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Draft

Abstract: A sulfur-decorated perylene derivative, 1-propanethiol-N, N'-dicyclohexyl perylene-3, 4, 9, 10-tetracarboxylic diimide (PTPDI), was facilely synthesized, and was fully characterized by ^1H -NMR, ^{13}C NMR, FT-IR, HRMS, UV-Vis absorption, fluorescence, fluorescence lifetime, fluorescence quantum yield, cyclic voltammetry, and thermogravimetric techniques. The optical, fluorescence, and scanning electron microscopies were employed to study its self-assembly process. The photophysical properties were affected strongly by modifying the propanethiol unit linking to the perylene core. Furthermore, the chromophore showed two irreversible oxidation and two quasi-reversible reductions in dichloromethane at modest potential. The optical properties of PTPDI in various conditions and complementary density functional theory (DFT) calculations were reported. Due to steric hindrance of bulky n-propyl mercaptan substituent, PTPDI molecules are arranged in slipped face-to-face fashion to form J-aggregates. Thus, the intermolecular π - π actions of the molecular are weak and causing its high luminescence efficiency. In the mean time, the space between perylene cores is very short (3.45 Å), which is favorable for the hopping transportation of charge carrier from one molecule to an adjacent one. PTPDI could be a candidate material for acquiring well defined organic nanostructure with excellent charge-transporting and light-emitting capabilities.

Keywords: Perylene diimide, Photophysical, Self-assembly, Electrochemical, Molecular packing

Introduction

Molecules of perylene diimides (PDIs) are a unique class of organic semiconductor.¹⁻⁴ The PDI derivatives have been extensively studied due to their excellent photochemical and thermal stabilities, high molar absorptivity, and high quantum yield of fluorescence.⁵ PDI derivatives are widely used in the fabrication of various optoelectronic devices.⁶ Typical examples include photovoltaics, thin-film transistors, light-emitting diodes, and liquid crystals.⁷⁻¹² Single-molecule devices such as fluorescence switches, molecular wires, sensors, and transistors could also be fabricated from PDI derivatives.¹³⁻¹⁵

Self-assembly of polycyclic organic molecules have received increased attention and have been forecasted as a tool for the design and synthesis of well defined organic nanostructures in recent years.^{16,17} As low-cost complement materials of carbon nanotubes and inorganic semiconductor nanowires or nanobelts,^{18,19} PDIs can be potentially used for processes such as printing, spin-coating, and evaporating. However, the solubilities of PDIs are generally poor because of their tendency to aggregate in most solvents.²⁰ Modifications on molecular structure of PDIs were usually achieved by introducing substituent at the bay position or the imide nitrogen atoms.²¹ Substitution at the bay position can increase the solubilities of PDIs in organic solvents and the derivatives are well compatible with plastic substrates.²² Also, substitutions at the bay position often lead to distortion of the perylene core, and thus alter the photo-physical properties of PDIs. Many PDIs with either electron-donating or electron-withdrawing groups at the bay position, such as piperidinyl-substituted PDIs, pyrrolidinyl-substituted PDIs, arylsubstituted PDIs, alkoxy-substituted PDIs, nitro-substituted PDIs, and cyano-substituted PDIs, etc. have been reported.²³⁻²⁸ PDIs modified with strong electron-withdrawing groups have been used as air-stable n-type organic semiconductors,^{29,30} and some of which containing electron-donating groups could also be used as near-infrared fluorescent dyes.³¹ Furthermore, incorporating heteroatom into the bay position can change the electronic structures and photochemical properties of PDIs dramatically.³²⁻³⁴ Many researchers have reported that modifying PDIs at imine sites could lead to formations of self-assembled nanostructures.³⁵ However, self-assembly of PDIs substituted in bay area has rarely been reported although such substituent can significantly change the electronic structures and photochemical properties of PDIs.³² It is because forming well-defined nanostructures were difficult for such PDIs due to distorted π - π stacking.³⁶ Additionally, PDI molecules are prone to form aggregates in the solid state, which lead to fluorescence quenching because of the effective intermolecular π - π action and/or attractive dipole-dipole effects. This characteristic will greatly limit their potential applications.³⁷

Scheme 1. The synthetic route of PTPDI.

In the present study, we report the design and synthesis of a PDI with substitution at the bay position: 1-propanethiol-N, N'-dicyclohexyl perylene-3, 4, 9, 10-tetracarboxylic diimide (PTPDI) (Scheme 1). The photophysical, electrochemical, self-assembly and molecular packing of PTPDI were investigated. The results showed that PTPDI possesses both well defined organic microstructure and high fluorescence quantum yield in solid state. Due to steric hindrance of bulky n-propyl mercaptan substituent, there was a huge transverse offset between adjacent PTPDI molecules. Thus, the intermolecular π - π actions of the molecular are weak and cause its high luminescence efficiency.

Experimental

Materials and equipments

The solvents were purchased from commercial source and used as received. N, N'-dicyclohexyl-1-nitroperylene-3, 4, 9, 10-tetracarboxylic acid diimide (compound **2**) was synthesized according to the literature procedure.³⁸

The ^1H NMR spectra was obtained on a Bruker 300 MHz spectrometer using TMS as standard. FT-IR spectrum was measured on a Bruker Tensor-27 spectrophotometer. Mass spectra were measured with a Bruker Maxis UHR-TOF mass spectrometer. UV-Vis absorption spectra were recorded on a Varian CARY-50

spectrophotometer. Emission spectra were recorded on a Hitachi FL-4500 spectrofluorometer. Fluorescence lifetimes in solutions (10 μ M in DCM) were measured with the Hamamatsu spectrometer C11367. Cyclic voltammetry was recorded with a CHI760E electrochemical analyzer using three electrode cell units, glassy carbon working electrode, Pt as counter electrode and Ag/AgNO₃ reference electrode. Tetrabutylammonium perchlorate (Bu₄NClO₄) was used as a supporting electrolyte. The scan rate employed was 100 mV/ s and the current sensitivity was given as 0.01 μ A. Thermogravimetric analysis (TGA) was measured with a TA Q50 instrument. The sample temperature of TGA was maintained at 10 $^{\circ}$ C/ min under a N₂ atmosphere. The quantum yields in the solid states were measured with the Hamamatsu spectrometer C11347 Quantaaurus-QY. Optical and fluorescence microscopic images were obtained with an Olympus (Japan) BH2 microscope. Scanning electron microscope (SEM) image was obtained using a FEI NOVA NANOSEM 450 microscope. The sample was prepared by casting a drop of the suspension on a glass cover slip, followed by drying in air and then annealed overnight in an oven at 40 $^{\circ}$ C. The dried sample was coated with gold prior to imaging. X-ray diffraction (XRD) measurement was performed on a Rigaku R-AXIS RAPID X-ray diffractometer.

Computation details

The Becke's three parameter gradient-corrected hybrid density function B3LYP method and the standard 6-31G (d) basis set were used for all of the structure optimization, the property calculations and the molecular arrangement in PTPDI solid based on two molecular models.^{39,40} All the calculations were performed using the Gaussian 03 program installed on a Windows PC.

Preparation of PTPDI.

Compound **2** (200 mg, 0.34 mmol) and K₂CO₃ (200 mg) were suspended in 20 mL *N*-methyl-2-pyrrolidone (NMP) at room temperature, and propanethiol (8.0 mL) was then added into the solution. The reaction mixture was kept stirring for 30 min at room temperature, and then poured into 100 mL of 2 M HCl. The precipitate was collected by vacuum filtration and washed with water three times (50 mL $\times$ 3). The

crude product was purified by silica gel column chromatography with CH_2Cl_2 /petroleum ether 4:1 as eluent to give a red solid (189 mg, 90%). Characterization data: ^1H -NMR (CDCl_3 , 300 MHz, TMS, ppm): δ = 8.57 (m, 3H), 8.46-8.35 (m, 3H), 8.23 (s, 1H), 4.96 (m, 2H), 3.06 (m, 2H), 2.50 (m, 5H), 1.74 (m, 4H), 1.64 (m, 6H), 1.41 (m, 8H), 0.80-1.00 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ = 163.64, 139.58, 130.47, 129.24, 128.41, 127.27, 126.51, 125.96, 123.11, 122.72, 121.99, 54.18, 37.95, 29.13, 26.60, 25.49, 21.91, 13.61. FT-IR (KBr, cm^{-1}): ν = 2922, 2845, 1691, 1651, 1611, 1415, 1343, 1307, 1257, 1179, 1000, 894, 853, 804, 735, 629, 578, 448, 416. MS (APCI): m/z 628.2 M^+ .

Results and discussion

Synthesis of dye

The compound **2** was achieved by a reaction of compound **1** with cerium (IV) ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) and 96% nitric acid under ambient temperature in dichloromethane (with a yield >90%). The substitution reaction of compound **2** could be carried out smoothly with propanethiol in N-methylpyrrolidone (NMP) (with a yield of ca 90%). The product was pure enough to be used in other reactions. However, in chloroform (CHCl_3), the mixture was refluxed for 10 h under argon atmosphere and the yield of the reaction was less than 30%.⁴¹ Compared with the similar reaction of monobromized PDI reacting over 100 °C,⁴² the substitution of nitro group by propanethiol group took place more quickly at room temperature. The reaction time could be shortened from 10 h to 0.5 h. The substitution of nitro group was easier and more effective than the substitution of halogen atom owing to its higher activity than halogenated PDI. The structure of compound PTPDI has been fully characterized through nuclear magnetic resonance (^1H NMR and ^{13}C NMR), fourier transform infrared spectroscopy (FT-IR) and mass spectroscopy (MS).

Optical properties of dye

The absorption and fluorescence spectra of PTPDI in dichloromethane at room temperature are shown in Figure 1. The photoelectric data is summarized in Table 1. The unsubstituted perylene diimide (compound **1**) was used for comparison. As

shown in Figure 1a, PTPDI showed two vibronic π - π^* transition absorption bands (542 nm and 504 nm) and a shoulder peak at 442 nm, which was in accordance with the characteristics of 0-0, 0-1, and 0-2 transition energy, respectively (0-0, 0-1, and 0-2 mean the transitions from ground state to the zero, first, and second excited state, respectively).⁴³ The incorporation of a propanethiol unit resulted in a strong intramolecular charge transfer (ICT) transition, which was indicated by a bathochromic shift of the onset absorption wavelength (about 15 nm) compared to the parent compound **1**. The optical bandgap estimated from the onset of the absorption spectra in solution is 2.28 eV. Introduction of alkoxy or amino group which has the electron donating group at the bay position of perylene shifted the absorption region to a longer wavelength.^{44,45}

PTPDI exhibited red photoluminescence with the emission wavelength at 617 nm, which was red-shifted by 74 nm compared to compound **1** (543 nm). It possesses a larger Stokes shift of about 75 nm, which is further manifested by lower rigidity of the perylene core after the introduction of propanethiol unit compared to **1** (16 nm). Clearly, the photophysical properties were affected strongly by modifying the propanethiol unit linking to the perylene core.

The fluorescence lifetime of PTPDI in dichloromethane solvent was measured (Figure 2). PTPDI exhibited a fluorescence lifetime with single exponential decay feature and the average fluorescence lifetime was 5.43 ns, which was longer than the fluorescence lifetime of perylene.⁴⁶ The longer lifetime could be originated from the energetically favorable process of the electron-transfer characteristic of the relaxed excited-state between propanethiol substituent and perylene core of PTPDI [30]. The fluorescence quantum yield (Φ_f) in CH_2Cl_2 solution was evaluated by using fluorescein as standard.⁴⁷ The Φ_f value of compound **1** was 0.97, while the Φ_f value of PTPDI decreased to 0.34, indicating an amplification factor ($\Phi_{f, \text{compound 1}}/\Phi_{f, \text{PTPDI}}$) of 2.85. Such a change may be caused either by electronic coupling between the electron richer substituent and the electron-deficient PDI core, or by substituent induced distortion of PDI core. Using the fluorescence quantum yield (Φ_f) and lifetime (τ) values, the rate constants of radiative (k_r) and nonradiative (k_{nr}) decay calculated

according to the equations (a) and (b) were 6.3 nS^{-1} and 12 nS^{-1} , respectively (Table 1).

$$k_r = \Phi_f / \tau \quad (\text{a})$$

$$k_{nr} = (1 - \Phi_f) / \tau \quad (\text{b})$$

Fig. 1. Normalized absorption (a) and fluorescence spectra (b) of PTPDI and compound 1 in dichloromethane recorded at room temperature.

Fig. 2. Lifetime decay curve of PTPDI.

Fig. 3. Normalized absorption (a) and fluorescence spectra (b) of PTPDI in

cyclohexane (red line, $\lambda_{\text{ex}} = 534 \text{ nm}$), ethyl acetate (green line, $\lambda_{\text{ex}} = 535 \text{ nm}$), tetrahydrofuran (blue line, $\lambda_{\text{ex}} = 537 \text{ nm}$) and dichloromethane (black line, $\lambda_{\text{ex}} = 542 \text{ nm}$).

PTPDI had a moderate solubility and can dissolve in common organic solvents such as cyclohexane (Cy), ethyl acetate (EA), tetrahydrofuran (THF) and dichloromethane (DCM). Spectroscopy properties of PTPDI in different solvents were investigated (Figure 3). When the solvent polarity increases (from cyclohexane to dichloromethane), the shapes of spectra were similar, but the longest wavelength absorption band and the fluorescence spectra of PTPDI exhibited a red shift of about 7 nm and 26 nm, respectively (Table 1). This phenomenon indicates strong intramolecular charge transfer (ICT) characteristics of PTPDI in excited states.⁴⁸

Table 1. Absorption and emission data of PTPDI.

Solvents	$\lambda_{\text{abs}}(\text{nm})$	$^a\epsilon(\text{M}^{-1} \text{ cm}^{-1})$	$\lambda_{\text{em}}(\text{nm})$	$^b\Phi_{\text{f}}$	$^a\Phi_{\text{f}}(\%)$	$^a\langle\tau\rangle(\text{ns})$	$k_{\text{r}}(\text{nS}^{-1})$	$K_{\text{nr}}(\text{nS}^{-1})$
DCM	542	32,900	617	0.34	0.34	5.43	6.3	12
Cy	534	-	590	-	-	-	-	-
EA	535	-	610	-	-	-	-	-
THF	537	-	612	-	-	-	-	-

^a Measured at 10^{-5} M . ^b Determined with fluorescein as standard ($\Phi_{\text{F}} = 0.85$, 0.1 M NaOH).

Electrochemical and thermal properties of dye

The electrochemical behavior of PTPDI was investigated by cyclic voltammogram (CV) in dichloromethane (Figure 4a). The chromophore showed two irreversible oxidation and two quasi-reversible reductions in dichloromethane at

modest potential. These two quasi-reversible reduction processes originated from successive reduction of the imide groups to form a radical anion (PTPDI^{•-}) in the first reduction step and a dianion (PTPDI²⁻) in the second step. The first reduction process increased the electron density on the carbonyl oxygen of one of the imide groups. The addition of an electron to another imide group was governed by two factors. The first was the capability of delocalizing the surplus electron density imposed on the molecule during the first reduction step, and the second was the coulombic repulsion between the introduced charges of the same sign. Table 2 summarized the redox potential, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels estimated from cyclic voltammetry (CV). The HOMO/ LUMO energy levels of PTPDI and compound 1 were estimated to be -6.42/-3.94 eV and -6.43/-3.89 eV, respectively. Also, we can see from Table 2 that the band gap of PTPDI estimated from the equation $E_{\text{gap}} \text{ (eV)}^b = E_{\text{red1}}^{0a} - E_{\text{ox}}^{0a}$ was similar to the optical band gap energy (E_g^b) (Table 3) derived from the onset absorption edge in solution.

Thermogravimetric analysis (TGA) of PTPDI was presented in Figure 4b. The decomposition temperature was 350 °C. PTPDI exhibited a lower thermal stability than that of other PDIs (~400 °C) due to its structural asymmetry [32]. The weight loss of PTPDI (about 12%) is in good agreement with the theoretical value (11.7%), and is plausibly ascribed to the fragmentation of propanethiol group. The amine group attached to the bay position of perylene was more easily decomposed, even at temperature lower than 200 °C.⁴⁵

Table 2. Cyclic voltammetry data and molecular orbital energies of PTPDI and compound 1 with respect to the vacuum level.

Molecule	E_{red1}^{0a}	E_{red2}^{0a}	E_{ox}^{0a}	LUMO (eV) ^b	HOMO (eV) ^b	E_{gap} (eV) ^b
PTPDI	-1.03	-1.35	1.45	-3.94	-6.42	2.48
PDI	-0.91	-1.29	1.63	-3.89	-6.43	2.54

^a Measured in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in

dichloromethane versus Ag/AgNO₃ (in V).

^b Calculated from $E_{\text{HOMO}} = -4.88 - (E_{\text{oxd}} - E_{\text{Fc/Fc}^+})$, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$.

Fig. 4. The cyclic voltammogram (a) and thermal degradation (b) of PTPDI.

Quantum chemistry computation

To gain further insight into the structural and electronic property of PTPDI, quantum chemical calculation was carried out with density functional theory (DFT) at the B3LYP/6-31G* level. Optimized ground state geometric conformation of PTPDI was shown in Figure 5. The ground state geometry of the perylene core of PTPDI had two core twist angles, and the approximate dihedral angles between the two naphthalene subunits that attached to the central benzene ring were about 5° and 3°, respectively. Thus, the introduction of alkyl sulfide into the perylene skeleton slightly broke down the original planar conformation of perylene core and enlarged the dihedral angles. The HOMO and LUMO frontier molecular orbital of PTPDI were delocalized on the perylene core and S heteroatom sites (Figure 6). Furthermore, the calculated HOMO-LUMO gap fit quite well to the value obtained by experiment. As tabulated in Table 3, the energy gap has been decreased for PTPDI compared to **1**.

Fig. 5. Optimized structure of PTPDI obtained by DFT calculation at the B3LYP/6-31G* level. The grey, blue, red, and yellow balls represent C, N, O and S atoms, respectively. The H atoms are omitted for clarity.

Fig. 6. Computed frontier orbital of PTPDI.

Table 3. Calculated and experimental parameters for PTPDI and compound 1.

Molecule	HOMO ^a	LUMO ^a	E _g ^a	λ _{max}	E _g ^b
PTPDI	-5.89	-3.54	2.35	542	2.29
Compound 1	-6.09	-3.62	2.47	527	2.35

^a Calculated by DFT/B3LYP (in eV); ^b At absorption maxima (E_g = 1240/λ_{max}, in eV).

Stacking behavior of dye in solution and solid state

For perylene diimides, the electronic absorption had a pronounced coupling to the vibronic features corresponding to $v = 0 \rightarrow v' = 0, 1$, and 2 transitions, where v and v' were quantum vibrational numbers of the ground and excited states, respectively. For a free monomer, the normal progression of Franck–Condon factors were $A^{0-0} > A^{0-1} > A^{0-2}$. However, as the monomer begins to aggregate, the 0–1 transition increased.⁴³ Figure 7 showed the concentration-dependent (from 10^{-6} M to 8×10^{-5} M) UV-Vis absorption, fluorescence, and normalized absorption spectra (for

comparing the peak shapes) of PTPDI in dichloromethane. Both the maximum absorption and emissive wavelengths were not shifted with the variation of concentration. The 0–1 transition absorption of PTPDI showed scarcely any increase in dichloromethane at a concentration from 10^{-6} to 8×10^{-5} M (Figure 7c), suggesting that the π – π interactions did not occur. This trend indicated that the flexibility n-propyl mercaptan substituent and the core twist angles of PTPDI can effectively improve the solubility of the rigid perylene dye and inhibit the aggregation of perylene cores by shielding the π faces.

Fig. 7. Concentration-dependent UV-Vis absorption (a), fluorescence (b), and normalized absorption spectra (c) of PTPDI in dichloromethane.

Fig. 8. Absorption (a) and normalized absorption spectra (b) of PTPDI in methanol/dichloroform mixture with different methanol fractions (f_w , by volume %).

The stacking behavior of PTPDI was further investigated in methanol/dichloroform mixture with different methanol fractions (f_w). The absorption bands of PTPDI in dichloroform solution (10^{-5} M) at 542 nm and 504 nm increased gradually with the increase of f_w from 0% to 50% (Figure 8a), while 0–1 transition

absorption did not show any increase (Figure 8b). When $f_w = 66\%$, the absorption coefficient and 0–1 transition absorption increased obviously, indicating the aggregation occurred. Self-assemblies with bathochromic shifts of absorption bands and significant band increase of absorption coefficient are typical characteristics of *J*-aggregation.⁴⁹

To facilitate molecular aggregation, a mixed solvent composed of methanol and dichloromethane was used. Methanol (with poor solvent power) was added atop a concentrated dichloromethane solution (with good solvent power) of PTPDI at a ratio of 2:1 in a glass vial. Within a few minutes, red aggregates formed at the interface of the two solvents, and they slowly diffused into the upper phase (methanol). Figure 9a showed optical photograph capturing the self-assemble process of PTPDI. The process was also monitored by absorption spectral assay (Figure 9b). The absorption peak decreased gradually, indicating the formation of nanostructures. Such a self-assembly approach takes the advantage of strong intermolecular π - π interaction, which will be enhanced in a solvent where the solvophobic interaction of the molecule is maximized. Similar methods have been reported for self-assembling of one-dimensional nanostructure of other PDI molecules.¹⁶

Fig. 9. Optical photograph capturing (a), absorption spectra (b), a large area SEM image (c), SEM image (d), fluorescence microscopic image (e), optical microscopic image (f) and solid optical spectra (g) of PTPDI nanosheets.

Figure 9c showed the SEM image of PTPDI nanosheets with uniform

morphology in terms of both width and thickness. The length was in the range of a few hundreds of micrometers, and the average width was 30 μm (Figure 9d). Optical microscopic image also supported the observed nanosheet morphology (Figure 9f). As shown in Figure 9e and g, PTPDI showed strong fluorescence with sharp peaks and large Stokes shift in solid state. The emission quantum yield (Φ) in solid state was 14.5%. The emission maxima band was at 690 nm with a large Stokes shift of 223 nm. The narrow solid-state emission band of PTPDI was also unusual and interesting because spectral broadening is a very common phenomenon for solid emitting materials. It was because that the introduction of the bulky *n*-propyl mercaptan substituent increased steric hindrance, which prevented the molecules from packing compactly to some extent and thus avoided the spectral broadening. Weak intermolecular interactions between PTPDI molecules and large Stokes shift provided favorable factors that eliminated self-quenching of PTPDI and enhanced the solid fluorescence. The red-shift (74 nm) of the solid emission maximum can be attributed to the increased intermolecular interactions in the solid state compared to that in the solution.

X-ray diffraction study and molecular packing of dye

The internal structure of the self-assembled PTPDI has been further investigated by X-ray diffraction (XRD) experiment (Figure 10). The XRD pattern of PTPDI shows two clear diffraction peaks at $2\theta = 5.62^\circ$ (1.56 nm) and $2\theta = 8.44^\circ$ (1.05 nm), which correspond to the diffractions from the (100) and (010) planes, respectively. The peak at $2\theta = 25.60^\circ$ (*d* spacing 0.34 nm) can be attributed to the π -stacking of the perylene segment because the distances of π -stacking between the perylene cores were approximately 0.35 nm.⁵⁰⁻⁵² A diffraction peak at $2\theta = 16.51^\circ$ (*d* spacing 0.52 nm) can be attributed to the α -form crystal.⁵³ The multiple orders of reflection indicated that the self-assembled structure of PTPDI was well-ordered and layered.

Fig. 10. X-ray diffraction analysis of PTPDI.

Combining the results of density functional theory (DFT), X-ray diffraction pattern, and the morphological analyses using SEM, the molecular arrangement of PTPDI crystal could be disclosed (Figure 11). PTPDI molecules remained the similar face-to-face π - π packing as all known PDIs adopted in their crystal structures. However, due to the steric hindrance of bulky *n*-propyl mercaptan substituent, there was a huge transverse offset between adjacent PTPDI molecules. About seven carbon atoms in a perylene core were close to the adjacent perylene core (a perylene core is composed of 20 carbon atoms). The overlapping area of successive π -conjugated perylene cores was merely 35%, indicating extraessential intermolecular π -stacking in this case. The spectral changes also indicated that PTPDI molecules were arranged in slipped face-to-face fashion to form *J*-aggregates (Figure 8). The interplanar distance between adjacent PTPDI molecules was found to be 3.45 Å, which was similar to that in other PDIs crystals (about 3.5 Å).⁵⁴ It can be proposed that the good photoluminescence property of PTPDI solid crystal originates from the weak intermolecular π - π actions. The short interplanar distance between perylene cores is favorable for the hopping transportation of charge carriers from one molecule to an

adjacent one.

Fig. 11. View of the single crystal structure of PTPDI.

Conclusions

In this study, we reported a perylene diimide derivative with bulky n-propyl mercaptan substituent. The product PTPDI possesses both well defined organic microstructure and high fluorescence quantum yield in solid state. Due to the steric hindrance of bulky n-propyl mercaptan substituent, the intermolecular π - π actions were weak, and so provided high luminescence efficiency. In the mean time, the interplanar distance between perylene cores was very short (3.45 Å), which is favorable for the hopping transportation of charge carrier from one molecule to an adjacent one. Therefore, this study would be helpful for designing and synthesizing novel organic semiconductive materials with potential applications in electrically pumped lasers which require high emission efficiency when large current density is applied.

Notes

The authors declare no competing interest.

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Figure captions

Scheme 1. The synthetic route of PTPDI.

Fig. 1. Normalized absorption (*a*) and fluorescence spectra (*b*) of PTPDI and compound 1 in dichloromethane recorded at room temperature.

Fig. 2. Lifetime decay curve of PTPDI.

Fig. 3. Normalized absorption (*a*) and fluorescence spectra (*b*) of PTPDI in cyclohexane (red line, $\lambda_{\text{ex}} = 534$ nm), ethyl acetate (green line, $\lambda_{\text{ex}} = 535$ nm), tetrahydrofuran (blue line, $\lambda_{\text{ex}} = 537$ nm) and dichloromethane (black line, $\lambda_{\text{ex}} = 542$ nm).

Table 1. Absorption and emission data of PTPDI.

Table 2. Cyclic voltammetry data and molecular orbital energies of PTPDI and compound 1 with respect to the vacuum level.

Fig. 4. The cyclic voltammogram (*a*) and thermal degradation (*b*) of PTPDI.

Fig. 5. Optimized structure of PTPDI obtained by DFT calculation at the B3LYP/6-31G* level. The grey, blue, red, and yellow balls represent C, N, O and S atoms, respectively. The H atoms are omitted for clarity.

Fig. 6. Computed frontier orbital of PTPDI.

Table 3. Calculated and experimental parameters for PTPDI and compound 1.

Fig. 7. Concentration-dependent UV-Vis absorption (*a*), fluorescence (*b*), and normalized absorption spectra (*c*) of PTPDI in dichloromethane.

Fig. 8. Absorption (*a*) and normalized absorption spectra (*b*) of PTPDI in methanol/dichloroform mixture with different methanol fractions (f_w , by volume %).

Fig. 9. Optical photograph capturing (*a*), absorption spectra (*b*), a large area SEM image (*c*), SEM image (*d*), fluorescence microscopic image (*e*), optical microscopic image (*f*) and solid optical spectra (*g*) of PTPDI nanosheets.

Fig. 10. X-ray diffraction analysis of PTPDI.

Fig. 11. View of the single crystal structure of PTPDI.

Scheme 1.

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Fig. 1.

Fig. 2.

Fig. 3.

Table 1.

Solvents	$\lambda_{\text{abs}}(\text{nm})$	$^a\epsilon(\text{M}^{-1} \text{ cm}^{-1})$	$\lambda_{\text{em}}(\text{nm})$	$^b\Phi_{\text{f}}$	$^a\Phi_{\text{f}}(\%)$	$^a\langle\tau\rangle(\text{ns})$	$k_{\text{r}}(\text{nS}^{-1})$	$K_{\text{nr}}(\text{nS}^{-1})$
DCM	542	32,900	617	0.34	0.34	5.43	6.3	12
Cy	534	-	590	-	-	-	-	-
EA	535	-	610	-	-	-	-	-
THF	537	-	612	-	-	-	-	-

^a Measured at 10^{-5} M. ^b Determined with fluorescein as standard ($\Phi_{\text{F}} = 0.85$, 0.1 M NaOH).

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Table 2.

Molecule	E_{red1}^{0a}	E_{red2}^{0a}	E_{ox}^{0a}	LUMO (eV) ^b	HOMO (eV) ^b	E_{gap} (eV) ^b
PTPDI	-1.03	-1.35	1.45	-3.94	-6.42	2.48
PDI	-0.91	-1.29	1.63	-3.89	-6.43	2.54

^a Measured in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane versus Ag/AgNO₃ (in V).

^b Calculated from $E_{\text{HOMO}} = -4.88 - (E_{\text{oxd}} - E_{\text{Fc/Fc}^+})$, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$.

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Fig. 4.

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Fig. 5.

Fig. 6.

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Table 3.

Molecule	HOMO ^a	LUMO ^a	E _g ^a	λ_{max}	E _g ^b
PTPDI	-5.89	-3.54	2.35	542	2.29
Compound 1	-6.09	-3.62	2.47	527	2.35

^a Calculated by DFT/B3LYP (in eV); ^b At absorption maxima ($E_g = 1240/\lambda_{\text{max}}$, in eV).

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Fig. 7.

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Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

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