EurJOC
European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201200980

Core Expansion of Perylenetetracarboxdiimide Dyes with Anthraquinone Units for Electron-Accepting Materials

Liang Xu,[a,b] Chao Liu,[a,b] Zhihong Qin,[a,b] Runsheng Jiang,[a,b] and Yongjun Li*[a]

Keywords: Dyes/pigments / Chromophores / Photovoltaic device / Electron transfer / Fused-ring systems / Cyclization / Electrochemistry / Density functional calculations

A perylenetetracarboxdiimide derivative containing an anthraquinone unit has been synthesized by the phototriggered intramolecular cyclization of 2-anthraquinone-substituted perylenetetracarboxdiimide. The anthraquinone-substituted perylenetetracarboxdiimide dyes showed excellent electron-accepting abilities with four reversible reduction potentials. Photovoltaic devices of ITO/PEDOT:PSS/P3HT:PDIs/Ca/Al were fabricated and power conversion efficiencies of 0.16 and 0.39 were obtained for **1** and **2**, respectively.

Introduction

Perylenetetracarboxdiimide derivatives (PDIs) as organic chromophores have been widely used in sensors,[1] logic gates,[2] molecular machines,[3] organic electronic devices,[4] organic photovoltaic devices,[5] organic field-effect transistors,[6] and NIR absorbing dyes[7] owing to their thermal and photochemical stabilities, high molar extinction coefficients, high fluorescence quantum yields, and exceptional electron-accepting abilities. To further improve their physical and chemical properties, considerable attention has been directed towards the modification of PDIs through high-yielding synthetic routes. Two approaches are usually adopted. One is to introduce substituents at the imide nitrogen atoms,[8] the other is to introduce substituents with electron-donor or -acceptor groups at the aromatic core in the bay region, which could dramatically change the properties of the PDIs. Not only the perylene core, but also the linkage between the substituents and the PDI can be twisted by direct C–C coupling of substituents in the bay positions. On the one hand, this twisting could help to improve the solubility of the PDIs by reducing π–π interactions between the PDIs,[4b] but on the other hand, the twisting might weaken the π-conjugative interactions due to the loss of planarity of the molecules. Usually, bay-functionalized perylenetetracarboxdiimides are obtained from the corresponding brominated derivatives.[9] Replacement of the bromo group is achieved by metal-catalyzed C–C coupling, such as Suzuki,[10] Stille,[11] and Sonogashira reactions,[12] or by traditional nucleophilic substitutions[13] and Diels–Alder reactions.[14] For bay-substituted PDIs, photocyclization is an efficient way to obtain ring-expanded molecules. We have previously prepared core-extended perylene chromophores by phototriggered intramolecular cyclization of perylenetetracarboxdiimides functionalized with a phenyl group, nitrogen-containing five-membered heteroaromatic rings (imidazole, 1,2,4-triazole, and pyrazole), and an anthracene group.[15]

In most cases, perylenetetracarboxdiimides are employed as electron-accepting units,[16] although on some occasions they can also be used as electron-donating units.[17] Whether a PDI acts as a donor or an acceptor clearly depends on the nature of the substituent.[17c] When good electron acceptors such as fullerenes are attached to PDIs, electron transfer from the PDI to the fullerene can be observed.[17a,18] As a traditional colorant, quinones are widely used in the dyestuff industry.[19] In addition, they are also involved in electron transport in biological systems and in the photosynthesis of bacteria and plants.[20] Recently, quinones have found applications in sensors,[19] optical recording media,[21] and solar energy conversion.[22] Among the derivatives of quinones, 9,10-anthraquinone (AQ) is widely known as an electron-accepting group with low reduction potentials.[20a] In addition, the preparation of AQ is relatively simple and it can be easily incorporated into π-conjugated systems.[23] In light of this, we designed two new PDI derivatives **1** and **2** with the 2-anthraquinone moiety attached to the bay region. The solubility of **2** was efficiently improved because of the reduced π–π interactions and the increased polarity of the molecule. Through the phototriggered intramolecular cyclization of 2-anthraquinone-substituted perylenetetracarboxdiimide **2**, we obtained zigzag constitutional compound **1** in which the aromatic π system of the perylenetetracarboxdiimide is length-

---

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100190, P. R. China
E-mail: liyj@iccas.ac.cn
Homepage: http://english.ic.cas.cn/
[b] Graduate University of Chinese Academy of Sciences,
Beijing 100049, P. R. China

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200980.

ened along the equatorial axis. The photo- and electrochemical properties of these perylenetetracarboxdiimide dyes were also investigated, as were their applications in photovoltaic devices.

Results and Discussion

Synthesis

The synthesis of compounds **2** and **1** is outlined in Scheme 1. One of the starting materials, 2-(9,10-dioxo-9,10-dihydroxy-2-anthryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**) was synthesized in two steps according to a literature report.[24] First, 2-aminoanthraquinone was converted into 2-bromoanthraquinone by the Sandmeyer reaction. Secondly, 2-bromoanthraquinone was treated with bis(pinacolato)diboron to give AQ-boronic ester **4**. Another starting material, 1-bromoperylenetetracarboxdiimide **3**, was again obtained according to the literature.[25] Suzuki coupling of compounds **4** and **3** gave compound **2** in 81% yield. Subsequent exposure to sunlight produced compound **1** in 90% yield within 5 min.

The colors and fluorescence emissions of unsubstituted PDI, **2**, and **1** are shown in Figure S2 in the Supporting Information. The unsubstituted PDI is an orange color and displays a light-yellow fluorescent emission. Introduction of the anthraquinone substituent in the bay position caused a redshift in the color, with **2** being a red color and exhibiting a light-red emission. Cyclization of **2** in sunlight led to a blueshift, with **1** a green-yellow color and displaying weak green-yellow fluorescence emission.

The UV/Vis absorption and fluorescent spectra of **2** and **1** are presented in Figure 1 and the data are summarized in Table 1. According to the literature,[11,26] unsubstituted PDI shows an absorption band (450–550 nm) peak at 527 nm with characteristic vibronic fine structure, which has been attributed to perylene core π→π* transitions.[27] The absorption band at the longer wavelength can be assigned to the electronic $S_0 \rightarrow S_1$ transition with the dipole moment along the long molecular axis, whereas the absorption band at the lower wavelength can be assigned to the electronic $S_0 \rightarrow S_2$ transition with the dipole moment perpendicular to the long molecular axis.[13,28] The AQ group exhibits an absorption band in the region 200–300 nm.[20b] The UV/Vis spectrum recorded for **2** shows a combination of an anthraquinone unit (200–300 nm) and a perylenetetracarboxdiimide unit (450–550 nm). Because of steric constraints, the anthraquinone moiety is rotated out of the perylene plane with a dihedral angle of 56.1° (see Figure S4 in the Supporting Information) and so the π-conjugative interactions are weakened; as a consequence, in comparison to the $\lambda_{\max}$ value of unsubstituted PDI (527 nm), the $\lambda_{\max}$ for **2** is only slightly redshifted by 3 nm to 530 nm. After cyclization, the $\lambda_{\max}$ value of **1** is blueshifted by 21 nm to 506 nm, partly due to the electron affinity of the anthraquinone moiety. The blueshifted absorption of **1** suggests that more energy is needed for the optical transition.[29] Meanwhile, a new absorption band peak at 346 nm can be seen. Compared with unsubstituted PDI and **2**, the absorption bands of **1** span a wider range in the UV/Vis spectrum. The maximum extinction coefficient for **2** is 41139 $\text{M}^{-1}\,\text{cm}^{-1}$, whereas that of **1** is 55816 $\text{M}^{-1}\,\text{cm}^{-1}$; the difference between these two values can be attributed to the large twist in compound **2**.

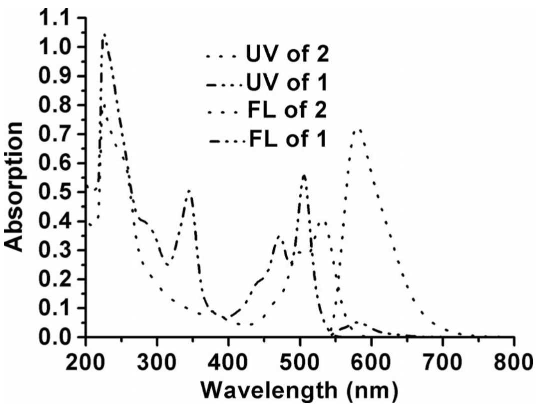
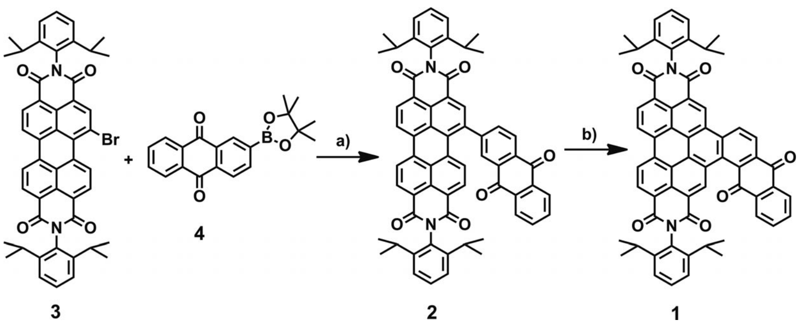


Figure 1. UV/Vis absorption and fluorescence emission spectra of **2** and **1** in CH_2Cl_2.

In comparison with unsubstituted PDI (534 nm), the maximum emission of **2** is redshifted by 45 nm to 579 nm, with a Stokes shift of 49 nm, and the fluorescent quantum yield is about 0.78, measured relative to unsubstituted PDI in CH_2Cl_2 solution as reference.[26a] Unsubstituted 9,10-anthraquinone itself shows no photoluminescence. The decrease in the fluorescence intensity of the perylene core in **2** is due to steric twisting of the perylene ring and the elec-



Scheme 1. Synthetic route to compounds **2** and **1**. Reagents and conditions: a) KCO_3, $[Pd(Ph_3P)_4]$, toluene/ethanol (3:1); b) *hν* (sunlight or sun lamp), CH_2Cl_2.

Table 1. Photophysical and electrochemical data for **2** and **1**.

Compound	**2**	**1**
Absorption[a] λ_{max} [nm]	530	506
ε[a] [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]	41139	55816
Fluorescence[b] λ_{max} [nm]	579	581
Φ_{fl}[c]	0.78	0.050
Stokes shift	49	75
E_{ox} [V vs. SCE][d]	1.71[e]	
E_{red} [V vs. SCE][d,e]	–0.55, –0.76, –1.04, –1.38	–0.60, –0.83, –1.16, –1.45
HOMO/LUMO [eV][f]	–6.11/–3.85	–/–3.80
E_g [eV][f]	2.26	

[a] Measured in CH_2Cl_2 solution (1.0×10^{-5} M). [b] Measured in CH_2Cl_2 solution (1.0×10^{-6} M) upon excitation at 500 nm. [c] In CH_2Cl_2, *N*,*N′*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide (unsubstituted PDI, Φ_{fl} = 1 in $CHCl_3$)[26a] was used as standard. [d] Performed in CH_2Cl_2 under N_2 by using $n\mathrm{Bu}_4\mathrm{NPF}_6$ (0.05 M) as the supporting electrolyte, platinum as the counter electrode, glassy carbon as the work electrode, and the saturated calomel electrode (SCE) as the reference electrode. [e] Half-wave potentials are given. [f] The HOMO and LUMO levels were obtained directly from CV according to the method reported in the literature.[36]

tron-accepting character of anthraquinone.[30] The cyclized product **1** shows a maximum emission at 581 nm, which is redshifted by 47 and 2 nm compared with unsubstituted PDI and **2**, respectively. Meanwhile, the fluorescent quantum yield of **1** is only 0.050. The significant quenching of the fluorescent intensity of **1** is possibly a result of efficient intramolecular electron transfer between the perylenetetracarboxdiimide donor and the anthraquinone acceptor induced by excitation of the electron-donating perylenetetracarboxdiimide chromophore.[31] The Stokes shift for **1** is 75 nm. The relatively large variation of the Stokes shift upon cyclization might be attributed to the stabilization of the HOMO by the anthraquinone acceptor and the destabilization of the LUMO by the perylenetetracarboxdiimide donor.[32]

The photophysical properties of **2** and **1** in different solvents were also investigated (see Figure S3 and Table S3 in the Supporting Information). Compared with the absorption spectra recorded in dichloromethane, blueshifts were only observed in cyclohexane and dibutyl ether. In cyclohexane, the absorption λ_{max} values of **2** and **1** are blueshifted by 12 and 10 nm, respectively, whereas in dibutyl ether blueshifts of 10 and 8 nm were observed. The absorption spectra show small changes in other solvents. The fluorescence spectra are also influenced by solvent polarity. Clear blueshifts were observed in the spectra recorded in cyclohexane and dibutyl ether, whereas redshifts were detected in methanol and DMF. In cyclohexane, the fluorescence emission λ_{max} values of **2** and **1** are blueshifted by 8 and 13 nm, whereas in dibutyl ether blueshifts of 5 and 10 nm occur. In contrast, the fluorescence emission λ_{max} values of **2** and **1** are redshifted by 6 and 3 nm in methanol, and by 4 and 4 nm in DMF. Meanwhile, significant fluorescence quenching was observed in strongly polar protonic solvents. For example, the fluorescent quantum yields of **2** and **1** are only 0.24 and 0.038 in methanol. The polarity and dipole moment are the major factors that affect the optical properties. Increasing the polarity of the solvent could lead to redshifts of the optical spectra and quenching of the fluorescence emission. Protonic solvents may facilitate the formation of hydrogen bonds between the anthraquinone unit and hydrogen proton, which might also cause weak redshifts.

The redox potentials of these compounds were determined by cyclic voltammetry in dichloromethane (Figure 2). The data are summarized in Table 1. According to the literature,[33] one reversible oxidation potential at 1.65 V (vs. SCE) and two reversible reduction potentials at –0.53 and –0.75 V (vs. SCE) were observed for unsubstituted PDI. For anthraquinone-substituted PDI **2**, one reversible oxidation potential and four reversible reduction potentials appeared, whereas for cyclized product **1**, only four reversible reduction potentials emerged. The oxidation potential versus SCE is 1.71 V for **2**. The reduction potentials versus SCE are –0.55, –0.76, –1.04, and –1.38 V for **2**, and –0.60, –0.83, –1.16, and –1.45 V for **1**. Compared with unsubstituted PDI, the oxidation potential of **2** is positively shifted by 0.06 V, which indicates that the electron-deficient anthraquinone moiety renders oxidation more difficult. Furthermore, after cyclization, the oxidation peak of **1** disappears, which may be due to intramolecular charge transfer from the perylenetetracarboxdiimide group to the anthraquinone group.[34] The electronic communication between the PDI and AQ units might be reduced significantly as a result of the large twisting of the conjugated core, as verified by theoretical calculations (see Figure S4 in the Supporting Information), and thus the two units are relatively independent such that the first two reduction potentials for **2** are almost the same as those of unsubstituted PDI.[5b] However, after cyclization, the first two reduction potentials of **1** are negatively shifted by 0.05 and 0.07 V compared with those of **2**, respectively. These shifts are probably due to the planar core of **1**, which facilitates electronic communication between the perylenetetracarboxdiimide and anthraquinone units and renders intramolecular charge transfer between the two units more efficient.[35] The extended π-conjugated system would increase the resonance energy and delocalize the negative charge more effectively, which could explain why the fourth reduction potential is closer to the third reduction potential in the case of **1**.

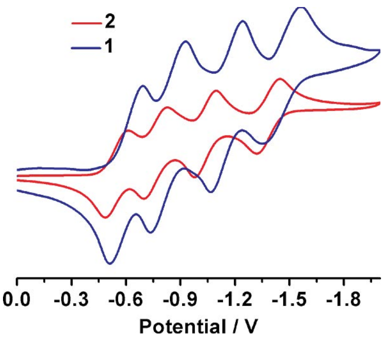


Figure 2. Cyclic voltammograms of **2** and **1** vs. SCE in CH_2Cl_2.

The HOMO and LUMO energy levels and the energy gap of **2** and the LUMO energy level of **1** were evaluated from the cyclic voltammograms. For unsubstituted PDI, the HOMO and LUMO levels are –6.05 and –3.87 eV, respectively, and the energy gap is 2.18 eV. The corresponding values for **2** are –6.11, –3.85, and 2.26 eV, whereas the LUMO level for **1** is –3.80 eV. Thus, the anthraquinone substituent in **2** lowers the HOMO level and moves the charge density from the HOMO of the perylenetetracarboxdiimide core to the LUMO of the anthraquinone substituent such that the positive charge density resides on the perylenetetracarboxdiimide core.[37] In this circumstance, better planarity of the molecules would result in greater charge transfer and delocalization leading to a LUMO with a higher energy.[38]

For the perylenetetracarboxdiimide core, the changes in optical and redox properties are primarily due to the inductive effect of the groups on the frontier orbitals. To investigate the spectroscopic properties of these compounds from a theoretical point of view, the molecular frontier orbitals of **2** and **1** were studied by DFT at the B3LYP/6-31tG* level of theory by using the Gaussian 03 program.[39] The molecular orbital (MO) map of **2** (Figure 3) shows that both the HOMO and LUMO are localized over the perylenetetracarboxdiimide moiety, which indicates that no charge transfer occurs in **2** in the ground state. As a result, in **2**, the PDI and AQ units maintain their individual optical characteristics. For **1**, the charge density in the HOMO and LUMO is not simply concentrated on the perylenetetracarboxdiimide ring, it is also located over the fused linkage between the perylenetetracarboxdiimide and the anthraquinone moiety. The calculated HOMO and LUMO energies and the energy gap of **2** are –5.99, –3.54, and 2.45 eV, which are in good agreement with the electrochemical experimental data, and the values calculated for **1** relative to **2** are the same. The anthraquinone moiety plays an important role in the LUMO+1 and LUMO+2 as a result of its electron-withdrawing nature (see Figure S4 in the Supporting Information). The quantum chemical calculations are in good agreement with the UV/Vis spectra and electrochemical data. The optimized configurations of **2** and **1** show that the mean plane of the anthraquinone ring is not parallel to the mean plane of the perylene ring, having dihedral angles of 56.1 and 5.5°. Thus, upon cyclization, the anthraquinone moiety and perylenetetracarboxdiimide ring in **1** lie approximately in one plane, which leads to better conjugation and electron delocalization.

We also investigated the photovoltaic properties of **2** and **1**. As we know, perylene diimide derivatives with large and tunable molar absorption coefficients have potential as light-absorbing materials rather than purely as transport materials,[40] exhibit good electron-accepting properties,[41] and may be highly conducting along the π–π stacking axis.[42] In addition, they are more easily functionalized than fullerenes.[43] Thus, PDIs provide a much larger choice of acceptor materials for use in bulk heterojunction (BHJ) solar cell devices.[5b,44] The electron-donating conjugated polymers used in BHJ solar cell devices at present are mainly poly(3-hexylthiophene)s (P3HT).[45] However, to date the performances of solution-processed devices based on P3HT and PDIs have been rather poor (normally below 0.05%).[4b] BHJ solar cell devices based on P3HT and commercially available unsubstituted PDI only exhibit efficiencies of 0.18%.[5b] Recently, BHJ solar cell devices composed of blends of P3HT and an asymmetric PDI derivative exhibited efficiencies of 0.37%.[4b]

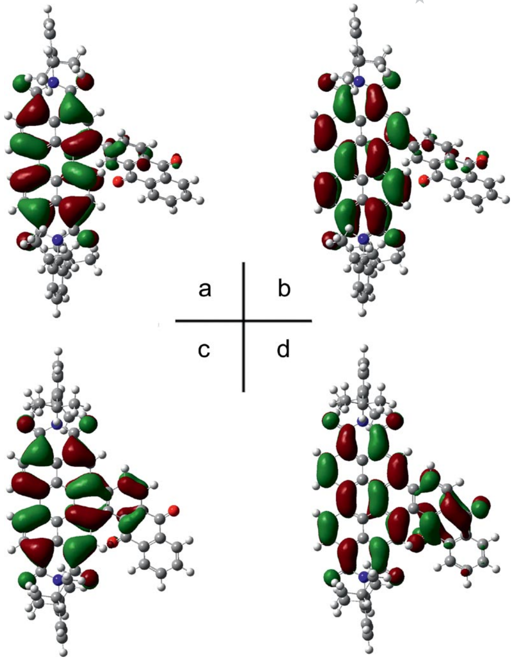


Figure 3. Calculated frontier orbitals for (a) the HOMO of **2**, (b) the LUMO of **2**, (c) the HOMO of **1**, and (d) the LUMO of **1**.

As we discussed earlier, the absorption ranges of **2** and **1** are located in the middle of the visible region with suitable extinction coefficients. The LUMO energies of **2** (–3.85 eV) and **1** (–3.80 eV) are close to that of PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) (–3.71 eV). The LUMO gap (1.17 or 1.22 eV) and HOMO gap (1.40 eV) between P3HT and **2** or **1** are large enough to guarantee efficient exciton dissociation.[46] The difference between the LUMO of **2** and the HOMO of P3HT is as large as 1.40 eV, which could lead to a high open circuit voltage (V_{OC}) for solar cells.[47] Thermogravimetric analysis (TGA) of **2** and **1** revealed that they are both thermally stable over 350 °C. Given the features of **2** and **1**, we investigated the performances of devices based on P3HT and **2** or **1**. The indium/tin oxide (ITO) (150 nm)/poly(ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS, CLEVIOS A1 4083) (50 nm)/P3HT:PDIs (100 nm)/Ca/Al devices were fabricated by spin-coating a thin-layer of PEDOT:PSS onto the ITO glass substrate. Figure 4 shows the *J–V* curves for the devices based on **2** and **1**.

The photovoltaic properties including open circuit voltages (V_{OC}), short circuit current densities (J_{SC}), fill factors (FF), and power conversion efficiencies (PCEs) of the devices with 1:1 donor/acceptor weight ratios are summarized in Table 2. Because V_{OC} is related to the gap between the LUMO of the acceptor and the HOMO of the donor,[48] an

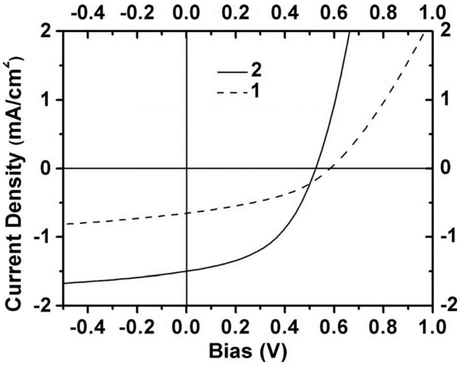


Figure 4. *J–V* curves for the P3HT/PDIs devices with SA and PTA treatment under AM 1.5 G illumination at 100 mW cm^{-2} (SA = solvent annealing; PTA = pre-thermal annealing).

acceptor with a lower LUMO causes a device to have a lower V_{OC}. This is borne out by the lower V_{OC} level of the device based on **2**. In general, large π systems such as PDIs are inclined to close molecular π–π packing, which has two effects on efficiency. On one hand, it may be beneficial to electron charge carriers and, on the other, it may aggravate the intermolecular charge recombination.[49] Therefore finding a balance between favorable molecular packing and a suitable distorted molecular geometry is a key goal to realizing a high efficiency. Thus, in our view, it seems that with the help of large substituents such as the anthraquinone group in the bay positions, the molecular packing of PDI could be largely suppressed and consequently the intermolecular charge recombination minimized. At the same time, this torsion of molecules does not lower the rate of charge carriers significantly. Perhaps this is the reason why the value of J_{SC} for **2** is higher than that for **1**. Finally, solar cells with **2** exhibited a power conversion efficiency of 0.39%, which is more than two-fold that of the efficiency (0.16%) achieved with **1**.

Table 2. Performance of ITO/PEDOT:PSS/P3HT:PDIs/Al bulk heterojunction photovoltaic devices[a] under a simulated photovoltaic light with 100 mW cm^{-2} illumination (AM 1.5 G).

Sample	PCE [%]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	Area [cm^2]
2	0.39	0.52	1.50	47.36	0.044
1	0.16	0.58	0.65	40.36	0.168

[a] The fabrication of photovoltaic devices of ITO/PEDOT:PSS/P3HT:PDIs/Ca/Al is described in the in the Supporting Information.

With respect to the light absorption range, charge carrier rate, and electron affinities, PDI dyes should outperform fullerenes in solar cells. However, the results show otherwise. The causes of the poor power conversion efficiencies achieved with our systems are not well understood. One explanation for this is that the close molecular packing may lead to the self-trapping of excitons.[5b] Another explanation is that the dissociation of the charge-transfer (CT) state into mobile charge carriers could be severely delayed by the efficient charge-recombination (CR) process.

Conclusions

Zigzag constitutional perylenetetracarboxdiimide derivative **1** containing an anthraquinone unit has been synthesized by phototriggered intramolecular cyclization of 2-anthraquinone-substituted perylenetetracarboxdiimide **2**. Significant visible color and fluorescence changes were observed after cyclization. The two materials exhibit strong electron-accepting abilities. Their application in organic solar cells was also investigated with power conversion efficiencies of 0.39 and 0.16 obtained for **2** and **1**, respectively. Although PDIs seem less suitable than fullerenes as components of photovoltaic cells, we still believe that the role of PDI dyes in organic solar cell devices remains bright.

Experimental Section

Materials and Characterization: All reagents were obtained from commercial suppliers and used as received unless otherwise noted. Column chromatography was performed on silica gel (160–200 mesh) and TLC was performed on precoated silica gel plates and observed under UV light. NMR spectra were recorded with Bruker Avance DPS-400 and DPS-600 spectrometers at room temperature (298 K). Chemical shifts are referenced to residual solvent peaks. MALDI-TOF MS was performed with a Bruker Biflex III mass spectrometer. Electronic absorption spectra were recorded with a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded with a Hitachi F-4500 fluorimeter.

Synthesis of 2: 1-Bromo-*N*,*N′*-bis(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxdiimide (**3**; 158 mg, 0.2 mmol) and 2-(9,10-dioxo-9,10-dihydro-2-anthryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**; 99 mg, 0.3 mmol) were dissolved in toluene/ethanol (30 mL/10 mL) and K_2CO_3 (42 mg) was added. [Pd(PPh$_3$)$_4$] (ca. 5 mg) was added after bubbling N_2 through the solution for 30 min. After stirring at 80 °C for 3 h, the reaction mixture was concentrated in vacuo. The resulting solid was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (20 mL), and dried with anhydrous Na_2SO_4. Concentrated in vacuo and purified by column chromatography (CH_2Cl_2/hexane as eluent), yield 148 mg, 81%, m.p. >400 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87–8.82 (m, 2 H), 8.79–8.76 (m, 2 H), 8.69 (s, 1 H), 8.54 (d, J = 8 Hz, 1 H), 8.49 (s, 1 H), 8.40 (d, J = 8 Hz, 1 H), 8.33 (d, J = 8 Hz, 1 H), 8.19 (d, J = 8 Hz, 1 H), 8.07 (d, J = 8 Hz, 1 H), 7.90–7.85 (m, 3 H), 7.53–7.45 (m, 2 H), 7.38–7.31 (m, 4 H), 2.80–2.71 (m, 4 H), 1.21–1.12 (m, 24 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.79, 182.56, 163.59, 163.56, 163.35, 163.29, 148.73, 145.77, 145.65, 139.73, 135.83, 135.54, 135.33, 134.82, 134.73, 134.59, 133.68, 133.58, 133.55, 133.30, 132.20, 132.10, 130.76, 130.66, 130.48, 129.90, 129.84, 129.69, 129.53, 128.56, 127.95, 127.70, 127.64, 124.24, 123.64, 123.50, 123.31, 123.02, 122.85, 32.05, 29.41, 29.29, 24.14, 22.82, 14.24 ppm. MS (MALDI-TOF): *m*/*z* = 916.3 [M]$^+$. $C_{62}H_{50}N_2O_4$ (887.09): calcd. C 81.20, H 5.28, N 3.05; found C 81.16, H 5.30, N 3.04.

Synthesis of 1: Compound **2** (92 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (100 mL) in a quartz vessel and irradiated in direct sunlight. The progress was monitored by TLC. About 5 min the photocyclization was finished and the reaction mixture was concentrated in vacuo. The crude product was purified by column chromatography (CH_2Cl_2 as eluent), yield 82 mg, 90%, m.p. >350 °C (decomp.). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.27 (s, 1 H), 9.85 (s, 1

H), 9.60 (d, J = 8.0 Hz, 1 H), 9.42–9.37 (m, 2 H), 9.22–9.17 (m, 2 H), 8.92 (d, J = 8.0 Hz, 1 H), 8.38 (t, J = 4.0 Hz, 1 H), 8.27 (t, J = 4.0 Hz, 1 H), 7.88 (t, J = 4.0 Hz, 2 H), 7.59–7.54 (m, 2 H), 7.43 (t, J = 4.0 Hz, 4 H), 2.96–2.87 (m, 4 H), 1.27–1.23 (m, 24 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.71, 181.79, 163.18, 163.02, 162.94, 162.87, 161.62, 144.88, 135.02, 134.69, 134.59, 134.24, 134.00, 133.78, 133.48, 133.38, 132.72, 131.39, 130.18, 129.76, 129.66, 128.99, 128.23, 127.91, 127.82, 127.56, 127.48, 127.08, 126.76, 126.50, 125.99, 125.89, 124.79, 124.00, 123.74, 123.37, 122.96, 122.81, 122.57, 122.01, 121.73, 119.86, 35.57, 30.53, 28.44, 23.16, 23.09 ppm. MS (MALDI-TOF): m/z = 937.5 $[M + Na]^+$. $C_{62}H_{48}N_2O_4$ (885.07): calcd. C 81.38, H 5.07, N 3.06; found C 81.33, H 5.09, N 3.04.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for **1** and **2**, photos of the visible colors and visual fluorescence colors of **1** and **2**, computational investigations on **1** and **2**, TGA profiles of **1** and **2**, and process for the fabrication of the solar cell devices, details of CV experiments.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (NSFC) (grant number 21031006), the Chinese–German NSFC–DFG joint fund (TRR 61), and the National Basic Research 973 Program of China (grant numbers 2011CB932302 and 2012CD932900).

---

[1] a) W. Wang, W. Wan, H.-H. Zhou, S. Niu, A. D. Q. Li, *J. Am. Chem. Soc.* **2003**, *125*, 5248–5249; b) L. Zang, R. Liu, M. W. Holman, K. T. Nguyen, D. M. Adams, *J. Am. Chem. Soc.* **2002**, *124*, 10640–10641; c) N. I. Georgiev, A. R. Sakr, V. B. Bojinov, *Dyes Pigm.* **2011**, *91*, 332–339; d) T. Heek, C. Fasting, C. Rest, X. Zhang, F. Würthner, R. Haag, *Chem. Commun.* **2010**, *46*, 1884–1886.

[2] a) X. Guo, D. Zhang, D. Zhu, *Adv. Mater.* **2004**, *16*, 125–130; b) Y. Li, H. Zheng, Y. Li, S. Wang, Z. Wu, P. Liu, Z. Gao, H. Liu, D. Zhu, *J. Org. Chem.* **2007**, *72*, 2878–2885.

[3] a) J. Baggerman, D. C. Jagesar, R. A. L. Vallée, J. Hofkens, F. C. De Schryver, F. Schelhase, F. Vögtle, A. M. Brouwer, *Chem. Eur. J.* **2007**, *13*, 1291–1299; b) B. J. Slater, E. S. Davies, S. P. Argent, H. Nowell, W. Lewis, A. J. Blake, N. R. Champness, *Chem. Eur. J.* **2011**, *17*, 14746–14751; c) Y. Li, H. Li, Y. Li, H. Liu, S. Wang, X. He, N. Wang, D. Zhu, *Org. Lett.* **2005**, *7*, 4835–4838.

[4] a) X. Zhan, A. Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R. Wasielewski, S. R. Marder, *Adv. Mater.* **2011**, *23*, 268–284; b) C. Huang, S. Barlow, S. R. Marder, *J. Org. Chem.* **2011**, *76*, 2386–2407; c) W. Lu, J. P. Gao, Z. Y. Wang, Y. Qi, G. G. Sacripante, J. D. Duff, P. R. Sundararajan, *Macromolecules* **1999**, *32*, 8880–8885.

[5] a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122; b) C. Li, H. Wonneberger, *Adv. Mater.* **2012**, *24*, 613–636; c) C. Ego, D. Marsitzky, S. Becker, J. Zhang, A. C. Grimsdale, K. Müllen, J. D. MacKenzie, C. Silva, R. H. Friend, *J. Am. Chem. Soc.* **2003**, *125*, 437–443; d) J. J. Dittmer, E. A. Marseglia, R. H. Friend, *Adv. Mater.* **2000**, *12*, 1270–1274; e) Z. Liang, R. A. Cormier, A. M. Nardes, B. A. Gregg, *Synth. Met.* **2011**, *161*, 1014–1021; f) B. A. Gregg, R. A. Cormier, *J. Am. Chem. Soc.* **2001**, *123*, 7959–7960; g) Y. Liu, N. Wang, Y. Li, H. Liu, Y. Li, J. Xiao, X. Xu, C. Huang, S. Cui, D. Zhu, *Macromolecules* **2005**, *38*, 4880–4887; h) Y. Liu, Y. Li, L. Jiang, H. Gan, H. Liu, Y. Li, J. Zhuang, F. Lu, D. Zhu, *J. Org. Chem.* **2004**, *69*, 9049–9054; i) A. J. Breeze, A. Salomon, D. S. Ginley, B. A. Gregg, H. Tillmann, H.-H. Horhold, *Appl. Phys. Lett.* **2002**, *81*, 3085–3087; j) H. Langhals, S. Saulich, *Chem. Eur. J.* **2002**, *8*, 5630–5643.

[6] a) B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem.* **2004**, *116*, 6523; *Angew. Chem. Int. Ed.* **2004**, *43*, 6363–6366; b) R. T. Weitz, K. Amsharov, U. Zschieschang, E. B. Villas, D. K. Goswami, M. Burghard, H. Dosch, M. Jansen, K. Kern, H. Klauk, *J. Am. Chem. Soc.* **2008**, *130*, 4637–4645; c) H. Z. Chen, M. M. Ling, X. Mo, M. M. Shi, M. Wang, Z. Bao, *Chem. Mater.* **2007**, *19*, 816–824; d) R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. da Silva Filho, J.-L. Brédas, L. L. Miller, K. R. Mann, C. D. Frisbie, *J. Phys. Chem. B* **2004**, *108*, 19281–19292; e) P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, W. Andreoni, *Appl. Phys. Lett.* **2002**, *80*, 2517–2519.

[7] a) N. G. Pschirer, C. Kohl, F. Nolde, J. Qu, K. Müllen, *Angew. Chem.* **2006**, *118*, 1429; *Angew. Chem. Int. Ed.* **2006**, *45*, 1401–1404; b) L. Fan, Y. Xu, H. Tian, *Tetrahedron Lett.* **2005**, *46*, 4443–4447; c) Y. Li, Z. Qing, Y. Yu, T. Liu, R. Jiang, Y. Li, *Chem. Asian J.* **2012**, DOI: 10.1002/asia.201200243; d) M. J. Lin, B. Fimmel, K. Radacki, F. Würthner, *Angew. Chem.* **2011**, *123*, 11039; *Angew. Chem. Int. Ed.* **2011**, *50*, 10847–10850.

[8] a) H. Quante, Y. Geerts, K. Müllen, *Chem. Mater.* **1997**, *9*, 495–500; b) F. Würthner, C. Thalacker, A. Sautter, *Adv. Mater.* **1999**, *11*, 754–758.

[9] P. Rajasingh, R. Cohen, E. Shirman, L. J. W. Shimon, B. Rybtchinski, *J. Org. Chem.* **2007**, *72*, 5973–5979.

[10] a) W. Qiu, S. Chen, X. Sun, Y. Liu, D. Zhu, *Org. Lett.* **2006**, *8*, 867–870; b) S. Muller, K. Müllen, *Chem. Commun.* **2005**, *32*, 4045–4046.

[11] Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Bohm, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 2357–2369.

[12] Y. Avlasevich, C. Li, K. Müllen, *J. Mater. Chem.* **2010**, *20*, 3814–3826.

[13] F. Würthner, *Chem. Commun.* **2004**, *14*, 1564–1579.

[14] H. Langhals, S. Kirner, *Eur. J. Org. Chem.* **2000**, 365–380.

[15] a) Y. Li, Y. Li, J. Li, C. Li, X. Liu, M. Yuan, H. Liu, S. Wang, *Chem. Eur. J.* **2006**, *12*, 8378–8385; b) Y. Li, L. Xu, T. Liu, Y. Yu, H. Liu, Y. Li, D. Zhu, *Org. Lett.* **2011**, *13*, 5692–5695.

[16] G. Horowitz, F. Kouki, P. Spearman, D. Fichou, C. Nogues, X. Pan, F. Garnier, *Adv. Mater.* **1996**, *8*, 242–245.

[17] a) Y. Liu, S. Xiao, H. Li, Y. Li, H. Liu, F. Lu, J. Zhuang, D. Zhu, *J. Phys. Chem. B* **2004**, *108*, 6256–6260; b) S. Suzuki, M. Kozaki, K. Nozaki, K. Okada, *J. Photochem. Photobiol. C: Photochem. Rev.* **2011**, *12*, 269–292; c) Y. Zhao, M. R. Wasielewski, *Tetrahedron Lett.* **1999**, *40*, 7047–7050.

[18] R. K. Dubey, A. Efimov, H. Lemmetyinen, *Chem. Mater.* **2011**, *23*, 778–788.

[19] R. M. F. Batista, E. Oliveira, S. P. G. Costa, C. Lodeiro, M. M. M. Raposo, *Org. Lett.* **2007**, *9*, 3201–3204.

[20] a) H. Görner, *Photochem. Photobiol.* **2003**, *77*, 171–179; b) J. Yang, A. Dass, A.-M. M. Rawashdeh, C. Sotiriou-Leventis, M. J. Panzner, D. S. Tyson, J. D. Kinder, N. Leventis, *Chem. Mater.* **2004**, *16*, 3457–3468.

[21] a) J. Fabian, H. Nakazumi, M. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197–1226; b) C. Kohl, S. Becker, K. Müllen, *Chem. Commun.* **2002**, *23*, 2778–2779.

[22] C. A. Wijesinghe, M. Niemi, N. V. Tkachenko, N. K. Subbaiyan, M. E. Zandler, H. Lemmetyinen, F. D'Souza, *J. Porphyrins Phthalocyanines* **2011**, *15*, 391–400.

[23] M. Mamada, J.-i. Nishida, S. Tokito, Y. Yamashita, *Chem. Commun.* **2009**, *16*, 2177–2179.

[24] J. Hankache, O. S. Wenger, *Chem. Commun.* **2011**, *47*, 10145–10147.

[25] M. Thelakkat, H.-W. Schmidt, *Adv. Mater.* **1998**, *10*, 219–223.

[26] a) C.-C. Chao, M.-k. Leung, Y. O. Su, K.-Y. Chiu, T.-H. Lin, S.-J. Shieh, S.-C. Lin, *J. Org. Chem.* **2005**, *70*, 4323–4331; b) F. O. Holtrup, G. R. J. Müller, H. Quante, S. De Feyter, F. C. De Schryver, K. Müllen, *Chem. Eur. J.* **1997**, *3*, 219–225.

[27] G. Seybold, G. Wagenblast, *Dyes Pigm.* **1989**, *11*, 303–317.

[28] R. Gvishi, R. Reisfeld, Z. Burshtein, *Chem. Phys. Lett.* **1993**, *213*, 338–344.
[29] a) J. Feng, D. Wang, H. Wang, D. Zhang, L. Zhang, X. Li, *J. Phys. Org. Chem.* **2011**, *24*, 621–629; b) S. Chai, S.-H. Wen, K.-L. Han, *Org. Electron.* **2011**, *12*, 1806–814.
[30] H. Langhals, T. Pust, *Eur. J. Org. Chem.* **2010**, 3140–3145.
[31] S. Chen, Y. Liu, W. Qiu, X. Sun, Y. Ma, D. Zhu, *Chem. Mater.* **2005**, *17*, 2208–2215.
[32] Y. Avlasevich, S. Müller, P. Erk, K. Müllen, *Chem. Eur. J.* **2007**, *13*, 6555–6561.
[33] S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Müllen, A. J. Bard, *J. Am. Chem. Soc.* **1999**, *121*, 3513–3520.
[34] S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M.-J. Blesa, P. Hudhomme, *J. Org. Chem.* **2005**, *70*, 6313–6320.
[35] Z. Yuan, Y. Xiao, X. Qian, *Chem. Commun.* **2010**, *46*, 2772–2774.
[36] a) D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53–59; b) Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu, A. J. Heeger, *Synth. Met.* **1999**, *99*, 243–248.
[37] S. M. Bonesi, M. Fagnoni, A. Albini, *J. Org. Chem.* **2004**, *69*, 928–935.
[38] H. Graaf, W. Michaelis, G. Schnurpfeil, N. Jaeger, D. Schlettwein, *Org. Electron.* **2004**, *5*, 237–249.
[39] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford, CT, **2004**.
[40] Y. Nagao, *Prog. Org. Coat.* **1997**, *31*, 43–49.
[41] E. E. Neuteboom, S. C. J. Meskers, P. A. van Hal, J. K. J. van Duren, E. W. Meijer, R. A. J. Janssen, H. Dupin, G. Pourtois, J. Cornil, R. Lazzaroni, J.-L. Brédas, D. Beljonne, *J. Am. Chem. Soc.* **2003**, *125*, 8625–8638.
[42] a) T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss, M. R. Wasielewski, *J. Am. Chem. Soc.* **2002**, *124*, 9582–9590; b) S.-G. Liu, G. Sui, R. A. Cormier, R. M. Leblanc, B. A. Gregg, *J. Phys. Chem. B* **2002**, *106*, 1307–1315.
[43] C. Liu, Y. Li, C. Li, W. Li, C. Zhou, H. Liu, Z. Bo, Y. Li, *J. Phys. Chem. C* **2009**, *113*, 21970–21975.
[44] G. D. Sharma, P. Suresh, J. A. Mikroyannidis, M. M. Stylianakis, *J. Mater. Chem.* **2010**, *20*, 561–567.
[45] a) W. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* **2005**, *15*, 1617–1622; b) G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, *4*, 864–868.
[46] a) J. Hou, Z. a. Tan, Y. Yan, Y. He, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916; b) C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. van Hal, R. A. J. Janssen, *Adv. Funct. Mater.* **2002**, *12*, 709–712.
[47] V. Dyakonov, *Appl. Phys. A* **2004**, *79*, 21–25.
[48] C. Liu, S. Xiao, X. Shu, Y. Li, L. Xu, T. Liu, Y. Yu, L. Zhang, H. Liu, Y. Li, *ACS Appl. Mater. Interfaces* **2012**, *4*, 1065–1071.
[49] Y. Yi, V. Coropceanu, J.-L. Bredas, *J. Mater. Chem.* **2011**, *21*, 1479–1486.

Received: July 24, 2012