Novel Isoindigo-Based Conjugated Polyelectrolytes: Synthesis and Fluorescence Quenching Behavior with Water-Soluble Poly(*p*-Phenylenevinylene)s

Chun Kou, Xiaolong He, Xueyu Jiang, Yifeng Ni, Ling Liu, Changxin Huangfu, Kuan Liu

College of Science, Sichuan Agricultural University, Yaan 625014, People's Republic of China Correspondence to: K. Liu (E-mail: cosmicer@live.cn)

Received 13 January 2015; accepted 21 May 2015; published online 30 June 2015 DOI: 10.1002/pola.27711

ABSTRACT: Two novel ID-based water-soluble conjugated polymers (+)-PIDPV and (-)-PIDPV were synthesized by Heck coupling reaction. These two polyelectrolytes are both consisted of isoindigo units and phenylenevinylene units. In the UV-vis absorption spectra, both (+)-PIDPV and (-)-PIDPV exhibit broad absorption bands that almost cover the whole visible region. Photophysical investigations reveal that the fluorescence of water-soluble PPV can be efficiently quenched by oppositely charged PIDPV at a very low concentration. Cationic PPV shows an efficient quenching effect with $K_{SV} = 1.01 \times 10^6$ M⁻¹ in the presence of (-)-PIDPV while the anionic PPV gives

a lager quenching constant with $K_{SV} = 1.71 \times 10^6 \ M^{-1}$ in the presence of (+)-PIDPV. Furthermore, the blend films of water-soluble PPVs and oppositely charged PIDPV also exhibit excellent quenching effect. These properties suggest that (+)-PIDPV and (-)-PIDPV are promising materials in the application of ionic photoactive layer in the organic solar cells. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 2223–2237

KEYWORDS: isoindigo; conjugated polyelectrolytes; copolymerization; synthesis; fluorescence quenching

INTRODUCTION Conjugated polyelectrolytes (CPEs) have drawn a great deal of interest because of their excellent solubility in water and other polar solvents which was achieved by modification of the side chains with a set of ionic pendants such as anionic carboxylates,¹ phosphonates,² sulfonates,^{3,4} and cationic quaternary ammonium salts.⁵ With the wonderful properties of strong and tunable absorption and photoluminescence, environment-friendly processability, water solubility, and aggregation phenomenon, CPEs have been applied in a variety of photoelectric devices including polymer light-emitting diodes (PLEDs),6-8 photovoltaic cells,9,10 organic field effect transistors (OFETs),11,12 and chemical and biological sensors.^{13,14} Conjugated polymersbased bulk-heterojunction (BHJ) solar cells have been studied widely due to their advantages for fabrication of lowcost, promising flexibility and processability but the low power conversion efficiency (PCE) has always been the essential drawback.^{15,16} Research on interface engineering¹⁷ demonstrates that the performance of the photovoltaic devices can be dramatically improved by introducing an interfacial layer between the active layer and the metal electrode. The inserted layer should be in ohmic contact to minimize the contact resistant and maximize the open-circuit voltage $(V_{\rm oc})$.¹⁸ It has been reported that CPEs are good candidates for the interfacial layer material because they can prevent

damage to the underlying organic soluble active layer and have environment-friendly processing capabilities. Furthermore, the ionic side groups of the polymers can induce large interfacial dipoles to reduce the work-function of the cathode and as a result the $V_{\rm oc}$ of the device is increased and the PCE is improved.^{19,20}

In the past few years, dye-based conjugated polymers have attracted great attention and almost all of these polymers exhibit excellent photoelectric properties due to their large conjugated system.²¹ Isoindigo (ID) is a kind of indigoid dyes as same as indigo and isatin, in which two indolin-2one units are connected by the central C=C bond in E configuration and two intramolecular hydrogen bonds occur between C=O and N-H groups.^{22,23} Investigation of the medicinal properties of ID derivatives reveals that ID derivatives such as 1-methylisoindigo (Meisoindigo) and 1-(tri-0acetylxylopyranosyl)-isoindigo (Natura) have a great anticancer potency.²⁴ Moreover, as same as other hydrogen-bond dyes, IDs are always modified with alkyl groups via N-alkylation, which can break the hydrogen-bond network and increase their solubility. Recently ID derivatives are used as copolymerization units to form internal donor-acceptor (D-A) structures in the synthesis of conjugated polymers due to its strong electron-deficient lactam rings.²⁵⁻²⁷ Introduction

© 2015 Wiley Periodicals, Inc.





SCHEME 1 Synthetic routes of monomers and polymers.

of soluble ID unit into conjugated polymers can not only optimize the electron structure but also lower the HOMO energy levels and the band gaps, thus the polymers can harvest a large number of solar photon. Most of these polymers exhibit broad absorption band in the visible region which makes them become important components of active layers in the organic solar cells.²⁸ In 2010 the first ID-based conjugated polymer was blended with PC₆₀BM to fabricate molecular BHJ solar cells with PCE of $1.76\%^{29}$ and now the highest PCE of the ID-based organic solar cells is 8.2%.³⁰ In addition, the ID-based polymers are also used in organic semiconductor memory devices where ID units act as electron-trapping moieties to improve the on/off ratios and in OFETs due to the relative high hole mobility of the polymers.³¹

However, none of ID-based conjugated polyelectrolytes has been reported yet. The ionic hydrogen bond dyes as watersoluble 1,4-diketopyrrolo[3,4-c]pyrrole (DPP) derivatives have been obtained by modified with carboxyl³² or sulfuric acid ester³³ on its *N*-alkyl side chain, but it gives a low yield and an unsatisfied purity. Recently, the strategy to transform such hydrogen-bond dyes as quinacridone³⁴ and DPP³⁵ into water-soluble derivatives with high yield and purity has been realized by alkylation with sultone, which makes it possible to synthesize water-soluble ID derivatives. And the sulfonated ID electrolytes must be important parts in the synthesis of anionic ID-based conjugated polyelectrolytes. On the other hand, few cationic conjugated polyelectrolytes were reported and almost all of these cationic polymers were prepared by quaternization after the polymerrization.³⁶ Completely charged cationic polyelectrolytes cannot be obtained through this indirect method because not all of the side groups of the polymers can be charged in this procedure. Therefore, the direct strategy was designed and achieved to afford the completely charged cationic polymers in our work in which the cationic monomer was prepared first via quaternization reaction followed by copolymerized with oil-soluble ID to give the cationic polymers.

Herein, we have successfully designed and synthesized two kinds of novel conjugated polyelectrolytes: anionic PIDPV ((-)-PIDPV) and cationic PIDPV ((+)-PIDPV). First, we accomplished the synthesis and the characterization of two ionic monomers 6,6-dibromo-N,N-bis(4-sulfonylbutyl)-isoindigo (Monomer 1) and 1,4-bis{3-(N,N,N-triethylammo-nium)-1-oxapropyl}-2,5-divinyl-benzene dibromide (Monomer 4). And then the two novel ionic compounds were



SCHEME 2 The chemical structures of (-)-PPV and (+)-PPV.

introduced into the backbone of (-)-PIDPV and (+)-PIDPV, respectively, via Heck coupling reaction. As similar with other ID-based conjugated polymers, (-)-PIDPV and (+)-PIDPV also exhibit broad absorption bands in the visible region but do not have fluorescence emission. Furthermore, we also synthesized two water-soluble poly(*p*-phenylenevinylene)s (PPVs): cationic PPV ((+)-PPV) and anionic PPV ((-)-PPV). Investigations of the optic properties of cationic and anionic PPV with oppositely charged PIDPV were carried out in the dilute aqueous solution and in the solid state. The results show that the fluorescence of the water-soluble PPVs was quenched with addition of the oppositely charged ID-based polymers.

EXPERIMENTAL

FT-IR spectra were recorded on a Shimadzu FTIR-8400S IR spectrometer. ¹H NMR and ¹³C NMR measurements were carried out on a Bruker Avance II-300MHz spectrometer with tetramethylsilane as the internal reference. Elemental analysis was performed on a CARLO ERBA 1106 elemental analyzer. The UV-vis spectra were performed on a UNICO-2102 UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 luminescence spectrophotometer.

6-bromooxindole, 6-bromoisatin, sodium hydride, 1,4-butane sultone, anhydrous potassium carbonate, *n*-butyl bromide, potassium tertbutoxide, poly(diallyldimethylammonium chloride) (PDDC), poly(sodium-*p*-styrenesulfonate) (PSS) were obtained from domestic chemical companies. All the chemicals were used as received. Toluene was distilled over sodium with benzophenone as indicator. *N*,*N*-dimethylform-amide was purified by distillation under vacuum.

The synthetic routes of Monomers 1–4 and polymers (–)-PIDPV and (+)-PIDPV are illustrated in Scheme 1. The Compounds 1–7 were synthesized according the literatures: 6,6dibromoisoindigo (1),²⁵ 1,4-dibutyloxy-benzene (2),³⁷ 1,4bisbromomethyl-2,5-dibutyloxy-benzene (3),³⁸ 2,5-dibutyloxy-1,4-xylylene-bis(triphenyl phosphonium bromide) (4),³⁸ 1,4bis{(*N*,*N*-diethyl-amino)-1-oxapropyl}c-benzene (5),³⁹ 1,4-bis {(*N*,*N*-diethyl-amino)-1-oxapropyl}c-benzene (5),³⁹ 1,4-bis {(*N*,*N*-diethylaminohydrochloride)-1-oxapropyl}-2,5-dichloromethane-benzene (6),³⁹ {1,4-bis(4'-2-(*N*,*N*-diethylamino)ethoxy)-2,5-xylene}bis(triphenylphosphonium chloride) dihydrochloride (7).⁴⁰ The two water-soluble poly(p-phenylenevinylene)s (+)-PPV and (–)-PPV were also prepared according to the methods which reported in the references. 36,41 The chemical structures of (+)-PPV and (-)-PPV are illustrated in Scheme 2.

Monomers' Synthesis

6,6-Dibromo-N,N-Bis(4-Sulfonylbutyl)-Isoindigo ((–)-ID, Monomer 1)

Under argon atmosphere, 6,6-dibromoisoindigo (0.6302 g, 1.5 mmol) and sodium hydride (0.096 g, 4 mmol) were stirred in N,N-dimethyl-formamide (45 mL) and heated to 40 °C. Then 1,4-butane sultone (0.456 mL, 4.5 mmol) was injected through a syringe. The mixture was stirred at 60 °C for 11 h and then poured into ethanol (300 mL). The solution was filtered and the precipitate was dissolved in water. The oil-soluble impurities were removed via filtration. The solvent was evaporated under reduced pressure and the residue was purified by recrystallization from potassium chloride solution (40 g/L) to give a brown solid. Finally the crude product was dried under vacuum at 80 °C for 12 h to give a dark brown solid. Yield: 0.4944 g, 44.8%. ¹H NMR (300 MHz, D_2O , δ): 8.39 (dd, J = 29.2, 8.6 Hz, 2H), 7.11–6.75 (m, 4H), 3.40 (s, 4H), 2.98-2.72 (m, 4H), 1.95 - 1.36 (m, 8H). ¹³C NMR (75 MHz, DMSO-d₆, δ): 166.98, 145.86, 132.07, 130.80, 126.37, 124.49, 119.88, 111.87, 50.91, 26.20, 22.61. (The signal of the carbon of N-CH₂ is covered by the heptet of DMSO-d₆ in the range of 40.35-38.69 ppm). IR (KBr): v = 2933 (vs; v_{as} (-CH₂-)), 1698 (s; v(C=O)), 1594 (s), 1473 (s; v(Ar_{C=C})), 1357 (vs; v(C-N)), 1178 (vs), 1042 (vs; v(sulfonate)), 726 cm⁻¹ (w, δ (- (CH₂)_n-)). Anal. calcd. for C24H24Br2N2Na2O8S2: C 39.15, H 3.01, N 3.80; found: C 39.06, H 2.94, N 3.77.

6,6-Dibromo-N,N-Dibutyl-Isoindigo ((N)-ID, Monomer 2)

Under argon atmosphere, 6,6-dibromoisoindigo (0.8402 g, 2 mmol) and anhydrous potassium carbonate (1.6584 g, 12 mmol) was stirred in N,N-dimethylformamide (40 mL) for 30 minutes. Subsequently, n-butyl bromide was injected through a syringe. The mixture was stirred at 100 °C for 15 h and then poured into water. The aqueous phase was extracted with dichloromethane and the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. The product was purified by recrystallization from dichloromethane/hexane (1/1) to give red needles. Yield: 0.5636 g, 53%. ¹H NMR (300 MHz, CDCl₃, δ): 9.07 (d, J = 8.6Hz, 2H), 7.17 (dd, J = 8.6, 1.8 Hz, 2H), 6.93 (d, J = 1.6 Hz, 2H), 3.74 (t, J = 7.3 Hz, 4H), 1.74-1.61 (m, 4H), 1.49-1.34 (m, 4H), 0.98 (t, J = 7.3 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 167.64, 145.67, 132.54, 131.15, 126.69, 125.07, 120.32, 111.24, 39.97, 29.39, 20.23, 13.74. IR (KBr): v = 2961 (vs; $v_{as}(-CH_{3}, -CH_{2}-))$, 2868 (vs; $v_{s}(-CH_{3}, -CH_{2}-))$, 1686 (s; v(C=0)), 1594 (s), 1473 (s; v(Ar_{C=C})), 1358 (vs; v(C-N)), 730 cm⁻¹ (w, δ (- (CH₂)_n-)). Anal. calcd. for C₂₄H₂₄Br₂N₂O₂: C 54.16, H 4.54, N 5.26; found: C 54.01, H 4.52, N 5.16.

1,4-Divinyl-2,5-Dibutyloxy-Benzene ((N)-DVB, Monomer 3)

Under argon atmosphere, 1,4-xylylene-bis(triphenylphosphonium bromide)-2,5-dibutyloxy (7.6601 g, 7.5 mmol),



dichloromethane (100 mL) and formaldehyde aqueous (30 mL) were stirred at 0 °C, then an aqueous solution of NaOH (20 wt%, 65 mL) was added dropwise in 1 h and the reaction mixture was stirred at room temperature for 24 h. The organic phase was separated and the aqueous phase was extracted with dichloromethane for three times. After the combined organic layer was washed with brine and water, the resulting solution was dried over anhydrous sodium sulfate. Subsequently, the solvent was removed by rotary evaporation and the residue was purified by recrystallization from ethanol to give a pale-yellow crystal. Yield: 1.7658 g, 85.8%. ¹H NMR (300 MHz, CDCl₃, δ): 7.13 – 7.01 (m, 2H), 6.99 (s, 2H) 5.72 (dd, J = 17.7, 1.2 Hz, 2H), 5.25 (dd, J = 11.1, 1.2 Hz, 2H), 3.97 (t, J = 6.4 Hz, 4H), 1.86-1.71 (m, 4H), 1.58–1.45 (m, 4H), 0.98 (t, J = 7.4 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 150.57, 131.48, 127.08, 113.93, 110.37, 68.89, 31.50, 19.34, 13.87. IR (KBr): v = 3105 (m; v (=C-H)), v = 2958 (vs; $v_{as}(-CH_3, -CH_2-)$), 2870 (vs; $v_s(-CH_3, -CH_2-)$) -CH₂-)), 1674 (w; v(C=C)), 1622-1418 (s; v(Ar_{C=C})), 1385 (s; δ (-CH₃)), 1307 (s; v(-CH₃)), 1204 (vs; v(C-0)), 897 (s; γ (=C-H)), 738 cm⁻¹ (v; δ (- (CH₂)_n-)). Anal. calcd. for C₁₈H₂₆O₂: C 78.79, H 9.55; found: C 77.72, H 9.64.

1,4-Bis{3-(N,N,N-Triethylammonium) – 1-Oxapropyl}-2,5-Divinyl-Benzene Dibromide ((+)-DVB, Monomer 4)

Under argon atmosphere, a mixture of 7 (3.0087 g, 3 mmol), dichloromethane (50 mL) and formaldehyde aqueous solution (40 wt%, 15 mL) was stirred at 0 °C, and then an aqueous solution of NaOH (20 wt %, 28 mL) was added dropwise in 1 h. After stirred for 24 h, the aqueous layer of resulting solution was extracted with dichloromethane for three times. The combined organic layer was washed with water and dried with anhydrous sodium sulfate. The final pale-yellow powder 8 was obtained after removing the solvent by rotary evaporation and then transferred into a threenecked flask. Under argon atmosphere, a mixture of bromoethane (2 g) and acetone (10 mL) was added to the former flask, which was stirred and heated to reflux for 2 days to give a white precipitate. The solid was filtered, washed with bromoethane and hot acetone repeatedly and finally dried under vacuum to afford a white powder. Yield: 0.35 g, 21%. ¹H NMR (300 MHz, D_2O , δ): 7.22 (s, 2H), 7.02 (dd, 2H), 5.85 (d, J = 17.7 Hz, 2H), 5.41 (d, J = 11.3 Hz, 2H), 4.53-4.43 (m, 4H), 3.81 - 3.72 (m, 4H), 3.46 (q, J = 7.2 Hz, 12H), 1.35 (t, J = 7.2 Hz, 18H). ¹³C NMR (75 MHz, D₂O, δ): 149.09, 129.99, 127.06, 115.97, 109.97, 62.07, 55.31, 53.51, 6.81. IR (KBr): v = 3071 (m; v = C - H), v = 2972 (vs; $v_{as} - CH_3$, $-CH_2$)), 2883 (vs; v_s(-CH₃, -CH₂-)), 1674 (w; v(C=C)), 1560-1462 (s; ν(Ar_{C=C})), 1353 (s; δ(-CH₃)), 1270 (s; ν(-CH₃)), 1213 (vs; v(C-0)), 875 cm⁻¹ (s; $\gamma(=C-H)$). Anal. calcd. for C₂₆H₄₆Br₂N₂O₂: C 53.98, H 8.02, N 4.84; found: C 53.91, H 8.14, N 4.81.

Polymers' Synthesis

(-)-PIDPV

Under argon atmosphere, a mixture of monomer 1 (0.3682 g, 0.5 mmol), monomer 3 (0.1372 g, 0.5 mmol), palladium(II) acetate (0.0068 g, 0.03 mmol), tri(*O*-toly)phos-

phine (0.0365 g, 0.12 mmol), triethylamine (2.5 mL) and dimethylsulfoxide (5 mL) was stirred at 100 °C for 18 h. The reaction solution was poured into the mixed solvent (ethanol/ethyl ether = 1/1) and then filtered. The precipitate was dissolved in dimethylsulfoxide and filtered by hydrophobic filter membrane. The solution was poured into the mixed solvent (ethanol/ethyl ether = 1/1) and then filtered by hydrophilic filter membrane again. Subsequently the residue was redissolved in deionized water and the concentrated solution was dialyzed against deionized water for 5 days using a 4KD MWCO cellulose membrane (Spectra/Por Cellulose Ester Membrane). Finally the solvent was removed by rotary evaporation and the crude product was dried under vacuum with P₂O₅ at 50 °C for 24 h to give a dark blue solid. Yield: 0.2048 g, 46.6%. ¹H NMR (300 MHz, DMSO-d₆, δ): 9.20-6.91 (m, 12H), 4.12 (d, J = 31.6 Hz, 4H), 3.78 (s, 4H), 2.77-2.52 (m, 4H), 1.85-1.43 (m, 16H), 0.98 (dd, J = 13.9, 6.5 Hz, 6H). IR (KBr): v = 3120 (m; v(=C-H)), v = 2954 (vs; $v_{as}(-CH_3, -CH_2-))$, 2869 (vs; $v_s(-CH_3, -CH_2-))$, 1703 (vs; v(C=O)), 1605-1490 (s; v(Ar_{C=C})), 1419 (s; δ(-CH₃)), 1359 (vs; v(C-N)), 1202 (vs), 1103 (vs; v(sulfonate)), 995 cm⁻¹ (w; γ (=C-H)).

(+)-PIDPV

Under argon atmosphere, a mixture of monomer 2 (0.2661 g, 0.5 mmol), monomer 4 (0.2892 g, 0.5 mmol), palladium(II) acetate (0.0068 g, 0.03 mmol), tri(0-toly)phosphine (0.0365 g, 0.12 mmol), triethylamine (5 mL), and dimethylsulfoxide (20 mL) was stirred at 80 °C for 6 h. The reaction solution was poured into the mixed solvent (ethyl ether/acetone = 5/4) and then filtered. The precipitate was dissolved in H₂O and then filtered by hydrophilic filter membrane. The concentrated solution was dialyzed against deionized water for 5 days using a 4KD MWCO cellulose membrane (Spectra/Por Cellulose Ester Membrane). Finally the solvent was removed by rotary evaporation and the crude product was dried under vacuum with P2O5 at 50 °C for 24 h to give a dark blue solid. Yield: 0.1447 g, 29.6%. ¹H NMR (300 MHz, DMSO-d₆, δ): 9.10 (d, J = 47.1 Hz, 2H), 7.88-6.89 (m, 10H), 4.49 (dd, J = 57.9, 20.2 Hz, 4H), 3.99-3.44 (m, 20H), 1.64 (d, J = 27.1 Hz, 4H), 1.38 (s, 4H), 1.35 -1.20 (m, 16H), 0.99 (d, J = 22.9 Hz, 8H). IR (KBr): v = 3048 (m; v = C - H), v = 2954 (vs; $v_{as} - CH_3$, $-CH_2$), 2869 (vs; v_s(-CH₃, -CH₂-)), 1699 (vs; v(C=0)), 1605 (s), 1456 (s; $v(Ar_{C=C})$, 1419 (s; $\delta(-CH_3)$), 1360 (vs; v(C-N)), 958 cm⁻¹ (w; γ (=C-H)).

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

Monomer 1 was obtained via *N*-alkylation reaction of 6,6dibromoisoindigo with 1,4-butane sultone, which is similar to the synthesis of the sulfonated DPP derivatives. Here, ID and DPP are both hydrogen-bond pigments with lactam rings in their molecular structure, so they should exhibit the same reactive site. In the procedure, 6,6-dibromoisoindigo was alkylated under alkaline condition using sodium hydride as the base and using anhydrous DMF as the solvent. DMF is



FIGURE 1 FT-IR spectra of 6,6-dibromoisoindigo (a), (-)-ID (b), and (N)-ID (c).

the frequently used solvent in the synthesis of oil-soluble derivatives of isoindigo. The use of the strong base sodium hydride can accelerate the reaction rate and increase the yield but the pyrrole rings of isoindigo may be destroyed in this alkali environment, resulting in a variety of impurities such as single substitution isoindigo and ring-open by-products. While the impurities mentioned above are hardly to be removed thoroughly by filtration and recrystallization from common organic solvents. Therefore, pure monomer 1 was successfully obtained by recrystallization from potassium chloride aqueous solution as same as the purification method of water-soluble DPP derivative reported in our previous work.³⁵ Monomer 4 was prepared via a five-step reaction, containing Williamson ether reaction, chloromethylation, Ylide reaction, Wittig reaction, and quaternization. As shown in Scheme 1, the product of the forth step was used directly for the subsequent reaction without further purification. And then after quaternization, the mixture was filtered and the solid was washed to give the target product as a white powder. At the same time, the triphenylphosphine oxide which was characterized as the main by-products of Wittig reaction was removed in the process of the purification of monomer 4, because the triphenylphosphine oxide is soluble in bromoethane and acetone but the target product monomer 4 is not.

The polymerization of the two polymers were both carried out via Heck coupling reaction using $Pd(OAc)_2$ as catalyst and $P(o-tolyl)_3$ as the corresponding ligand.⁴² Considering the excellent solubility of monomer 1 and monomer 4 in water and other polar solvents, the strong organic polar solvent DMSO which is the common solvent to synthesize CPEs in the Heck reaction was used. During the procedure of the copolymerization, the conjugated length of (–)-PIDPV and (+)-PIDPV which was detected by the UV-vis spectrum was adjusted to be almost identical by controlling the polymerization time. The polymers were collected by filtration after precipitating in the mixed solvent (ethanol/ethyl ether = 1/1 and ethyl ether/acetone = 5/4), respectively, and purified by



FIGURE 2 FT-IR spectra of (-)-ID (a), (N)-DVB (b), and (-)-PIDPV (c).

dialyzed against deionized water. The methods are similar to the polymerization of DPP-based CPEs reported in our previous work.³⁵ Water solubility of (+)-PIDPV, (-)-PIDPV, (+)-PPV and (-)-PPV are around 11.8 mg mL⁻¹ ([repeat unit]=1.21 × 10⁻² M), 12.5 mg mL⁻¹ ([repeat unit] = 1.42 × 10⁻² M), 120.7 mg mL⁻¹ ([repeat unit] = 0.132 M) and 115.2 mg mL⁻¹ ([repeat unit] = 0.159 M) at room temperature, respectively.

The Structure Characterizations of Monomers and Polymers

Figure 1 shows the FT-IR spectra of 6,6-dibromoisoindigo (a), (-)-ID (b) and (N)-ID (c). The absorption peak at 3136 cm⁻¹ in the Figure 1(a) which is attributed to the N—H vibration disappears in Figure 1(b,c), indicating that nitrogen hydrogen has been substituted completely in the synthesis procedure of monomer 1 and 2. In addition, the peak at 2933 cm⁻¹ in the Figure 1(b) is attributed to the --CH₂— vibration of sulfonylbutyl of (-)-ID and the peaks at 2961 and 2868 cm⁻¹ in the Figure 1(c) are, respectively,



FIGURE 3 FT-IR spectra of (N)-ID (a), (+)-DVB (b), and (+)-PIDPV (c).



FIGURE 4 ¹H NMR spectra of (-)-ID, (N)-DVB, and (-)-PIDPV.

attributed to the $-CH_3$, $-CH_2$ - vibration of butyl of (N)-ID. And the two peaks appear at 1178 and 1042 cm⁻¹ in Figure 1 (b) are attributed to the sulfonate. The results mentioned above prove that the 6,6-dibromoisoindigo has been translated into (-)-ID and (N)-ID via *N*-alkylation. Figure 2(a) and at 1202, 1103 cm⁻¹ in Figure 2(c) are attributed to the sulfonate. While the peaks at 1358 and 1700 cm⁻¹ both appear in Figure 2(a,c) are due to the C—N and C=O stretching vibration of isoindigo, respectively. All these prove that the (-)-ID unit has been introduced into the (-)-PIDPV. The absorption peaks at 3105 cm⁻¹ in Figure 2(b) and at 3120 cm⁻¹ in Figure 2(c) are attributed to the C—H vibration of C=C double bond, demonstrating that the

Figure 2 shows the FT-IR spectra of (-)-ID (a), (N)-DVB (b) and (-)-PIDPV (c). The peaks at 1178, 1042 cm⁻¹ in



FIGURE 5 ¹H NMR spectra of (N)-ID, (+)-DVB, and (+)-PIDPV.



FIGURE 6 UV-vis spectra of (-)-ID (9.749 \times 10⁻⁵ M in DMSO), (N)-DVB (1.058 \times 10⁻⁴ M in CH₂Cl₂), and (-)-PIDPV (5.255 \times 10⁻⁵ M in DMSO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vinylene structure in the main chain of (-)-PIDPV has been obtained via Heck reaction. Similarly, the peak at 3071 cm⁻¹ in the Figure 3(b) which is attributed to the C—H vibration of C=C double bond of (+)-DVB can also be observed in the IR spectrum of (+)-PIDPV in Figure 3(c). Furthermore, the C=O and C—N stretching vibration of isoindigo at 1686 and 1358 cm⁻¹, respectively, also have been characterized in Figure 3(c). These signals indicate that another conjugated polyelectrolyte (+)-PIDPV has been obtained.

Figure 4 shows the ¹H NMR spectra of (–)-ID, (N)-DVB and (–)-PIDPV while Figure 5 gives the ¹H NMR spectra of (N)-ID, (+)-DVB and (+)-PIDPV. According to the spectra of (–)-ID and (N)-ID, the peak at 2.86 ppm of (–)-ID in Figure 4 is attributed to the hydrogen of S—CH₂, while the peak at 0.98 ppm of (N)-ID in Figure 5 is attributed to the methyl hydrogen. The signals of other structures of the two compounds are basically the same. In the ¹H NMR spectrum of (–)-ID, the peak at 3.40 ppm is attributed to the hydrogen of N—CH₂, and the signals in the region of 1.95 to 1.36 ppm are due to the alkyl hydrogen in the middle of carbon chain of sulfonylbutyl unit. The aromatic hydrogen of the bromophenyl appears at 8.39 ppm and 7.11–6.75 ppm.

In the ¹H NMR spectrum of (N)-DVB in Figure 4, the singlet at 6.99 ppm is attributed to the aromatic hydrogen of the phenyl. The triplet at 7.05 ppm and doublets at 5.72, 5.25 ppm are attributed to the vinyl and terminal vinyl, respectively. In addition, the hydrogen of O-CH₂ appears at 3.97 ppm. In the ¹H NMR spectrum of (+)-DVB in Figure 5, the signals of those structures mentioned above are basically the same as (N)-DVB. Furthermore, the peaks at 1.79 ppm, 1.50 ppm and the triplet at 0.98 ppm of (N)-DVB are due to the hydrogen of butoxy unit. Compared with (N)-DVB, the signal at 3.77 ppm with quartet at 3.46 ppm of (+)-DVB in the Figure 5 is attributed to the hydrogen.

In the ¹H NMR spectrum of (-)-PIDPV (Fig. 4), the presence of the peaks at 4.12 ppm and 3.78 ppm which are respectively attributed to O-CH2 and N-CH2 of (-)-PIDPV shows the (-)-ID and (N)-DVB units have been introduced into the main chain of (-)-PIDPV. These results can also be found in the spectrum of (+)-PIDPV in Figure 5. Furthermore, the signal of S–CH₂ appears at 2.58 ppm in the ¹H NMR spectrum of (-)-PIDPV also proves that (-)-PIDPV was successfully synthesized. In the ¹H NMR spectrum of (+)-PIDPV, the peak at 3.44 ppm is attributed to the hydrogen of N-CH₂ corresponding to the signal appears at 3.46 ppm of (+)-DVB. Moreover, the ¹H NMR spectra of (+)-PIDPV and (-)-PIDPV both show small signals in the region of 5-6 ppm which are attributed to the terminal vinyl hydrogen of (+)-DVB and (N)-DVB, respectively.^{43,44} All these results indicate that the polymerizations of these two kinds of copolymers (-)-PIDPV and (+)-PIDPV have been accomplished successfully by using the synthetic methods shown in Scheme 1.

Figure 6 shows the UV-vis spectra of (-)-ID, (N)-DVB and (-)-PIDPV while Figure 7 gives the UV-vis spectra of (N)-ID, (+)-DVB and (+)-PIDPV. It has been found that the two polymers and monomers of (-)-ID and (N)-ID have no fluorescence emission, which is the same with other oil-soluble ID derivatives and ID-based conjugated polymers.⁴⁵ As shown in this two figures, (-)-PIDPV and (+)-PIDPV give broad absorption bands in the visible region. The absorption peaks at 592 nm in the spectrum of (-)-PIDPV in Figure 7 are associated with the π - π * transitions of the large π -conjugated backbone of the two polymers, respectively. Moreover, compared with the monomers, the absorption of (-)-PIDPV and (+)-PIDPV both exhibit a remarkable red-shift due to their long π -conjugated structures in the main chain.

It is well-known that conjugated polyelectrolytes can aggregate in its solution and that aggregated CPEs may be easily



FIGURE 7 UV-vis spectra of (N)-ID (4.379 \times 10⁻⁵ M in CH₂Cl₂), (+)-DVB (1.057 \times 10⁻⁴ M in DMSO) and (+)-PIDPV (9.654 \times 10⁻⁵ M in DMSO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 UV-vis spectra of (+)-PPV in aqueous solution under different concentration of (-)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbed on the chromatography column, so it is difficult to get precise molecular weight information of CPEs from gel permeation chromatography (GPC). The key reason is that it is very hard to find a suitable solvent to meet the requests of the measurement. Furthermore, owing to the aggregation phenomenon of CPEs, light scattering which is the common technique to measure the molecular weight as same as GPC is not available, too.⁴⁶ In this paper, the two CPEs (-)-PIDPV and (+)-PIDPV were dialyzed against deionized water using a 4KD MWCO cellulose membrane, which is the same with the method reported in our previous work.³⁵ This approach can not only remove impurities but also ensure that the molecular weight of (-)-PIDPV and (+)-PIDPV are more than 4000 (at least four constitutional repeating units). Although we can only get a general result in this way, but it is enough to prove that the polymerization of the two CPEs has been completed successfully and to satisfy the requirement of photophysics measurement.

Fluorescence Quenching Investigation of PPV/PIDPV Complexes

Poly(*p*-phenylenevinylene) (PPV) has been used as the electron donor in the polymer solar cells and as the active layer in light emitting diodes (LEDs) due to its excellent processability and favorable electronic and spectroscopic properties in the past years. Poly[2-methoxy-5-(2-ethyl)hexoxy-1,4-phenylenevinylene] (MEH-PPV) is the first conjugated polymer to use in the BHJ solar cells⁴⁷ and double layers organic solar cells,⁴⁸ and now it has become a kind of typical electron donor materials. Furthermore, the negatively charged PPV such as poly(5-methoxy-2-(3-sulfopropoxy)-1,4-phenyl-enevinylene) (MPS-PPV)⁴⁹ was obtained by modified with sulfonyl chloride groups and it created a brand new research field of novel synthetic method and frontier applications for conjugated polyelectrolytes. Compared with MPS-PPV, the cationic PPV was prepared by quaternization of the neutral

PPV in bromoethane, and the neutral PPV was synthesized by Gilch reaction. However, the synthesis of completely charged cationic PPV can not be achieved because the low boiling point of bromoethane prevents the nucleophilic substitution reaction from being carried out at elevated temperature, which results in an incompletely guaternization. Most of the PPVs can exhibit strong fluorescence emission and the fluorescence can be effectively quenched by different quenchers, which provides a potential for PPVs to apply as materials in the chemical and biological sensors. Furthermore, the first observed quenching effect in CPEs was in the investigation of the fluorescence quenching of MPS-PPV by methyl viologen (MV^{2+}) .⁵⁰ We have mentioned that ID is an excellent electron-withdrawing group which suggests that the two ID-based CPEs (+)-PIDPV and (-)-PIDPV have the ability of accepting electrons. Here, the fluorescence quenching effects of PPV/PIDPV complexes were investigated to reveal the interactions between PPV and oppositely charged PIDPV.

Fluorescence Quenching Mechanisms

Two standard mechanisms⁵¹ are used to explain the fluorescence quenching effect: (1) static quenching (a) which is due to the formation of fluorophore/quencher complexes in the ground state; (2) dynamic quenching (b) which results from the random collision between the fluorophore and quencher, so the dynamic quenching is also called collisional quenching. Static and dynamic quenching can be distinguished by

$$F + Q \stackrel{K_{a}}{\longrightarrow} [F, Q] \stackrel{h_{\nu}}{\longrightarrow} [F^*, Q] \to F + Q$$
(1)

$$F^* + Q \xrightarrow{k_q} F + Q \tag{2}$$

the absorption spectra of the fluorophore. No changes of the absorption spectra can be observed in the dynamic quenching because it only affects the excited states of the fluorophore. However, in the static quenching the formation of ground-state complex will exhibit different absorption behavior and result in perturbation of the absorption spectra.^{51,52}

As shown in the equations (a) and (b), F^* is an excited-state fluorophore, Q is a quencher, κ_q is the bimolecular quenching rate constant and K_a is the association constant for formation of the ground-state complex [*F*, *Q*].

And both quenching mechanisms can be quantitatively described by the Stern–Volmer equation:

$$I_0/I = 1 + K_{SV} [Q]$$

where I_0 and I are the fluorescence intensities of the system in the absence and presence of the quencher, respectively, and K_{SV} is the Stern–Volmer quenching constant. I_0/I versus [Q] is expected to give a linear plot according to the Stern– Volmer equation. JOURNAL OF POLYMER SCIENCE Chemistry



FIGURE 9 UV-vis spectra of (-)-PPV in aqueous solution under different concentration of (+)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fluorescence Quenching of PPV

As shown in Scheme 2, the level of the quarternization of (+)-PPV is determined to be 50% which is a rough estimate according the NMR and the value is the same with the result in our previous work.³⁶ Investigations of the optic properties of (+)-PPV/(-)-PIDPV and (-)-PPV/(+)-PIDPV complexes in the aqueous solution were carried out. As shown in Figure 8, with addition of (-)-PIDPV, the absorption of (+)-PPV at 386 nm is overlapped with the absorption of (-)-PIDPV at 370 nm leading to an increase of absorbance at 380 nm. The new absorption at 580 nm appearing in the spectra is attributed to the (-)-PIDPV. (-)-PPV gives a similar phenomenon in Figure 9 in the presence of (+)-PIDPV. These properties indicate that interaction between PPVs and the oppositely charged PIDPV does not exist in the ground state and the



FIGURE 10 PL spectra of (+)-PPV in aqueous solution under different concentration of (-)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 11 Stern–Volmer plot for the fluorescence quenching of (+)-PPV under different concentration of (–)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbance of the PPVs just exhibits a linear superposition with increasing concentration of the oppositely charged PIDPV. Furthermore, according to the absorption spectra of PPVs, it can be concluded that dynamic quenching is the leading factor of the quenching mechanism between PPVs and oppositely charged PIDPV.

Figure 10 shows the photoluminescence (PL) spectra of (+)-PPV in the presence of (-)-PIDPV which was measured with excitation wavelength at 440 nm. Figure 11 gives the Stern-Volmer plot for the fluorescence quenching of (+)-PPV by (-)-PIDPV with detection wavelength at 528 nm. It is obvious that the PL intensity of (+)-PPV is quenched effectively with addition of (-)-PIDPV (0-10 \times 10⁻⁷ M with repeat units) to the dilute solution of (+)-PPV ($c = 5 \times$ 10^{-5} M with repeat units). As shown in Figure 11, the Stern-Volmer plot for fluorescence quenching of (+)-PPV is linear with $K_{SV}\,{=}\,1.01\,\times\,10^{6}~M^{-1}$ for the concentration of (-)-PIDPV in the range of $0-6 \times 10^{-7}$ M. The results show that the fluorescence emission of (+)-PPV is quenched effectively by the (-)-PIDPV at a very low concentration, which suggests that (+)-PPV exhibits a very high sensitivity to the oppositely charged quencher (-)-PIDPV. With the increasing concentration of (-)-PIDPV, the Stern-Volmer plot has a tendency to be curved upward and this phenomenon indicates that besides dynamic quenching some other processes are involved in the quenching behavior of (+)-PPV/(-)-PIDPV system, including static quenching,⁵³ ion-pair complex formation between the PPV and the quencher, interchain exciton diffusion in the complex of (+)-PPV/(-)-PIDPV,⁵⁴ chromophore aggregation and variation with varying concentration of guencher.55

Herein, we display a model to explain the fluorescence quenching mechanism between PPV and oppositely charged PIDPV. As shown in Figure 12, ID and DVB segments are,



FIGURE 12 The assumed model of the fluorescence behavior of (+)-PPV/(-)-PIDPV complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively, stand for isoindigo unit and 1,4-divinyl-benzene unit while PPV and PIDPV segments are, respectively, represent the backbone of poly(*p*-phenylenevinylene) and ID-based conjugated polymer synthesized in this article. At such a low concentration of $c = 5 \times 10^{-5}$ M with repeat units, the (+)-PPV aggregates very weakly in the aqueous solution and thus exhibits strong fluorescence emission, but when the (-)-PIDPV was added into its dilute solution, ion-pair complexes of (+)-PPV and the quencher (-)-PIDPV were induced to be formed by Coulombic attraction between the ionic units. Upon absorption of light, the excitions can transfer from the fluorophore (+)-PPV to the quencher (-)-PIDPV due to the excellent electron accepting properties of the isoindigo in the main chain of (-)-PIDPV.



FIGURE 13 PL spectra of (-)-PPV in aqueous solution under different concentration of (+)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fluorescence of (+)-PPV was efficiently quenched in the presence of (–)-PIDPV, and the ultrafast interchain transfer of the excitions within the fluorophore-quencher system results in a large K_{SV} value.

The optical spectra of (–)-PPV shows similar properties with (+)-PPV. Figure 13 gives the photoluminescence (PL) spectra of (–)-PPV in the presence of (+)-PIDPV which was measured with excitation wavelength at 370 nm. Figure 14 gives the Stern-Volmer plot for the fluorescence quenching between (–)-PPV and (+)-PIDPV with detection wavelength at 502 nm. Addition of (+)-PIDPV (0–10 × 10⁻⁷ M with repeat units) into the dilute solution of (–)-PPV ($c = 5 \times 10^{-5}$ M with repeat units) results in an efficient fluorescence



FIGURE 14 Stern–Volmer plot for the fluorescence quenching of (–)-PPV under different concentration of (+)-PIDPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 15 UV–vis spectra of (–)-PPV in aqueous solution under different concentration of PDDC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quenching of (-)-PPV at a low concentration. As shown in Figure 14, the Stern-Volmer plot for the fluorescence quenching of (-)-PPV shows a linear response with $K_{\rm SV} = 1.71 \times 10^6 \, {\rm M}^{-1}$ for the concentration of (+)-PIDPV in the range of 0-6 $\times 10^{-7}$ M and it tends to be curved upward with the increasing concentration of (+)-PIDPV. The mechanisms of this quenching effect of (-)-PPV is similar with (+)-PPV. The research on the fluorescence quenching of PPVs/CPEs complexes using CPE as the quencher provides a possibility to research on the quenching effect between the oppositely charged polymers.

To further study the interactions between PPVs and polyelectrolytes, we also investigate the optic properties of (-)-PPV in the presence of poly(diallyldimethylammonium chloride)



FIGURE 16 UV-vis spectra of (+)-PPV in aqueous solution under different concentration of PSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 17 PL spectra of (–)-PPV in aqueous solution under different concentration of PDDC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(PDDC) and of (+)-PPV in the presence of poly(sodium-*p*-styrenesulfonate) (PSS). PDDC and PSS are cationic and anionic polymers respectively, and they are two conventional polyelectrolytes but not conjugated polymers.

As shown in Figure 15, unconspicuous changes are observed in the UV-vis spectra of (-)-PPV with addition of PDDC. Figure 16 gives a similar phenomenon of (+)-PPV in the presence of PSS. Figure 17 shows the PL spectra of (-)-PPV in the presence of PDDC which was measured with excitation wavelength at 370 nm and Figure 18 gives the PL spectra of (+)-PPV in the presence of PSS which was measured with excitation wavelength at 440 nm. It is obvious that the fluorescence of (-)-PPV is violently quenched by PDDC while the fluorescence of (+)-PPV exhibits an insignificant enhancement with addition of PSS. The results may be caused by the different charge density of the two conventional polymers. According to the report, the charge density



FIGURE 18 PL spectra of (+)-PPV in aqueous solution under different concentration of PSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 19 The assumed model of the fluorescence behavior of (+)-PPV/PSS complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PDDC is calculated to be 6.19 mmol/g (meg/g) which is higher than PSS. As a result, the electronic attraction between (–)-PPV and PDDC is much stronger than the attraction force between (+)-PPV and PSS so that the formation of (–)-PPV/PDDC complexes by ion pairing is very tight and the fluorescence of (–)-PPV is drastically quenched.^{56,57}

Two assumed models are displayed here to illustrate the interactions between the water-soluble PPVs and the oppositely charged conventional polymers. The model of (+)-PPV/PSS complexes is shown in Figure 19 where PSS and PPV segmers are, respectively, stand for poly(sodium-*p*-styrenesulfonate) and the backbone of poly(*p*-phenylenevinylene). When PSS was added into the dilute aqueous solution of (+)-PPV, the formation of complexes between (+)-PPV and PSS are induced by electrostatic attraction of the ionic side groups and as a result the distance of the main chains of (+)-PPV is increased slightly. Finally, the exciton transfer between the main chains is avoided by the inserted PSS chains and the self-quenching of (+)-PPV is inhibited to a certain extent. Thus, the PL spectrum of (+)-PPV shows a weak fluorescence enhancement in the presence of PSS.

Moreover, the model of (-)-PPV/PDDC complexes is displayed in Figure 20 where PDDC and PPV segmers are respectively stand for poly(diallyldimethylammonium chloride) and the backbone of poly(*p*-phenylenevinylene). We have mentioned that PPV only aggregates weakly in the aqueous solution with a low concentration thus exhibits strong fluorescence emission. When PDDC is added,



FIGURE 20 The assumed model of the fluorescence behavior of (–)-PPV/PDDC complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 21 UV-vis spectra of (+)-PPV, (-)-PIDPV films and their blend film ((+)-PPV/(-)-PIDPV = 1/1, c/c [repeat unit], on quartz substrate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

complexes of (-)-PPV and PDDC are formed due to the electrostatic attraction between the ionic units and the attraction force is very strong because of the high charge density of PDDC. Driven by the strong attraction the two polymers twist tightly so that the complexes may form a colloid in the aqueous solution. In the circumstances the solution is not a real solution but a colloidal solution, therefore, the fluorescence of (-)-PPV is almost quenched completely.⁵⁸ The results indicate that the fluorescence quenching effect of (-)-PPV/PDDC complexes is completely different from the quenching mechanism of the PPV-PIDPV system which is governed by the standard quenching mechanisms.

Furthermore, we have also investigated the optic properties of the polymers in the solid state. Figures 21 and 22,



FIGURE 22 PL spectra of (+)-PPV film and the blend film of (+)-PPV and (-)-PIDPV ((+)-PPV/(-)-PIDPV = 1/1, c/c [repeat unit], on quartz substrate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 23 UV-vis spectra of (-)-PPV, (+)-PIDPV films and their blend film ((-)-PPV/(+)-PIDPV = 1/1, c/c [repeat unit], on quartz substrate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively, show the UV-vis and PL spectra of (+)-PPV, (-)-PIDPV films and their blend film ((+)-PPV/(-)-PIDPV = 1/1, c/c [repeat unit]). It is obviously that the fluorescence of (+)-PPV is completely quenched in the presence of (-)-PIDPV in the solid state while the UV-vis spectrum of the blend film just show a superposition of (+)-PPV and (-)-PIDPV, which proves that the interaction between the two oppositely charged polymers does not exist in the ground state. (-)-PPV and (+)-PIDPV give a similar result as shown in Figures 23 and 24. The fluorescence emission of (+)-PIDPV is almost completely quenched with addition of (+)-PIDPV in the solid state while the UV-vis spectrum of the blend film show a superposition of (-)-PPV and (+)-PIDPV. The phenomena mentioned above indicate the photo-induced electron transfer and exciton diffusion between the



FIGURE 24 PL spectra of (–)-PPV film and the blend film of (–)-PPV and (+)-PIDPV ((–)-PPV/(+)-PIDPV = 1/1, c/c [repeat unit], on quartz substrate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chains of oppositely charged PPVs and PIDPV.⁵⁹ These properties suggest that (+)-PIDPV and (-)-PIDPV can be used as the active matrix in the construction of CPE-based photovoltaic cells.

CONCLUSIONS

Two novel ID-based conjugated polyelectrolytes (+)-PIDPV and (-)-PIDPV were synthesized and characterized, and they both have favorable coverage of the visible light region. The fluorescence of water-soluble PPV can be quenched by the oppositely charged PIDPV at a very low concentration. (+)-PPV shows an efficient quenching effect with $K_{SV} = 1.01 \times$ 10^6 M^{-1} in the presence of (-)-PIDPV while (-)-PPV gives a lager quenching constant with $K_{SV} = 1.71 \times 10^6 \text{ M}^{-1}$ in the presence of (+)-PIDPV. The Stern–Volmer plot of the two PPVs both are curved upward. In the absorption spectra, PPVs only exhibit a linear superstition with addition of the oppositely charged PIDPV, which suggests that dynamic quenching process is dominant in the mechanisms of the quenching effect. Two conventional polyelectrolytes PDDC and PSS were also used to investigate the fluorescence quenching between PPV and polyelectrolytes. The results show great difference with PPV/PIDPV complexes. The fluorescence of (-)-PPV is strongly quenched by PDDC while (+)-PPV exhibits a weak enhancement with addition of PSS. Moreover, in the solid state the fluorescence of the watersoluble PPVs is also effectively quenched by the oppositely charged PIDPV. The excellent optic properties which (-)-PIDPV and (+)-PIDPV exhibit suggest that the two polymers can become important materials in the fabrication of ionic double layers solar cells.

ACKNOWLEDGMENTS

This work is financially supported by the "Shuangzhi" project of Sichuan Agricultural University (No. 00770105).

REFERENCES AND NOTES

1 T. I. Wallow, B. M. Novak, *J. Am. Chem. Soc.* **1991**, *113*, 7411–7412.

2 C. Qin, Y. Cheng, L. Wang, X. Jing, F, Wang. *Macromolecules* 2008, *41*, 7798–7804.

3 Z. Gu, Y.-J. Bao, Y. Zhang, M. Wang, O.-D. Shen, *Macromolecules* **2006**, *39*, 3125–3131.

4 X. Xu, W. Cai, J. Chen, Y. Cao, *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1263–1272.

5 B. S. Harrison, M. B. Ramey, J. R. Reynolds, K. S. Schanze, *J. Am. Chem. Soc.* **2000**, *122*, 8561–8562.

6 O. Onitsuka, A. Fou, M. Ferreira, B. Hsieh, M. Rubner, J. Appl. Phys. 1996, 80, 4067–4071.

7 J. W. Baur, S. Kim, P. B. Balanda, J. R. Reynolds, M. F. Rubner, *Adv. Mater.* **1998**, *10*, 1452–1455.

8 A. Kimyonok, E. Tekin, G. Haykır, F. Turksoy, *J. Lumin.* 2014, *146*, 186–192.

9 J. Baur, M. Durstock, B. Taylor, R. Spry, S. Reulbach, L. Chiang, *Synth. Met.* **2001**, *121*, 1547–1548.

10 V. Tamilavan, K. H. Roh, R. Agneeswari, D. Y. Lee, S. Cho, Y. Jin, S. H. Park, M. H. Hyun, J. *Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 3564–3574.

11 J. H. Seo, A. Gutacker, B. Walker, S. Cho, A. Garcia, R. Yang, T.-Q. Nguyen, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.* **2009**, *131*, 18220–18221.

12 K. Manoli, M. M. Patrikoussakis, M. Magliulo, L. M. Dumitru, M. Y. Mulla, L. Sabbatini, L. Torsi, *Org. Electron.* **2014**, *15*, 2372–2380.

13 J. You, T. Park, J. Kim, J. S. Heo, H.-S. Kim, H. O. Kim, E. Kim, *ACS Appl. Mater. Interfaces* **2014**, *6*, 3305–3311.

14 J. H. Lee, D. G. Kim, N. Y. Kwon, G. S. Jang, J. H. Son, M. Lee, H.-J. Cho, H.-S. Kweon, T. S. Lee, *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 138–146.

15 S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324–1338.

16 P. W. Blom, V. D. Mihailetchi, L. J. A. Koster, D. E. Markov, *Adv. Mater.* **2007**, *19*, 1551–1566.

17 L.-M. Chen, Z. Xu, Z. Hong, Y. Yang, *J. Mater. Chem.* 2010, 20, 2575–2598.

18 Z. He, C. Zhong, X. Huang, W. Y. Wong, H. Wu, L. Chen, S. Su, Y. Cao, *Adv. Mater.* **2011**, *23*, 4636–4643.

19 S. H. Oh, S. I. Na, J. Jo, B. Lim, D. Vak, D. Y. Kim, *Adv. Funct. Mater.* **2010**, *20*, 1977–1983.

20 K. Yao, L. Chen, Y. Chen, F. Li, P. Wang, *J. Mater. Chem.* 2011, *21*, 13780–13784.

21 M. J. Robb, S.-Y. Ku, F. G. Brunetti, C. J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1263–1271.

22 M.-S. Yuan, Q. Fang, L. Ji, W.-T. Yu, *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2007**, *63*, 04342–04342.

23 S. Luňák Jr, B. Frumarová, P. Horáková, *Chem. Phys. Lett.* 2009, 477, 116–121.

24 X. K. Wee, W. K. Yeo, B. Zhang, V. B. Tan, K. M. Lim, T. E. Tay, M.-L. Go, *Biorg. Med. Chem.* **2009**, *17*, 7562–7571.

25 G. Zhang, Y. Fu, Z. Xie, Q. Zhang, *Macromolecules* **2011**, *44*, 1414–1420.

26 X. Xu, P. Cai, Y. Lu, N. S. Choon, J. Chen, X. Hu, B. S. Ong, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 424–434.

27 W. Elsawy, H. Kang, K. Yu, A. Elbarbary, K. Lee, J.-S. Lee, *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2926–2933.

28 P. Salvatori, E. Mosconi, E. Wang, M. Andersson, M. Muccini, F. De Angelis, *J. Phys. Chem. C* **2013**, *117*, 17940–17954.

29 J. Mei, K. R. Graham, R. Stalder, J. R. Reynolds, *Org. Lett.* **2010**, *12*, 660–663.

30 Y. Deng, J. Liu, J. Wang, L. Liu, W. Li, H. Tian, X. Zhang, Z. Xie, Y. Geng, F. Wang, *Adv. Mater.* **2014**, *26*, 471–476.

31 P. Sonar, H.-S. Tan, S. Sun, Y. M. Lam, A. Dodabalapur, *Polym. Chem.* **2013**, *4*, 1983–1994.

32 F. Guo, S. Qu, W. Wu, J. Li, W. Ying, J. Hua, *Synth. Met.* **2010**, *160*, 1767–1773.

33 M. Behnke, B. Tieke, Langmuir 2002, 18, 3815-3821.

34 T. V. Pho, P. Zalar, A. Garcia, T.-Q. Nguyen, F. Wudl, *Chem. Commun.* **2010**, *46*, 8210–8212.

35 H. Shen, C. Kou, M. He, H. Yang, K. Liu, J. *Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 739–751.

36 K. Liu, Y. Li, G. Zhang, X. Lv, M. Yang, *Sens. Actuators, B: Chem.* **2009**, *135*, 597–602.

37 D. A. M. Egbe, H. Tillmann, E. Birckner, E. Klemm, *Macromol. Chem. Phys.* **2001**, *202*, 2712–2726.

38 S. Xiao, S. Wang, H. Fang, Y. Li, Z. Shi, C. Du, D. Zhu, *Macromol. Rapid Commun.* **2001**, *22*, 1313–1318.

39 Y. Gao, C.-C. Wang, L. Wang, H.-L. Wang, *Langmuir* **2007**, *23*, 7760–7767.

40 O.-L. Fan, S. Lu, Y.-H. Lai, X.-Y. Hou, W. Huang, *Macromolecules* **2003**, *36*, 6976–6984.

41 B. Xie, M. Bagui, R. Guo, K. Li, O. Wang, Z. Peng, J. *Polym. Sci.*, *Part A: Polym. Chem.* **2007**, *45*, 5123–5135.

42 Y.-J. Cheng, T.-Y. Luh, J. Organomet. Chem. 2004, 689, 4137–4148.

43 J. A. Mikroyannidis, K. M. Gibbons, A. P. Kulkarni, S. A. Jenekhe, *Macromolecules* **2008**, *41*, 663–674.

44 G. Zhang, H. Xu, K. Liu, Y. Li, L. Yang, M. Yang, *Synth. Met.* 2010, *160*, 1945–1952.

45 S. Luňák Jr, P. Horáková, A. Lyčka, *Dyes Pigments* **2010**, *85*, 171–176.

46 M. R. Pinto, K. S. Schanze, Synthesis 2002, 1293–1309.

47 G. Yu, J. Gao, J. Hummelen, F. Wudl, A. Heeger, *Science* **1995**, *270*, 1789–1791.

48 N. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. Heeger, G. Stucky, F. Wudl, *Appl. Phys. Lett.* **1993**, *62*, 585–587.

49 S. Shi, F. Wudl, *Macromolecules* 1990, 23, 2119–2124.

50 L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson, F. Wudl, D. G. Whitten, *Proc. Natl. Acad. Sci. U.S.A.* 1999, *96*, 12287–12292.

51 J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 2nd ed., Kluwer Academic/Plenum Publishers, New York, **1999**. Chapter *8*, pp 238–264.

52 Y. Liu, K. Ogawa, K. S. Schanze, J. Photoch. Photobio. C 2009, 10, 173–190.

53 J. W. Hong, H. Benmansour, G. C. Bazan, *Chem. Eur. J.* 2003, *9*, 3186–3192.

54 X. Zhao, H. Jiang, K. S. Schanze, *Macromolecules* 2008, *41*, 3422–3428.

55 C. Tan, E. Atas, J. G. Müller, M. R. Pinto, V. D. Kleiman, K. S. Schanze, *J. Am. Chem. Soc.* 2004, *126*, 13685–13694.

56 G. Marcelo, M. P. Tarazona, E. Saiz, Polymer 2005, 46, 2584-2594.

57 Y. Li, X. Liu, X. Zeng, X. Liu, B. Kong, W. Wei, S. Luo, *Electrochim. Acta* 2011, *56*, 2730–2734.

58 G. Nizri, S. Lagerge, A. Kamyshny, D. T. Major, S. Magdassi, J. Colloid Interface Sci. 2008, 320, 74–81.

59 J. W. Baur, M. F. Durstock, B. E. Taylor, R. J. Spry, S. Reulbach, L. Y. Chiang, *Synth. Met.* **2001**, *121*, 1547–1548.

