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A photochromic diarylethene dyad based on perylene diimide

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A new photochromic diarylethene dyad based on perylene diimide (PDI-DTE) has been synthesized. The photochromic reaction of PDI-DTE induced the significant change of the absorption spectra and fluorescence intensity. The color of PDI-DTE in THF solution was not changed obviously upon ultraviolet irradiation, while the fluorescence intensity is increased unexpectedly with the photochromic cyclization of the diarylethene units. With not visible change of color accompanied to the enhanced fluorescence, PDI-DTE can be potentially applied to anti-counterfeiting technology.

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1. Introduction

In recent years, many countries and companies research variety of anti-counterfeiting technology in order to combat fake and inferior products. Especially, more efforts are focused on the banknotes and the anti-counterfeiting packaging of brand-name products. Thus demands promoted the research and development of the anti-counterfeiting technology. Photochromic materials, with special ink marker and high anti-counterfeiting features, have aroused extensive attention. Generally, there are three kinds of anti-counterfeiting technology: 1) visible without fluorescence; 2) visible with significant fluorescence under ultraviolet light irradiation; 3) not visible with significant fluorescence under ultraviolet light irradiation. Organic photochromic compounds just as spiropyran and fulgide derivatives have been applied as anti-counterfeiting materials, they all belong to the second kind [1]. But the application used dithienylethene (DTE) is extremely rare. Diarylethene derivatives, the promising families of photochromic compounds, substituted with fluorescent chromophore, exhibit fluorescence modulation upon irradiation with ultraviolet and visible light [2–5]. On the other hand, perylene diimides (PDIs) are outstandingly versatile fluorescent chromophores [6] with exceptional thermal and photochemical stability, strongly absorb visible light and high fluorescence quantum yield [7,8]. Also, the photophysical properties of PDIs can be conveniently modified through substitution in the aromatic core and bay region [9,10]. The modulation of PDIs properties based on photochromic reactions has been studied [11–15]. Here we report on a reversible fluorescence modulation by photoinduced reaction with the diarylethene unit linking to the aromatic region of the perylene unit (Fig. 1). The final product PDI-DTE show significant fluorescence after ultraviolet irradiation while the visible color is the same. PDI-DTE can be potentially used as the third kind of anti-counterfeiting materials.

2. Experimental

2.1. Chemicals and instruments

N-*N*-(*n*-butylamino)-1,7-Dibromoperylenetetracarboxylic acid diimide was synthesized according to the literature [16]. Other reagents were commercially available and used without further purification.

^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethyl silane (TMS) as internal reference. MS were recorded on EI or ESI mass spectroscopy. Absorption spectra were measured on a Varian Cary500 UV–Vis spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. The optical switch experiments were carried out using a photochemical reaction apparatus with a 200 W Hg lamp. Luminescence lifetime measurements were performed on an Edinburgh FL 900 Fluorescence Spectrometer equipped with a blue laser ($\lambda = 440$ nm).

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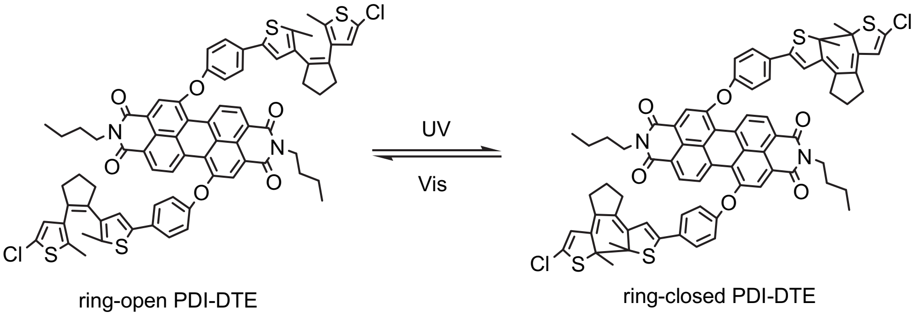

Fig. 1. The photochromic reaction of compound PDI-DTE.

2.2. Synthesis

2.2.1. 1-{(2-methyl-5-(4-hydroxyl)phenyl)thien-3-yl}-2-(5-chloro-2-methylthien-3-yl) cyclopentene(DTE)

To a stirred solution of 1, 2-Bis(5-chloro-2-methylthien-3-yl) cyclopentene (1 g, 3 mmol) in THF (10 ml) at −78 °C under Ar in the absence of light was added dropwise 2.9 M *n*-BuLi in hexane (0.17 g, 3 mmol), and the reaction mixture was stirred at −70 °C for further 30 min. Then tributyl borate (0.7 g, 3 mmol) was quickly added in one portion. This reddish solution was stirred for 1 h at room temperature, and was then used in the Suzuki coupling reaction without any workup because the product is deboronized during isolation.

A mixture of 4-iodophenol (0.67 g, 3 mmol), the catalyst Pd $(PPh_3)_4$ and 10 ml THF was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (8 mL, 2 M) was added. The reactive mixture was heated at a temperature of 60 °C, and the solution of bis (boronic) esters prepared from 1, 2-Bis(5-chloro-2-methylthien-3-yl) cyclopentene was added dropwise via a syringe. Subsequently, the mixture was refluxed for 2 h and cooled to room temperature. The reactive mixture was poured into H_2O and extracted with ether, and the organic layer was collected and dried with anhydrous $MgSO_4$. After concentration, the compound was purified by column chromatography on silica (petroleum ether−ethyl acetate = 2:1 v/v) to yield compound DTE (0.618 g), yield 56%. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.38 (d, 2H, $J = 8.8$ Hz, phenyl C−H), 6.87 (s, H, thienyl C−H), 6.83 (d, 2H, $J = 6.8$ Hz, phenyl C−H), 6.63 (d, 1H, $J = 5.4$ Hz, thienyl C−H), 4.84 (s, 1H, hydroxyl −OH), 2.82 (t, $J = 5.2$ Hz, 2H, $-CH_2-$), 2.79 (t, 2H, $J = 5.2$ Hz, $-CH_2-$), 2.07 (m, 2H, $-CH_2-$), 1.99 (s, 3H, $-CH_3$), 1.90 (s, 3H, $-CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.83, 139.63, 136.19, 135.41, 135.18, 133.61, 133.47, 133.25, 127.59, 126.86, 126.82, 124.93, 122.80, 115.67, 38.44, 38.34, 29.69, 22.91, 14.30, 14.17. TOF-MS: calculated for $(C_{21}H_{19}Cl_2NOS_2)$ 386.9580, found: 386.0550.

2.2.2. Synthesis of PDI-DTE

N-*N*-(*n*-butylamino)-1,7-Dibromoperylenetetracarboxylic acid diimide (0.33 g, 0.5 mmol) was stirred under argon with compound DTE (0.407 g, 1.06 mmol) in NMP (20 ml) at 100 °C in a 100 mL round flask in the presence of powdered anhydrous K_2CO_3 (400 mg, 3 mmol). The temperature was maintained at 100 °C overnight under argon. The reaction mixture was allowed to cool to room temperature and was poured into aqueous hydrochloride acid (50 ml, 1 M). The precipitated product was filtered under suction, and was then purified by column chromatography to give a red solid PDI-DTE (70 mg, 6.8%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 9.58 (d, 2H, $J = 8.0$ Hz, perylene C−H), 8.63 (d, 2H, $J = 8.0$ Hz, perylene C−H), 8.37 (s, 2H, perylene C−H), 7.56 (d, 4H, $J = 8.7$ Hz, phenyl C−H), 7.53 (d, 4H, $J = 8.7$ Hz, phenyl C−H), 6.97 (s, 2H, thienyl C−H), 6.65 (s, 2H, thienyl C−H), 4.17 (t, 4H, $J = 8.0$ Hz, $-CH_2-$), 2.84 (t, 4H, $J = 7.2$ Hz, $-CH_2-$), 2.77 (t, 4H, $J = 8.0$ Hz, $-CH_2-$), 2.09 (m, 4H, $-CH_2-$), 2.04 (s, 6H, $-CH_3$), 1.92 (s, 6H, $-CH_3$), 1.712 (m, 4H, $-CH_2-$), 2.45 (m, 4H, $-CH_2-$), 0.99 (t, 6H, $J = 7.2$ Hz, $-CH_3$), ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 163.3, 162.9, 155.0, 154.0, 138.6, 136.5, 135.2, 135.0, 134.8, 134.0, 133.3, 132.1, 131.7, 130.3, 129.3, 128.9, 127.8, 127.4, 126.8, 125.2, 125.0, 124.1, 123.9, 122.3, 119.8, 40.4, 38.4, 38.3, 31.9, 30.1, 29.7, 22.9, 22.6, 20.3, 14.4, 14.2, 13.8; MOLDI-TOF: calculated for $(C_{74}H_{60}Cl_2N_2O_6S_4)$ 1271.4440, found:1271.3481.

3. Results and discussion

3.1. Design and synthesis of PDI-DTE

In this work, a photochromic dithieylethene unit was linked to perylene bisimide and the photochromic behaviors were investigated in detail. Two reference compounds DTE and PDI were also prepared. PDI-DTE was synthesized from the typical dithienylethene unit, 2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (DTE) (Fig. 2). Compound DTE was prepared by a Suzuki coupling reaction with 4-iodophenol with a yield of 56%. The target compound PDI-DTE was involved a phenoxylation of *N*-*N*-(*n*-butylamino)-1,7-Dibromoperylenetetracarboxylic acid diimide [9] by treatment with phenol function group of DTE [17]. The product was purified by silica-gel-column chromatography. The structure was identified by ^1H NMR, ^{13}C NMR spectroscopes and MOLDI-TOF (see Supporting Information).

3.2. Absorption spectral change of DTE and PDI-DTE

The photochromic behavior of dithienylethene compound DTE and perylene derivative PDI-DTE was examined in THF solution. The absorption spectra change of DTE upon photoirradiation is shown in Fig. 3. After 254 nm ultraviolet light irradiation, the THF solution of DTE turned colorless to orange. The absorption maximum located at 290 nm for the open form decreased, while a new absorption band appeared at ca. 490 nm after ultraviolet (UV) irradiation. The absorption at 300 nm of the open form is ascribed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the phenol and thiophene rings. Upon 254 nm irradiation, the new absorption band appearing at 490 nm was assigned as absorption of the closed form, resulting from the enlargement of the π conjugation by photocyclization.

After introducing photochromic dithienylethene unit into the aromatic region of perylene diimide, the derivative PDI-DTE is also shown photochromic behavior in THF solution. Perylene is a well-known red dye, and the THF solution of PDI-DTE has not changed the red color after irradiation with 254 nm ultraviolet light. But the difference after ultraviolet light irradiation is shown obviously in the absorption and fluorescence spectra (Figs. 4 and 5). Similarly to DTE, in the UV region the open form of PDI-DTE shows absorption

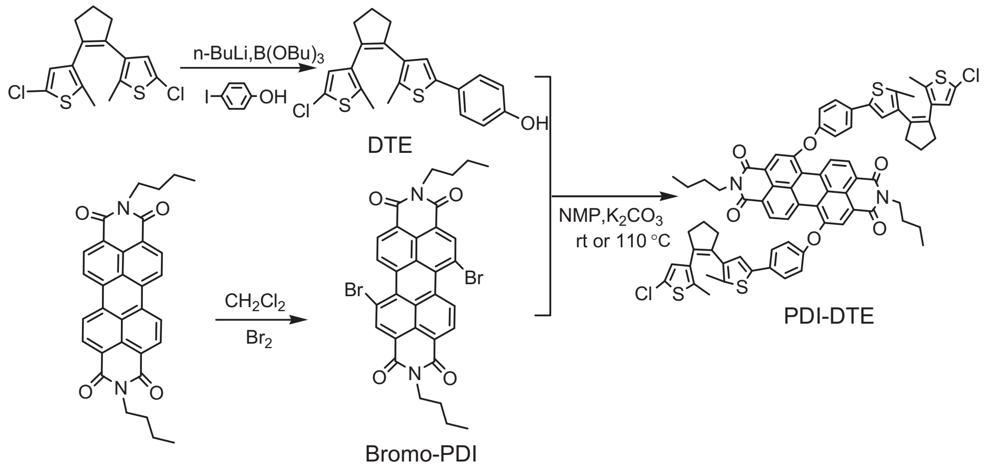

Fig. 2. The synthetic route of compound PDI-DTE.

band at 290 nm ascribed to dithienylethene unit. And the characteristic absorption band of perylene unit located at 533 nm, 502 nm, 390 nm and 270 nm, just similar to the reference compound *N*,*N*′-di(*n*-butyl)-1,7-di (4-phenal) perylene-3,4,9,10-tetracarboxylic acid bisimide (PDI) at 533 nm, 499 nm, 396 nm and 268 nm. After irradiation of 254 nm UV light, the characteristic absorption band blue-shift to 520 nm and 490 nm with the interaction of the photocyclization of the dithienylethene unit. A new absorption band appeared at about 585 nm ascribed to the enlargement of the π conjugation. Also the absorption peak at 290 nm increased with the cyclization of the dithienylethene unit. The transformation ratios corrected for the active conformer for the photocyclization were determined [DTE, $\Phi_{254} = 0.28$, PDI-DTE, $\Phi_{254} = 0.18$], which were found to be comparable to those for photocycloreversion [DTE, $\Phi_{510} = 0.35$, PDI-DTE, $\Phi_{586} = 0.26$].

3.3. *The fluorescence change of PDI-DTE*

Since perylene diimide derivatives are well-known with their excellent ability to accept electrons, standout stability, high molar extinction coefficient and fluorescence quantum yield, the fluorescence behavior of PDI-DTE is also investigated (Fig. 5). PDI-DTE is similar to PDI with the fluorescence maximum at 565 nm. After the irradiation of 254 nm ultraviolet light the intensity increased 750% [$\Phi_{\text{em open form}}$ (λ_{ex} 480 nm) = 0.05, $\Phi_{\text{em closed form}}$ (λ_{ex} 480 nm) = 0.37, using PDI as Φ_{em} (λ_{ex} 480 nm) = 1]. For the structure of PDI-DTE, each diarylethene unit is intimately connected to the perylene unit only through one oxygen atom in PDI-DTE. That conformation leads to the existence of a strong electronic interaction between the perylene unit and the diarylethene units. The fluorescence of the open form of PDI-DTE was very weak. After 254 nm UV light irradiation, the fluorescence of PDI-DTE was increased. The electrons of the diarylethene units flowing towards the perylene unit were pulled back due to the forming of the π conjugation of the closed diarylethene. As a result, the fluorescence of the PDI unit was increased. But the fluorescence intensity of PDI-DTE is still smaller than that of PDI. This was probably due to the 50% of parallel formation of the open form of DTE units without cyclization process. The fluorescence life time is also measured and the results are shown in Supporting Information.

3.4. *The computational study of PDI-DTE*

To enhance the understanding of the effect of the diarylethene unit on the PDI-DTE compound, we carried out molecular orbital calculation on PDI, the open and closed forms of PDI-DTE. These experimental data were complemented by B3LYP/6-31G(d).

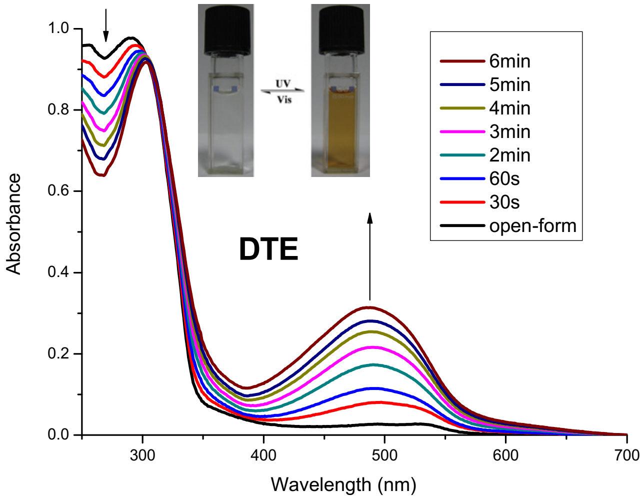

Fig. 3. UV–Vis absorption spectral changes of DTE (5×10^{-5} M in THF) at 298 K upon irradiation with 254 nm UV light.

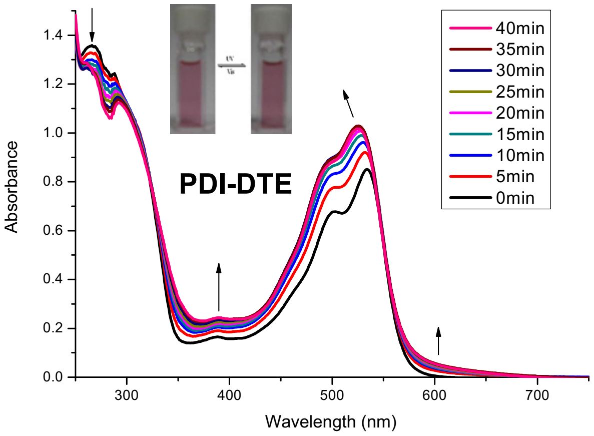

Fig. 4. UV–Vis absorption spectral changes of PDI-DTE (5×10^{-5} M in THF) at 298 K upon irradiation with 254 nm UV light.

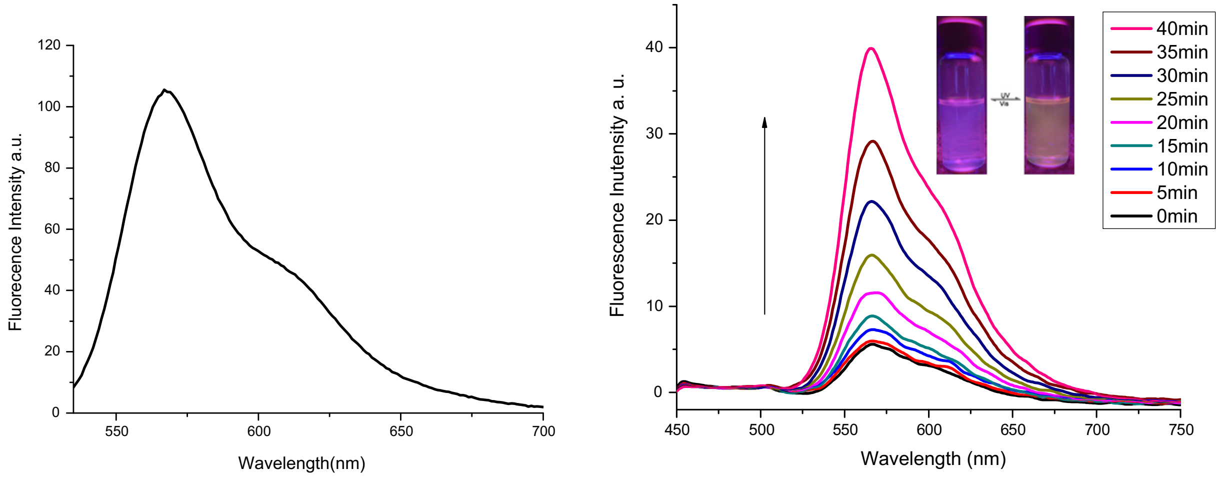

Fig. 5. Emission spectra changes of PDI and PDI-DTE (5×10^{-5} M in THF at 298 K) upon excited at 480 nm.

The calculated HOMOs and LUMOs of the geometry optimized structures are shown in Fig. 6 and indicate qualitatively different electronic structures for these compounds. In contrast to the open form of PDI-DTE, the closed form shows a clear spatial separation of its HOMO and LUMO, consistent with optical excitation resulting in the formation of an intramolecular charge separated state of the closed diarylethene unit. The electron at the phenoxyl thiophene unit tends to join the large π conjugation of the perylene unit at the open form. After irradiation with UV light, the cyclization of the diarylethene unit leads to the electron back to form π conjugation of the closed ring [18].

According to the calculation results (Table 1), incorporation of the open form of diarylethene unit onto the aromatic region of the perylene unit increases the energy level of LUMO, the energy gap between HOMO and LUMO is similar to PDI. While after photocyclization of the diarylethene unit, a significant positive shift in the energy level of the HOMO while the energy level of LUMO negative shift, leading to a decrease in the HOMO–LUMO gap. The

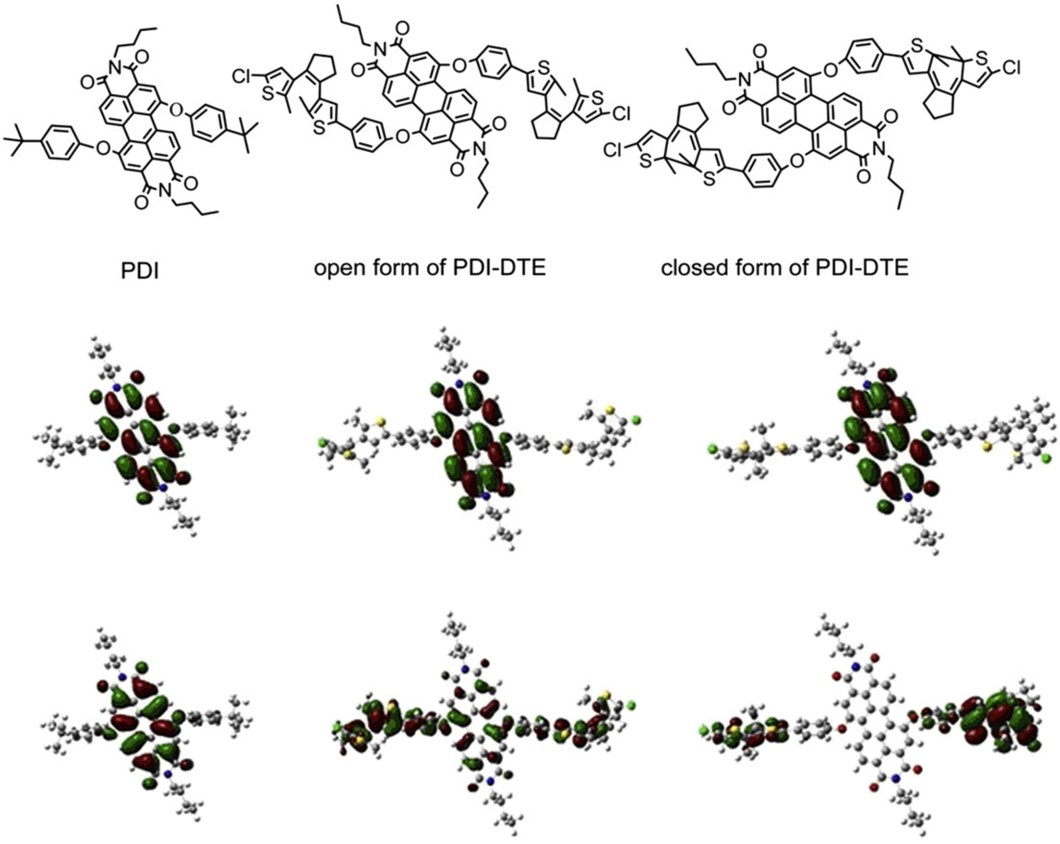

Fig. 6. The calculated LUMOs (middle) and HOMOs (bottom) for molecules (top).

Table 1
Calculated HOMO and LUMO Energy of PDI-DTE and PDI.

Compound	HOMO (eV)	LUMO (eV)	Twisting angle (°)
PDI	−5.51	−3.09	17.5
Open form of PDI-DTE	−5.50	−3.20	17.2
Closed form of PDI-DTE	−4.75	−3.25	17.4

calculated data is just consistent with the result of the electrochemical studies mentioned below.

Time-dependent density functional theory (TDDFT) calculations are also performed by using the PBE0 functional and the 6-31G(d) basis set, to further investigate the excited states of the PDI-DTE. The TDDFT results are listed in Supporting Information(Table S1). Upon excitation at 480 nm, the fluorescence of the open form of PDI-DTE is quenched via internal conversion of the excited state. While in the closed form of PDI-DTE, there is a significant energy gap between the excited states, which prevents the internal conversion from the higher excited states to the lower excited states. And the strong fluorescence of the PDI unit preserves.

A schematic representation of the excitation process of the open form of PDI-DTE is shown in Fig. 7. Upon excitation at 480 nm, the open form of PDI-DTE is excited to the S_3 (H-2 → L) state which may convert to S_1 (H → L) state via internal conversion. Since the HOMO of the open form of PDI-DTE is extended over the whole molecule, the fluorescence from the LUMO → HOMO transition is expected to be diminished, in accordance with experimental observations.

Fig. 8 shows the excitation process of the closed form of PDI-DTE. Upon 480 nm excitation, the closed form of PDI-DTE is excited to the S_5 state, which does not convert to the lowest S_1 state due to the energy gap between the S_1/S_2 and the S_3/S_4/S_5 excited states, and the strong fluorescence of the PDI unit preserves. In the closed form of PDI-DTE, the HOMO and HOMO-1 orbitals are almost degenerate, which also contribute to the absorption band around 500 nm (see Table S1 and Fig. S3).

3.5. The cyclic voltammograms of PDI-DTE and PDI

The redox potentials of PDI-DTE, as well as DTE and PDI, were measured with cyclic voltammetry in anhydrous tetrahydrofuran (THF), in a N_2 atmosphere, using Bu_4NPF_6 as the electrolyte, glassy carbon electrode as work electrode, platinum as the counter electrode, and the Ag/AgCl as the reference electrode (Fig. 9). Ferrocence is the internal standard. The scan rate is 100 mV/s. The inconspicuous first reduction potential, with $E^1{}_{Red} = -0.48$ V, and the second reduction potential $E^2{}_{Red} = -0.75$ V, which are more positive than those of PDI ($E^1{}_{Red} = -0.53$ V, $E^1{}_{Red} = -0.82$ V), were

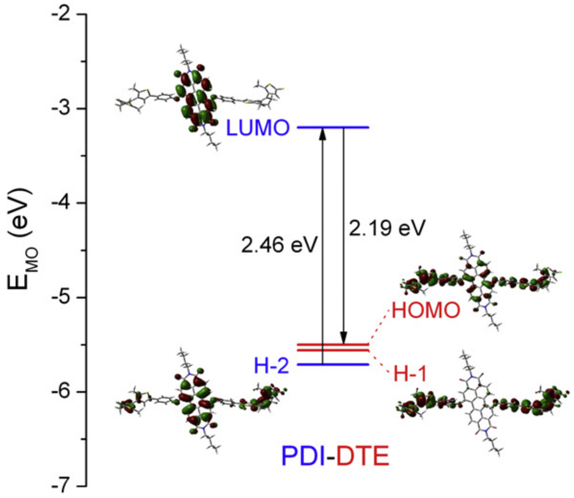

Fig. 7. Excitation process of the open form of PDI-DTE.

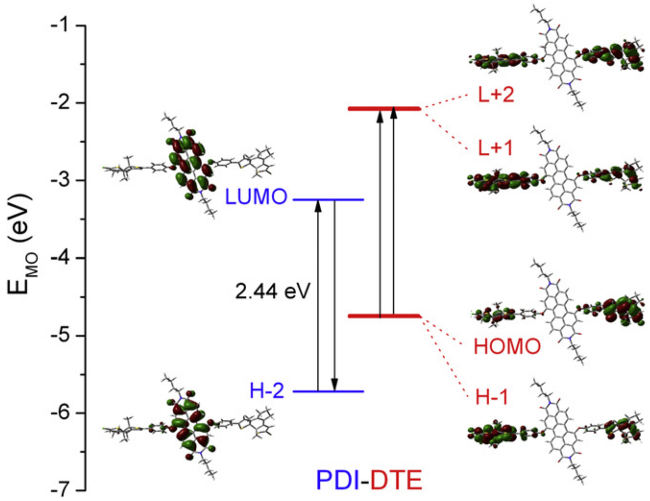

Fig. 8. Excitation process of the closed form of PDI-DTE.

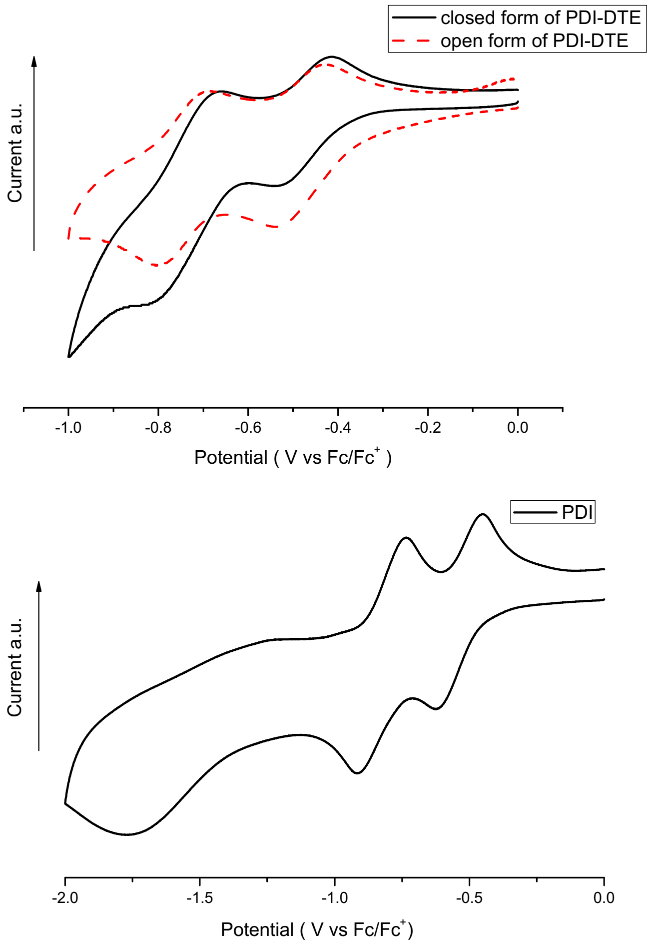

Fig. 9. The cyclic voltammograms of PDI-DTE, PDI in THF(under N_2 atmosphere, scanning rate 100 mV/s) using Bu_4NPF_6 as electrolyte, glassy carbon electrode as work electrode, platinum as the counter electrode, and the Ag/AgCl as the reference electrode (vs Fc/Fc$^+$).

detected for PDI-DTE. Therefore, these electrochemical results also suggested that the DTE and PI units of PDI-DTE strongly interacted with each other in the ground state. But for the closed form of PDI-DTE, the first reduction potential $E^1{}_{\mathrm{Red}} = -0.47$ V, and the second reduction potential $E^2{}_{\mathrm{Red}} = -0.82$ V. That result also demonstrated the electron change ascribed to the cyclization reaction of PDI-DTE with the ultraviolet light irradiation.

4. Conclusions

The photochromic and fluorescence properties of a perylene derivative PDI-DTE with a diarylethene unit at the aromatic region have been investigated. Successful tuning of the absorption spectra and fluorescence intensity has been realized by the photochromic reaction. Consequently, the fluorescence intensity is increased unexpectedly upon photochromic cyclization. With not visible change of color accompanied to the enhanced fluorescence, PDI-DTE can be potentially applied to the anti-counterfeiting technology.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2010.03.020.

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