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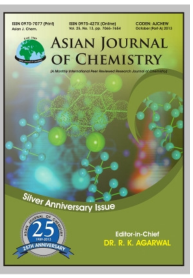

Synthesis and Photoelectric Properties of a Novel Perylene Diimide Derivative

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A novel donor-acceptor-donor (D-A-D) perylene diimide derivative 1,7-*bis*-[*N,N*-*bis*-(4-methoxy phenyl)aniline]perylene diimide (PDI2) had been successfully synthesized by means of bromination, condensation, Suzuki-crossing reaction. 1,7-*Bis*-[*N,N*-*bis*-(4-methoxy phenyl)aniline]perylene diimide exhibits excellent solubility in common solvents. The absorption maxima of PDI2 shows a bathochromic shift and absorption bands span widen to 890 nm, due to the introduction of electron donating *bis*-(4-methoxyphenyl)phenylamine moiety. A pronounced fluorescence quenching was observed due to the intramolecular charge transfer. Cyclic voltammograms of PDI2 display a couple of reversible redox peaks. The LUMO and HOMO levels of PDI2 were calculated as -3.88 eV and -5.13 eV, respectively.

Key Words: Synthesis, Solubility, Ambipolar transport material, Organic solar cells.

INTRODUCTION

The increasing energy demand and the concerns about climate changes have led to a great focus on renewable energy sources during the last years. So conversion of solar energy into electricity has been one of the important areas for scientific research[1]. Recently, organic solar cells have attracted much attention due to the broad range of small and large area applications, which will benefit from its unique features such as being flexible, light weight and low cost[2]. Nevertheless, one important factor that governs the performance of organic solar cells is the absorption spectrum of the organic semiconductors used for device fabrication. In an ideal situation, the absorption spectrum of solar cell materials should completely cover the region of terrestrial solar irradiation[3].

Perylene diimides have been investigated extensively in many research areas. The key application of perylene diimides so far is in laser dyes[4]. such as the famous perylene orange and red dyes[5]. because of the excellent fluorescent properties with high photoluminescence quantum yields[6]. More recently, perylene diimides have been applications in optoelectronic devices, such as photovoltaic devices[7]. Organic field-effect transistors[8] and light-emitting diodes[9], because of their good *n*-type semiconducting properties[10]. For the development of such applications, in particular soluble perylene diimides based organic solar cells are attractive because of enhanced light absorption due to their high molar extinction coefficient and good electron transport properties. Moreover, high electron mobility through π-π stacking favours intermolecular charge transfer and increases the charge separation[11]. However, a key issue for perylene diimides is their solvent solubility, which restricts their thin-film-forming capability and potential applications as solution processable semiconductors[12]. Therefore, various strategies dealing with the incorporation of solubility-increasing electron donating groups into various positions of the perylene structure have been proposed[13]. Previous studies have shown that introduction of bulky alkyl, alkoxy, aryloxy and triphenylamine moiety into the perylene diimides backbone can enhance solubility in many aprotic solvents and exhibited excellent thin-film-forming capability[14].

Triphenylamine and its derivatives are well known hole transport materials in organic photoelectronic devices due to their ability to form stable radical cations and high drift mobility[15]. In addition, triphenylamine derivatives exhibited lower oxidation potential and the formed cation radical was stabilized when electro-donating groups (methyl, methoxy) substituted at the *para*-phenyl positions[16]. Moreover, the long alkoxy chains which have also been further derivatized to modify specific optical properties such as electronic energy levels and absorption wavelength. In this context, amino and alkoxy groups extend absorption to longer wavelengths and lower the band gap[17]. Recently, the substitution in the bay region of perylene diimide through C-C or C-N coupling is a simple route to modify the HOMO-LUMO level renders to cover the whole visible-NIR region have been investigated and reported[18].

Here we report the synthesis, absorption, fluorescence and electrochemical behaviour of 1,7-*bis*-[*N,N*-*bis*-(4-methoxy phenyl)aniline]perylene diimide (PDI2), which use *bis*-(4-methoxy-phenyl)phenylamine and 3-(2-ethyl-hexoxy) propylamine attach perylene carboxylic dianhydride (PCD) to bridge a donor-acceptor-donor configuration of perylene diimide.

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 ^{1}H NMR spectral data of synthesized samples were recorded on a Bruker ACF 300 spectromete operating at 400 MHz for ^{1}H nucleus, using $CDCl_3$ solvent and TMS as internal standard, respectively.

The absorbance and fluorescenc spectra were recorded on a Shimadzu 3101 PC spectrophotometer and Hitachi F-4600 spectrofluorometer, respectively. Dichloromethane solutions of perylene diimide derivatives in 10×10 mm^3 quartz cells were used for UV-Vis and luminescence measurements.

Cyclic voltammograms measurements have been carried out using 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte in dichloromethane 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 synthesized routes of perylene diimides were shown in **Scheme-I**. The detailed synthetic procedures are as follows.

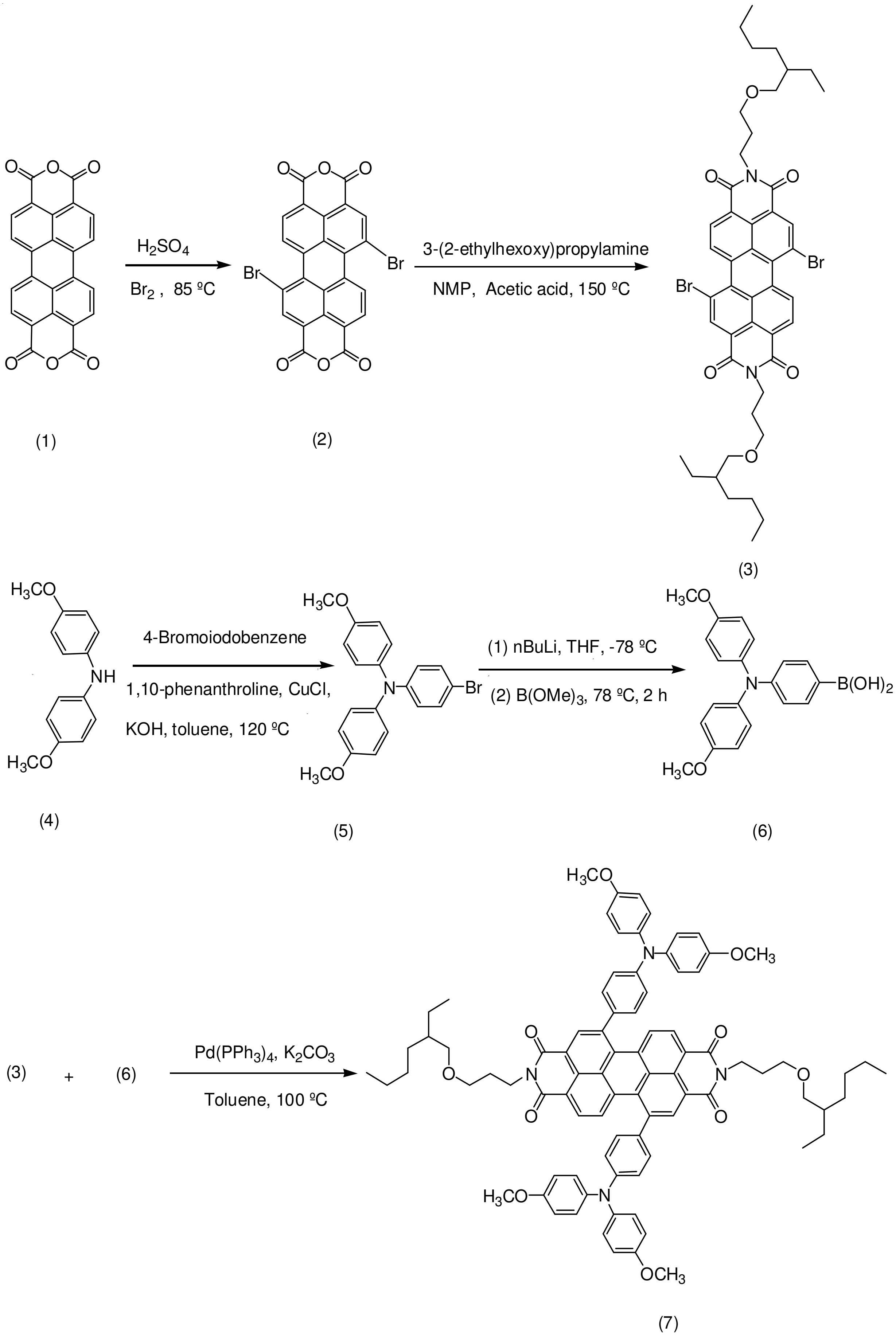
1,7-Dibromo-3,4,9,10-perylenetetracarboxylic dianhydride(2): A mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (20 g, 51.02 mmol) and 300 mL concentrated sulfuric acid was stirred for 12 h at room temperature and subsequently I_2 (0.48 g, 1.89 mmol) was added. The reaction mixture was heated to 85 ºC and bromine (5.83 mL, 113.77 mmol) was added dropwise over a time period of 8 h. After bromine addition, the reaction mixture was heated for an additional 10 h at 85 ºC and cooled to room temperature. The excess bromine was removed by a gentle stream of N_2 gas 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, yield 85 %. IR (KBr, cm^{-1}) 1771, 1739, 1726, 1592, 1376, 1286, 1230, 1166, 1139, 1037, 957, 859, 805, 734, 694.

1,7-Dibromo-*N,N'*-(3-(2-ethylhexyloxy) propylamine) -perylenetetracarboxylic acid diimide (PDI1) (3): Compound **2** (2.20 g, 4 mmol), NMP (60 mL), *n*-butyric acid (40 mL) and 3-(2-ethylhexoxy)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 ºC under N_2 purge. After being cooled, the mixture was poured into 100 mL methanol and stored at temperature of -10 ºC a 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, yield 70 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.37 (d, J = 8.0 Hz, 2 H), 8.83 (s, J = 8.0 Hz, 2 H,), 8.61 (d, J = 6.4 Hz, 2 H), 4.16 (t, J = 5.2 Hz, 4 H), 3.56 (t, J = 5.6 Hz, 4 H), 3.26 (t, J = 5.6 Hz, 4 H), 2.04 (t, J = 6.0 Hz, 4 H), 1.15 (m, 18 H), 0.75 (m, 12 H). Calcd. for $C_{46}H_{52}Br_2N_2O_6$: C, 62.17; H, 5.90; N, 3.15. found: C, 62.06; H, 5.98; N, 3.09.

4-Bromo-*N,N*-*bis*-(4-methoxyphenyl)aniline (5): 4,4'-Dimethoxydiphenylamine (2.05 g, 8.9 mmol), 4-bromoiodobenzene (2.97 g, 10.6 mmol) and 1,10-phenanthroline (0.27 g, 1.5 mmol)were dissolved in toluene (30 mL). After the solution was heated to 100 ºC, CuCl (0.15 g, 1.5 mmol) and KOH (1.23 g, 22.0 mmol) were added under N_2 purge. The mixture was refluxed for 48 h at 120 ºC. After being cooled, the mixture was washed with H_2O (50 mL) three times and the organic phase was dried over Na_2SO_4. After removal of the solvent, the residual was purified on a silica gel column with ethyl acetate:petroleum (v:v, 1:40) as eluent, yield 46 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 7.18 (d, 2 H, J = 8.0 Hz), 6.56 (d, J = 8.0 Hz, 4 H), 6.36 (d, J = 8.0 Hz, 6 H), 3.40 (s, 6 H).

4-[*Bis*-(4-methoxyphenyl)amino]phenylboronic acid (6): To a 50 mL three-necked flask containing the compound **5** (0.86 g, 2.3 mmol) in dried THF (20 mL) equipped with a magnetic stirrer, a N_2 purge and at -78 ºC acetone-dry ice bath were dropwise added to *n*-BuLi (2.1 mL, 3.2 mmol, 1.5 M) while maintaining a good stirring. After stirring for 1 h, trimethyl borate (0.36 mL, 3.2 mmol) was carefully added. After stirring at room temperature for another 2 h, water was first added to the reaction mixture and then HCl (6 M) was added in a dropwise fashion until an acidic mixture was obtained. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried with anhydrous Mg_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography using CH_2Cl_2 : ethyl acetate (v:v, 10:1) as eluent, yield 47 %. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.88 (s, 2 H), 7.66 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 4H), 7.06 (d, 4 H), 6.86 (d, J = 8.0 Hz, 2 H), 3.40 (s, 6 H).

1,7-*Bis*-[*N,N*-*bis*-(4-methoxyphenyl)aniline]-*N,N'*-*bis*-[3-(2-eshylhexyloxy)propylamine]-perylenetetracarboxylic acid diimide (PDI2) (7): Compound **6** (1.06 g, 1.2 mmol), compound 6 (0.93 g, 2.7 mmol), $Ph(PPh_3)_4$ (0.23 g. 0.2 mmol), K_2CO_3 water solution (10 mL, 2 M) and dried toluene (30 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 ºC under N_2 purge. After being cooled, the mixture was poured into 100 mL methanol and stored at temperature of -10 ºC a 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, 5:1) as eluent, yield 80 %. IR (KBr, ν_{max}, cm^{-1}) 2957, 2925, 2854, 1695, 1654, 1592, 1504, 1408, 1329, 1241, 1178, 1107, 1028, 855, 831, 758, 712; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 8.50 (s, 2 H), 8.14 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 4 H), 7.08 (d, J = 8.0 Hz, 8 H), 6.87 (d, J = 8.0 Hz, 4 H), 6.82 (d, J = 8.0 Hz, 8 H), 4.22 (t, J = 6.4 Hz, 4 H), 3.74 (S, 12 H), 3.46 (t, J = 6.0 Hz, 4 H,), 3.20 (t, J = 5.6 Hz, 4 H), 1.94 (m, 4 H), 1.14 (m, 18 H), 0.72 (m, 12 H). Anal. calcd. for $C_{86}H_{88}N_4O_{10}$: C, 77.22; H, 6.63; N, 4.19. Found: C, 76.95; H, 6.65; N, 4.32.



Scheme-I: Reagents and conditions for the synthesis of PDIs

RESULTS AND DISCUSSION

Synthesis: The synthesis of PDI2 began with the I_2-catalyzed bromination of 3,4,9,10-perylenetetracarboxylic dianhydride in 98 % conc. sulfuric acid. The synthetic approach of compound 1,7-dibromo-3,4,9,10-perylene tetracarboxylic dianhydride[19]. 4-bromo-*N,N*-*bis*-(4-methoxyphenyl)aniline, 4-[*bis*-(4-methoxyphenyl)amino]-phenylboronic acid[20], were mentioned in previous. Imidization of the anhydride with 3-(2-ethylhexoxy) propylamine was carried out in the presence of acetic acid as catalyst and *N*-methyl pyrrolidone as solvent at 150 ºC under nitrogen atmosphere reflux conditions for 24 h to smoothly produce PDI1 with a yield of 70 %. In the ^1H NMR spectrum of PDI1, only one singlet appears at 8.83 ppm in the aromatic region, the result is consistent with the highly symmetric structure of PDI1, the elemental analysis also are in good agreement with the chemical structure.

Suzuki coupling is known to be an effective approach for introducing aryl side groups to the perylene diimide core[21]. Even though steric hindrance is expected to be high, Suzuki counpling of PDI1 and compound **6** with $Pd(PPh_3)_4$ as catalyst and toluene as solvent at 100 ºC under nitrogen atmosphere reflux conditions for 24 h, successfully produces PDI2 with a high yield of 80 % by a relatively easy procedure for the common synthetic laboratory. The chemical structure of PDI2 was fully characterized by IR, ^1H NMR spectra, elemental analysis, *etc*. In the ^1H NMR spectrum of PDI2, only one singlet appears at 8.50 ppm in the aromatic region. This proton signal undergo up field shifting relative to that of compound PDI1 (8.83 ppm), the elemental analysis also are in good agreement with the chemical structure.

Solubility: The solubility behaviour of resulting perylene derivatives was tested qualitatively and the results are summarized in Table-1.

TABLE-1
SOLUBILITY OF PERYLENE DERIVATIVES

	Perylene solvent					
	$CHCl_3$	Toluene	DMF	THF	NMP	CH_2Cl_2
PCD	-	-	+ +	+	+ +	-
PDI1	+ +	+ +	+	+ +	+	+ +
PDI2	+ +	+ +	+ +	+ +	+ +	+ +

[a]Solubility: + +, soluble at room temperature; +, soluble on heating; -, insoluble even on heating

All compound exhibited highly soluble in aportic solvent except for PCD. As compared with PCD, PDI1 can better dissolve in common solvents such as $CHCl_3$, toluene, THF, CH_2Cl_2 *etc.*, which is due to the PCD unit was modified by 3-(2-ethylhexoxy)propylamine to increase it solubility. PDI2 exhibited more excellent solubility which resulted from the *bis*-(4-methoxyphenyl)phenylamine unit was introduced as compared to PDI1. Such excellent solubility in common organic solvents are competitive as candidates for solution processable semiconductor.

Absorption spectra: The absorption spectra of the solutions of perylene diimides with a concentration of 10^{-6} M and of spin coated thin films were shown in Fig. 1. The values of absorption maxima and optical band gaps are given in Table-2.

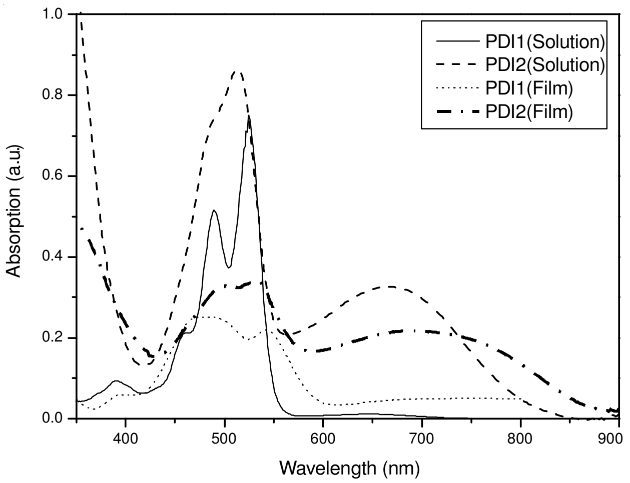


Fig. 1. Normalized absorption spectra of the solutions of PDIs with a concentration of 10^{-6} M and of spin coated thin films

TABLE-2
ABSORPTION SPECTRA OF PDIs

	Solution		Thin film	
Derivative	λ_{abs}(nm)	E_g^{opt} (eV)	λ_{abs}(nm)	E_g^{opt} (eV)
PDI1	458/489/524	2.20	392/483/543	2.06
PDI2	489/512/672	1.49	498/533/706	1.39

The optical band gap (E_g^{opt}) values were calculated from the onset of the absorption spectra ($E_g^{opt} = 1240/\lambda_{onset}$)[22]. The substitution of electron donating groups in the bay region of the perylene diimide core has changed the characteristic optical properties of the perylene diimide. PDI1 showed two absorption maxima at 485 and 521 nm, which corresponds to S_0-S_1 transition, with clear vibronic fine structure[11].

PDI2 starts absorption from 890 nm region with a lower optical band gap of 1.39 eV, which is due to lowering of the HOMO levels by electron donating substituents, resulting in a significant decrease as compared with PDI1 (2.06 eV). Additional, PDI2 undergo a significant bathochromic shift along with considerable band broadening and shows dual bands in visible region, in which the first band peaked at 672 nm is tentatively attributed to the charge-transfer absorption involving the electronic transition from the *bis*-(4-methoxy phenyl)phenylamine groups to the electron-deficient perylene core. The second band peaked at 512 nm and showed a characteristic vibronic coupling pattern and is assigned to the perylene π-π^* transition[23]. The two absorption bands span a wide range of the visible spectrum from 420 to 890 nm, covered the whole visible light region and broadened to near infrared region. Hence, the absorption spectra of PDI2 could well match the solar spectra, improving the utilization of sunlight.

As compared to those of the solutions, the absorption bands of the films were shifted to the higher wavelength region. The absorption pattern appears without any vibronic fine structure due to solid state aggregation and increasing amorphous nature. The optical band gaps were reduced as compared to those observed for the solution state.

Fluorescence spectra: The fluorescence spectra in dichloromethane solution and spin coated thin films of PDI1 were shown in Fig. 2.

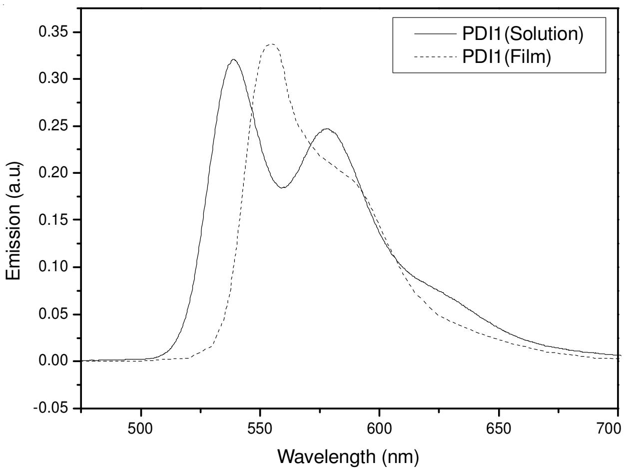


Fig. 2. Normalized fluorescence spectra in dichloromethane solution (solid line) and spin coated thin films (dotted line) of PDI1

The PDI1 showed two emission maxima at 537 and 576 nm, respectively. But in the PDI2 no visible fluorescence emission was observed. This fluorescence quenching behaviour is the result of an extremely rapid charge-transfer process from the electron donor *bis*-(4-methoxyphenyl)phenyl-amine moiety to the electron acceptor perylene diimide moiety, which leads to a charge separation state that lowers the energy of the more accessible empty orbitals in the phenyl subunit in the solution and the solid state[24]. In principle, intramolecular charge separation can be followed either by recombination on the same molecule or by intermolecular charge separation, which is necessary for solar energy conversion purposes in the solid state[25].

Electrochemical behaviour: The electrochemical behaviour of derivatives have been investigated using 0.1 M tetrabutylammonium perchlorate as an electrolyte at room temperature in dichloromethane solutions were shown in Fig. 3. The corresponding electrochemical properties of perylene diimides are summarized in Table-3.

As observed from the above results, PDI1 didn't show any observable oxidation potential. The HOMO level, calculated using the optical band gap, was found to be 6.07 eV. It implies that the incorporation of electron donating substituents does not significantly alter the position of the LUMO level. As compared to PDI1, PDI2 showed reversible redox cycle at $E_{ox} = 0.81$ V and $E_{red} = 0.71$ V, the electrochemical band gap (E_g^{elc}) was calculated as 1.25 eV, which is comparable to the optical band gap. The decrease in electrochemical band gap is due to the introduction of electron donating groups at the bay region increase in the π-conjugation of substituents as compared to the PDI1. The electrochemical properties reveal the ambipolar behaviour of PDI2, which the LUMO and LUMO levels were calculated as -3.88 eV and -5.13 eV, respectively, which the LUMO levels is very close to the most commonly electron acceptors material PCBM (-3.90 eV)[27] and the HOMO levels is very close to the most commonly electron donors material P3HT (-5.20 eV)[28]. Therefore, it has the potential to be used as ambipolar transport material application in organic solar cells.

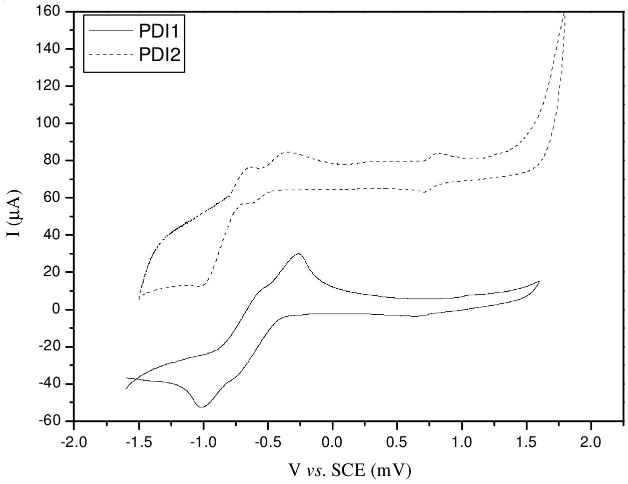


Fig. 3. Cyclic voltammograms of perylene diimides in dichloromethane/(TBAP 0.1 M) at a scan rate of 100 mV/s

TABLE-3
ELECTROCHEMICAL PROPERTIES OF PDIs

PDIs	E_{oxi}(V)	E_{red}(V)	E_{HOMO} (eV)[a]	E_{LUMO} (eV)[b]	E_g^{elc} (eV)[c]
PDI1	-0.54, -0.27	-1.01, -0.74	-6.07d	-4.01	-
PDI2	-0.64, -0.35, 0.81	-0.99, -0.63, 0.71	-5.13	-3.88	-1.25

aCalculated from empirical formula: $E_{HOMO} = -\left(E_{onset}^{ox} + 4.44\text{eV}\right)$. [b]Calculated by $E_{LUMO} = -\left(E_{onset}^{red} + 4.44\text{eV}\right)$.[26] [c]Determined by $E_g^{elc} = E_{HOMO} - E_{LUMO}$ [d]$E_{HOMO} = E_{LUMO} - E_g^{opt}$, calculated using optical band gap

Conclusion

In summary, a novel donor-acceptor-donor perylene-diimide derivative PDI2 has been successfully synthesized with a high yield. PDI2 exhibits excellent solubility in common solvents.The absorption spectra properties reveal that considerable bathochromic shift and absorption bands span a wide range of the visible spectra from 420 to 890 nm, displaying a low optical band gap of 1.39 eV. The cyclic voltammetry studies show that the LUMO and HOMO levels of PDI2 are -3.88 eV and -5.13 eV, respectively and exhibits an ambipolar behaviour. Hence, it has the potential to be used as ambipolar transport material application in organic solar cells.

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