

Core-Extended Terrylene Diimide on the Bay Region: Synthesis and Optical and Electrochemical Properties

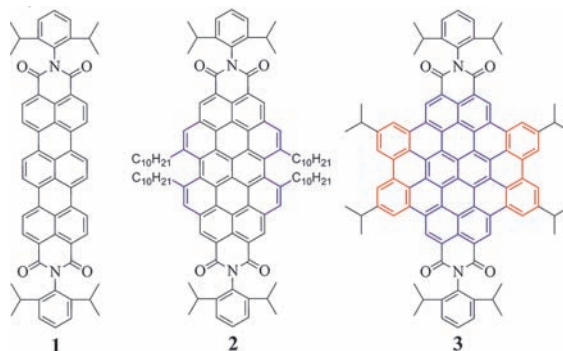
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ABSTRACT



Two novel core-extended terrylene diimides on the bay region (CETDIs) were synthesized via annulation of the four additional ethylene units or benzene units on the bay region of the terrylene diimide core. The optical and electrochemical properties of the two compounds were investigated. These CETDIs exhibited broad absorption spectra with high extinction coefficients, which span a wide range in the ultraviolet and visible spectrum from 300 to 700 nm. Furthermore, the redox process of the CETDIs increased from two waves to four waves, and the lowest unoccupied molecular orbital (LUMO) levels were enhanced from -4.00 to -3.59 eV.

Perylene diimides (PDIs) have received considerable attention in dye chemistry,¹ supramolecular assemblies,² and optoelectronic applications³ because of their exceptional properties, such as photochemical stabilities, high

quantum yields,⁴ and ability to self-assemble into ordered supramolecular structures.⁵ Modifications of PDIs have been concentrated on the bay regions, at which chemical

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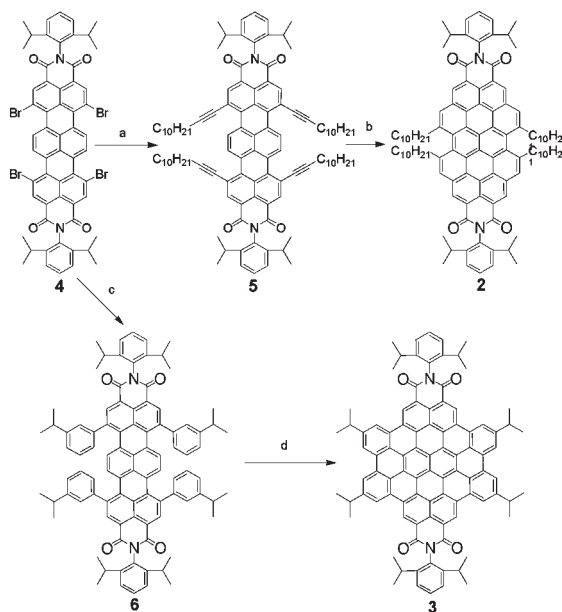
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substitution can dramatically alter the intermolecular interactions and the optical electronic properties.^{6,7} Furthermore, the core-extended of **PDI**s attract huge interest and offer access to various biological⁸ as well as organic electronic applications.^{9,10} Core bay-extended **PDI**s include annulated hydrocarbon aromatic rings¹¹ and diverse heterocycles such as sulfur-,¹² pyridyl-, and N-heterocyclic¹³ substituted **PDI**s.

The higher **PDI** homologues, terylene diimides (**TDI**s), exhibit the same attractive properties, such as brilliant color; high extinction coefficients, a high fluorescence quantum yield of 90%, and high thermal, chemical, and photochemical stabilities, which are generally required for practical use.^{7a,14,15} However, core-extended terylene diimides on the bay region remain unexploited. Our current interests are development of the core-enlarged terylene diimide on the bay region for use as stable fluorophores.¹⁶ While this work was in progress, Klaus Müllen and co-workers reported the synthesis and chiroptical properties of a partially core-extended terylene diimide.¹⁷ In this paper, the synthesis of the fully core-extended terylene diimides on the bay region (**CETDI**s) was present, and their optical and electrochemical properties were further investigated.

Scheme 1. Synthesis of Core-Extended Terylene Diimides^a



^a (a) CuI, Pd(PPh₃)₄, TEA, toluene, 80 °C, 24 h; (b) DBU, toluene, 80 °C, 24 h; (c) Pd₂(dba)₃, DPEPhos, K₂CO₃, H₂O, toluene, ethanol, 95 °C, 36 h; (d) FeCl₃, nitromethane/CH₂Cl₂, 25 °C for 0.5 h.

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The synthetic approach for **CETDI**s is outlined in Scheme 1. Tetrabromoterylenedicarboximide **4** was prepared according to literature procedures.¹⁸ Under Sonogashira conditions, the reaction of compound **4** with 1-dodecyne yielded the intermediate compound **5**, which was not isolated but was converted to the **CETDI 2** through the addition of DBU to the reaction mixture. Some cyclization of intermediate compound **5** to the final product was observed prior to the addition of DBU.^{6c}

Suzuki coupling of compound **4** with 3-isopropylphenylboronic acid produced the terylene diimides **6** with a 63% yield. Intramolecular oxidative cyclodehydrogenation reactions were then performed on compound **6** using FeCl₃ as an oxidant. With 40 equiv of FeCl₃ (3.3 equiv per hydrogen to be removed), the completely closed **CETDI 3** was obtained within 30 min with a 70% yield.^{19,20} These **CETDI** compounds show good solubility in common organic solvents such as cyclohexane, dichloromethane, chloroform, tetrahydrofuran, and toluene. The **CETDI**s have been fully characterized by H NMR spectroscopy, C NMR spectroscopy, and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS).

The ¹H NMR spectrum of **CETDI 2** in CDCl₃ (Figure S1A in Supporting Information) shows the resolved resonances of the fourteen aromatic protons with four signals. However, eight protons H1 (Ar-CH₂) of **CETDI 2** show two distinct signals at 4.37–4.32 and 4.19–4.14 ppm, which were assigned by the aid of ¹H–¹³C COSY NMR data. It suggests that protons Ar-CH₂ are not equivalent

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(19) At room temperature, the color of the reaction solution changed three times, suggesting that the cyclodehydrogenation reaction is a stepwise mechanism. However, this cyclodehydrogenation condition using 20 equiv of FeCl₃ (1.7 equiv per hydrogen to be removed) did not produce the completely closed **CETDI 3**, even after the reaction time was extended to 48 h. The formation of partially closed compound **6** is due to the hindrance induced by the twisting of the terylene diimides **6**.

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due to conformational restrictions, with a possible contribution from the anisotropic magnetic current. Furthermore, four C1 of **CETDI 2** have the same chemical shift at 37 ppm (Figure S1C in Supporting Information).

In contrast to **CETDI 2**, the chemical shifts of aromatic protons H4 of **CETDI 3** show two sets of signals, a doublet signal at low field of 7.87 ppm with a large coupling constant of 9.0 Hz and another doublet signal at high field of 7.47 ppm with a small coupling constant of 7.2 Hz (Figure S1B in Supporting Information). It is very surprising that the chemical shifts of the aliphatic CH and (CH₃)₂ groups of **CETDI 3** respectively show two sets of signals with a 0.4 to 1.8 ppm interval. The protons H3 of 2,6-diisopropylphenyl on the imide show two sets of signals with a 0.4 ppm interval, a doublet signal at low field of 2.24 ppm and another doublet signal at high field of 1.84 ppm. The protons H1 and H2 of isopropyl on the aromatic core have four sets of signals with 1.8 and 1.5 ppm intervals, respectively. The protons H1 and H2 of the substituted group near the large aromatic core have a long ppm interval. However, the protons H3 and H4 of the substituted group far from the large aromatic core have a short ppm interval. The ring-current effects of the large aromatic π -systems, which result in the anisotropic magnetic current, are possibly responsible for the two sets of signals of the same substituted group.²¹

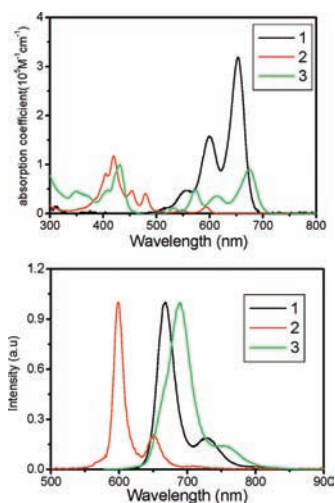


Figure 1. UV–vis spectra (top) and fluorescence emission spectra (bottom) of **CETDIs** in chloroform.

The UV–vis absorption spectra and fluorescence spectra of the **CETDIs** in chloroform are shown in Figure 1, and the photophysical data are summarized in Table 1. The UV–vis spectra of the **CETDIs** show a multippeak band with defined structures. Compared with **TDI 1**, **CETDI 2**

has a significantly blue-shifted absorbance maximum at 419 nm with four low intensity bands at 592, 548, 479, and 453 nm. It is already known that an extension of the core of **PDIs** in some cases induces a shift to shorter wavelengths in their absorption spectra, which is in contrast to the extension along their long molecular axis.^{7,11a} Furthermore, the extinction coefficient of **CETDI 2** is lower than that of **TDI 1** but still remains high ($\epsilon = 115\,000\text{ M}^{-1}\text{ cm}^{-1}$).

The absorption band of **CETDIs** is red-shifted after the annulation of four additional benzene units in the bay region of the terylene diimide core. At the shorter wavelength region, **CETDI 3** shows a slightly red-shifted absorption band with a comparable extinction coefficient (Table 1). However, the longest absorbance maximum of **CETDI 3** is significantly red-shifted by 84 nm (from 592 to 674 nm) with highly improved extinction coefficients (from 15 000 to 91 000 $\text{M}^{-1}\text{ cm}^{-1}$). It is noteworthy that the **CETDI 3** has seven absorption bands with high extinction coefficients, which span a wide range of the UV–vis spectra from 300 to 700 nm. The broad spectrum and high extinction coefficient of **CETDI 3** make it a potential compound for organic solar cells.^{12b,22}

Table 1. Optical and Electrochemical Properties of **CETDIs**

Compd	$\lambda_{\text{max}}/\text{nm}$ (log ϵ)	$\lambda_{\text{em}}/\text{nm}$ (Φ)	E_{HOMO} eV ^a	E_{LUMO} eV ^a	E_{g} eV ^b
1	652 (5.50), 600 (5.20), 556 (4.67)	667, 730 (0.90)	−5.58	−4.00	1.82
2	592 (4.16), 548 (3.85), 479 (4.61) 453 (4.67), 4.19 (5.07), 404 (4.91)	597, 650 (0.10)	−5.72	−3.79	2.08
3	674 (4.95), 614 (4.55), 5.73 (4.69), 532 (4.03), 429 (5.00), 406 (4.66)	689, 756 (0.55)	−5.29	−3.59	1.77

^aEnergy level of HOMO and LUMO according onset of first oxidation potential and reduction potential: 1.18 V and −0.40 V for **1**; 1.32 V and −0.61 V for **2**; 0.89 V and −0.81 V for **3**. ^bOptical band gap according UV/vis absorption.

The emission spectra of all **CETDIs** are recorded, and the wavelength of the emission maxima is given in Table 1. **TDI 1** in chloroform exhibits a deep red fluorescence with a quantum yield of 90%.¹⁴ Annulation of the four additional ethylene units on the core bay led to the hypsochromic shift of the emission maxima by 70 nm (from 667 to 597 nm), leading to orange red fluorescence with a low quantum yield of 10%. Further fusion of the four benzene units on the core bay resulted in the red shift of emission maxima of **CETDI 3** by 92 nm (from 597 to 689 nm). The fluorescence quantum yield of **CETDI 3** increased by 55% but is still lower than that of **TDI 1**. Furthermore, the two **CETDI** compounds display small Stokes shifts of approximately 5 nm to 15 nm. In the case of the terylene diimides core twist, small Stokes shifts are possibly responsible for the decrease in the fluorescence quantum yield. The small

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Stokes shift results in a strong reabsorption effect which lowers the fluorescence quantum yield.

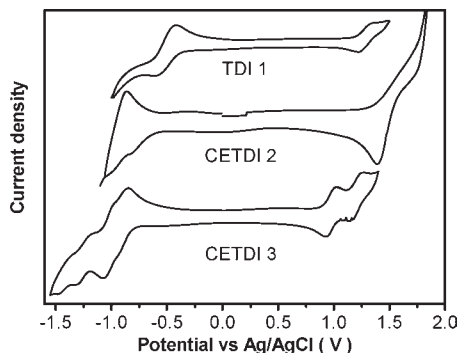


Figure 2. Cyclic voltammograms of compound **CETDI**s in dichloromethane at a scan rate of 0.1 V/s.

The electrochemical properties of the **CETDI**s in dichloromethane were studied by cyclic voltammetry (CV). Figure 2 shows the CV curves of the **CETDI**s. **TDI 1** shows one reversible oxidation potential at 1.35 V vs Ag/AgCl and one reversible reduction potential at -0.56 V vs Ag/AgCl. **CETDI 2** exhibits one irreversible reduction potential at -0.89 V, whereas **CETDI 3** exhibits two reversible reduction potentials at -1.0 and -1.30 V, respectively. These **CETDI**s show a continuous decrease of the first reduction potential, indicating that the electron-accepting power becomes weaker. **CETDI 3** exhibits two reversible oxidation potentials at 1.01 and 1.26 V respectively. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) were estimated from the onset of the first reduction potentials and first oxidation potentials.²³ The HOMO and LUMO levels of the

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three compounds were calculated as -5.29 to -5.58 eV and -3.59 to -4.00 eV, respectively. The continuously enhanced LUMO levels are ascribed to the terrylene diimides core twist, which weaken the electronic coupling between two of the electron-deficient imides.²⁴ Compared with **TDI 1**, **CETDI 2** has lower HOMO levels. However, **CETDI 3** shows enhanced HOMO levels, suggesting that the electron-donating property of **CETDI 3** becomes stronger.

In conclusion, we reported the synthesis of the core bay-extended terrylene diimides by the palladium-catalyzed coupling reaction and ring annulation reaction. The optical and electrochemical properties of the two compounds were investigated. Fused with four ethylene units in the bay region of the terrylene diimides, **CETDI 2** has a significantly blue-shifted absorbance and emission maximum with low extinction coefficients and fluorescence quantum yields. **CETDI 3**, after annulation of an additional four benzene units on the bay region of the terrylene diimides, shows red-shifted absorbance and emission maxima with a high extinction coefficient and moderate fluorescence quantum yield. **CETDI 3** has seven absorption bands with high extinction coefficients, which span a wide range of the UV and visible spectrum from 300 to 700 nm. Furthermore, the redox process of the **CETDI**s increased from two to four waves, and the LUMO levels were enhanced from -4.00 to -3.59 eV.

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Supporting Information Available. Detailed synthetic procedures and characterization, general procedures, and supporting spectroscopic and microscopic images. This material is available free of charge via the Internet at <http://pubs.acs.org>.