while a Diels–Alder strategy influenced the regiochemistry of cyclization to afford the linear precursor of a new acene.

During the past decade, scientists have developed morphologies for synthesizing and characterizing many new conjugated hydrocarbons with extended polycyclic frameworks.¹ Acenes such as anthracene and pentacene have received much attention as optical and electronic materials.² Interest in the synthesis of acenes larger than pentacene, such as hexacene,³ heptacene,^{3b,4} octacene⁵ and

nonacene,⁶ is growing which is expected to increase the conjugated length for tuning electronic structure, aromaticity, and HOMO–LUMO gaps for molecular electronic application.^{1d} Understanding the structure–property relationships that relate specifically to these molecules could lead to new design rules for producing high-performance conjugated molecules. Anthony's group observed that heptacene is a stable and synthetically accessible molecule if it is protected by significantly bulky groups.^{3b} Wudl et al. have explored different synthetic methods to functionalize heptacenes.^{4c} Bettinger's group reported the synthesis and spectroscopic detection of unsubstituted octacene and nonacene under conditions of matrix isolation.⁵ Later, Miller's group reported a persistent substituted nonacene with a very small HOMO–LUMO gap of 1.12 eV.⁶ Still, the design and synthesis of novel structure acenes with a controlled electronic structure is a significant and ongoing challenge within molecular electronics.⁷

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Perylene tetracarboxdiimide derivatives are relatively easy to functionalize at main or bay positions, leading to soluble dyes for applications in organic photovoltaic devices,⁸ artificial light-harvesting complexes,⁹ organic electronic devices,¹⁰ light-emitting diodes,¹¹ and fluorescent¹² or NIR dyes.¹³ Benzannulation of the bay region of perylene bisimide expanded π -systems along the equatorial axis enabled new chromophores with significant hypsochromic absorption shifts,¹⁴ while the excellent photostabilities and high fluorescence quantum yields are retained. The benzannulation can be realized through the palladium-catalyzed ring annulation reaction^{14b,15} or phototriggered intramolecular cyclization.¹⁶ Core-extended perylene chromophores, naphthoperylene tetracarboxdiimide (**NP**),¹⁶ dibenzocoronene tetracarboxdiimide analogues (**BC**),^{16,17} and nitrogen heterocoronene tetracarboxdiimide analogues^{14c} are obtained by phototriggered intramolecular cyclization (Figure 1). We reasoned that by further extending the perylene bisimide along the equatorial axis and then removing the diimide unit, we could produce a new analogue of acene-like structure: perylene superimposed acenes (red core of **4** in Figure 1).

The high reactivity of anthracene rendered fruitful chemistry for anthracene derivatives.¹⁸ Here we reported the synthesis strategies to enlarge the aromatic π -system of perylene bisimide along the equatorial axis to give a precursor of a pentacene or nonacene analogue by the phototriggered intramolecular cyclization of 2-anthracene substituted perylene bisimide. In addition to the synthesis strategies, also discussed are the optoelectronic profiles of these molecules.

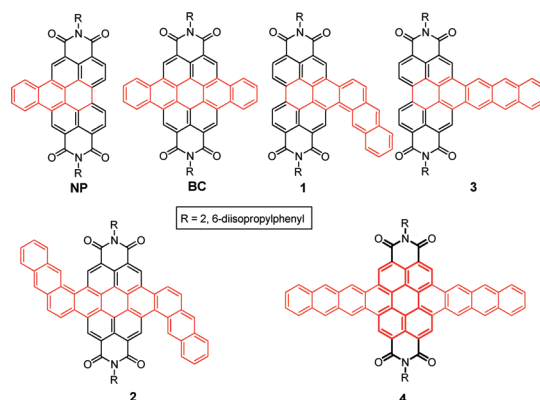


Figure 1. Molecular structures of the perylene bisimide superimposed acenes.

Coupling 2-anthracen-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane¹⁹ with 1-bromoperylene bisimide²⁰ or 1,7-dibromoperylene bisimide²¹ through Suzuki reaction gave donor–acceptor molecules **PDI-AN** and **PDI-2AN** in which photoinduced electron transfer (PET) between the perylene bisimide unit and the anthracene unit could occur (Scheme 1). The initial attempts to access the perylene bisimide superimposed acenes with the photocyclization reaction led to the zigzag constitutional compounds **1** and **2** in high yield, which is induced by the higher reactivity of the 1-position of the anthracene unit than that of the 3-position. Instead, we introduced a directing group generated at the 9,10-position of the anthracene moiety by Diels–Alder cycloaddition with *N*-3-hydroxypropyl maleimide, which tuned the reactivity of the phenyl ring connected with perylene bisimide by breaking the conjugation of anthracene. Positions 1 and 3 should have similar reactivity, but the steric effect induced by the directing group will enhance the possibility of position 3 to couple with perylene bisimide (Scheme S2). For instance, photocyclization of the endo- and exo-adduct **PDI-AN-DA** would lead to endo/exo-**PDI-AN-C**, totally cyclized at position 3. Followed by a re-Diels–Alder reaction, the linear constitutional compound **3** can be generated (Scheme 1). Perylene bisimide superimposed nonacene **4** can be obtained in the same way, but detailed characterization of **4** cannot be performed owing to the relatively rapid degradation in solution; only MS spectra can be obtained. In the synthesis procedure, the endo/exo-cycloaddition intermediates would lead to the same target. Spectral analysis of the mono- or dicyclized product by HRFAB mass spectrometry indicated the expected mass ion with the loss of two or four hydrogen atoms. The zigzag compounds **1** and **2** showed two characteristic doublet peaks of protons 3/4 of the anthracene unit, and the linear compound **3** exhibited two singlet peaks for protons 1/4,

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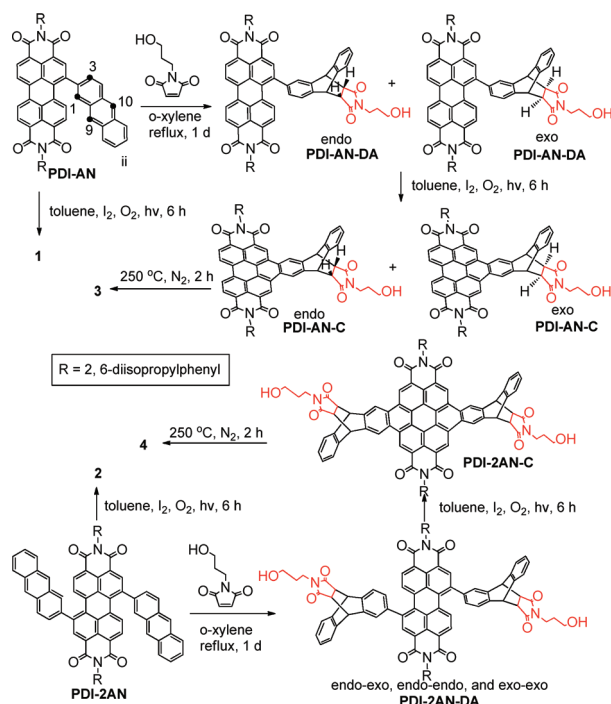
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9/10 of anthracene. All of these compounds except **2** and **3** were soluble in various organic solvents, such as CH₂Cl₂, CHCl₃, toluene, and acetone. ¹³C NMR spectra of **2** and **3** cannot be well resolved due to poor solubility. The cyclized compounds **1**, **2**, and **3** showed high thermal stability, with their decomposition temperature at up to 450 °C.

Scheme 1. Synthesis of the Anthracene Substituted Perylene Diimides and Their Photocyclization



The UV–vis absorption spectra and fluorescent spectra of **PDI-AN**, **1**, **3**, **PDI-2AN**, and **2** are presented in Figure 2. The UV–vis spectrum of **PDI-AN** shows a combination of an anthracene unit (325–400 nm) and red-shifted perylene bisimide absorption (530 nm). Dianthracene substituted **PDI-2AN** shows similar but broader absorbance in the long wavelength region (450–650 nm). After cyclization, the zigzag compound **1** showed a multipeak band with defined structures at a shorter wavelength (250–410 nm). A typical perylene vibronic structure with λ_{max} at 495 nm (high intensity band) and a shoulder absorbance band at $\lambda_{\text{max}} = 570$ nm (low intensity band) was observed in the longer wavelength region, which is similar to the UV–vis absorption of the coronenebis-(dicarboximide)s.^{14a} Interestingly, the low intensity band at 570 nm is solvent-dependent, which has a defined structure in cyclohexane (Figure S10a). For **2**, the absorption in the shorter wavelength region (320–430 nm) is increased, while in the region of longer wavelengths, the absorbances at 475 and 598 nm show similar intensity. For linear compound **3**, a broad band between 550 and 720 nm, a perylene like band at 475 nm, a sharp band at 380 nm, and an intensive band at 290–350 nm were observed.

PDI-AN emitted at 535 nm ($\phi = 0.212$ in CH₂Cl₂, with a lifetime of 4.17 ns), and a dimeric band at 575 nm appeared with increasing concentration (Figure S11). **PDI-2AN** emitted at 520 nm weakly ($\phi = 0.086$), which was induced by the PET from the anthracene unit to PDI. After cyclization, the anthracene units and perylene plane in **1** and **2** are twisted, which decreased the conjugation between them. **1** showed two emission bands at 520 and 645 nm in cyclohexane. The short wavelength emission is due to the perylene core which has a lifetime of 4.10 ns in CH₂Cl₂. The emission band at a longer wavelength showed a solvato-kinetic effect (Figure S10b), which is due to the charge transfer from an anthracene unit to a perylene unit, with a lifetime of 7.61 ns in CH₂Cl₂ ($\phi = 0.532$). With increasing solvent polarity, this band red-shifted and the emission intensity decreased; it disappeared in acetonitrile, DMF, and DMSO. Compound **2** emitted strongly at 650 nm ($\phi = 0.97$), with a lifetime of 7.71 ns in CH₂Cl₂. However, the linear compounds **3** did not emit, which was due to the strong intramolecular charge transfer.

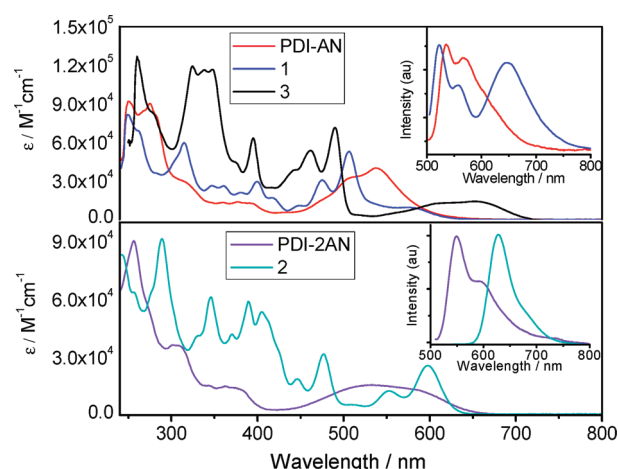


Figure 2. UV–vis absorption and fluorescence emission (inset) spectra of **PDI-AN**, **1**, **3**, **PDI-2AN**, and **2** in CH₂Cl₂.

To obtain the theoretical aspect of the spectroscopic properties of these compounds, the B3LYP/6-31+G* level using the Gaussian 03 program²² functional calculations of the molecular orbits of **1**, **2**, **3**, and **4** was studied. The HOMO and LUMO orbitals from the calculation are depicted in Figure 3 (Figure S2). For **1** and **2**, the density in the HOMO concentrated in the anthracene ring, while the density in the LUMO did not simply concentrate on the perylene bisimide ring; it was on the plane of perylene bisimide fused with one or two ethylenes in the bay region. For linear compounds **3** and **4**, the molecular orbits showed different behavior. In the case of **3**, the density in the HOMO still concentrated in the anthracene ring and the density in the LUMO concentrated on the perylene

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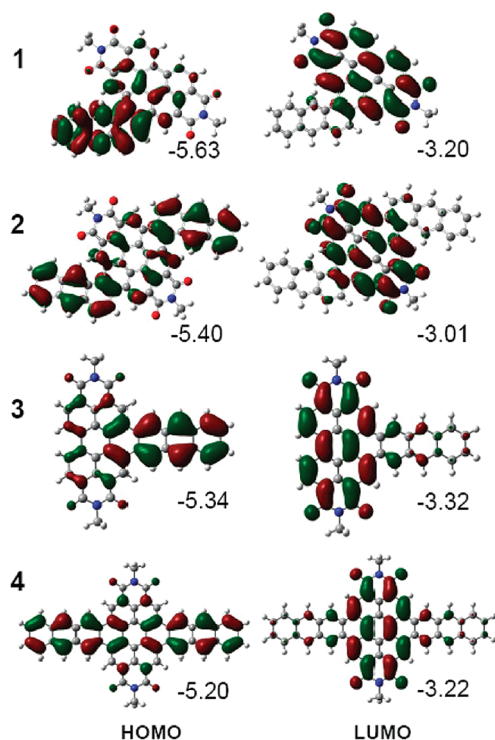


Figure 3. HOMO and LUMO of **1**, **2**, **3**, and **4** calculated by the B3LYP/6-31+G* method.

bisimide ring, but the gradual delocalization between these two moieties indicated the stronger conjugation in **3** than **1**. For **4**, the surfaces of the HOMO has a clear node in the center. Theoretical calculation was also carried out by the TD-DFT method at the B3LYP/6-31+G* level to investigate the electronic transitions (Figure S3–S6, Table S1–S4). The electronic transition analysis of compound **1** suggests that the band at 570 nm is caused by a transition from an anthracene-like HOMO to a perylene-like LUMO.^{17b} The second band at 495 nm shows the typical vibronic fine structure of perylene bisimide, as this band is related to the transition between the perylene-like HOMO–1 and the perylene-like LUMO. The 320–430 nm region absorbances are due to a HOMO→LUMO+1 transition. The transition of **3** is similar to **1**, except that the HOMO→LUMO transition is red-shifted for 80 nm and the HOMO–1→LUMO transition is blue-shifted for 18 nm. For **2**, the absorbance at about 600 nm is caused by the transition from HOMO to LUMO and the band at 550 nm is due to the transition of HOMO–2→LUMO.

On the basis of the onset of the longest-wavelength absorption, the optical HOMO–LUMO gaps for perylene bisimide superimposed acenes were calculated to be 2.04 (**1**), 1.98 (**2**), 1.75 (**3**), which are 0.2–0.4 eV smaller than the

predicted value (2.43 (**1**), 2.39 (**2**), 2.02 (**3**)). The band gap widths were further confirmed by cyclic voltammetry (Table S5). Upon cyclization, there existed two one-electron reduction waves for zigzag compounds **1** (–1.14 and –1.35 V) and **2** (–1.26 and –1.44 V). Compared with that of **PDI-AN** (–0.98 V) and **PDI-2AN** (–1.00 V), the first reduction potential of **1** was negatively shifted by about 160 mV and that of **2** was negatively shifted about 260 mV. The oxidation process was irreversible, which was attributed to oxidation processes that involved the anthracene unit (1.04 V for **1**, 0.96 and 1.10 V for **2**). The band gaps based on cyclic voltammetry were 2.18 and 2.22 eV for **1** and **2**. For linear compounds **3**, the reduction and oxidation processes are all irreversible, the electrodonation ability is enhanced ($E_{\text{ox}} = 0.58$ V, negatively shifted about 400 mV compared with that of **1**). The band gap of linear **3** (1.80 eV) is smaller than that of the zigzag **1**, further supporting the claim that the twisting of the aromatic cores driven by steric congestion between 9-H on anthracene and the neighboring hydrogen atoms on the perylene core (Figure S1) greatly reduced the electronic communication between the anthracene and perylene units in the zigzag constitutional compounds.

In conclusion, we demonstrated a facile method for the synthesis of an anthracene-fused perylene bisimide from the cyclization of an anthracene unit pendant to a perylene diimide scaffold. The direct cyclization led to a zigzag molecule, while a Diels–Alder strategy influenced the regiochemistry of cyclization to thus afford ultimately the linear molecule. Although we have not yet succeeded in the isolation of **4**, we expect that the stable analogue can be obtained by protection of the anthracene unit. These acene-like compounds showed mainly the properties of the perylene bisimide core; the low energy absorbance for the central acene-like core was not evident. However, success in the synthesis of this kind of functionalized acene-like structures will help to stimulate significant new synthetic targets; for example, after removal of the diimide unit, structures with more acene-like properties should be expected.

Acknowledgment. We are grateful for financial support from the National Nature Science Foundation of China (21031006, 20971127, 90922017, 20831160507), NSFC-DFG joint fund (TRR 61), and the National Basic Research 973 Program of China.

Supporting Information Available. Detailed experimental procedures, characterization data, UV–vis absorption spectra, electrochemistry data, and results of theoretical calculation, complete ref 22. This material is available free of charge via the Internet at <http://pubs.acs.org>.