

Optical and Electronic Properties of 3,4-Dialkylthiophene-Based *p*-/*n*-Alternating Copolymers

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Received 16 July 2010; accepted 16 September 2010

DOI 10.1002/app.33407

Published online 3 January 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Four novel highly soluble *p*-/*n*-poly[(2,5-divinyl-3,4-dialkylthiophene)-alt-2,6-pyridine] (PA₂TV-Py) and poly[(2,5-divinyl-3,4-dialkylthiophene)-alt-(2,5-diphenyl-1,3,4-oxadiazole)] (PA₂TV-OXD) are prepared by Heck coupling approach to compare their photoelectric properties. Characterizations of the copolymers include FT-IR, ¹H-NMR, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), UV-vis spectroscopy, photoluminescence (PL), and electroluminescence (EL). Four alt-copolymers exhibit excellent solubility in common organic solvents (e.g., CHCl₃, THF) and good thermal stabilities, losing less than 5% on heating to ~ 250°C. The optical properties depict that the band-gap energy of PA₂TV-Py and PA₂TV-OXD is similarly, ranging from 2.68 to 2.80 eV in solid film and 2.90–2.97 eV in CHCl₃ solution. PA₂TV-Pys can emit bright turquoise light with quantum efficiencies (QE) of 30.6 and 53.9%, which about 10–18

times higher than that of homopolymer in CHCl₃ solution. Furthermore, the QE of two PA₂TV-OXDs (purple fluorescence) are increased to 43.6 and 68.5%, respectively, about 1.3–1.4 times higher than that of PA₂TV-Pys. Electrochemical results indicate that the electron affinity (*E_a*) of four alt-copolymers range from 2.79 to 3.09 eV, which are propitious to electrons injecting and transporting from the cathode. As a result, these novel copolymers present expected good electroluminescence (EL) performance in their single layer polymer light-emitting device (PLED) with configuration of ITO/polymer/Al, which turn-on voltages are between 4.0 and 5.8 V and emit bright green-yellow (538 nm) and yellow (545–552 nm) EL light. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2678–2684, 2011

Key words: 3,4-dialkylthiophene; copolymer; quantum efficiency; electroluminescence; PLED

INTRODUCTION

Conjugated polymers have attracted intensive attention in the last years on account of their unique electrical and optical properties.¹ Polythiophene is a sort of conjugated polymer with excellent thermal and environmental stability as well as high electrical conductivity when doped.² The processability and the optoelectronic properties of the resultant polymers can be taken by introducing lateral pendant groups in polythiophene. Attachment of suitable pendant groups at both the 3- and 4- positions of the thiophene ring afforded a convenient approach in minimizing the occurrence of structural defects (such as branching and crosslinking arising from irregular β-couplings) in the backbones of polythiophenes.³

However, polythiophenes have a π-excessive nature, which are typical *p*-doped type polymers with much greater tendency for transporting holes than for transporting electrons,⁴ and polythiophenes are very sensitive to the values of the ground state dipole moments which following the charge transfer determines the electronic properties.⁵ This charge transfer imbalance highly limits the EL quantum efficiency (QE) of PLEDs. On the other hand, 1,3,4-oxadiazole or pyridine units with electron-deficient abilities have been found to be efficient in promoting the electron-transport property when incorporated into the PTs main chain or as side substituents.^{6–9} Therefore, a novel alternating copolymer with 3,4-dialkylthiophene and oxadiazole (or pyridine) units in ordered arrangement is synthesized via a “bridge” of vinyl by means of Heck coupling^{10–13} method. The optoelectronic properties are discussed and comparatively studied.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 21075015.

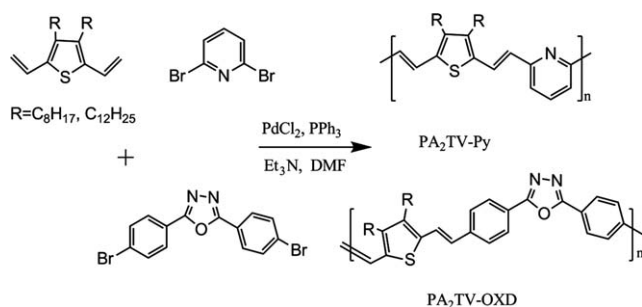
Contract grant sponsor: Jiangsu Province Science and Technology; contract grant number: BE 2009150.

Journal of Applied Polymer Science, Vol. 120, 2678–2684 (2011)
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EXPERIMENTAL

Materials

PdCl₂ and tetrabutylammonium perchlorate (TBAP, 98%) were purchased from Aldrich Chemical.



Scheme 1 Synthetic procedure of PA₂TV-Py and PA₂TV-OXD.

Triphenylphosphine (PPh₃), triethylamine, and *N,N*-dimethylformamide (DMF) were purchased from Wan Qin Chemical Reagent grade solvents were dried when necessary and were purified by distillation. 2,5-divinyl-3,4-dioctylthiophene and 2,5-divinyl-3,4-didodecylthiophene were synthesized by our group according to literature methods.¹⁴ 2,5-bis(*p*-bromophenyl)-1,3,4-oxadiazole and 2,6-dibromopyridine were synthesized according to literature methods.^{15,16}

Instruments

Gel permeation chromatography (GPC) was performed with a Perkin–Elmer series 200 apparatus (a mixed 10 μm PS column with a length of 750 mm, refractive index detector). Tetrahydrofuran (THF) was acted as the eluant at a flow rate of 1.0 mL min⁻¹ at 40°C. Polymer solution was filtered through a 0.45 μm PTFE filter prior to injecting into the column. Calibration was conducted with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a DuPont 9900 analyzer (DuPont Instrument, Wilmington, Germany) with a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. UV–vis spectra of the polymers were recorded on a Cary 5000 (Varian, America) in a laboratory atmosphere at room temperature. Photoluminescence (PL) spectra were recorded on a Perkin–Elmer LS-50B and photoluminescence QE was detected by using quinine sulfate (1 × 10⁻⁵ M solution in 0.5M H₂SO₄, QE is 55.0%) as a standard solution. Electroluminescence spectra were recorded on Hitachi M-850 double beam fluorophotometer (Hitachi, Japan). I–V characteristics were measured using an assembly consisting of HT-1712G dc-power supply (Shijiazhuang, China).

Cyclic voltammetry (CV) studies were performed using a standard three-electrode cell. Platinum disk was used as counter and 213 platinum slice was used as working electrodes. Ag/AgCl (0.1M AgNO₃ in acetonitrile) was used as a reference electrode. Measurements were recorded using a CHI660B CV voltametric analyzer (Chenhua, Shanghai, China) at

a scan rate of 50 mV s⁻¹. The Ag/AgCl electrode was connected to the electrochemical cell through a salt bridge and was calibrated before each experiment by CV measurement in a ferrocene containing solution.

Preparation of copolymers

General procedure for the synthesis procedure of poly[(2,5-divinyl-3,4-dialkylthiophene)-alt-2,6-pyridine] (PA₂TV-Py) and poly[(2,5-divinyl-3,4-dialkylthiophene)-alt-(2,5-diphenyl-1,3,4-oxadiazole)] (PA₂TV-OXD) is shown in Scheme 1.

Poly[(2,5-divinyl-3,4-dioctylthiophene)-alt-2,6-pyridine] (PO₂TV-Py)

About 65.6 mg (0.27 mmol) triphenylphosphine (PPh₃), 0.7 mL triethylamine(Et₃N) and 5.0 mL *N,N*-dimethylformamide (DMF) were added to a flask purged with N₂ and stirred. About 360 mg (1.00 mmol) 2,5-divinyl-3,4-dioctylthiophene, 237mg (1.00 mmol) 2,6-dibromopyridine, and 5.0 mg PdCl₂ were added subsequently. The mixture was stirred at 115°C for 12 h and 140°C for 2 h under N₂ atmosphere. The reaction mixture was filtered and the filtrate solution was poured into methanol. The deposition was dried under vacuum and extracted in a Soxhlet apparatus using hexane to remove oligomers. The final reactant was dried under vacuum after being further purified by redissolving in CHCl₃ and precipitating into methanol. The yield of a fawn powder was 39.5%. ¹H-NMR (*d*-acetone, δ): 0.88 (*t*, 6H, *J* = 6.2 Hz); 1.28 (*m*, 20H); 1.74 (*m*, 4H); 2.85 (*m*, 4H); 6.50–6.85 (*m*, 4H); 7.56–7.70 (*m*, 3H). FT-IR (KBr pellet, cm⁻¹): 2955, 2920, 2850, 1722, 1658, 1540, 1456, 1380, 1159, 1075, 790.

Poly[(2,5-divinyl-3,4-didodecylthiophene)-alt-2,6-pyridine] (PDD₂TV-Py)

PDD₂TV-Py was obtained following a procedure similar to that described for PO₂TV-Py. A brown powder was obtained with yield of 37.8%. ¹H-NMR (*d*-acetone, δ): 0.87 (*t*, 6H, *J* = 6.2 Hz); 1.28–1.40 (*m*, 36H); 1.68 (*m*, 4H); 2.85 (*m*, 4H); 6.40–6.78 (*m*, 4H); 7.68–7.75 (*m*, 3H). FT-IR (KBr pellet, cm⁻¹): 2955, 2917, 2850, 1719, 1655, 1592, 1463, 1383, 1255, 1165, 1075, 771.

Poly[(2,5-divinyl-3,4-dioctylthiophene)-alt-(2,5-diphenyl-1,3,4-oxadiazole)] (PO₂TV-OXD)

PO₂TV-OXD was obtained following a procedure similar to that described for PO₂TV-Py and 2,5-bis(*p*-bromophenyl)-1,3,4-oxadiazole was chosen to instead of 2,6-dibromopyridine. The yield of a red brown powder was 46.3%. ¹H-NMR (*d*-acetone, δ): 0.88

TABLE I
Solubility in Organic Solvents, Average Molecular Weights, Polydispersity Index, Polymerization Degree, and TGA Properties of Polythiophene Derivatives

Polymer	Solvent				GPC				T_{5d} (°C)
	CHCl ₃	THF	Toluene	Xylene	M_w	M_n	PDI	DP	
PO ₂ TV-Py	++	++	+	+	8176	7481	1.09	19	258
PDD ₂ TV-Py	++	++	+	+	6075	5591	1.08	11	280
PO ₂ TV-OXD	++	++	+	+	4495	3059	1.46	8	257
PDD ₂ TV-OXD	++	++	+	+	6896	5110	1.34	10	275

++, easily soluble at room temperature; +, partially soluble at room temperature; and T_{5d} (°C), decomposition temperature determined by TGA in N₂ atmosphere at 5% weight loss.

(*t*, 6H, *J* = 6.2 Hz); 1.26 (*m*, 20H); 1.70 (*m*, 4H); 2.45 (*m*, 4H); 7.64–7.88 (*m*, 4H); 8.04 (*m*, 8H). FTIR (KBr pellet, cm⁻¹): 3052, 2959, 2920, 2850, 1652, 1601, 1543, 1476, 1399, 1261, 1072, 1011, 832, 736.

Poly[(2,5-divinyl-3,4-didodecylthiophene)-alt-(2,5-diphenyl-1,3,4-oxadiazole)] (PDD₂TV-OXD)

PDD₂TV-OXD was obtained following a procedure similar to that described for PO₂TV-OXD. A red brown powder was obtained with yield of 40.8%. ¹H-NMR (*d*-acetone, δ): 0.87 (*t*, 6H, *J* = 6.6 Hz); 1.20–1.39 (*m*, 36H); 1.73 (*m*, 4H); 2.80 (*m*, 4H); 7.45–7.78 (*m*, 4H); 8.09 (*m*, 8H). FT-IR (KBr pellet, cm⁻¹): 3058, 2949, 2923, 2850, 1674, 1601, 1543, 1489, 1383, 1264, 1072, 1008, 829, 745.

RESULTS AND DISCUSSION

Physical properties

From ¹H-NMR spectra, multiple peaks are obtained in the range of 6.40–6.85 for PA₂TV-Py and 7.45–7.88 for PA₂TV-OXD, respectively, which reflect that the vinylene group between moiety of thiophene ring and oxadiazole is in both structures (a mixture of *cis* and *trans*).

The solubility, GPC, and TGA results of polymers are assembled in Table I. All of them are easily soluble in common solvents such as CHCl₃ and THF, but partially soluble in toluene and xylene. The polymers are of relatively low polymerization degree, which is attributed to the steric exclusion of the substitution in side chains.¹⁷ However, all the copolymers have relatively narrow molecular weight distributions (polydispersity = 1.08–1.46).

The stability of four polymers is also apparent through their resistance to photodecomposition and photo-isomerization with intense irradiation at 330–355 nm. This implies the polymers are relatively stable with respect to the light.

The thermal stability of the polymers is investigated with TGA under a nitrogen atmosphere. All of the polymers exhibit a good thermal stability, losing

less than 5% of their weight on heating to 258, 280, 257, and 275°C for PO₂TV-Py, PDD₂TV-Py, PO₂TV-OXD, and PDD₂TV-OXD, respectively. The excellent thermal stability of the polymers might be propitious to the application in optoelectronic device.

UV-vis spectroscopy

Among conjugated polymers, the extent of conjugation directly affects the observed energy of the π–π* transition, which appears as the maximum absorption.^{18,19} As shown in Figure 1(a), in CHCl₃ solution (1 × 10⁻⁷ M), the π–π* transitions of PO₂TV-Py, PDD₂TV-Py, PO₂TV-OXD, and PDD₂TV-OXD are exhibited by the absorption with maximum wavelength (λ_{max}) lying at 304, 308, 318, and 310 nm, respectively. Interestingly, the absorption of four copolymers showed the characteristics of oxadiazole or pyridine moieties and completely absented the absorption of the thiophene units. This imply that more electrons are lean to oxadiazole or pyridine moieties. In the film state, the absorption peaks of four copolymers [Fig. 1(b)] shows λ_{max} at a longer wavelength than that for the CHCl₃ solution. This imply that the conformation of PA₂TVs in solution would be that of a coil with a small effective conjugation length, and that of the solid state would be a more extended structure with more extensive electronic delocalization.²⁰ The optical band gap (E_g) of the polymers is calculated according to the formula: $\alpha h\nu = B(h\nu - E_g)^n$ where α is the absorbance coefficient, h is the Planck constant, and n (the value is 0.5) is the transition type, respectively.^{21–23} So a $(h\nu A)^2 - h\nu$ curve can be drawn and the band-gap energy is obtained by extending the linearity edge of absorbance to intersect with energy axis. The comparison data of optical band-gap energy for the copolymers are listed in Table II. The E_g of polymers in solution is higher than that of solid state. Meanwhile, the E_g of PO₂TV-Py (2.80 eV) and PDD₂TV-Py (2.70 eV) are 0.07–0.02 eV higher than that of PO₂TV-OXD(2.73 eV) and PDD₂TV-OXD (2.68 eV) in the solid film. These results are coincident with the variations of UV-vis maximum absorption.

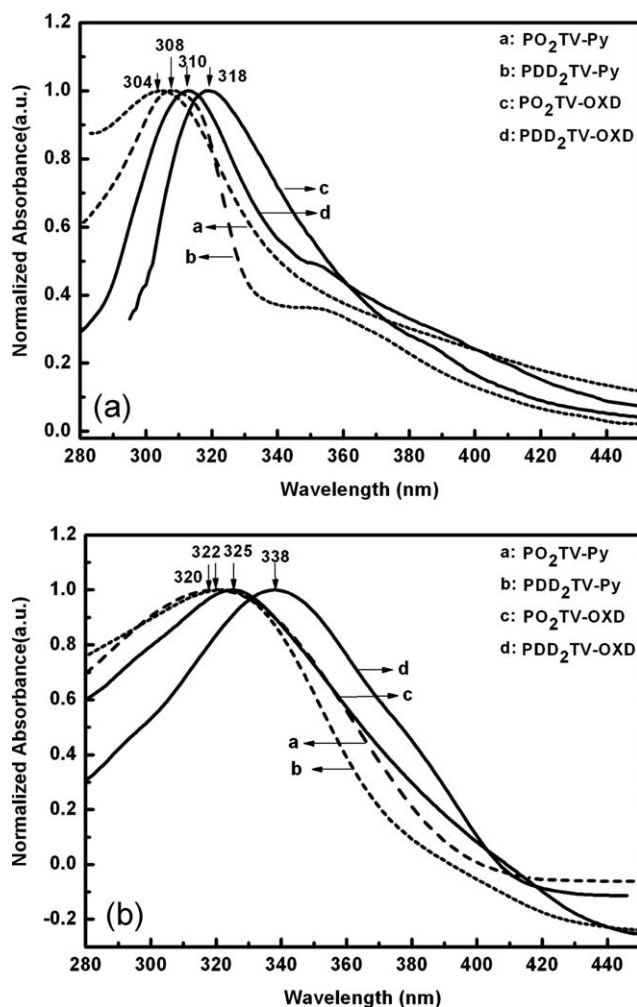


Figure 1 (a) UV-Vis spectra of PO₂TV-Py, PDD₂TV-Py, PO₂TV-OXD, and PDD₂TV-OXD in CHCl₃ solution (1×10^{-7} M) and (b) UV-Vis spectra of PO₂TV-Py, PDD₂TV-Py, PO₂TV-OXD, and PDD₂TV-OXD in solid film.

Photoluminescence properties

PL spectra can provide a good deal of information on the electronic structures of the conjugated polymers. Compared with the UV-vis absorption spectra, the excited maximum peaks of copolymers (Fig. 2) are red-shifted by 12–31 nm in CHCl₃ solution and 11–33 nm in solid film, respectively, which may

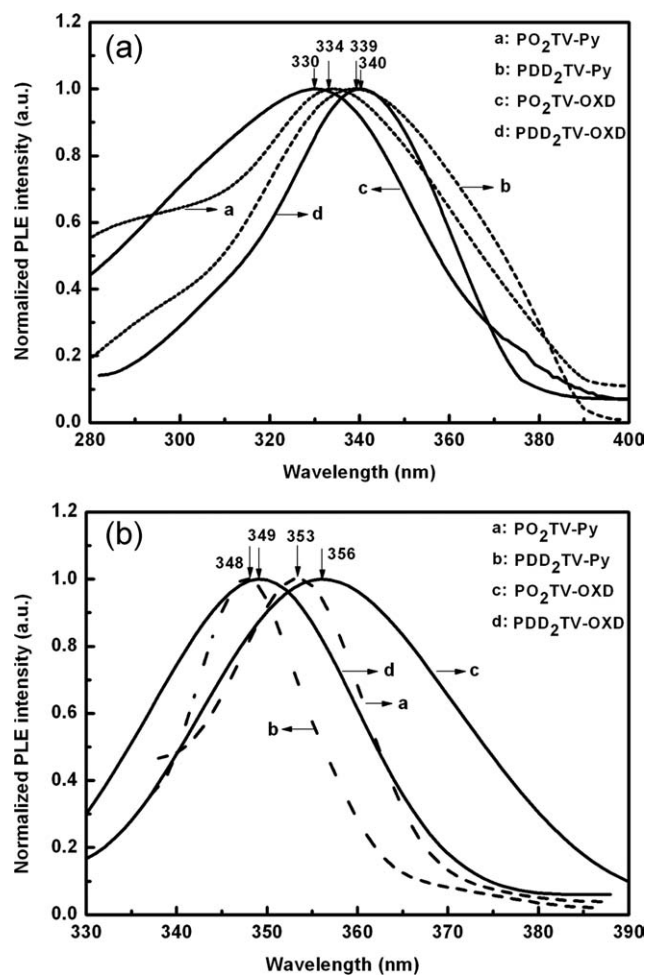


Figure 2 (a) PL excitation spectra of the polymers in CHCl₃ solution (1×10^{-7} M) and (b) PL excitation spectra of the polymers in solid film.

attribute to the partial energy transferring from the oxadiazole or pyridine moieties to the thiophene backbone under high energy laser.²³

The emission maximum of PO₂TV-Py, PDD₂TV-Py, PO₂TV-OXD, and PDD₂TV-OXD lies at 482, 471, 390, and 395 nm [Fig. 3(a)], with corresponding stock's shift is 178, 163, 72, and 85 nm respectively, in CHCl₃ solution. Among four copolymers, PA₂TV-Py displays the PL characteristics of polyalkylthiophene

TABLE II
Optical Data of Copolymers in CHCl₃ (1×10^{-7} M) and in Solid Film

Polymer	CHCl ₃ solution						Solid film				
	λ_{\max} (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	E_g^{opt} (eV)	QE (%)	Stock's shift (nm)	λ_{\max} (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	E_g^{opt} (eV)	Stock's shift (nm)
PO ₂ TV-Py	304	334	482	2.97	30.6	178	320	353	511	2.80	191
PDD ₂ TV-Py	308	339	471	2.95	53.9	163	322	348	518	2.70	196
PO ₂ TV-OXD	318	330	390	2.92	43.6	72	325	356	470	2.73	145
PDD ₂ TV-OXD	310	340	395	2.90	68.5	85	338	349	496	2.68	158

λ_{\max} , the absorption maxima of UV-vis; $\lambda_{\max}^{\text{ex}}$, the excitation maxima of PL; $\lambda_{\max}^{\text{em}}$, the emission maxima of PL; E_g^{opt} , the optical band gap.

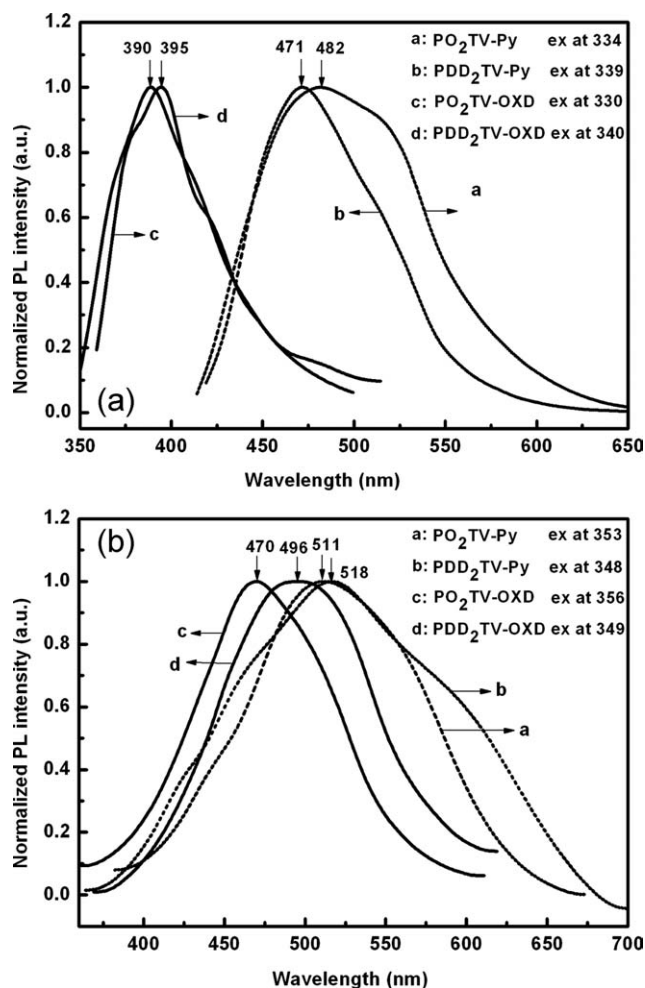


Figure 3 (a) PL emission spectra of the polymers in CHCl_3 solution ($1 \times 10^{-7} \text{ M}$) and (b) PL emission spectra of the polymers in solid film.

homopolymers (466–473 nm),²⁴ whereas the emission maximum wavelength of $\text{PA}_2\text{TV-OXD}$ is larger than that of oxadiazole moiety²⁵ but less than that of thiophene units. Examining polymers in the solid state [Fig. 3(b)], the emission maximum of $\text{PO}_2\text{TV-Py}$ (511 nm), $\text{PDD}_2\text{TV-Py}$ (518 nm), $\text{PO}_2\text{TV-OXD}$ (470 nm), and $\text{PDD}_2\text{TV-OXD}$ (496 nm) is red shifted by 29, 47, 80, and 101 nm compared with that of in CHCl_3 solution, respectively. The emission of $\text{PA}_2\text{TV-Py}$ is similar to that of polyalkylthiophene homopolymers (515–521 nm),²⁴ as well as emission from oxadiazole units (378 nm)²⁵ is not observed in PL of $\text{PA}_2\text{TV-OXD}$ which $\lambda_{\text{max}}^{\text{em}}$ is shifted to a longer wavelength. The stock's shift of four copolymers is 191, 196, 145, and 158 nm. These indicate that energy transferring from oxadiazole or pyridine to thiophen is suggested and more distinct in the solid state than that in solution. In addition, the energy transferring extent of $\text{PA}_2\text{TV-OXD}$ differs from that of $\text{PA}_2\text{TV-Py}$ because of their different electron-withdrawing ability leading to dissimilar ground and excited state

dipole moment.²⁶ All optical data are summarized in Table II.

PL QE is another important feature of the optical properties for conjugated polymers. Here, using quinine sulfate ($1 \times 10^{-5} \text{ M}$ solution in $0.5 \text{ M H}_2\text{SO}_4$, QE is 55.0%) as a standard solution, the PL QE of four copolymers are calculated according to the literature method²⁷ and listed in Table II.

In our previously work, the PL QE of poly(3-octylthiophene) (P3OT) was lower than 3% in CHCl_3 solution. Here, to our expectations, by introducing electron transporting moiety of 1,3,4-oxadiazole, the PL QE of $\text{PO}_2\text{TV-OXD}$ is increased evidently with reaching to 43.6%, about 14 times higher than that of P3OT. Similarly, a 68.5% QE of $\text{PDD}_2\text{TV-OXD}$ is about 23 times higher than that of P3OT. The results imply that the formation of a *p/n*-alternating copolymer can enhance the rigidity of polymers and compatibilize the immiscible pair of the two homopolymers effectively. In addition, the donor conjugated polymers being combined with electron accepting phases may provide the paths for both hole and electron transporting.²⁸ Therefore, increased rigid structure of copolymer and equilibrium of charge transfer along polymer's backbone both take a crucial role in luminescent efficiency.²⁹ Meanwhile, the PL QE of $\text{PO}_2\text{TV-Py}$ and $\text{PDD}_2\text{TV-Py}$ are also increased remarkable, ranging from 30.6 to 53.9%, about 10–18 times than P3OT. Comparing two different kinds of acceptors, the PL emission maximum of $\text{PA}_2\text{TV-OXD}$ s is blue shifted 92 and 76 nm with respect to that of corresponding $\text{PA}_2\text{TV-Py}$, however, their QE are 1.3–1.4 times higher than those of $\text{PA}_2\text{TV-Py}$ in CHCl_3 solution. This indicates that the electron injection and transporting capability of oxadiazole is more efficient than that of pyridine. On the other hand, examining the same acceptor unit, the QE of $\text{PDD}_2\text{TV-OXD}$ is larger than that of $\text{PO}_2\text{TV-OXD}$, as well as $\text{PDD}_2\text{TV-Py}$ larger than $\text{PO}_2\text{TV-Py}$, which is because the QE of polymer is enhanced according to the increasing length of pendant group in thiophene ring.²⁹

Electroluminescence properties

The singer layer PLED devices based on the four polymers with the configuration of ITO/polymer/Al are fabricated to investigate the electroluminescent properties. The film thickness of the emissive polymer is ~ 70 – 100 nm . Four singer layer devices display good commutated performance of classical diodes, and turn-on voltage of $\text{PO}_2\text{TV-Py}$ (5.8 V) and $\text{PDD}_2\text{TV-Py}$ (5.5 V) are 1.6–1.5 V higher than that of $\text{PO}_2\text{TV-OXD}$ (4.2 V) and $\text{PDD}_2\text{TV-OXD}$ (4.0 V) respectively. The results are agreed with the optical properties. In Figure 4, the EL maximum peak of $\text{PO}_2\text{TV-Py}$, $\text{PDD}_2\text{TV-Py}$, $\text{PO}_2\text{TV-OXD}$, and $\text{PDD}_2\text{TV-OXD}$ is lying

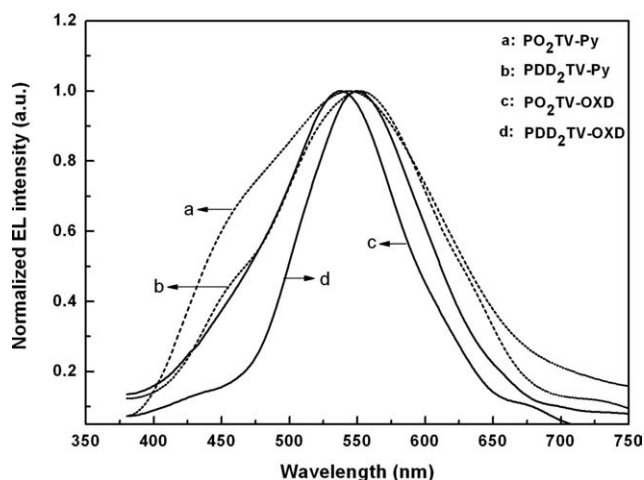


Figure 4 EL spectra of the polymers in devices of configuration with ITO/polymer/Ag.

at 545, 552, 538, and 548 nm, which color vary from green–yellow to yellow. A 34–68 nm larger wavelength for EL than that of PL can attribute to the increased congregation of copolymers in the singer layer PLED.²⁹

Electrochemical study

The electrochemical behaviors of the polymers are studied by cyclic voltammetry (CV) and their potential obtained with Ag/AgCl was converted to it against a saturated calomel electrode. The energy levels were calculated with the following empirical equations:^{30–32}

$$I_p = |E_{\text{HOMO}}| = E_{\text{onset}}^{\text{ox}} + 4.68 \text{ eV}$$

$$E_a = |E_{\text{LUMO}}| = E_{\text{onset}}^{\text{red}} + 4.68 \text{ eV}$$

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$$

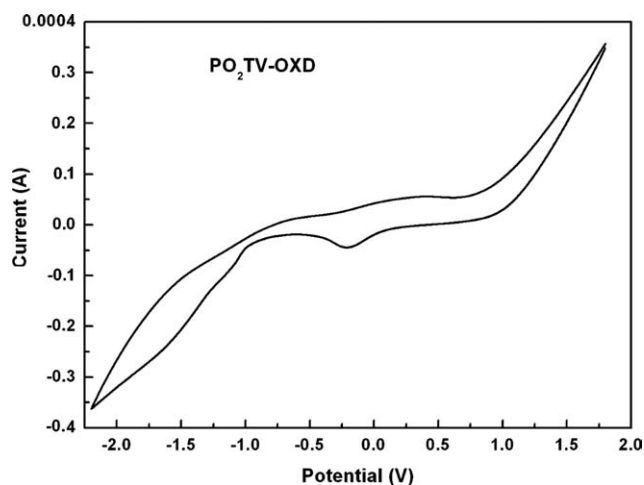


Figure 5 The cyclic voltammogram of PO₂TV-OXD.

TABLE III
The HOMO, LUMO, Band Gap, and Other Optical Data of Copolymers

Polymer	$E_{\text{onset}}^{\text{ox}}$	E_{HOMO} (eV)	I_p	$E_{\text{onset}}^{\text{red}}$	E_{LUMO} (eV)	E_a (eV)	E_g^{el}
PO ₂ TV-Py	1.08	-5.76	5.76	-1.87	-2.81	2.81	2.95
PDD ₂ TV-Py	1.15	-5.83	5.83	-1.89	-2.79	2.79	3.04
PO ₂ TV-OXD	1.19	-5.87	5.87	-1.63	-3.05	3.05	2.82
PDD ₂ TV-OXD	1.16	-5.84	5.84	-1.59	-3.09	3.09	2.75

$E_{\text{onset}}^{\text{ox}}$, the onset oxidation potential; $E_{\text{onset}}^{\text{red}}$, the onset reduction potential.

Examining the voltammogram of PO₂TV-OXD (showed in Fig. 5), an increase of oxidation current is observed with an onset at 1.19 V yielding an ionization potential (I_p) of 5.87 eV and corresponding reduction process displays a small peak relating to a *n*-doping process with an onset at -1.63 V. The similar electrochemical properties are also observed for PO₂TV-Py, PDD₂TV-Py, and PDD₂TV-OXD and results are showed in Table III. These indicate that the novel alternating copolymers are provided with capability of both electron transporting and hole transporting abilities. Moreover, the electron affinity (E_a) of PA₂TV-Py ranging from 2.79 to 2.81 eV is lower than that of PO₂TV-OXD (3.05 eV) and PDD₂TV-OXD (3.09 eV), imply that PA₂TV-OXD possess much better electron transporting properties³³ which will be effectively beneficial to balancing charges motion and enhancing the efficiency of functional optoelectronic devices. The E_g^{el} mensurated from CV is about 0.07–0.34 eV higher than that of the optical method (E_g^{opt}), because the charges transfer through polymer film might consume more energy during electrochemical determining.³⁴ The difference between E_g^{el} and E_g^{opt} is in good agreement with the theoretical error (<0.5 eV).³⁵

CONCLUSION

Four alternating π -conjugated copolymers combining with electron donor (2,5-divinyl-3,4-dialkylthiophene) and electron acceptor (2,5-diphenyl-1,3,4-oxadiazole and 2,6-pyridine) have been studied with respect to their optical and electronic properties. Energy transfer from the heteroaromatic moieties to the polythiophene backbone is suggested. An *n*-doping process reveals that the alternating copolymer is capable of electron transfer, besides their inherent hole transferring ability. A remarkable increase in the PL QE of PA₂TV-Py and PA₂TV-OXD compared with the homopolymer indicates that increased rigid structure of conjugated polymer and equilibrium of charge transfer among polymer take on a crucial role in the luminescence efficiency. In different electron-drawing moieties, 1,3,4-oxadiazole with relatively high E_a can

possess much better electron transporting properties which benefit to balancing charges motion and enhancing the efficiency of PL and EL. On the basis of these results, these novel *p*-/*n*- alternating copolymers with both electron-transporting and hole-transporting abilities might be a promising material for applications in high efficiency, low cost optoelectronic devices.

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