

Synthesis and Photoelectric Properties of Donor-Acceptor-Donor Molecule Containing Perylene Diimide

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In this paper, a novel perylene diimide derivative 1,7-bis[N,N-bis(4-phenyl)aniline]perylene diimide (PDI-TPA) was synthesized and characterized by IR spectroscopy, ^1H NMR and elemental analysis. Besides, solubility and photoelectric properties of 1,7-bis[N,N-bis(4-phenyl)aniline]perylene diimide were studied. Results show that 1,7-bis[N,N-bis(4-phenyl)aniline]perylene diimide exhibits excellent solubility in common solvents. The absorption bands span a wide range of the visible spectra and optical band gap is 1.68 eV. In addition, 1,7-bis[N,N-bis(4-phenyl)aniline]perylene diimide exhibits an ambipolar behaviour, the highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) energy level are -5.64 eV and -3.94 eV, respectively.

Keywords: Perylene diimide, Synthesis, Photoelectric properties.

INTRODUCTION

Recently, perylene diimides (PDIs) have been application extensively in molecular electronic devices such as photo-voltaic cells, organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs), because of their favorable properties for this purpose, such as migrational, photochemically, thermally stability and so forth. These materials have excellent fluorescent properties with high photoluminescence quantum yields¹⁻⁵. However, a key issue for perylene diimides is their solvent solubility, which restricts their thin-film-forming capability and potential applications as solution processable semi-conductors⁶⁻⁸. Previous studies⁹⁻¹² have shown that introduction of bulky alkyl, alkoxy, aryloxy moiety into the perylene diimides backbone can enhance solubility in many aprotic solvents and exhibited excellent thin-film-forming capability.

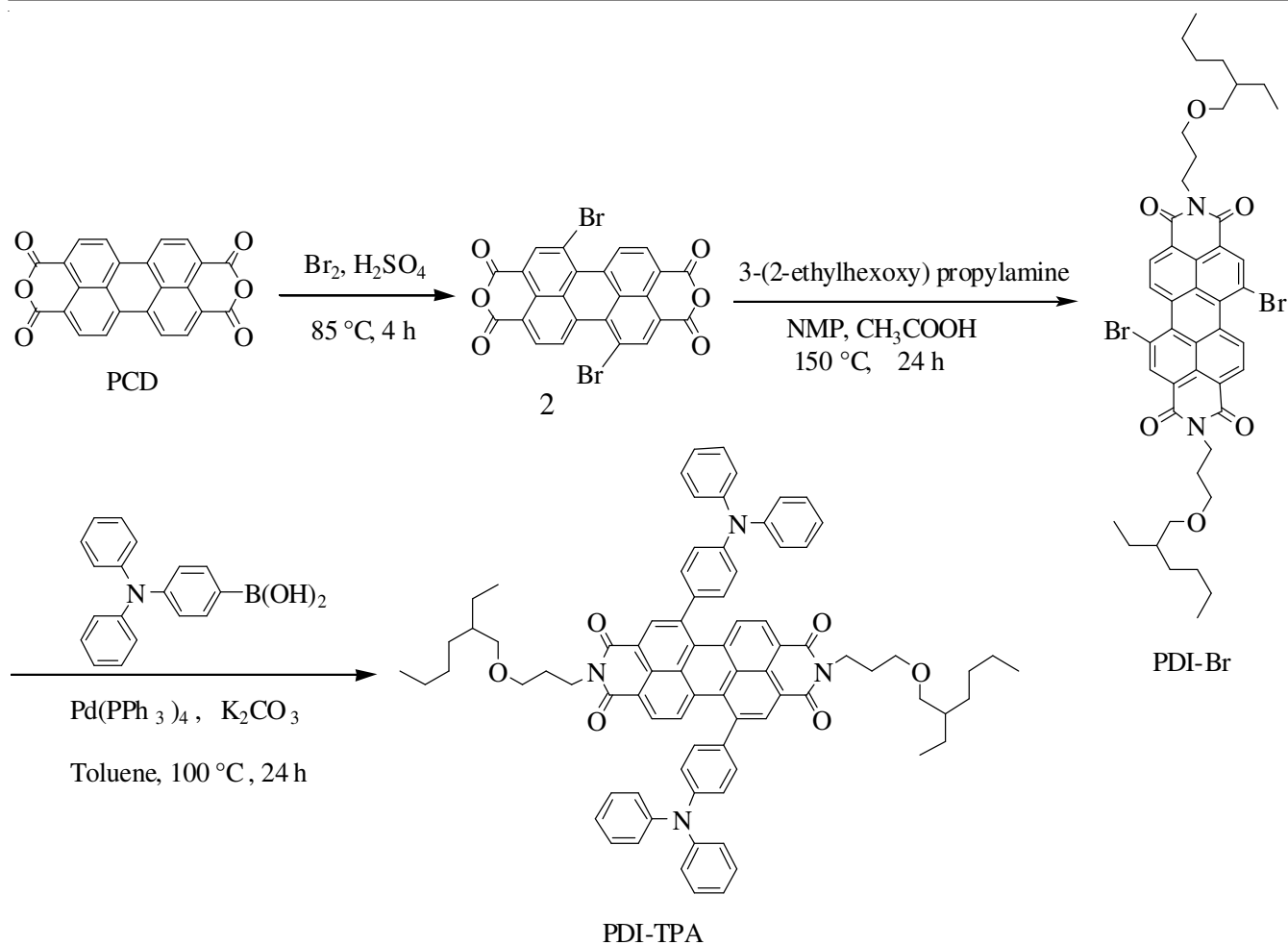
In addition, the long alkoxy chains and triphenyl amine moiety have also been further derivatised to modify specific optical properties such as electronic energy levels and absorption wavelength^{13,14}. In this paper, we have used perylene tetracarboxylic dianhydride (PCD) as raw materials *via* Suzuki-coupling reaction to obtain a novel donor-acceptor-donor (D-A-D) molecule PDI-TPA. Effects of 3-(2-ethyl-hexoxy) propylamine and triphenyl amine moiety on solubility and photoelectric properties of perylene diimides were investigated.

EXPERIMENTAL

All other chemicals and reagents were purchased from Aladdin and used as received without any further purification unless otherwise specified. All the reactions were accomplished in distilled anhydrous solvents under inert atmosphere. The ^1H NMR spectral data of synthesized samples were recorded on a Bruker ACF 300 spectrometer operating at 400 MHz for ^1H nucleus, using CDCl_3 solvent and TMS as internal standard, respectively. The absorbance and fluorescence spectra were recorded on a Shimadzu 3101 PC spectrophotometer and Hitachi F-4600 spectrofluoro-meter, respectively. Cyclic voltamograms measurements have been carried out using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in dichloro-methane solutions at a scan rate of 100 mV/s. The electrochemical cell composed of three electrode system, glassy carbon as working electrode, platinum rod as a counter electrode and saturated calomel as reference electrode.

The synthetic route of 1,7-bis[N,N-bis(4-phenyl)aniline]perylene diimide (PDI-TPA) is shown in **Scheme-I**.

Synthesis of compound 2: A mixture of perylene tetracarboxylic dianhydride (PCD) (19.6 g, 0.05 mol) and 300 mL concentrated sulfuric acid was stirred for 12 h at room temperature and subsequently I_2 (0.48 g, 1.89 mmol) was added. The reaction mixture was heated to 85 °C and bromine (5.83 mL, 0.1 mol) was added dropwise over a time period of 8 h. After bromine addition, the reaction mixture was heated for



Scheme-I: Synthetic routes of PDI-TPA

an additional 10 h at 85 °C and cooled to room temperature. The excess bromine was removed by a gentle stream of N_2 and 50 mL of water was added carefully. The resulting precipitate was separated by filtration through a funnel, washed with 300 mL of 86 % sulfuric acid and a large amount of water and dried in a vacuum to obtain the compound **2** (23.85 g, 85 %). IR (KBr, ν_{max} , cm^{-1}) 1771, 1739, 1726, 1592, 1376, 1286, 1230, 1166, 1139, 1037, 957, 859, 805, 734, 694.

Synthesis of compound PDI-Br: Compound **2** (2.20 g, 4 mmol), NMP (60 mL), *n*-butyric acid (40 mL) and 3-(2-ethyl hexoxy)propylamine (2.64 mL, 12 mmol) were mixed in a 250 mL three-neck flask while maintain a good stirring. The mixture was degassed and refluxed for 24 h at 150 °C under N_2 purge. After being cooled, the mixture was poured into 100 mL methanol and stored at -10 °C whole night. The formed precipitate was collected by filtration and washed with methanol. The precipitate was purified on a silica gel column with CH_2Cl_2 : petroleum (v:v, 10:1) as eluent to afford the dye PDI-Br as red solid (2.46 g, 70 %). ^1H NMR (400 MHz, CDCl_3 , δ ppm) 9.37(d, $J = 8.0$ Hz, 2H), 8.83 (s, $J = 8.0$ Hz, 2H), 8.61(d, $J = 6.4$ Hz, 2H), 4.16 (t, $J = 5.2$ Hz, 4H), 3.56 (t, $J = 5.6$ Hz, 4H), 3.26 (t, $J = 5.6$ Hz, 4H), 2.04 (t, $J = 6.0$ Hz, 4H), 1.15 (m, 18H), 0.75 (m, 12H). Anal. Calcd for $\text{C}_{46}\text{H}_{52}\text{N}_2\text{O}_6\text{Br}_2$: C, 62.17; H, 5.90; N, 3.15. found: C, 62.06; H, 5.98; N, 3.09.

Synthesis of compound PDI-TPA: Compound PDI-Br (2.66 g, 3 mmol), 4-(diphenyl-amino)phenylboronic acid

(1.83 g, 6.33 mmol), $\text{Pd(PPh}_3)_4$ (0.1 g, 0.08 mmol), K_2CO_3 water solution (17.4 mL, 2 M) and dried toluene (80 mL) were added to a 50 mL three-neck flask while maintain a good stirring. The mixture was degassed and refluxed for 24 h at 100 °C under N_2 purge. After being cooled, the mixture was poured into 100 mL methanol and stored at -10 °C whole night. The formed precipitate was collected by filtration and washed with methanol. The precipitate was purified on a silica gel column with CH_2Cl_2 : petroleum (v:v, 1:1) as eluent to afford compound PDI-TPA (2.30 g, 63 %). IR (KBr, ν_{max} , cm^{-1}) 2958, 2927, 2858, 1696, 1658, 1587, 1493, 1274, 1182, 1109, 861, 812, 694. ^1H NMR (400 MHz, CDCl_3 , δ ppm) 8.63 (s, $J = 8.0$ Hz, 2H), 8.23 (d, $J = 8.0$ Hz, 2H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.32 (m, 12H), 7.20 (m, 8H), 7.13 (m, 8H), 4.30 (t, $J = 6.4$ Hz, 4H), 3.54 (t, $J = 6.0$ Hz, 4H), 3.26 (t, $J = 5.6$ Hz, 4H), 2.03 (m, 4H), 1.19-1.33 (m, 18H), 0.77-0.84 (m, 12H). Anal. Calcd for $\text{C}_{82}\text{H}_{80}\text{N}_4\text{O}_6$: C, 80.89; H, 6.62; N, 4.60; found: C 80.51; H, 7.35; N, 5.15.

RESULTS AND DISCUSSION

Synthesis: Synthesis of PDI-TPA began with the I_2 -catalyzed bromination of perylene tetracarboxylic dianhydride in 98 % conc. sulfuric acid¹⁵. PDI-Br could be conveniently obtained in good yield by direct condensation using NMP and acetic acid as the solvent. Suzuki coupling of PDI-Br and 4-(diphenyl-amino)phenyl boronic acid with $\text{Pd(PPh}_3)_4$ as

catalyst and toluene as solvent at 100 °C under nitrogen atmosphere reflux conditions for 24 h, successfully produces PDI-TPA with a high yield. The chemical structure of PDI-TPA was fully characterized by IR, ^1H NMR spectra, elemental analysis, etc. The ^1H NMR spectrum is depicted in Fig. 1.

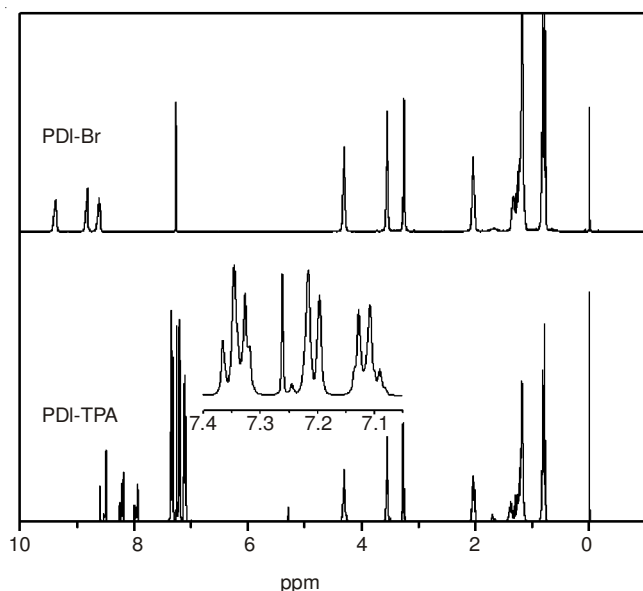


Fig. 1 ^1H NMR spectra of perylene diimides (PDIs)

PDI-Br has only one singlet appears at 8.83 ppm in the aromatic region, the result is consistent with the highly symmetric structure. The proton of PDI-TPA aromatic region appears at 7.1–8.2 ppm due to the triphenyl amine moiety had been introduced. The elemental analysis is also in good agreement with the chemical structure.

Solubility: Solubility behavior of resulting perylene diimides was tested qualitatively and the results are summarized in Table-1. PDI-TPA exhibited highly soluble in common solvents such as CHCl_3 , $\text{C}_6\text{H}_5\text{CH}_3$, THF, CH_2Cl_2 etc compare with PCD, which is due to the introduction of the bulky 3-(2-ethyl-hexoxy)propylamine unit directly attached to the perylene core reduces the π -stacking ability of the perylene moieties, thus increasing its solubility¹⁶. 1,7-Bis[N,N-bis(4-phenyl)aniline]-perylene diimide such excellent solubility in common organic solvents are competitive as candidates for solution processable semiconductor.

Absorption spectra properties: Absorption spectra of the solutions of perylene diimides with a concentration of 10^{-6} M and of spin coated thin films are depicted in Fig. 2.

TPA-Br shows an absorption band peak at 524 nm with characteristic vibronic fine structure which is attributed to the perylene core π - π^* transition¹⁷. The $\lambda_{\text{max}} = 630$ nm of PDI-TPA is red shifted about 106 nm compared with that of PDI-Br

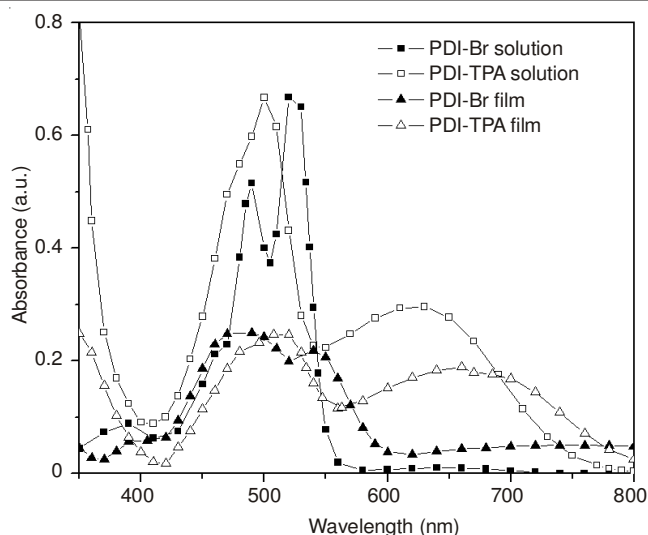


Fig. 2. Normalized absorption spectra of the solutions and thin films of perylene diimides (PDIs)

because the introduction of triphenylamine units enhanced the degree of intramolecular charge transfer. As compare to those of in the solutions, the absorption bands of the films are shifted to the higher wavelength region due to solid state aggregation and increasing amorphous nature. In addition, in the case of PDI-TPA, the starts absorption from 740 nm region with a lower optical bandgap of 1.68 eV compare to PDI-Br (2.19 eV), which is due to effective π - π conjugation of electron rich triphenylamine unit¹⁸.

Fluorescence spectra properties: Emission spectra of the dilute solutions at fixed optical density using an excitation wavelength of 330 nm are shown in Fig. 3.

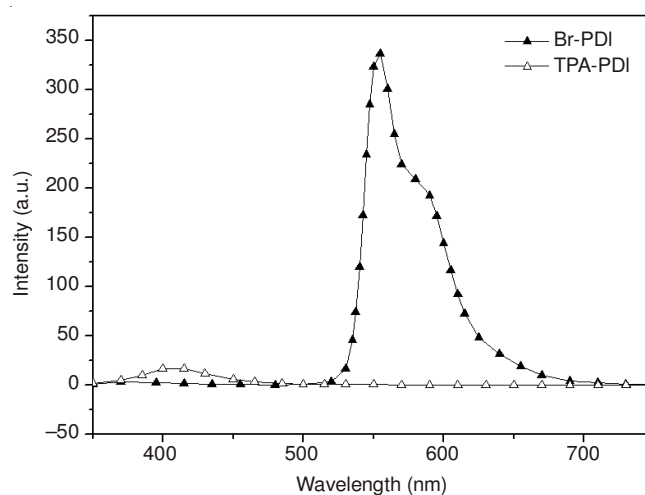


Fig. 3. Normalized emission spectra of perylene diimides (PDIs)

TABLE-1
SOLUBILITY OF PERYLENE DERIVATIVES

	CHCl_3	$\text{C}_6\text{H}_5\text{CH}_3$	DMF	THF	NMP	CH_2Cl_2
PCD	-	-	++	+	++	-
PDI-Br	++	++	+	++	+	++
PDI-TPA	++	++	+	+	++	++

Solubility: ++, Soluble at room temperature; +, Soluble on heating; -, Insoluble even on heating

PDI-Br shows two emission maxima at 554 and 588 nm. However, PDI-TPA have no fluorescence emission was observed, possibly due to fluorescence quenching attributed by efficient intramolecular charge transfer from electron-donating triphenylamine to electron deficient perylene diimide core¹⁹.

Electrochemical properties: The electrochemical behaviour of perylene diimides has been investigated using 0.1M TBAP as electrolyte at room temperature in dichloromethane solutions was depicted in Fig. 4.

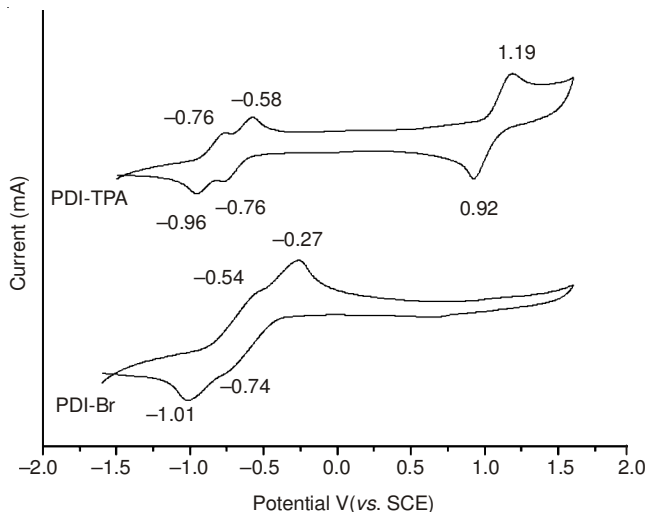


Fig. 4. Cyclic voltammograms of perylene diimides (PDIs)

PDI-Br has no oxidation wave could be detected, the HOMO level calculated using the optical bandgap was found to be -6.07 eV. Two clear quasi reversible one electron reduction waves could be found, which can be attributed to the reduction of the perylenediimide moiety and show the good electron acceptor ability of these materials^{20,21}. PDI-TPA shows the ambipolar behaviour, the onset potential for reduction and oxidation occurs at -0.80 and 0.90 V, which the LUMO and HOMO levels were calculated as -3.60 and -5.30 eV, respectively. The electrochemical band gap was calculated as -1.70 eV^{22,23}, which is the lower value. The decrease in electrochemical band gap is due to the introduction of electron donating triphenylamine unit which increase the π -conjugation of substituents as compared to the PDI-Br.

Conclusion

A novel D-A-D perylene diimide derivative PDI-TPA has been successfully synthesized. PDI-TPA exhibits excellent solubility in common solvents which is propitious to form film due to the introduction of the bulky 3-(2-ethylhexoxy)propylamine unit. The absorption bands span a wide range of the visible spectra and extend to the infrared region, which can greatly improve the utilization of the solar spectrum. In addition, PDI-TAP exhibits an ambipolar behaviour, the HOMO and LUMO energy level are -5.64 and -3.94 eV, respectively.

It has the potential to be used as electron donating and accepting materials application in OSCs.

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