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Synthesis and Characterization of Molecular Dyads Containing a Carbazolyl Based-Donor and Perylenediimide Based-Acceptor

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Synthesis and Characterization of Molecular Dyads Containing a Carbazolyl Based-Donor and Perylenediimide Based-Acceptor

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New molecular dyads containing perylenediimide (PTCDI) as an electron acceptor and carbazolyl derivative as an electron donor have been successfully synthesized. Cyclic voltammetry and absorption spectroscopy show that both electroactive units preserve their intrinsic nature, whereas photophysical investigations display a efficient fluorescence quenching. The molecular dyads such as **4** *and* **5** *exhibited unique electronic energy levels to facilitate the photoinduced electron transfer process.*

Keywords: acceptor; donor; molecular dyad; photoinduced electron transfer; photoluminescence

INTRODUCTION

Photoinduced electron transfer has is the fundamental process in which photosynthesis realize and it also provides the basis of molecular electronics [1]. The organic semiconductors are capable of tuning the absorption and emission properties, electron affinity or HOMO–LUMO molecular energy levels by controlling the molecular architecture. They have motivated the synthesis of a variety of molecular architectures combining electron donor and accepting moieties

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through a covalent bond and exhibiting the transfer of one electron from the donor to the acceptor unit after photoexcitation [2–4].

Perylenediimide (PTCDI) are well-known as a liquid crystalline n-type molecule and a photostable dye suitable for applications in solar cells. Thus, PTCDIs have been recently tethered to conjugated molecules or polymers as the electron acceptor for inducing photoinduced electron transfer [5–10]. These molecular dyads are often claimed as promising candidates for the construction of molecular rectifier, organic solar cells [11], either as active layers or to be used as light-harvesting antenna; or as models for the investigation of the fundamentals of photoinduced electron transfer.

One important characteristic to consider in these dyads is the stabilization of the charge separated state. The employment of carbazolyl-based donors in combination with PTCDIs can be quite useful, as carbazolyl group undergoes oxidation to afford thermodynamically stable radical ionic species. In this respect, the substitution of carbazolyl derivatives could be advantageous, considering the additional improvement in the stability of radical ion pairs produced by carbzaole unit. Thus, we decided to synthesize the molecular dyads, **4** and **5** in which a PTCDI electron accepting unit has been covalently attached to an electron donor through a relatively flexible alkylene spacer.

Here we report the synthesis and photophysical properties of novel donor-acceptor dyad systems carrying carbazolyl group as a donor and perylenediimide derivative (PTCDI) as an acceptor.

EXPERIMENTAL

Instrumental Analysis

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 Hz spectrometer using deuterated chloroform ($CDCl_3$-*d*) purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. Time-of flight mass spectrometry (MALDI-TOF) was performed using a Voyager-DESTR MALDI-TOF (matrix; DHB) mass spectrometer.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10°C/min. The redox properties of molecular dyads were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

Synthesis

Synthesis of Compound 1

6-Amino-1-pentanol (0.85 g, 8.20 mol) and zinc acetate (1.5 mg, 0.041 mmol) were dissolved in N,N-dimethylacetamide (150 mL) and the mixture was heated to 110°C under a nitrogen atmosphere. N-(1-Nonyldecyl)perylene-3,4,9,10-tetracarboxylic Acid 3,4-Anhydride 9,10-Imide (2.60 g, 4.10 mmol) was added and the reaction mixture was allowed to stir at 110°C for 18 hr. After cooling the mixture, the excess solvent was distilled off. The concentrated mixture was purified by silica gel column chromatography using chloroform. The material was precipitated into methanol. The product was filtered and dried in a vacuum oven. Yield: 3.41 g (87.7%).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.70 (br, J = 6.0 Hz, 2H). 8.66 (m, J = 6.0 Hz, 6H), 5.18 (m, 1H), 4.24 (t, J = 8.0 Hz, 2H), 3.69 (t, J = 6.0 Hz, 2H), 2.21 (m, 2H), 1.82 (m, 4H), 1.58 (m, 6H), 1.20 (m, 28H), 0.80 (t, J = 6.0 Hz, 6H).

Synthesis of 6-(3-((E)-4-((E)-2-(9-Hexyl-9H-Carbazol-3-Yl)vinyl)styryl)-9H-Carbazol-9-Yl)hexanoic Acid, 2

An oven dried, mag.-stirred, 100 mL RBF was charged with a solution of 9-hexyl-9H-carbazole-3-carbaldehyde (0.966 g, 3.30 mmol), methyl 6-(3-formyl-9H-carbazol-9-yl)hexanoate (1.02 g, 3.30 mmol) and tetraethyl 1,4-xylylenediphosphonate (1.24 g, 3.28 mmol) in 100 mL freshly distilled THF. The reaction was allowed to stir for 0.5 h followed by addition of potassium *tert*-butoxide (4.16 g, 37.1 mmole). The mixture was neutralized with HCl and extracted with 200 mL methylene chloride (MC). The organic layer was then dried over Na_2CO_3, filtered, and the solvent was removed *in vacuo*. The resulting crude product was then purified by silica gel column chromatography (MC:ethylacetate = 7:1) to yield 0.8 g (37.0%) of a solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 8.25 (s, 2H), 8.14 (d, J = 6.0 Hz, 2H), 7.70 (d, J = 6.0 Hz, 2H), 7.58 (s, 4H), 7.48 (t, J = 9.0 Hz, 2H), 7.41 (d, J = 3.0 Hz, 2H), 7.38 (d, J = 3.0 Hz, 2H), 7.33 (s, 3H), 7.24 (d, J = 3.0 Hz, 1H), 7.17 (d, J = 18.0 Hz, 2H), 4.32 (t, J = 9.0 Hz, 4H), 3.65 (s, 4H), 2.29 (t, J = 9.0 Hz, 4H) 1.92 (m, 4H), 1.68 (m, 4H), 1.46–1.41 (m, 4H).

Synthesis of 6-(3-((E)-3,5-Bis((E)-2-(9-Hexyl-9H-Carbazol-3-Yl)vinyl)styryl)-9H-Carbazol-9-Yl)hexanoic Acid, 3

9-Hexyl-9H-carbazole-3-carbaldehyde (3.46 g, 12.4 mmol), methyl 6-(3-formyl-9H-carbazol-9-yl)hexanoate (2.00 g, 6.19 mmol) and [1,2,4,5-tetra-(diethoxy-phosphorylmethyl)-benzyl]-phosphonic acid diethyl ester (3.27 g, 6.18 mmol) were dissolved in 100 mL freshly distilled THF. The reaction was allowed to stir for 0.5 h followed by addition of potassium *tert*-butoxide (4.16 g, 37.1 mmole). The mixture was neutralized with HCl and extracted with 200 mL MC. The organic layer was then dried over Na_2CO_3, filtered, and the solvent was removed *in vacuo*. The resulting crude product was then purified by silica gel column chromatography (MC:ethylacetate = 7:1) to yield 1.5 g (26%) of a solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) 8.28 (s, 3H), 8.16 (d, J = 8.0 Hz, 3H), 7.73 (d, J = 8.0 Hz, 3H), 7.63 (s, 3H), 7.48 (t, J = 8.0 Hz, 4H), 7.36–7.42 (m, 8H), 7.20–7.28 (m, 6H), 4.27 (t, J = 8.0 Hz, 6H), 2.33 (t, J = 8.0 Hz, 2H), 1.83–1.92 (m, 6H), 1.64–1.72 (m, 2H), 1.27–1.47 (m, 15H), 0.87 (t, J = 8.0 Hz 6H).

EA analysis calcd for C66H67N3O2; C, 84.85; H, 7.23; N,4.50, found; C, 84.77; H, 7.43; N, 4.44.

Synthesis of Compound 4

Compound 2 (0.127 g, 0.193 mmol), compound 1 (0.221 g, 0.309 mmol), dicyclohexylcarbodiimide (DCC, 0.067 g, 0.328 mmol), and 4-(dimethylamino)-pyridium-4-toluene sulfonate (DPTS, 0.091 g, 0.309 mmol) were dissolved in 100 mL of 1,2-dichloromethane at room temperature under argon. The reaction mixture was allowed to stir for 24 h. After completing the reaction, the solution was concentrated to the crude solid. Using chloroform, dissolution and filtration were repeated for removing white dicyclohexyl urea. The resulting mixture was poured into methanol to make the precipitate and the crude product was obtained after filtration. The resulting product was purified by silica gel column chromatography (chloroform:ethyl acetate = 50:1) and soxhlet extraction (methanol, 24 h). Yield : 0.21 (81.2 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 8.54 (s, 2H), 8.41 (m, 6H), 8.08 (m, 4H), 7.96 (d, J = 3.9 Hz, 1H), 7.56 (m, 4H), 7.48 (s, 4H), 7.15–7.44 (m, H), 7.04 (m, 2H), 5.17 (m, 1H), 4.04–4.28 (m, 9H), 2.25 (t, J = 6.0 Hz, 3H), 1.673 (m, 5H) 1.21–1.35 (m, 42H), 0.80–0.93 (m, 9H).

MALDI-TOF MS m/z calcd $C_{92}H_{98}N_4O_6$ $(M)^+$ 1355.79, Found 1355.7633.

Synthesis of Compound 5

Compound 3 (0.228 g, 0.140 mmol), compound 1 (0.160 g, 0.224 mmol), DCC (0.049 g, 0.238 mmol), and DPTS (0.066 g, 0.224

mmol) were dissolved in 150 mL of 1,2-dichloromethane at room temperature under argon. The reaction mixture was allowed to stir for 24 h. After completing the reaction, the solution was concentrated to obtain the crude solid. Repeated issolution in chloroform and filtration were performed for removing white dicyclohexyl urea. The resulting mixture was poured into methanol to make the precipitate and the crude product was filtered. The resulting product was purified by silica gel column chromatography (chloroform:ethyl acetate = 50:1) and soxhlet extraction (methanol, 24 h). Yield: 0.18 (78.8 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 8.55 (d, J = 8.1 Hz, 2H), 8.43 (m, 2H), 8.26 (d, J = 7.8 Hz, 2H) 8.12 (s, 4H), 8.20 (d, J = 7.8 Hz, 2H) 8.00 (d, J = 7.8 Hz, 4H), 7.73 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 2H), 7.48 (t, J = 7.2 Hz, 4H), 7.36–7.42 (m, 8H), 7.20–7.28 (m, 6H), 6.91 (d, J = 16.2, 2H), 5.23 (m, 1H), 4.28 (m, 5H), 3.98 (m, 4H), 2.28 (t, J = 6.9 Hz, 3H), 1.83 (m, 6H), 1.64 (m, 2H), 1.27–1.47 (m, 15H), 1.21–1.43 (m, 54H), 0.80–0.91 (m, J = 8.0 Hz, 12H).

MALDI-TOF MS m/z calcd $C_{112}H_{119}N_5O_6$ $(M)^+$ 1631.17, Found 1630.9987.

Absorption and Photoluminescence Spectroscopy

Studying absorption and PL spectral behavior, thin films of the molecular dyads were fabricated on quartz substrates as follows. The solution (2 wt%) of each molecule in chloroform was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 80°C for 24 hours under vacuum. Absorption spectra of film samples were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm. PL spectra were recorded with a Hitachi F-7000 FL spectrophotometer.

RESULTS AND DISCUSSION

We report the synthesis and photophysical properties of novel donor-acceptor dyad systems carrying carbazole-based donor (**2** or **3**) and perylene diimide type (**1**, PTCDI) acceptor. The donor and acceptor moieties were linked by an aliphatic ester bridge in order to isolate two moieties. The molecular structures are quite intriguing for us to employ a carbzaole-based donor, especially because carbazole derivatives are used as organic hole conductor materials in various applications. Furthermore, PTCDI is well-known as a liquid crystalline n-type molecule and a photostable dye suitable for applications in solar cells [12]. We successfully synthesized individual p-type and

TABLE 1 Measured and Calculated Parameters for the Synthesized Compounds

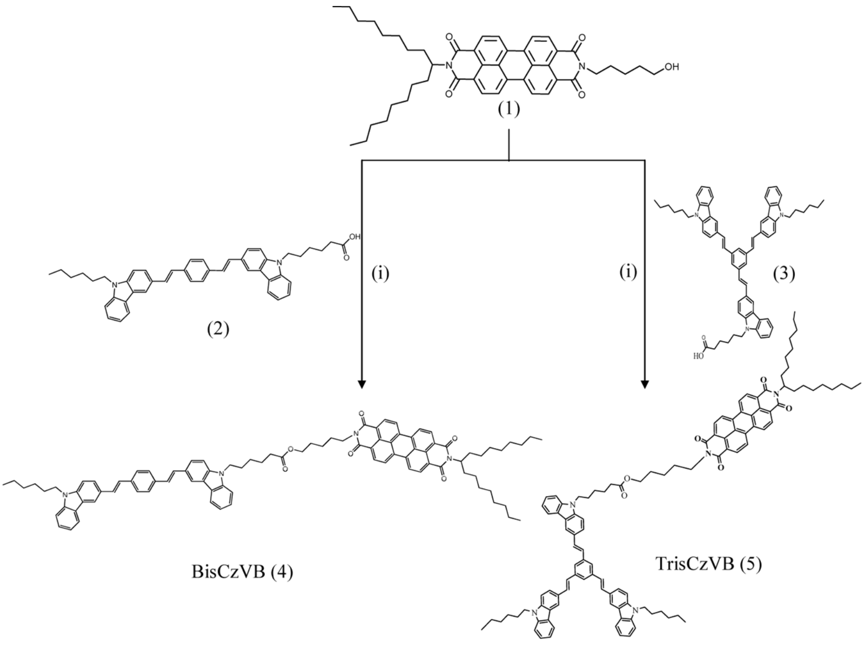
			Absorption		Emission				
	T_g	T_d	Solution λ_{max} (nm)	Film λ_{max} (nm)	Solution λ_{max} (nm)	Film λ_{max} (nm)	HOMO[a] (eV)	LUMO[a] (eV)	E_g[a] (eV)
(1)	67	415	459, 490, 527	496, 539	537, 573	603	−6.17	−3.29	2.88
(2)	–	–	373, 393	375, 397	440, 471	478	−5.21	−2.21	3.00
(3)	–	–	345	350	431	435, 536	−5.14	−2.40	2.74
(4)	70	429	394, 491, 527	398, 499, 539	537, 574	593	−5.09	−3.69	1.40
(5)	75	438	307, 350, 492, 528	307, 350, 499, 537	411, 533, 574	420	−5.06	−3.59	1.47

[a] The parameters were measured by using cyclic voltammogram.

n-type conducting moieties bearing reactive site and couple them suitably to get soluble, well-defined donor-acceptor large dyad molecules. The synthesized molecules are thoroughly characterized using spectroscopic analysis such as ^{1}H-NMR. These synthetic dyads were found to have a good self-film-forming property and showed good solubility in various organic solvents such as chloroform, xylene, chlorobenzene, and tetrahydrofuran (THF).

The thermal properties of the two molecular dyads were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Compounds **4** and **5** exhibits no discernible crystalline-isotropic transitions observed in DSC thermograms (see Table 1). The glass transition temperatures (T_gs) of the two molecules are 70 and 75°C for **4** and **5**, respectively. This indicates that two molecular dyads exhibit an amorphous morphology in solid films.

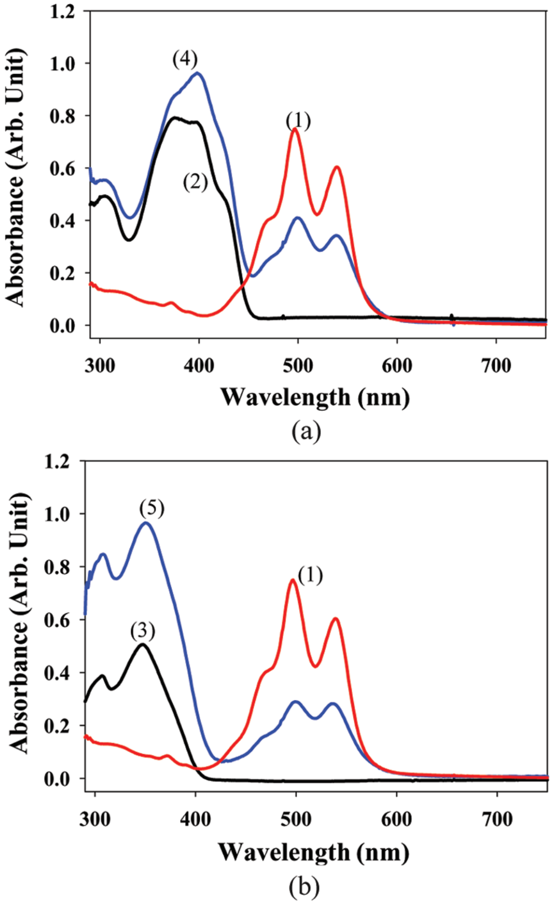
When comparing two glass transition temperatures, we found the fact that the molecular linearity of **4** induced lower glass transition temperature. TGA measurements at a heating rate of 10°C/min under nitrogen revealed good thermal stability. Two molecular dyads are thermally stable up to 429–438°C (see Table 1).



SCHEME 1 Synthetic route for two molecular dyads containing an electron donor and acceptor. (i) DCC, DPTS, MC, rt.

Using steady-state absorption and fluorescence measurements, we examined the photoinduced electron transfer (PET) processes. Figure 1 displays the absorption spectra of all the synthesized compounds in solid films. The absorption maximum wavelength ($\lambda_{\max}$) of **1** and **2** appeared 490 (459, 527) nm and 373(393) nm in solution, respectively. In the ground state of the solution, two molecular dyads do not exhibit high molecular interaction.

The UV–vis absorption spectra of **1, 2**, and **4** illustrated that coupled compound showed the simply additive spectral behavior



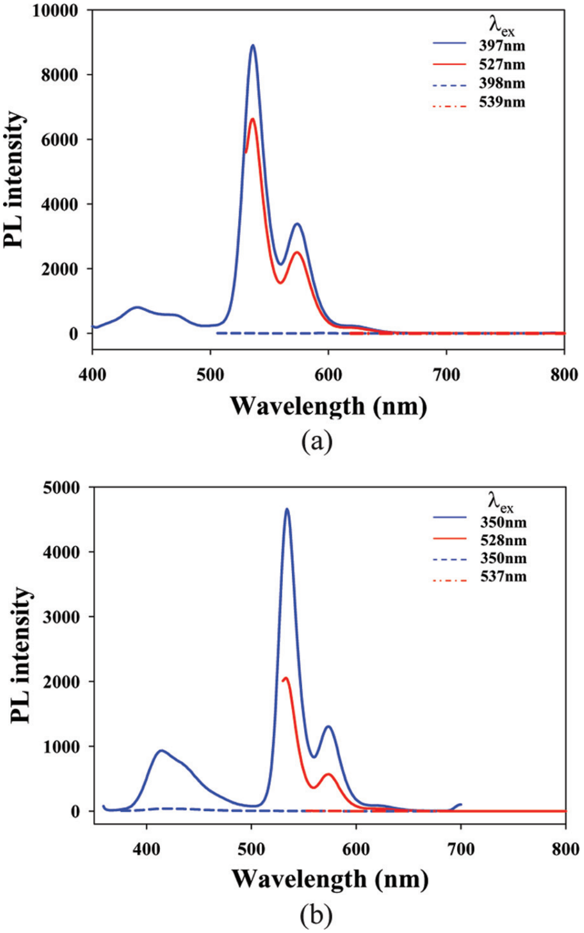
(a)

(b)

FIGURE 1 Absorption spectra of the molecular dyads. A: 1, 2, and 4, B: 1, 3, and 5. The number in parenthesis is same as the compound number in Scheme 1. *sample: Film (thickness: 70–90 nm).

without having clear charge transfer band. Just like the spectrum of **4**, the absorption spectrum of **5** also consists of the approximate superposition of the absorption features of its constitutive units, confirming the minimal interaction between the chromophores in the ground state, in agreement with the electrochemical analysis results.

Fluorescence emission spectra of the compounds, 4 and 5 were measured both in solution and film states using different excitation wavelengths. (4: $\lambda_{ex} = 350$, 527 nm for solution, $\lambda_{ex} = 350$, 527 nm for films;



(a)

(b)

FIGURE 2 PL spectra of the molecular dyads. A: 4; B: 5. The number in parenthesis is same as the compound number in Scheme 1. *sample: solid lines (solution states), dotted lines (film state, thickness: 70–90 nm).

5: $\lambda_{ex} = 350$, 528 nm for solution, $\lambda_{ex} = 350$, 537 nm for films). In dilute solution, two compounds showed two emission peaks; one is due to carbazole based donor. The other is due to PTCDI electron acceptor). Therefore, intramolecular electron transfer process does not affect the PL behavior significantly (see solid lines in Fig. 2). However, in films states, we could observe the emission behavior in two compounds commonly. It indicates that a quantitative quenching (ca. >99%) of the fluorescence emission in solid states is strongly governed by the

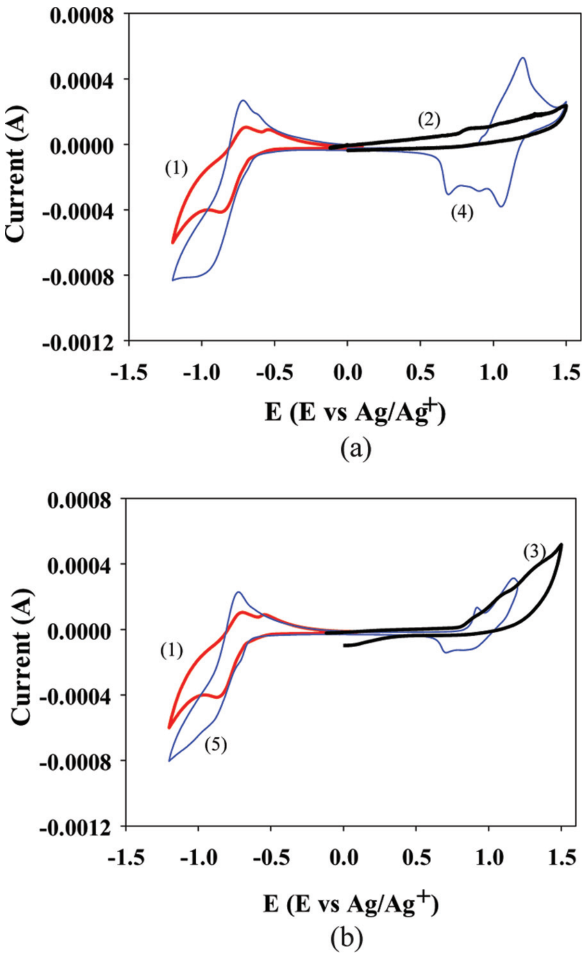


FIGURE 3 Cyclic voltammograms of compounds 1, 2, 3, 4, and 5. *sample: film on Pt electrode.

intermolecular photoinduced electron transfer process (see dotted lines in Fig. 2).

Electrochemical characterization of these molecules as films evidenced that their oxidation and reduction are quasi-reversible, which is a necessary condition for an electroactive material (Fig. 3). Voltammograms of **4** and **5** in the film state show that their lowest oxidative waves are at +0.66 and +0.69 V, respectively. As shown in Table 1, compounds **1, 4** and **5** have HOMO levels of −5.06 and −5.09 eV, respectively. The relatively higher HOMO levels should endow the material with better environmental stability. In addition, **4** and **5** have LUMO energy levels of −3.69 and −3.59 eV, respectively. The energy levels are almost consistent with the HOMO level of carbazolyl donor and LUMO level of PTCDI unit. After covalent bonding between two different electronic moieties, no significant variation of electronics property was observed.

CONCLUSION

We have successfully synthesized and characterized new donor-acceptor type molecular dyads that are well soluble in organic solvents. Upon UV-Vis absorption spectroscopy of **4** and **5**, the potoinduced electron transfer process was clearly observed in solid films state. These newly synthesized molecular dyads are composed of carbazolyl donor and perylenediimide type acceptor which are proper units for allowing the efficient photoinduced electron transfer process. The new molecular dyads are employed to fabricate the photovoltaic devices and the characterization is in progress.

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