Synthesis and Surfactochromicity of 1,4-Diketopyrrolo[3,4-c]pyrrole(DPP)-Based Anionic Conjugated Polyelectrolytes

DPP,

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ABSTRACT: Two novel anionic conjugated copolyelectrolytes PSDPPPV and PSDPPPE were synthesized via Heck/Sonogashira coupling reactions and characterized by FT-IR, ¹H NMR, UV-vis, and PL spectroscopy. The two polymers are respectively constituted of 2,5-diethoxy-1,4-phenyleneethynylene (DPV) and 2,5-di ethoxy-1,4-phenyleneethynylene (DPE) with 1,4-diketo-2,5-bis (4-sulfonylbutyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole (SDPP) which is a novel water soluble diketopyrrolopyrrole derivative. PSDPPPV and PSDPPPE show broad absorption band in visible region and they exhibit strong fluorescence quenching in aqueous solution. The fluorescence of their aqueous solutions can be enhanced in the presence of cationic surfactant or polymer nonionic surfactant. Fluorescence enhancement by introduction of polyvinylpyrrolidone (PVP) shows linear response. This result provides a controllable method to increase fluorescence intensity of dipyrrolopyrrole-based conjugate polyelectrolytes in aqueous phase. The optical properties suggested that PSDPPPV and PSDPPPE which are negatively charged conjugated polymers can assemble with positively charged photovoltaic materials to form ionic photoactive layer. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 739–751

KEYWORDS: conjugated polymers; conjugated polyelectrolytes; copolymerization; diketopyrrolopyrrole; optics; surfactochromicity

A general strategy to synthesize conjugated polymers with

excellent coverage of visible region is to combine dye molecules with another monomer via copolymerization.^{26,27}

copolymerization monomer precursor, is a kind of tradi-

tional hydrogen bond pigment along with indigo compounds and quinacridone, and its derivatives are already

an

appropriate

1,4-diketopyrrolo[3,4-c]pyrrole,

INTRODUCTION Conjugated polyelectrolytes (CPEs) which are functionalized conjugated polymers (CPs) with ionic side-chain, have received considerable interest in past decades because of their main chain controlled electronic/optical properties,¹⁻³ surfactochromicity,4-6 and environment-friendly solvent processability.⁷⁻⁹ With designed backbones and appropriate regions of absorption or emission, variety of CPEs have attracted extensive interest in photoelectronic applications such as polymer light-emitting diodes (PLEDs),^{10,11} chemosensors¹²⁻¹⁴ and photovoltaic devices.^{15,16} With the excellent solubility in water, CPEs are advanced used in biological fluorescent sensors¹⁷⁻¹⁹ and interface controlled bulk heterojunction solar cells.^{20,21} During the recent years, CPEs based self-assembly solar cell has been focus in application of photovoltaic materials.²²⁻²⁴ In these devices, the polyelectrolytes are assembled with other organic electrolytes^{23,24} or inorganic quantum dots²⁵ by intimate electrostatic attraction to form electron acceptor-donor pair in the photoactive layer. The power conversion efficiency of these photovoltaic devices is enhanced because of the extensive interfacial charge transfer area between the combined electron acceptor and electron donor.²⁵ However, owing to the hardness of purification and limited synthesis strategies, conjugated polyelectrolytes only appeared with several kinds of main chain structure. Design and synthesis of novel CPEs with excellent optical properties is an important mission in recent research.

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commercialized as high performance dyes and pigments.²⁸ DPPs are composed of large conjugated system as chromophore and a lactam structure as auxochromes with exceptional light, weather and heat stability. Thus, DPPs have been considered as electron acceptor unit to optimize the energy-level structure and reduce the band gap of conjugated polymers.^{29,30} These DPP-based polymers exhibit outstanding optical properties such as red light emission,^{31,32} large-scale visible light covered absorption^{33,34} and large Stokes shift.³⁵ DPPs are always modified with functional side chains to adapt common solvent via the alkylation reaction on its nitrogen atom. These soluble polymers provide a possibility to become film by traditional process and the film can be used as the active layer of the devices. For aforementioned advantages, a variety of DPP-based polymers have been investigated thoroughly in application of bulk heterojunction semiconductor devices such as solar cells.36-38

However, few publications concerning DPP-based conjugated polyelectrolytes were reported. The only discussed cationic one was obtained by indirect method.³⁹ It was synthesized though copolymerization of a non-electrolyte DPP unit and the aminated fluorene unit first and then made the aminated side chain into ammonium via quaternization reaction. The polyelectrolyte derived from this indirect strategy is considered as an incomplete charged product because not all the side chains of the polymer are translated into cationic group. DPP unit of this polymer is still a traditional oilsoluble N-alkyl substitution form but not directly charged. On the other hand, ionic DPP derivatives always appeared as small molecules. They are mostly modified with carboxyl⁴⁰ or sulfuric acid ester⁴¹ on their N-alkyl side chain by multistep reactions with low yield and unsatisfied purity. Recently, alkylation with alkane sultone is considered as a novel strategy to make hydrogen bond pigments into electrolytes with high yield and purity. This process was only realized on the functionalization of guinacridone.⁴² This novel method is expected to applied in alkylation of DPP to acquire a sulfonyl modified DPP which can adapt wide pH conditions and have perfect water solubility. Furthermore this kind of novel DPP electrolyte could act as an important DPP-based monomer which can couple with other π conjugated organic molecules to make different anionic **DPP-based CPEs.**

In our contribution, a novel negatively charged DPP monomer 1,4-diketo-2,5-bis(4-sulfonylbutyl)-3,6-bis(4-bromophe nyl)pyrrolo[3,4-c]pyrrole (monomer 3) has been designed, synthesized and purified. This water soluble DPP derivative has been copolymerized with two traditional monomers based on phenylenevinylene (PV)/phenyleneethynylene (PE) structure via palladium catalyzed Heck/Sonogashira coupling reactions to afford two novel anionic alternating conjugated polyelectrolytes PSDPPPV and PSDPPPE. As same as other DPP-based conjugated polymers, PSDPPPV and PSDPPPE exhibit red emission and large Stokes shift. On the other hand, similar as other conjugated polyelectrolytes, the optical properties of these two polymers show solvent-dependency, and the fluorescence of these two polymers can be enhanced by the addition of oppositely charged surfactant and nonionic polymer surfactant polyvinylpyrrolidone (PVP). PSDPPPV and PSDPPPE with excellent optical properties and electrolyte modified side chains are suggested to be a kind of photovoltaic materials which have potential in interface control and self-assembly to enhance the photoelectric conversion efficiency in application of bulk heterojunction solar cells.

EXPERIMENTAL

FT-IR spectra were recorded on a Shimadzu FTIR-8400S IR spectrometer. ¹H NMR measurements were carried out on a Bruker Avance II-300MHz spectrometer. UV-vis spectra were performed on a UNICO-2102 UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 luminescence spectrophotometer.



SCHEME 1 Synthetic routes of monomer 1–3, PSDPPPV and PSDPPPE.

4-Bromobenzonitrile, diisopropyl succinate, potassium *tert*butoxide, and 1,4-butane sultone were obtained from domestic chemical companies. All the chemicals were used as received. *tert*-Amyl alcohol and triethylamine were distilled over calcium hydride. Toluene was distilled over sodium with benzophenone as indicator. *N*,*N*-Dimethylformamide was purified by distillation under vacuum. Pd(PPh₃)₂Cl₂ was synthesized according to method described in literature.⁴³

The synthetic routes of the monomer 1–3, PSDPPPV and PSDPPPE are illustrated in Scheme 1. The following compounds were synthesized according to the procedure in the literature: 1,4-diethyloxy-benzene,⁴⁴ 1,4-bisbromomethyl-2,5-diethyloxy-benzene,⁴⁵ 2,5-diethyloxy-1,4-xylylene-*bis*(triphenyl phosphonium bromide)⁴⁶ and 1,4-diiodo-2,5-diethyloxy-benzene.⁴⁷

Monomers' Synthesis

1,4-Divinyl-2,5-diethyloxy-benzene (Monomer 1)

Under argon atmosphere, a mixture of 2,5-diethoxy-1,4-xylylene-bis(triphenyl phosphonium bromide) (6.57 g, 7.50 mmol), dichloromethane (100 mL) and formaldehyde aqueous (30 mL) was stirred at 0 °C, then aqueous solution of NaOH (20 wt %, 65 mL) was added dropwise in 1 h. The reaction mixture was stirred at room temperature for 24 h. The organic phase was separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was washed with water and dried over anhydrous sodium sulfate. Subsequently, the solvent was removed by rotary evaporation, and the residue obtained was purified by recrystallization from ethanol to afford a pale yellow crystal. Yield: 1.05 g, 64.13%.

¹H NMR (300 MHz, CDCl₃, δ): 7.00–7.10 (dd, J_1 = 11.13 Hz, J_2 = 17.76 Hz, 2H; vinyl-H), 7.00 (s, 2H; Ar-H), 5.73 (d, J = 17.7 Hz, 2H; vinyl-H(terminal)), 5.26 (d, J = 11.1 Hz, 2H; vinyl-H(terminal)), 4.04 (q, J = 7.0 Hz, 4H; 0-CH₂), 1.43 (t, J = 7.0 Hz, 6H; -CH₃); IR (KBr): v = 3090 (m; v(=C-H)), 2980 (vs), 2924 (vs; v_{as} (-CH₃, -CH₂-)), 2875 (vs; v_{s} (-CH₃, -CH₂-)), 1620-1429 (s; v(Ar_{C=C})), 1392 (s; δ (-CH₃)), 1269 (s; v(-CH₃)), 1205 (vs; v(C-O)), 999 (s), 910 cm⁻¹(s; γ (=C-H)).

1,4-Bis(3-methyl-3-hydroxybut-1-ynyl)-2,5-diethyloxybenzene (Monomer 2)

Under argon atmosphere, a solution of 1,4-diiodo-2,5-diethoxybenzene (5.86 g, 14.02 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol) and CuI (0.06 g, 0.32 mmol) in dry triethylamine (100 mL) was stirred in a three-neck flask at room temperature. 2-methyl-3-butyn-2-ol (3.62 mL, 0.05 mol) was added dropwise in 20 min, and the reaction mixture was stirred at 90 °C for 24 h. Subsequently, the precipitate was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica using ether as the eluent and then the crude product was recrystallized from hexane/chloroform (1:1) to afford a white crystal. Yield: 1.20 g, 25.90%.

¹H NMR (300 MHz, CDCl₃, δ): 6.86 (s, 1H; Ar-H), 4.02 (q, J = 7.0 Hz, 2H; -CH₂-), 2.24 (s, 1H; -OH), 1.64 (s, 6H; -CH₃), 1.43 (t, J = 7.0 Hz, 3H; -CH₃ (ethoxy)); IR (KBr): v = 3541 (s), 3450 (s), 3292 (s; v(0-H)), 2980 (vs), 2930 (vs; v_{as} (-CH₃, -CH₂-)), 2870 (vs; v_{s} (-CH₃, -CH₂-)),2223 (w; v(C=C)), 1502 (s), 1475 (s; v(Ar_{C=C})), 1392 (s; δ (-CH₃)), 1273 (s; v(-CH₃)), 1219 (vs; v(C-O)), 1159 (s; v(C-O)), 1047 (w), 864 (w), 590 cm⁻¹(w; δ (Ar-H)).

14-Diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole

Under argon atmosphere, sodium (2.21 g, 96 mmol), FeCl₃ (0.10 g) and dry *tert*-amylalcohol (50 mL) were stirred and heated to 90 °C until the sodium was dissolved completely. The solution was cooling to 50 °C and 4-bromobenzonitrile (8.74 g, 48 mmol) was added portionwise. Then the mixture was heated to 90 °C again. A solution of succinic acid diisopropyl ester (3.88 g, 19 mmol) in dry *tert*-amylalcohol (20 mL) was added dropwise in 1 h. After stirring at 90 °C for 24 h, the dark red mixture was cooled to 60 °C, and then



IR (KBr): v = 3147 (vs; v (N-H)), 1643 (s; v(C=O)), 1602 (s), 1554 (s; v(Ar_{C=C})), 1394 cm⁻¹ (vs; v(C-N)).

1,4-Diketo-2,5-bis(4-sulfonylbutyl)-3,6-bis(4-bromophenyl) pyrrolo[3,4-c]pyrrole (monomer 3)

Under argon atmosphere, 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole (4.46 g, 10 mmol) and potassium *tert*butoxide (1.76 g, 22 mmol) in dry DMF (150 mL) were heated to 60 °C; 1,4-butane sultone (3.10 mL, 30 mmol) was added dropwise in 10 min. The mixture was stirred at 90 °C for 12 h and subsequently the hot solution was poured into ethanol (1 L). The precipitate was collected by filtration and dissolved in hot water (200 mL). Then the solution was filtrated to remove the oil soluble impurity. The solvent was removed by rotary evaporation and the residue obtained was purified by recrystallization from aqueous solution of potassium chloride to give an orange crystal. Finally this hydrated crystal was dried under vacuum at 120 °C for 12 h to give a dark red solid. Yield: 1.55 g, 19.51%.

¹H NMR (300 MHz, D₂O, δ) : 7.60 (d, *J* = 8.5 Hz, 4H; DPP aromatic H), 7.44 (d, *J* = 8.4 Hz, 4H; DPP aromatic H), 3.67 (t, *J* = 6.0 Hz, 4H; N-CH₂), 2.69 (t, *J* = 7.3 Hz, 4H; S-CH₂), 1.49 (m, 8H; methylene); IR (KBr): *v* = 2937 (vs; *v*_{as}(-CH₃, -CH₂-)), 2872 (vs; *v*_s(-CH₃, -CH₂-)), 1676 (s; *v*(C=O)), 1603 (s), 1551 (s; *v*(Ar_{C=C})), 1371 (vs; *v*(C-N)), 1184 (vs), 1045 (vs),1007 (vs, *v*(sulfonate)), 735 cm⁻¹(w, δ (-(CH₂)_n-)).

Polymers' Synthesis

PSDPPPV

Under argon atmosphere, monomer 1 (0.22 g, 1.00 mmol), monomer 3 (0.79 g, 1.00 mmol), palladium(II) acetate (0.0135 g, 0.06 mmol), tri(o-tolyl)phosphine (0.0730 g, 0.24 mmol) and triethylamine (5 mL) were dissolved in a mixture of H₂O (3 mL) and dimethylsulfoxide (8 mL). The reaction mixture was stirred at 100 °C for 18 h and subsequently cooled to room temperature and then filtered. The filtrate was poured into the mixed solvent (ethyl ether/acetone/ methanol = 5/4/1). The precipitate was isolated by filtration and then redissolved in deionized water (10 mL). The resulting solution was dialyzed against deionized H₂O for 3 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 further dried under vacuum with P2O5 at 50 °C for 2 days to afford a dark purple powder. Yield: 0.34 g, 39.94%.

¹H NMR (300 MHz, DMSO- d_6 , δ) : 7.80-7.95 (DPP aromatic H), 7.48-7.65 (vinyl-H), 7.42 (DVB aromatic H), 4.20 (O-CH₂), 3.72-3.76 (N-CH₂), 2.33 (S-CH₂), 1.24,1.47 (-CH₃ and -CH₂-); IR (KBr): v = 3045 (m; v(=C-H)), 2931 (vs; $v_{as}(-CH_3, -CH_2-)$), 2872 (vs; $v_s(-CH_3, -CH_2-)$), 1664 (s; v(C=O)), 1593 (s), 1541

(s; $v(Ar_{C=C})$), 1388 (s; $\delta(-CH_3)$), 1367 (vs; v(C-N)), 1180 (vs), 1041 (vs; v(sulfonate)), 964 (m; $\gamma(=C-H, trans)$), 725 cm⁻¹ (w; $\delta(-(CH_2)_n-)$).

PSDPPPE

Under argon atmosphere, monomer 2 (0.0991 g, 0.30 mmol), monomer 3 (0.2384 g, 0.30 mmol), Pd(PPh₃)₂Cl₂ (0.0184 g, 0.0263 mmol), CuI (0.0190 g, 0.1 mmol), PPh₃ (0.0378 g, 0.14 mmol) and potassium carbonate (1.14g, 8.25mmol) were dissolved in dimethylsulfoxide (10 mL). The reaction mixture was stirred at 100 °C for 14 h and subsequently cooled and then filtered. The filtrate was poured into the mixed solvent (ethyl ether/ methanol = 1/1). The precipitate was isolated by filtration and then redissolved in deionized water (10mL). The resulting solution was dialyzed against deionized H₂O for 3 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 further dried under vacuum with P_2O_5 at 50 °C for 2 days to afford a dark purple powder. Yield: 0.0461 g, 18.15%.

¹H NMR (300 MHz, DMSO- d_6 , δ): 7.98-6.97 (Ar-H), 4.16-4.04 (O-CH₂), 3.74 (N-CH₂), 2.37-2.34 (CH₂-SO₃⁻), 1.52-1.47 (-CH₂-), 1.41-1.33 (-CH₃); IR (KBr): v = 2976 (vs), 2926 (vs; v_{as} (-CH₃, -CH₂-)), 2874 (vs; v_s (-CH₃, -CH₂-)), 2201 (w; $v(C\equiv C)$), 1662 (s; v(C=0)) 1510 (s), 1472 (s; $v(Ar_{C=C})$), 1390 (s; δ (-CH₃)), 1275 (s; $v(-CH_3)$), 1209 (vs; v(C-O)), 1171 (vs), 1041 (vs; v(sulfonate)), 845 cm⁻¹ (w; δ (Ar-H)).

RESULTS AND DISCUSSION

Synthesis of Monomer 3 and Polymers

Monomer 3 was obtained via N-alkylation reaction with alkane sultone as same as the synthesis of oil soluble derivatives of DPP with alkyl halide.48 Here, reaction yield and product purity not only depend on temperature but also the variety of solvent and the strength of the base. DMF was used as the solvent because it is the most used one which has the similar chemical structure with DPP. Potassium tertbutoxide was adopted as the base because it is a strong base which can make lactams of DPP into nitrogen anions immediately in the solution and this ion can accelerate the nucleophilic substitution process. Although tert-butoxide anion can make this alkylation fast and afford a higher yield rate, the pyrrole rings of DPP can be easily destroyed in this situation and give a variety of impurities. The usual impurities such as single substitution DPP and ring-opened product which are hardly soluble in water can be removed by filtration. And other water soluble impurities which are considered as sulfonate species have been removed completely by recrystallization. The result shows that monomer 3 has an excellent solubility in polar solvent and can be crystallized in oversaturated aqueous solution. However, reducing the solubility of the target product by admixture of organic solvent such as ethanol or acetone can not give the crystal from recrystallization. Finally, pure N-sulfonylalkyl DPP hydrate crystal with low concentration was successfully obtained by recrystalliza-



FIGURE 1 IR spectra of (a) 1,4-diketo-3,6-*bis*(4-bromophenyl)pyrrolo[3,4-c]pyrrole and (b) monomer 3.

tion from potassium chloride aqueous solution which provide high concentration of potassium ion.

In order to increase the solubility of polymers in water, monomer 1 and monomer 2 have been modified with short alkoxyl substituent like ethyoxyl. In their synthetic route, most of the solvents which are used for reactions and recrystallizations should be high polar or large quantity. To synthesize PSDPPPV, the traditional aqueous phase Heck coupling reaction which reported in the reference⁴⁶ has been successfully achieved in this polymerization. On the other hand, the synthesis of PSDPPPE was completed by modifying the procedure of Heck-Sonogashira coupling reaction in oil soluble system.49 The traditional phase transfer system of the solvent and the base has been replaced by strong polar solvent DMSO and potassium carbonate which is a solid weak base, respectively, and this reaction condition makes this polymerization faultless. Water solubility of PSDPPPV and PSDPPPPE are respectively around 4.7 mg mL⁻¹ ([repeat unit] = $5.52 \times$ 10^{-3} M) and 4.6 mg mL⁻¹ ([repeat unit] = 5.42 × 10^{-3} M) at room temperature.

The Structure Characterizations of Monomers and Polymers

Figure 1 shows the FT-IR spectra of 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole and monomer 3. Compared with Figure 1(a), the absent absorption peak at 3147 cm⁻¹ in Figure 1(b) is attributed to the N-H vibration of the lactam structure. In addition, two new absorption peaks at 1184 cm⁻¹ and 1007 cm⁻¹ in Figure 1(b) are attributed to the sulfonate. Those transformations prove that monomer 3 has been successfully translated into a sulfonate functionalized molecular with hydrophilic side chain via alkylation on nitrogen atoms. The absorption peaks at 1643 cm⁻¹ and 1394 cm⁻¹, which have been characterized in both Figure 1(a,b) are due to the typical C=O and C-N stretching modes of DPP unit. This result proves that the DPP lactam ring has been preserved in monomer 3 during the synthesis in the presence of the strong base potassium *tert*-butoxide.



FIGURE 2 IR spectra of (a) monomer 1, (b) PSDPPPV, (c) monomer 2 and (d) PSDPPPE.

Figure 2 shows the FT-IR spectra of monomer 1, PSDPPPV, monomer 3 and PSDPPPE. The absorption peak at 3090 cm^{-1} in Figure 2(a) and 3045 cm^{-1} in Figure 2(b) are attributed to the C-H vibration of the C=C double bond. These peaks intuitively prove that the vinyl in monomer 1 has been coupled with monomer 3 successfully to give the vinylene structure in the main chain of PSDPPPV via Heck coupling reaction. In Figure 2(b), the absorption peak at 1674, 1367 cm⁻¹ are attributed to lactam unit, and 1180, 1041 cm⁻¹ are attributed to sulfonate. These signals prove that sulfonate functionalized DPP unit has been preserved in PSDPPPV. Similarly, these characteristic absorption peaks which are attributed to sulfonate modified DPP structure can also be observed in the IR spectrum of PSDPPPE. Furthermore, the 0-H stretching vibration at 3292 cm^{-1} of monomer 2 is disappeared in Figure 2(d), and the C \equiv C vibration at 2201 cm⁻¹ has been obviously conserved. These results prove that another DPP-containing anionic conjugated polyelectrolyte PSDPPPE which has ethynylene structure in main chain has been successfully obtained.

Figure 3 shows the ¹H NMR spectra of monomer 1, monomer 3 and PSDPPPV. And Figure 4 gives the ¹H NMR of monomer 2, monomer 3 and PSDPPPE. In the ¹H NMR spectrum of monomer 3, the doublets at 7.60 ppm and 7.44 ppm are attributed to the AB spin-spin coupling system of two kinds of aromatic hydrogen in bromophenyl unit. Doublets at 3.67 ppm and 2.69 ppm are respectively attributed to the hydrogen of N-CH₂ and S-CH₂. The signals of other alkyl hydrogen in the middle of the carbon chain of sulfonylbutyl unit appears in the region of 1.60 ppm to 1.36 ppm. Here, the ¹H NMR spectrum of monomer 3 has got a considerable purity. It is identified as a valuable monomer to synthesize DPP-based conjugated copolyelectrolytes via the synthetic route in Scheme 1.

In the ¹H NMR spectrum of monomer 1 (Fig. 3), the quartet at 4.04 ppm with triplet at 1.43 ppm is attributed to the hydrogen of ethyloxy unit. As same, the ¹H NMR spectrum of monomer 2 in Figure 4 also shows these peaks. The other structure signals of monomer 1 and monomer 2 are as same as their homologs which have longer hydrocarbon chains linked to the oxygen atoms.^{35,46} In the ¹H NMR spectra of PSDPPPV (Fig. 3), the doublets of terminal vinyl of monomer 1 at 5.73 ppm and 5.26 ppm are absent. It is verified that all the vinyl has been transformed into vinylene structure in its backbone. In Figure 4, the singlet at 2.24 ppm and 1.64 ppm which attributed to the hydrogen of the hydroxyl unit and the methyl hydrogen in monomer 2 are invisible in the ¹H NMR of PSDPPPE. This transformation indicated that the isopropanol protection unit in monomer 2 has been removed and the ethynylene structure was introduced into the backbones of PSDPPPE. The signals of aromatic unit of PSDPPPV and PSDPPPE in the range of 7.98 to 6.97 ppm both show



FIGURE 3 ¹H NMR spectra of monomer 1, monomer 3 and PSDPPPV.

Materials



FIGURE 4 ¹H NMR spectra of monomer 2, monomer 3 and PSDPPPE.

larger chemical shift compared with their monomers because of the stronger deshielding effect of their π -conjugated backbones. Above mentioned translation indicated that the polymerizations in Scheme 1 were accomplished.

As some references reported, the molecular weight data is not available from common techniques such as gel permeation chromatography (GPC) or light scattering method due to the aggregation phenomenon of CPEs.³ It is difficult to find an appropriate solvent which lead to weak aggregation of CPEs with high concentration to finish the GPC measurement. Furthermore, aggregated CPEs may be easily adsorbed on the chromatographic column to give the imprecise results. In this investigation, solutions of PSDPPPV and PSDPPPE were dialyzed by 4kD MWCO cellulose membrane, which is the normal method to remove the oligomers and impurities. This approach can ensure that the molecular weight of PSDPPPV and PSDPPPE are more than 4000 (at least four constitutional repeating units). However, the actual molecular weights of these polyelectrolytes are much more than we imagined. Moreover, the absorption/emission peaks in ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra of the polymers exhibit remarkable red shift compared with the monomers. These results also prove that the polymerization of PSDPPPV and PSDPPPE has been successfully completed with the eligible molecular weight.

Basic Optical Properties of the Monomers and the Polymers

In this part, all the UV-vis and PL spectra have been respectively normalized to the same maximum values for better comparison. The photo of monomers and polymers in different solvent is shown in Figure 5. And all the absorption and emission maxima of polymers and monomers are listed in Table 1.

Figure 6 shows the UV-vis and PL spectra of monomer 1, monomer 3 and PSDPPPV. PSDPPPV shows broad absorption

band which can cover most visible light region ideally. In the UV-vis spectrum of PSDPPPV, The absorption peak at 421 nm is associated with 1,4-phenylenevinylene segments and the absorption maximum at 524 nm is attributed to the electron transitions of the largest π -conjugated backbones. Compared with its monomers, the absorption maximum of PSDPPPV exhibits a great red shift due to the longer conjugation length which has been acquired via the coupling reaction. On the other hand, PSDPPPV exhibits pale pink color fluorescence and shows red-shifted emission maximum at 609 nm compared to monomer 3. As same as other DPP-based conjugated polymer,^{31,32} the strength of fluorescence is decreased observably after the polymerization of monomer 3. This phenomenon suggests that there is a



FIGURE 5 Photo of the solutions, (a) monomer 1 in chloroform, (b) monomer 2 in DMSO, (c) monomer 3 in water, (d) PSDPPPV in DMSO, (e) PSDPPPE in DMSO, (f) PSDPPPV in water and (g) PSDPPPE in water.

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Polymer

Polymers	Solvent	UV-Vis (nm)	PL (nm)	Stokes Shift (nm)
Monomer 1	Chloroform	344	404	60
Monomer 2	DMSO	335	382	47
Monomer 3	Water	465	534/554 ^a	69/ 89 ^a
	DMSO	476	548	72
PSDPPPV	Water	547	-	-
	DMSO	524	609	85
	LAS/water: 16 μ g mL ⁻¹	547 ^b	_ ^b	_b
	CTAB/water: 16 μ g mL ⁻¹	544 ^b	721 ^b	177 ^b
	PVP/water: 16 μ g mL ⁻¹	558 ^b	668 ^b	110 ^b
PSDPPPE	Water	522	636	114
	DMSO	507	593	86
	LAS/water: 16 μ g mL ⁻¹	522 ^b	616 ^b	94 ^b
	CTAB/water: 16 μ g mL ⁻¹	528 ^b	641 ^b	113 ^b
	PVP/water: 16 μ g mL ⁻¹	530 ^b	636 ^b	106 ^b

TABLE 1 Optical Properties of Monomer 1-3, PSDPPPV, PSDPPPE

^a The concentration of monomer 3 is higher than 0.75 mmol L^{-1} .

^b The concentration of PSDPPPV or PSDPPPE is fixed on 0.01 mg mL⁻¹.

remarkable fluorescence self-quenching on polymer mainchain. In the backbone of PSDPPPV, DPP is considered as an acceptor unit due to the electron deficient lactam structure and phenylenevinylene (PV) segment is considered as a weak electron donor. The energy of excitons is partly dissipated by the electron transfer between the copolymerization units rather than translated into light emission. So, PSDPPPV has a similar framework with donor-acceptor structure $\mbox{CPs}^{35,50}$ which has narrow band gap, large Stokes shift and weak fluorescence.

Figure 7 shows the UV-vis and PL spectra of monomer 2, monomer 3 and PSDPPPE. As same as PSDPPPV, the UV-vis and PL maxima of PSDPPPE both show large red shift compared to its monomers. PSDPPPE exhibits the absorption

maximum at 507 nm and emission maximum at 593 nm, and those peaks both have a shorter wavelength than that of PSDPPPV. The difference suggests that the C=C double bond own a better conjugation degree compared to the $C \equiv C$ triple bond segments. In the mainchain of PSDPPPE, energy of excitons may not be dissipated effectively as PSDPPPV due to the $C \equiv C$ triple bond. As reference reported, p-phenylene ethynylene (PPE) typed conjugated polymers always show shorter wavelength of absortion/emission maxima and higher fluorescence quantum efficiency compared to the p-phenylene vinylene (PPV) typed CPs³⁵ which have the similar structures.

In addition, the optical properties of PSDPPPV and PSDPPPE vary dramatically with the solvent composition. Figure 8



FIGURE 6 UV-vis and PL spectra of monomer 1 (in chloroform), monomer 3 (in water) and PSDPPPV (in DMSO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 UV-vis and PL spectra of monomer 2 (in DMSO), monomer 3 (in water) and PSDPPPE (in DMSO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 UV-vis and PL spectra of PSDPPPV in different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows the UV-vis and PL spectra of PSDPPPV in water and DMSO. In contrast, when the solvent is changed from DMSO to water the absorption maximum has been red-shifted from 524 nm to 547 nm, and its fluorescence has been quenched completely. This transformation suggests that PSDPPPV has been translated to a higher conjugated state and the excitons may have different dissipation forms in aqueous solution. In water, PSDPPPV is aggregated strongly by π - π stacking as same as other reported conjugated polyelectrolytes⁵¹⁻⁵³ and this stacking has been entitled the J-aggregate.⁵⁴ It is a model that the backbones of the polyelectrolytes have been stacked mutually with conjugated layers because of the hydrophobicity. And the hydrophilic electrolyte side chains of them have been stretched freely between the backbones and water molecules. J-aggregate causes the conjugated polyelectrolytes to have a higher conjugation degree and the excitons can transfer easily between the mainchains. This new form of energy dissipation due to the exciton transfer may be one reason why the fluorescence of PSDPPPV is quenched completely.

Figure 9 shows the UV-vis and PL spectra of PSDPPPE in these two different solvents. The absorption maximum of PSDPPPE also shows an obvious red shift form 507 nm to 522 nm in aqueous solution. However, the fluorescence of PSDPPPE does not exhibit drastically quenching, and it can be seen that the emission maximum has been red shifted from 593 nm to 636 nm in aqueous solution. The red shifts of absorption and emission maxima of PSDPPPE are also attributed to the J-aggregate as same as other CPEs.^{51,52,54} And the incomplete fluorescence quenching of PSDPPPE may be mainly due to the higher fluorescence quantum efficiency of phenyleneethynylene (PE) segment than phenylenevinylenes (PV) segment. Following the previous studies, polyphenyleneethynylenes (PPEs) always have higher fluorescence quantum efficiency (about two times) than polyphenylenevinylenes (PPVs).55,56 As another reason, PSDPPPE may have less intermolecular exciton migration than PSDPPPV in aqueous solution. It is because the aggregation degree of PSDPPPE may be lower than PSDPPPV.



FIGURE 9 UV-vis and PL spectra of PSDPPPE in different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The π - π staking of PSDPPPE may less than PSDPPPV due to its lower conjugation level.³⁵ When the solvent is changed from DMSO to water, the absorption maximum of PSDPPPE is red-shifted by 15 nm as short as 23 nm of PSDPPPV. This difference may be due to the rigidity of the CPEs. DMSO is considered as a good solvent that makes the backbones free and independently, and water is considered as a pool solvent that makes the backbones form J-aggregates. PSDPPPE has more rigid backbones, so there is an unobvious change of its conformation when the solvent changes. The conjugated level only increased a little after its aggregation compared to PSDPPPV.

Fluorescence Enhancement by Surfactant

Another important research about conjugated polyelectrolyte (CPE) was focused on its surfactochromicity.⁴ With the involvement of oppositely charged surfactant, the homoaggregates between conjugated mainchains are broken and the heteroaggregates obviously form between polymer and surfactant. When the J-aggregate has been destroyed, excitons can not transfer easily between the mainchains, resulting in the increasing fluorescence strength of CPE due to the lower energy dissipation. On the other hand, the conjugation degree of the polymer has been changed because of the new shape of backbones upon the addition of surfactant. The UVvis and PL spectra of CPEs always show complex changes with the involvement of surfactant in a stepwise manner. Abovementioned properties are considered as the characteristic of CPEs which can verify that the polymers have electrolyte side chains and the potential to be self-assembly materials.25

Figures 10 and 11 show the UV-vis and PL spectra of PSDPPPV and PSDPPPE in aqueous solution upon the addition of sodium dodecyl benzene sulfonate (SDBS), respectively. The optical spectra show inconspicuous response with the complex of anionic surfactant. This result suggests that SDBS can not break the J-aggregate of PSDPPPV and PSDPPPE in their aqueous solution effectively because the



FIGURE 10 UV-vis and PL spectra of PSDPPPV in aqueous solution (0.01 mg mL⁻¹) under different concentration of SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

negative charged surfactant exhibits repulsive force with these anionic CPEs.

Compared with SDBS, addition of hexadecyl trimethyl ammonium bromide (CTAB) generates strong response in the emission spectra of PSDPPPV and PSDPPPE. Figure 12 shows the UV-vis and PL spectra of PSDPPPV in aqueous solution under different concentration of CTAB. With this cationic surfactant, an emission peak appears progressively at 721 nm. This phenomenon suggests that CTAB has the ability to interrupt the J-aggregate of PSDPPPV. However, this effect levels off at a surfactant concentration of 12 μ g mL⁻¹. On the other hand, the absorption spectra of PSDPPPV exhibits unobvious blueshift and the absorbance of the spectra are decreased gradually upon the addition of CTAB. These properties are similar to other anionic CPEs which were described by Wu et al.⁵⁷ As same as the model discussed, the CTAB bilayers insert into the homoaggregates of PSDPPPV gradually between the



FIGURE 11 UV-vis and PL spectra of PSDPPPE in aqueous solution (0.01 mg mL⁻¹) under different concentration of SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 12 UV-vis and PL spectra of PSDPPPV in aqueous solution (0.01 mg mL⁻¹) under different concentration of CTAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

anion side chains when the CTAB concentration is under 12 μ g mL⁻¹. In this process, CTAB bilayers avoid the exciton transfer between the backbones and there is a considerable enhancement of the fluorescence emission of this polymer because the energy of exciton can not dissipate between mainchains. However, it is believed that the homoaggregates of PSDPPPV has been completely destroyed when there is overmuch CTAB. When the concentration of CTAB is higher than 12 μ g mL⁻¹, the involvement of CTAB can not lead to responses anymore. In this situation, surfactant bilayers have already surrounded the entire polymer to form heteroaggregates and make the conjugated mainchain independently with the surrounded surfactant in aqueous solution.

The optical spectra of PSDPPPE show similar response compared to PSDPPPV in the presence of CTAB. Figure 13 gives the UV-vis and PL spectra of PSDPPPE in aqueous solution under different concentration of CTAB. There is also a large



FIGURE 13 UV-vis and PL spectra of PSDPPPE in aqueous solution (0.01 mg mL⁻¹) under different concentration of CTAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 14 UV-vis and PL spectra of PSDPPPV in aqueous solution (0.01 mg mL⁻¹) under different concentration of PVP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fluorescence enhancement and the emission peak can be at 3.4 times as strong as the original intensity by the addition of CTAB up to 8 μ g mL⁻¹. On the other hand, the absorption spectra do not show obvious blue-shift as same as PSDPPPV. In contrast, these two polymers show different limited point of fluorescence enhancement (PSDPPPV at 12 μ g mL⁻¹ and PSDPPPE at 8 μ g mL⁻¹) and different feature of absorption response. This result may be attributed to the different rigidity of these two polymers. The conformation of the conjugated mainchain of PSDPPPE may own a lower distorted degree than PSDPPPPV upon the complex of CTAB. Although these two polymers exhibit independent mainchains in both DMSO and CTAB aqueous solution, PSDPPPV and PSDPPPE shows different wavelength of their absorption and emission maximum. This disagreement may suggest that the optical properties solvent-dependency of the PSDPPPV and PSDPPPPE is not only caused by the aggregation phenomena.



FIGURE 15 Linear analysis between intensity of emission maximum of PSDPPPV (0.01 mg mL^{-1}) and concentration of PVP in aqueous solution.

As same as CTAB, the presence of non-ionic polymer surfactant also causes an interesting response in the optical spectra of PSDPPPV and PSDPPPE. Figure 14 shows the UV-vis and PL spectra of PSDPPPV in aqueous solution under different concentration of polyvinylpyrrolidone (PVP). As shown, not only the absorbance but also the PL intensity of PSDPPPV can be enhanced by the addition of PVP. The fluorescence enhancement of PSDPPPV exhibits linear response with the increasing concentration of PVP compared to that of CTAB. Figure 15 gives the linear fit plot of the relationship between the concentration of PVP and the PL intensity of PSDPPPV. In this analysis, the excitation wavelength has been fixed on 540 nm and the detection wavelength has been fixed on 668 nm. The result shows excellent correlation coefficient (R=0.9965) when the concentration of PVP is between 0 μ g mL⁻¹ and 16 μ g mL⁻¹. This regular response may be attributed to the quantificational



FIGURE 16 The assumed model of the heteroaggregates between PVP and PSDPPPV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 17 UV-vis and PL spectra of PSDPPPE in aqueous solution (0.01 mg mL⁻¹)under different concentration of PVP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction between PVP and PSDPPPV. Otherwise, the absorption maximum of PSDPPPV exhibits red shift and the peak which has the largest wavelength is narrowed gradually after the addition of PVP. Abovementioned properties have a notable difference with the responses caused by CTAB. It is suggested that the heteroaggregates between PSDPPPV and PVP have a different form with the heteroaggregates between PSDPPPV and CTAB. Here CTAB is a cationic surfactant, thus heteroaggregates between PSDPPPV and CTAB was caused by the electrostatic force between the alkylammonium cation on CTAB and the sulfonate anions on the side chain of PSDPPPV.⁵⁷ However, PVP is a nonionic polymer surfactant. Heteroaggregates between PSDPPPV and PVP was caused by the dispersion force between polar groups like lactam structure on both main chains of PSDPPPV and PVP.^{58,59}

The assumed model of the heteroaggregates between PVP and PSDPPPV is shown in Figure 16. In this figure, SDPP and DPV segments are respectively stand for 1,4-diketo-2,5-bis(4-sulfonylbutyl)-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole unit and 2,5-diethoxy-1,4-phenyleneethynylene unit in the mainchain of PSDPPPV. Polyvinylpyrrolidone, which has the similar lactam structure with DPP unit can attract PSDPPPV backbones and interrupt the J-aggregate directly by dispersion force. This attraction is different from the indirect ionic interaction between anion side chains and cationic surfactant. The exciton transfer between the mainchains has been avoided efficiently by the inserted PVP chains. And the fluorescence of PSDPPPV has been recovered because the energy can not dissipate by exciton transfer between backbones anymore. On the other hand, PVP may provide a flexible support to the conjugated backbones and this effect could prevent the mainchains twisting overmuch. So, the presence of PVP also decreases the distorted degree of the conjugated backbones and makes PSDPPPV into a higher conjugation level.

The optical spectra of PSDPPPE also show linear response with PVP. Figure 17 gives the UV-vis and PL spectra of



FIGURE 18 Linear analysis between intensity of emission maximum of PSDPPPE (0.01 mg mL^{-1}) and concentration of PVP in aqueous solution.

PSDPPPV in aqueous solution under different concentration of polvvinylpyrrolidone (PVP) and Figure 18 gives the linear fit plot of the relationship between the concentration of PVP and the PL intensity of PSDPPPE. In the linear analysis of PSDPPPE, the excitation wavelength has been fixed on 450 nm and the detection wavelength has been fixed on 633 nm. The fluorescence enhancement of PSDPPPE also shows excellent correlation coefficient (R = 0.9906). When the concentration of PVP is up to 16 μ g mL⁻¹, the absorption maximum of PSDPPPE is red-shifted by 8 nm as short as 14 nm in the response of PSDPPPV. This difference suggests that there is only a little change in the distorted level of PSDPPPE due to the phenyleneethynylene (PE) unit which is more structurally rigid than phenylenevinylene (PV) unit. Although there is an obvious response in PL spectra of PSDPPPV and PSDPPPPE by the addition of PVP, the wavelengths of their emission maxima of these two polymers never shift in this process. Thus, the fluorescence peaks at 668 nm of PSDPPPV and 633 nm of PSDPPPE are respectively attributed to their intrinsic emission due to the constant wavelength and the linear relationship of their PL intensity upon the concentration of PVP. In conclusion, fluorescence enhancement by PVP provides a controllable method to enhance the fluorescence of PSDPPPV and PSDPPPE in conceivable confine. And this process is predicted to be a method that can avoid the lower fluoresquantum efficiency of DPP-based cence conjugate polyelectrolytes.

CONCLUSIONS

Two novel water soluble anionic DPP-based conjugated polyelectrolytes PSDPPPV and PSDPPPE have been synthesized successfully. The polymers are dark purple solid and exhibit excellent solubility in water and DMSO. In DMSO, PSDPPPV exhibits absorption maximum at 524 nm and emission maximum at 609 nm, and PSDPPPE shows absorption maximum at



507 nm and emission maximum at 593 nm. The optical properties show obvious solvent-dependency. Aqueous solutions of PSDPPPV and PSDPPPE respectively exhibit their absorption maximum at 547nm and 522nm which show a notable red shift compared to their DMSO solutions. The emission of PSDPPPV and PSDPPPE both show remarkable fluorescence quenching in aqueous solution. PSDPPPV exhibits no fluorescence, but the intrinsic emission at 668 nm in aqueous solution appears by addition of PVP. PSDPPPE shows the emission maximum at 636 nm in aqueous solution which also has a large red shift compared to its DMSO solution. Furthermore, the addition of cationic surfactant CTAB and polymer nonionic surfactant PVP can effectively increase the emission intensity of their aqueous solution in a certain range. Fluorescence enhancement caused by PVP shows linear response with the increasing concentration of PVP and provides a controllable method to enhance the fluorescence of DPP-based conjugate polyelectrolytes in aqueous phase. This strategy could make the polymers be water soluble conjugated polymer materials with red light emitting. Finally, these two polymers have favourable coverage of the visible light region and this property suggests they are promising material in applications of self-assembly solar cells.

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