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Synthesis and Properties of Ethylene-Annulated Di(perylene diimides)

Yan Li,[†] Can Wang,[§] Cheng Li,[†,‡] Simone Di Motta,[∥] Fabrizia Negri,[*,∥] and Zhaohui Wang[*,†]

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, Graduate School of the Chinese Academy of Sciences, Beijing, China, Department of Chemistry, Wuhan University, Wuhan, China, and Dipartimento di Chimica 'G. Ciamician' and INSTM, UdR Bologna, Università di Bologna, Bologna, Italy

**fabrizia.negri@unibo.it; wangzhaohui@iccas.ac.cn*

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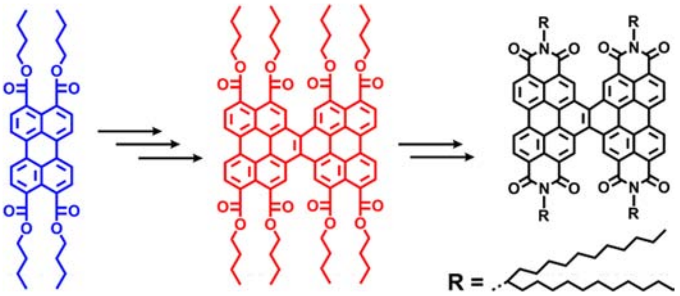
ABSTRACT



A new synthetic method toward ethylene-annulated di(perylene diimides) from easily available ethylene-annulated di(perylene esters), which is conducted by ICl-induced cyclization and Mizoroki–Heck coupling of ethynylene-linked di(perylene esters), is reported.

Due to their remarkable electro-optical properties,[1] perylene-3,4:9,10-tetracarboxylic acid diimides (PDIs, **1**, Figure 1) have received a great deal of attention as promising organic n-type semiconductors which have found applications such as in light-harvesting arrays,[2] field effect transistors,[3] light-emitting diodes,[4] and photovoltaics[5] in recent decades. To achieve air-stable, high performance organic electron transport materials, the design and synthesis of novel oligo-PDIs with extended conjugated cores to lower the LUMO level and more electron-withdrawing substituents to maintain good processability is considered to be a critical issue. In recent years, many efforts have been made in this area, but because of the difficulties in developing synthetic methodology for fully conjugated oligo-PDIs, only perylene diimide units conjugatively linked by phenylene, ethynylene, or a butadiynylene spacer via Suzuki, Sonogashira, and Glaser coupling are available.[6]

We are particularly interested in the design and synthesis of novel π-extended electron-poor molecules based on rylene diimides. Recently, we reported a facile one-pot synthesis of hybrid rylene diimide arrays via a combination of Stille coupling and C–H transformation and tetracene tetracarboxylic diimides via direct double ring extension of electron-deficient NDIs involving metallacyclopentadienes.[7]

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

[‡] Graduate School of the Chinese Academy of Sciences.

[§] Department of Chemistry, Wuhan University.

[∥] Department of Chemistry and INSTM, UdR Bologna, University of Bologna.

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Meanwhile, we also reported the facile homocoupling of tetrahalogenated PDIs to give triply linked fully conjugated oligo-PDIs via Ullmann reaction and C−H transformation,[8] which have been applied as exceptionally high performance n-type semiconductors and photosensitizers for singlet oxygen generation.[9]

In order to obtain oligo-PDIs which have unique electro-optical properties, good processability, and strong electron-accepting ability, and inspired by the previous creation of fused aromatic rings, we have designed, synthesized, and investigated the electro-optical properties of novel oligo-PDIs, namely ethylene-annulated di(perylene diimides) (**2**, Figure 1) from ethylene-annulated di(perylene esters), utilizing ICl-induced cyclization and Mizoroki-Heck coupling of ethynylene-linked di(perylene esters).

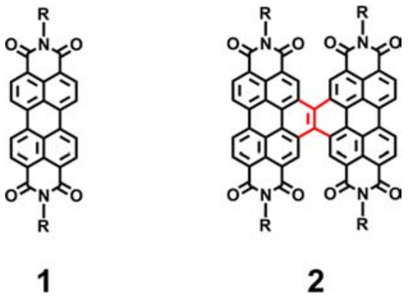
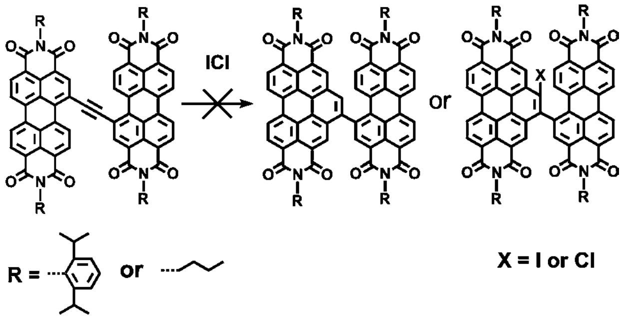
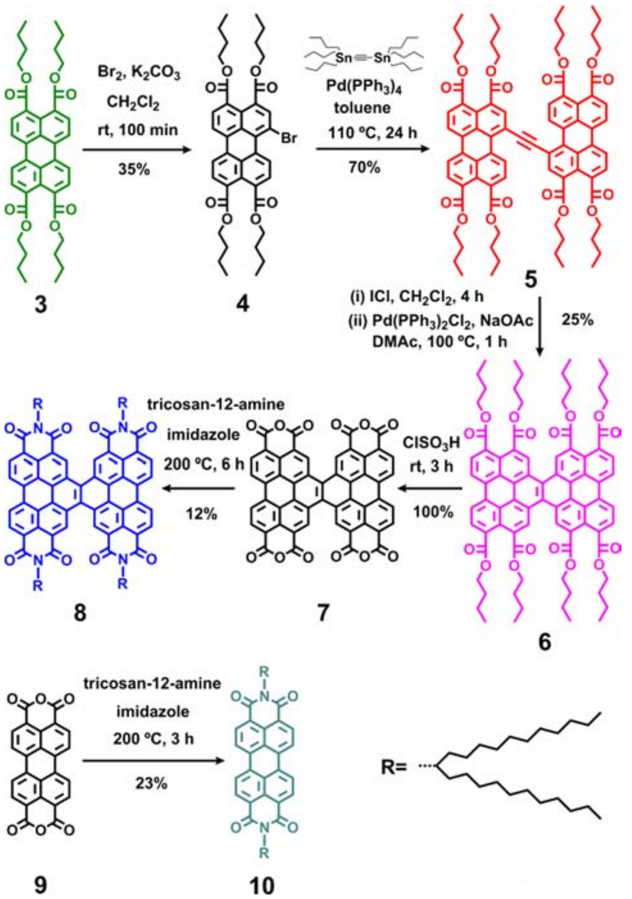


Figure 1. Perylene diimides (**1**) and ethylene-annulated di(perylene diimides) (**2**).

Scheme 1. Synthesis of Fused-Ring Structures via ICl-Induced Cyclization of Ethynylene-Linked Di(perylene diimides)



Scheme 2. Synthesis of Ethylene-Annulated Di(perylene diimides)



Iodine, ICl, and iodonium salt induced[10] intramolecular acetylene cyclization reactions have been widely used to synthesize polycyclic aromatic hydrocarbons (PAHs), especially dibenzo[*g*,*p*]chrysenes, with high quantum yields, small Stoke shifts, and long-lived excited states, and dibenzo[*a*,*j*]anthrancene.[11,12] However, this efficient method to make extended fused-ring structures is usually

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useful only for electron-rich aromatic systems and is rarely used for electron-deficient aromatic molecules. In order to obtain well-defined ethylene-annulated di(perylene diimides), we initially focused our attention on ethynylene-linked di(perylene diimides) as potential precursors for the targets. These were synthesized by palladium-catalyzed *Stille* cross-coupling of monobromo-PDI with bis(tributylstannyl)acetylene. After screening various reaction conditions of acetylene cyclization, however, we did not get the desired product (Scheme 1). It was conjectured that PAHs bearing weak electron-withdrawing groups may be more inclined to undergo the cyclization.

The synthesis of ethylene-annulated di(perylene diimides) is shown in Scheme 2. The key starting material was 3,4;9,10-tetra(*n*-butoxycarbonyl)perylene **3**, which was obtained in 92% yield via esterification of perylene-3,4;9,10-tetracarboxylic dianhydride (PTCDA) with alkanol and alkyl halide in a homogeneous solution.[13] Bromination of **3** in dichloromethane at room temperature for 100 min provided versatile building blocks, namely the monobrominated perylene esters (**4**, 35%) and dibrominated perylene esters (10%, mixture of isomers) for the construction of ethylene-annulated oligo-PDIs. Ethynylene-linked di(perylene esters) **5**, which have weak electron-withdrawing groups, are then available via *Stille* cross-coupling of monobrominated perylene ester **4** and bis(tributylstannyl)acetylene.

When ICl was added to a dichloromethane solution containing compound **5** at −78 °C and stirred at room temperature for 3.5 h, the reaction afforded an intermediate fused-ring structure,[11b−d] which has moderate stability in air. Treatment of the intermediate fused-ring molecule with $Pd(PPh_3)_2Cl_2$ and sodium acetate in DMAc (*N*,*N*-dimethylacetamide) at 100 °C for 1 h afforded the desired ethylene-annulated di(perylene esters) **6** in 25% yield. It should be noted that the utility of sequential ICl-induced cyclization and Mizoroki−Heck coupling is sometimes limited by the skeleton of the aromatic substrates and the electronic character of the substituents. Typically, bis(biaryl)acetylenes containing unsubstituted and electron-rich substituents[11b] are more active in the cyclization, whereas cyclization under these conditions does not work for more complicated and electron-deficient PAHs,[14] while coronene diimides synthesized via ICl-induced cyclization of diethynyl PDIs were only reported recently.[15] Thus, the successful ICl-promoted cyclization and Pd-catalyzed annulation of ethynylene-linked di(perylene esters) **5** to afford the desired product ethylene-annulated di(perylene esters) **6** is particularly interesting.

Hydrolysis of **6** in chlorosulfonic acid was carried out smoothly at room temperature and produced almost quantitatively the corresponding ethylene-annulated di(perylene dianhydrides) **7**, which are highly insoluble in common organic solvents even at high temperature. The condensation of **7** with tricosan-12-amine in imidazole led to ethylene-annulated di(perylene diimides) **8** in 12% yield, while this method is reported to be effective for the synthesis of related annulated diPDIs.[6b] In order to compare the opto-electrical properties between **1** and **2**, perylene diimide **10** was synthesized via condensation of perylene dianhydride and tricosan-12-amine under the same reaction conditions, which was also afforded in low yield (23%). So optimizing the reaction conditions is very important for achieving a high yield of soluble ethylene-annulated di-PDIs.

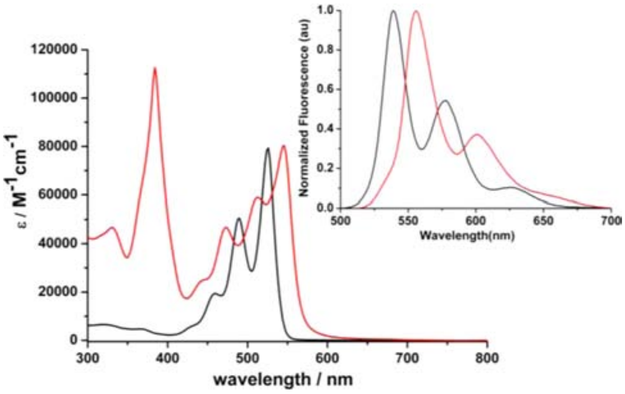

Figure 2. UV/vis absorption spectra of **10** (black) and **8** (red) in $CHCl_3$ (1×10^{-5} M) at room temperature. Inset: emission spectra of **10** (black) and **8** (red).

Figure 2 shows the comparison between the absorption and emission spectra of perylene diimide **10** and ethylene-annulated di(perylene diimides) **8** in $CHCl_3$, both of which have very good solubility in common organic solvents such as *n*-hexane, CH_2Cl_2, $CHCl_3$, and toluene. Ethylene-annulated di(perylene diimides) **8** shows four major bands in the 400−600 nm range with low-energy maxima at 546 nm, bathochromically shifted by 20 nm relative to that of perylene diimide **10**. Furthermore, in contrast with perylene diimide **10**, which shows absorption only in the 400−550 nm range, ethylene-annulated di(perylene diimides) **8** exhibits a high molar extinction coefficient at 384 nm.

An analysis in terms of the orbital nature of the TD-CAM-B3LYP/6-31G* computed electronic transitions of **8** (see Tables S1−S3 and Figure S3 for a comparison between computed and observed spectra) sheds more light on the nature of the lowest energy transitions of **8**. As seen in Figure 3, the frontier molecular orbitals of **8** correspond to linear combinations of the HOMO and LUMO orbitals of **10**, as already pointed out for triply linked PDIs.[8d] In addition, however, the presence of the ethylenic bridge contributes considerably to the frontier orbitals H−2 and L+2 in Figure 3. As a result, the lowest energy transition, dominated by the HOMO→LUMO excitation, is a typical PDI transition, shifted to lower energy on account of the electronic and excitonic coupling between the two PDI

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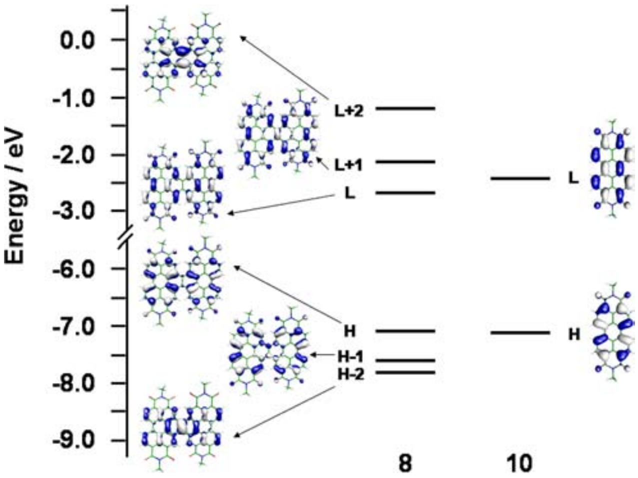

Figure 3. Energies and shapes of CAM-B3LYP/6-31G* frontier π orbitals of models for compounds **8** and **10**, showing the dominant orbital parentage.

units in **8**. The next, higher intensity transition observed at ca. 384 nm is dominated by the H→ L+2 electronic excitation where the L+2 orbital is considerably localized on the ethylenic bridge and located at low energy compared to other diPDIs.

The fluorescence spectra of **10** and **8** are also exhibited in Figure 2. Both of these compounds show high fluorescence in solution with a maximum at 539 nm for **10** and 556 nm for **8**, corresponding to a Stokes shift of 13 and 10 nm, respectively. The small Stokes shift between the absorption and emission bands of ethylene-annulated di(perylene diimides) **8** is probably due to the rigid conjugated structure.

The electrochemical properties of **10** and **8** are also investigated by cyclovoltammetry in dichloromethane (vs Ag/AgCl), and their reductive potentials and the energy levels are shown in Table 1. Perylene diimide **10** and ethylene-annulated di(perylene diimides) **8** exhibit two reversible reduction waves, whereas within the accessible scanning range no oxidation waves could be detected. The first and second reduction waves for **8** are observed at −0.54 and −0.69 V vs Ag/AgCl, respectively, which implies a stronger electron-accepting ability, a smaller E_g, and a LUMO level closer to [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$) being dominantly used as the acceptors in polymer solar cells,[16] compared with perylene diimides **10**.

Table 1. Electronic Properties and Energy Levels of Perylene Diimides and Ethylene-Annulated Di(perylene diimides)

	E_{1r}[a]	E_{2r}[a]	LUMO[b]	HOMO[c]	E_g[d]
10	−0.60	−0.85	−3.89	−6.16	2.27
8	−0.54	−0.69	−3.92	−6.08	2.16

[a] Half-wave reductive potentials (in V vs Ag/AgCl) measured in CH_2Cl_2 at a scan rate of 0.2 V/s with ferrocene as an internal potential marker. [b] Estimated from the onset potential of the first reduction wave (in eV). [c] Estimated from LUMO levels and E_g (in eV). [d] Obtained from the edge of the absorption spectra (in eV).

In summary, we reported a new synthetic method toward ethylene-annulated di(perylene diimides) from easily available ethylene-annulated di(perylene esters), which is conducted by ICl-induced cyclization and Mizoroki–Heck coupling of ethynylene-linked di(perylene esters). In light of the unique electro-optical properties, good processability, and electron-accepting ability, ethylene-annulated di(perylene diimides) are very promising for use as novel electron-acceptor materials in organic thin film transistors and polymer solar cells. Extension of this synthetic strategy to higher ethylene-annulated oligo-PDIs and applications in electronic devices are currently underway.

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

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The authors declare no competing financial interest.