Polymer Communication

A fluorene-containing water-soluble poly(p-phenyleneethynylene) derivative: Highly fluorescent and sensitive conjugated polymer with minor aggregation in aqueous solution

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Abstract

A novel cationic fluorene-containing water-soluble poly(p-phenyleneethynylene) (PPE) derivative, poly[(9,9-bis{6′-[(N,N-diethyl)-N-methylammonium]hexyl}-2,7-fluorenyleneethynylene)-alt-co-(2,5-bis{3′-[(N,N-diethyl)-N-methylammonium]-1′-oxapropyl}-1,4-phenylene)] tetraiodide (**P1′**), was synthesized through Sonogashira reaction and a post-polymerization treatment. **P1′** emits bright blue fluorescence in H_2O with a high photoluminescence quantum yield ($\Phi_{pl}=26\%$). Studies on the optical properties and quenching experiments with $Fe(CN)_6^{4-}$ in H_2O and MeOH show that **P1′** presents minor aggregation and high Stern–Volmer constant ($K_{sv}=2.4\times10^8\ M^{-1}$) in aqueous solution. The remarkably reduced tendency towards aggregation, relative to previously reported water-soluble PPEs, made the optical properties of **P1′** almost insensitive to the disturbance from the common ions (non-quencher) in the solution.
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Keywords: Water-soluble conjugated polymer; Aggregation; Fluorescence

1. Introduction

Water-soluble conjugated polymers (WSCPs) have shown great potential as highly sensitive fluorescent sensory materials for a variety of chemical analytes and biomolecules [1–5]. Compared with other WSCPs, water-soluble poly(p-phenyleneethynylene)s (PPEs) [6–8] have recently attracted more attention in chemo/bioanalysis because of the high delocalization of singlet exciton and rapid energy migration along the conjugated backbone of PPEs [9,10]. In addition, they are widely applied to study quenching–structure relationships owing to their good optical response to environmental variation through the relatively free internal rotation of alkyne–aryl single bond and facile interchain π-aggregation [11–14]. However, water-soluble PPEs usually suffer from their intrinsic defects, especially low photoluminescence (PL) quantum efficiency ($\Phi_{pl}<10\%$) and strong tendency towards aggregation in aqueous solution (disturbing the detection results and lowering the PL quantum efficiency because of self-quenching) [11–14]. Moreover, as a general property of WSCPs, the tendency towards aggregation will make their optical properties sensitive to the common ions (non-quencher) in the buffer solution, which dramatically limits their biosensor applications [14,15]. Thus, developing novel WSCPs such as PPE-based systems, but with reduced tendency towards aggregation, higher photoluminescence and higher Stern–Volmer constant (K_{sv}) is remarkably desired.

Herein, our work on a novel fluorene-containing water-soluble PPE derivative suggested that this molecular platform could be promising for this purpose. Poly(fluorenyleneethynylene)s (PFEs), a type of conjugated polymers with similar backbone structure to PPEs, exhibit higher quantum efficiency than PPEs, which may be attributed to the strong intrachain delocalization for the existence of fluorene [10,16].

Furthermore, in comparison with the planar and linear main chain of PPEs, the angle between the linkage positions of 2,7-fluorenyl unit induces a less planar and 'zigzag-like' shape of main chain, which is expected to disfavor close, efficient packing between adjacent chains [10,16]. Therefore, we suggest that introducing fluorene units into water-soluble PPEs would result in a material with less aggregation. In this communication, we synthesized a fluorene-containing water-soluble PPE derivative functionalized with ammonium side groups (Scheme 1), which presents minor aggregation, high PL quantum yield and K_{sv} in aqueous solution.

2. Experimental section

2.1. Materials

All chemical reagents used were purchased from ACROS or Aldrich Chemical Co. Toluene was purified by distillation from sodium in the presence of benzophenone. Other organic solvents were used without any further purification. 1,4-Diiodo-2,5-hydroquinone was synthesized according to the literature procedures [9].

2.2. General methods

NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. UV–vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Elemental microanalyses were carried out on a Vario EL III CHNOS Elemental Analyzer. Molecular weight measurements were performed by Shimadzu LC-10A VP gel permeation chromatography (GPC) with polystyrenes as the standard and tetrahydrofuran (THF) as the eluant. Time-correlated single photon fluorescence studies were performed using an Edinburgh Instruments LifeSpec-PS spectrometer. The Life-Spec-PS comprises a 371 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hammamatsu microchannel plate photomultiplier (R3809U-50). Lifetimes were determined from the data using the Edinburgh Instruments software package.

The optical properties of all the compounds were studied in dilute solutions ($c = 1\ \mu M$, repeat unit concentration for
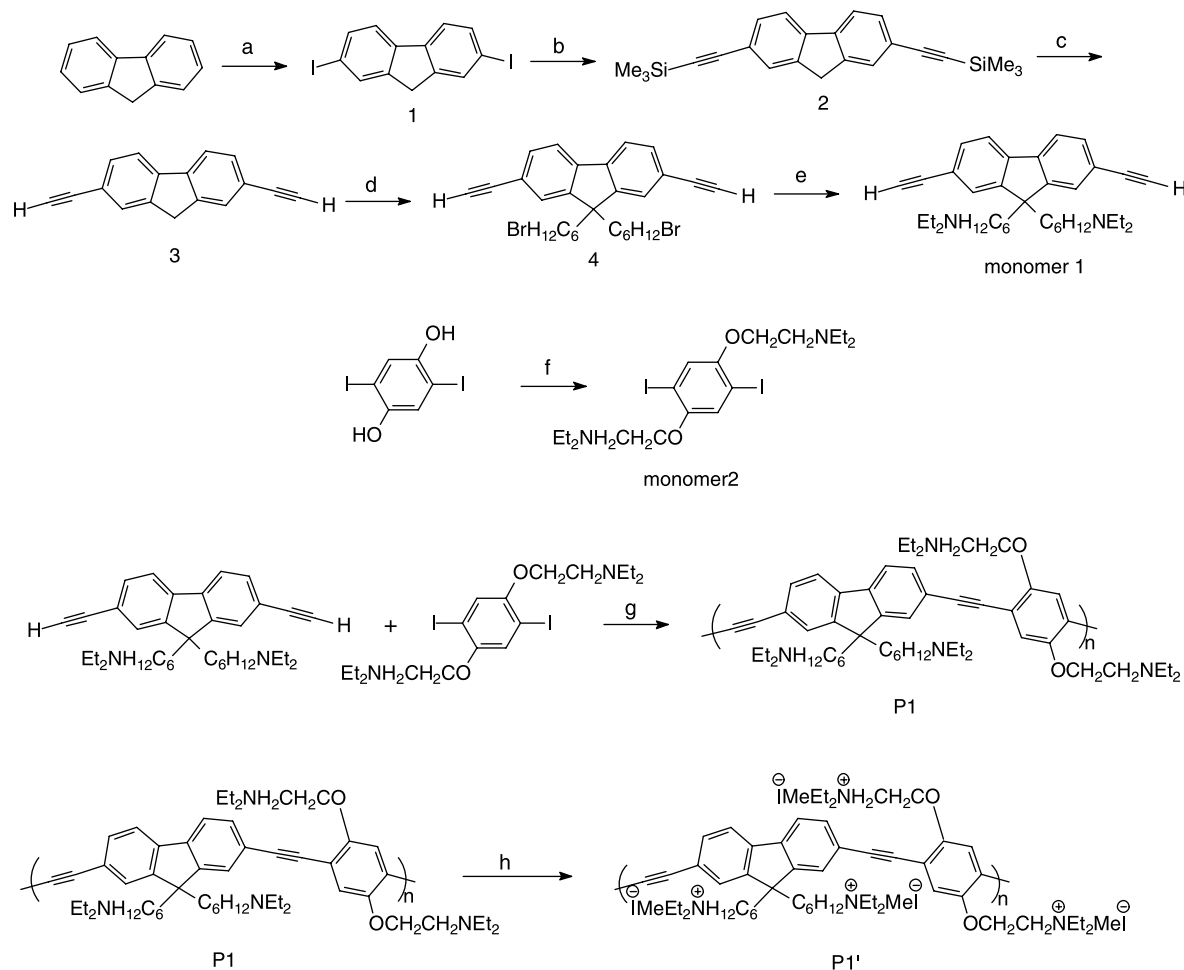
Scheme 1. Reagents and conditions: (a) I$_2$, KIO$_3$, AcOH, H$_2$SO$_4$, H$_2$O, 80 °C, 10 h; (b) (CH$_3$)$_3$SiCCH, (PPh$_3$)$_2$PdCl$_2$, CuI, diisopropylamine, 6 h; (c) KOH, CH$_3$OH–THF, room temperature, 1 h; (d) BrC$_6$H$_{12}$Br, KOH, H$_2$O, Bu$_4$NBr, 75 °C, 15 min; (e) HNEt$_2$, reflux, 24 h; (f) 2-chlorotriethylamine hydrochloride, K$_2$CO$_3$, acetone, reflux, 3 days; (g) iodobenzene, Pd(PPh$_3$)$_4$, CuI, diisopropylamine, 24 h; (h) CH$_3$I, THF–DMF–H$_2$O, room temperature, 5 days.

polymer). The quenching behavior was studied by comparing the fluorescence intensities of polymer solutions in the presence of quenchers with different concentrations. Milli-Q water used in preparing the aqueous solutions of the polymers and quenchers was purged with nitrogen for 4 h before use.

2.3. Synthesis of 2,7-diethynyl-9,9-bis[6'-(N,N-diethylamino)-hexyl]fluorene (monomer 1)

2,7-Diethynyl-9,9-bis(6'-bromohexyl)fluorene (4) (3 g, 5.5 mmol) was dissolved in 20 mL boiling diethylamine and the reaction mixture was refluxed for 10 h. After the removal of excess diethylamine, water was added to dissolve the precipitate and then extracted with ether for three times. The combined organic layer was dried over anhydrous sodium sulfate. After removing the solvent, the residue was purified by silica gel column chromatography (ethyl acetate/methanol/triethylamine = 120:20:1) to give a yellow oil (2.13 g, Yield: 73.1%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 0.54–0.60 (m, 4H), 0.96 (t, 12H, $J = 7.2$ Hz), 1.00–1.08 (m, 8H), 1.20–1.28 (m, 4H), 1.90–1.95 (m, 4H), 2.25–2.29 (m, 4H), 2.45 (q, 8H, $J = 7.2$ Hz), 3.14 (s, 2H), 7.44 (s, 2H), 7.47 (d, 2H, $J = 7.6$ Hz), 7.62 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (CD$_3$OD, 100 MHz): δ (ppm) 9.91, 23.36, 25.21, 26.86, 29.24, 39.83, 46.38, 52.25, 55.21, 77.94, 83.89, 119.99, 121.71, 126.30, 131.20, 141.89, 150.97. Analysis Calcd C$_{37}$H$_{52}$N$_2$: C, 84.68; H, 9.99; N, 5.34. Found: C, 84.76; H, 10.13; N, 5.01.

2.4. Synthesis of 1,4-bis[3'-(N,N-diethylamino)-1'-oxapropyl]-2,5-diiodobenzene (monomer 2)

A 250 mL round-bottom flask with magnetic stirring bar was charged with anhydrous potassium carbonate (24.84 g, 0.18 mol), 1,4-diiodo-2,5-hydroquinone (10.86 g, 0.03 mol), and 150 mL of acetone. The stirred mixture was sparged with nitrogen for 15 min and then refluxed for about 30 min. After 30 min refluxing, 2-chlorotriethylamine hydrochloride (12.38 g, 0.072 mol) was added into the round-bottom flask and the mixture was then refluxed for 3 days. The precipitate mixture was filtered away and the filtrate was rotary evaporated. The residue was poured into water and extracted with ether three times, and the combined organics were washed with 10% aqueous sodium hydroxide twice, water twice, and brine once. The solution was dried over magnesium sulfate, filtered and stripped of solvent by rotary evaporation to yield crude solid. The crude product was recrystallized from hexane to afford colorless crystals (12 g, yield: 71%). Mp: 76–78 °C (from hexane). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.10 (t, 12H, $J = 6.8$ Hz), 2.67 (q, 8H, $J = 6.4$ Hz), 2.93 (t, 4H, $J = 6.4$ Hz), 4.02 (t, 4H, $J = 6.4$ Hz), 7.23 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 12.6, 48.4, 52.0, 69.8, 86.5, 123.4, 153.4. Analysis Calcd C$_{18}$H$_{30}$I$_2$N$_2$O$_2$: C, 38.59; H, 5.40; N, 5.00. Found: C, 38.99; H, 5.32; N, 4.84.

2.5. Synthesis of poly{9,9-bis[6'-(N,N-diethylamino)hexyl]-2,7-fluorenyleneethynylene}-alt-co-{2,5-bis[3'-(N,N-diethylamino)-1'-oxapropyl]-1,4-phenylene} (P1)

Under nitrogen protection, degassed diisopropylamine/toluene (1:2, 15 mL) was added to a 25 mL round-bottom flask containing 0.16 g (0.31 mmol) of monomer 1 and 0.168 g (0.3 mmol) monomer 2, 13 mg of iodobenzene (0.064 mmol), 15 mg of Pd(PPh$_3$)$_4$ (0.013 mmol), and 3 mg (0.016 mmol) of CuI. After the reaction mixture was stirred at 70 °C for 24 h, iodobenzene (61.2 mg, 0.3 mmol) was added for end-capping the polymer for an additional 2 h. Upon cooling to room temperature, the reaction mixture was subjected to a CHCl$_3$/H$_2$O workup. The organic phase was washed with water for three times, then dried over anhydrous sodium sulfate. After the solution was concentrated, it was poured into methanol (300 mL). The precipitate was filtered, dissolved in chloroform, and reprecipitated in methanol twice to obtain a fibrous solid (yield: 71%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 0.45–0.78 (br, 4H), 0.80–1.25 (m, 36H), 1.78–2.15 (br, 4H), 2.19–2.39 (m, 4H), 2.40–2.50 (m, 8H), 2.65–2.76 (m, 8H), 2.96–3.06 (m, 4H), 4.10–4.22 (m, 4H), 7.08 (s, 2H), 7.40–7.58 (m, 4H), 7.60–7.72 (m, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 11.79, 12.47, 24.00, 27.08, 27.64, 30.28, 40.08, 47.00, 48.27, 51.26, 53.05, 55.41, 68.67, 86.56, 96.23, 114.01, 116.88, 120.24, 122.33, 126.08, 131.02, 140.99, 151.13, 153.70. Analysis Calcd C$_{55}$H$_{80}$N$_4$O$_2$: C, 79.58; H, 9.64; N, 6.75. Found: C, 79.05; H, 9.27; N, 6.38.

2.6. Synthesis of poly[(9,9-bis{6'-[(N,N-diethyl)-N-methylammonium]hexyl}-2,7-fluorenyleneethynylene)-alt-co-(2,5-bis{3'-[(N,N-diethyl)-N-methylammonium]-1'-oxapropyl}-1,4-phenylene)] tetraiodide (P1')

Methyl iodide (1.0 g, 7 mmol) was added to P1 (70 mg, 0.085 mmol) dissolved in 5 mL THF and 5 mL DMF at room temperature. After 1 min stirring, some precipitate was observed, which was redissolved by addition of 2 mL H$_2$O. After 5 days, the reaction mixture was concentrated and then poured into acetone causing a precipitate to form. The collected precipitate was redissolved with methanol. The solution was concentrated and poured into acetone again to yield P1' as a yellow solid (93 mg, yield: 79%). ^{1}H NMR (CD$_3$OD, 400 MHz): δ (ppm) 0.52–0.73 (br, 4H), 1.20–1.36 (br, 20H), 1.39–1.48 (br, 12H), 1.50–1.62 (br, 4H), 2.10–2.35 (br, 4H), 2.95 (s, 6H), 3.18–3.40 (br, 18H), 3.60–3.78 (br, 8H), 3.97–4.05 (br, 4H), 4.61–4.75 (br, 4H), 7.54–7.62 (br, 4H), 7.80–7.95 (br, 4H). Analysis Calcd for C$_{55}$H$_{80}$N$_4$O$_2$: C, 50.69; H, 6.59; N, 4.00. Found: C, 50.14; H, 6.56; N, 3.81.

3. Results and discussion

3.1. Synthesis and characterization

The cationic water-soluble polymer P1' was obtained by quaternization of the neutral polymer P1. P1 is composed of [9,9-bis(6'-N,N-diethylamino)hexyl]fluorene and 1,4-bis

[3'-(N,N-diethylamino)-1'-oxapropyl]benzene, which are alternatively linked by ethynylene bond (Scheme 1). Pd/CuI catalyzed cross-coupling of 2,7-diethynyl-9,9-bis[6'-(N,N-diethyl)hexyl]fluorene (monomer 1) and 1,4-bis[3'-(N,N-diethylamino)-1'-oxapropyl]-2,5-diiodobenzene (monomer 2) via the Sonogashira reaction afforded P1 (Supporting information for details on the synthesis and NMR spectral data). P1 readily dissolved in common organic solvents such as $CHCl_3$ and THF. Gel permeation chromatography (GPC) analysis showed a molecular weight of $M_n = 9800$ g/mol and a polydispersity of 1.28 for P1. According to ^{1}H NMR spectra of P1 and P1' shown in Fig. 1, the quaternization degree of P1' is 100%, because nearly all signals of P1 moved to the lower field after quaternization.

The aggregate conformation of water-soluble PPEs in water generally results from hydrophobic interaction between adjacent conjugated backbones [11–14]. In order to optimize hydrophobic interactions, the adjacent chains of these polymers align with their long axes parallel and phenylene rings stacking face-to-face. This interchain π-aggregation will allow the hydrophilic side chains to extend more fully into the aqueous solution and consequently improve the water-solubility of polymers. Thus, increasing the hydrophilic property of water-soluble conjugated polymers is anticipated to decrease their π-aggregated states. Consequently, compared with previously reported water-soluble PPEs [11–14], which present only (1+) or less than (1+) charge per phenylene ring, P1' features (4+) charges per three aromatic rings, i.e. about (1.3+) charges per phenylene ring. Therefore, the charge density of P1' is higher, which may make it exist in a better dissolved state in H_2O. Solubility experiments demonstrated that P1' has good solubility in DMSO, MeOH and satisfactory solubility in H_2O (2 mg/ml), but it is insoluble in $CHCl_3$ and THF.
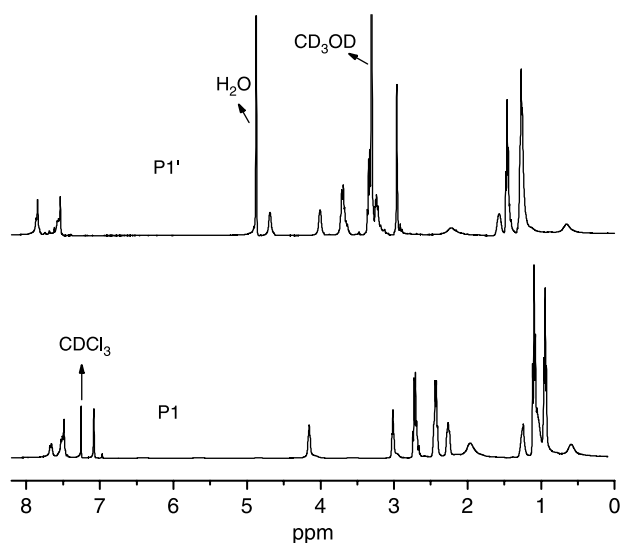
3.2. Optical properties

Monomer 1 in $CHCl_3$ featured a structured UV–vis absorption spectrum with a sharp peak at 329 nm, and its PL spectrum exhibited an emission peak at 331 nm, along with a clearly resolved vibrational band at 348 nm (shown in Fig. 2, the detailed data refer to Table 1). By contrast, the absorption and PL spectra of P1 and P1' (shown in Fig. 3) red-shifted and lost structured shape due to the extended π-conjugation of their backbones. Interestingly, P1 in $CHCl_3$ and P1' in MeOH and H_2O all displayed similar spectra in terms of shape and wavelength of the absorption and emission peaks. It is also noteworthy that all the emission peaks still retained clearly resolved vibrational shoulders at about 460 nm, which indicated the absence of strong π-aggregation in aqueous solution [11]. Additional information concerning the solvent effect of water on P1' comes from the UV–vis absorption and PL spectra of P1' in MeOH, MeOH/H_2O (1:1) and H_2O. With increased volume fraction of H_2O in the solvent, the absorption and emission features of P1' changed little except for the moderately decreased PL intensity, suggesting that no strong π-aggregation of the polymer chains was formed [11,13]. On the contrary, the previously reported water-soluble PPEs, for example, PPE–SO_3^-, presented significantly decreased PL intensity, progressively red-shifted absorption and broader, longer-lived fluorescence with increased volume fraction of H_2O, which are prominent characteristics of conjugated polymer aggregation [11]. In H_2O, the fluorescence decay time of PPE–SO_3^- was wavelength dependent, which consisted of two long-lived component ($\tau = 1.5$ and 6.0 ns, amplitude% = 44 and 56%, respectively), on the red side of the band and a short-lived component ($\tau = 550$ ps) on the blue side. Furthermore, the long-lived decay component was considered as a result of emission from the 'excimer-like' aggregated state [11,13]. However, the fluorescence decay of P1' in both MeOH and H_2O was nearly wavelength independent and it was dominated by a short-lived component with $\tau = 325$ ps, which is another powerful evidence for the absence of strong π-aggregation.
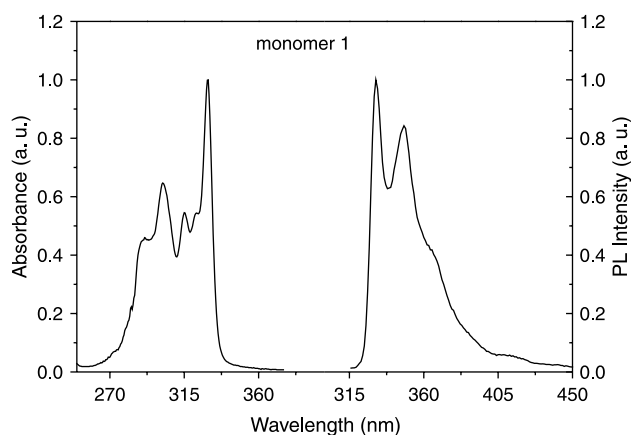

Fig. 1. ^{1}H NMR spectra of P1 and P1'.

Fig. 2. UV–vis absorption and PL spectra of monomer 1 in $CHCl_3$.

Table 1
Optical properties of monomer **1**, **P1** and **P1**′

Entry	Absorption λ_{max} (nm)			Emission λ_{max} (nm)		
	CHCl₃	CH₃OH	H₂O	CHCl₃	CH₃OH	H₂O
Monomer **1**	302, 329			331, 348		
P1	404			439, 461		
P1′		406	403		435, 457	436, 457

It has been reported that additions of multivalent ions may tend to increase the aggregation of WSCPs and consequently result in spectral changes and fluorescence decrease [1,17]. However, we added Na₂SO₄ to the aqueous solution of **P1**′ and when [SO₄²⁻]:[**P1**′] ratio went up to 10:1, both absorption and PL spectra still exhibited few change in terms of shape, wavelength and intensity. Moreover, considering that WSCPs with extensive aggregation in aqueous solution are very sensitive to ionic strength [14], we compared the absorption and PL spectral changes of **P1**′ in H₂O with the addition of NaCl. Until [NaCl] reached 0.1 M, the ionic strength did not significantly affect both spectra except that PL intensity decreased by less than 3%. For contrast, PPE-NEt₃⁺ has been found to display evidently red-shifted absorption and PL spectra, and obvious changes of PL intensity with the addition of NaCl, which were interpreted as the results of changes in aggregation [14]. Therefore, the remarkably reduced tendency towards aggregation made the optical properties of **P1**′ almost insensitive to disturbance from the environment, which is highly favored in sensor application.

In contrast to the planar phenylene ring and linear main chain of PPEs, the fluorenylene unit in **P1**′ resulted in a little torsional plane and 'zigzag-like' main chain, both of which may impede the efficient π-aggregation between adjacent chains. On the basis of our above arguments, the absence of strong π-aggregation is also likely in part due to the enhanced hydrophilic property of **P1**′, which resulted from its increased charge density. In addition, we speculate the moderately decreased PL intensity of **P1**′ in aqueous solution may be related with the impediment of planarization in the excited state [17,18]. However, one of the most attractive properties of **P1**′ is just its high PL quantum yield (Φ_{pl}) in H₂O. In aqueous solution, the Φ_{pl} of **P1**′ is up to 26%[1], which is much higher than the previously reported water-soluble PPEs ($\Phi_{pl} < 10\%$) [8,11,13,19]. We considered such a high Φ_{pl} of **P1**′ could be attributed to its minor aggregation in H₂O [1,13,14] and the introduction of strongly fluorescent fluorene units into the backbone [16,20].

Stern–Volmer (SV) quenching of **P1**′ by $Fe(CN)_6^{4-}$ in H₂O ($c = 1$, 5 μM) and MeOH ($c = 1$, 10 μM) was investigated. The SV curves are linear at low quencher concentrations and their K_{sv} values are 2.4×10^8, 4.9×10^7,

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[1] The quantum yields were measured using a Shimadzu RF-5301 PC spectrofluorophotometer with dilute solutions ($A < 0.05$) at room temperature [22]. Quinine sulfate solution ($c = 2$ μM) in 0.05 M H₂SO₄ ($\Phi_{pl} = 56.4\%$) was used as a standard.
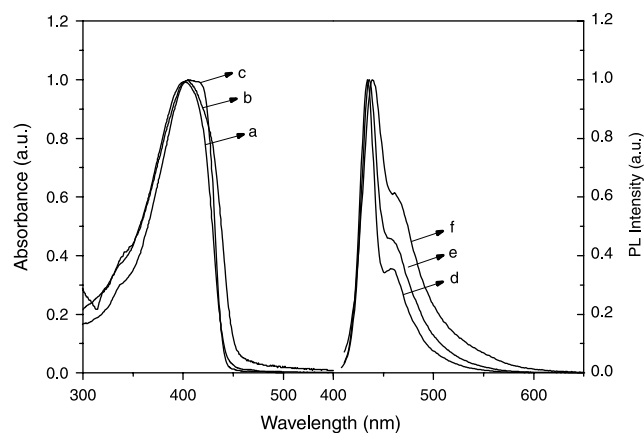

Fig. 3. UV–vis absorption and PL spectra of **P1** in CHCl₃, **P1**′ in MeOH and H₂O. (a) UV of **P1**′ in H₂O, (b) UV of **P1** in CHCl₃, (c) UV of **P1**′ in MeOH, (d) PL of **P1**′ in MeOH, (e) PL of **P1**′ in H₂O, (f) PL of **P1** in CHCl₃.

1.3×10^6, and 3×10^5 M⁻¹, respectively (Supporting information). It is noteworthy that $Fe(CN)_6^{4-}$ caused amplified fluorescence quenching concomitant with almost unchanged absorption spectra as shown in Fig. 4. This result was quite different from the usually red-shifted spectra of water-soluble PPE with the addition of quencher [11], suggesting that quencher-induced aggregation may be minimal and accordingly contributed little to the quenching of **P1**′ by $Fe(CN)_6^{4-}$. From the application point of view, this important feature will ensure further the reliability of detection results. Although some researchers have reported that interchain aggregation could lead to further amplification of fluorescence quenching through the occurrence of interchain exciton migration [11,13,14], **P1**′ still exhibited a very high K_{sv} in H₂O, which makes it possible to detect this quencher easily at concentrations <1 nM. On the other hand, we found that the K_{sv} values of **P1**′ are larger at lower polymer concentrations. According to the previous research [21], at lower polymer concentration the iodide ions are better dissociated away from the positively charged
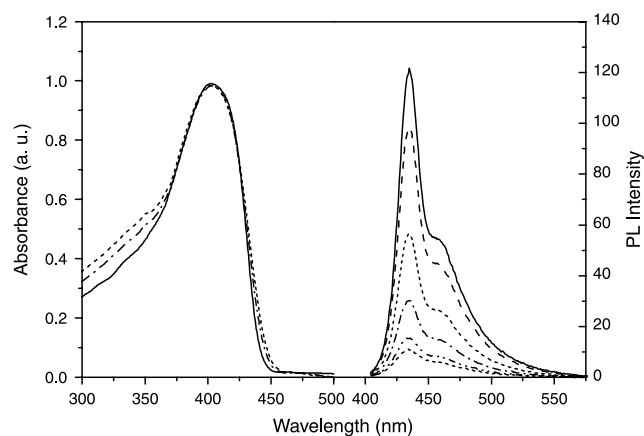

Fig. 4. UV–vis absorption (left) and PL spectra (right) of **P1**′ in H₂O with added $Fe(CN)_6^{4-}$. [**P1**′] = 1 μM. Absorption [$Fe(CN)_6^{4-}$] = 0, 10, and 16 nM. PL: [$Fe(CN)_6^{4-}$] ranges from 1 to 16 nM (from top to bottom).

polymer. This removal of ions decreases electrostatic screening around polymer and favors close proximity between the polymer and quencher. Moreover, proximity and ion-pairing of the polymer and quencher are important preconditions of amplified quenching [11,13]. Similar arguments may also be applicable for explaining the larger K_{sv} values in H_2O than in MeOH because water would be a better medium of ionization for polyelectrolytes. Although some researchers believe that stronger aggregation in H_2O may be the reason for the larger K_{sv} values compared with those in MeOH [11], this explanation may be unsuitable for our case.

4. Conclusion

In conclusion, we have synthesized a novel cationic fluorene-containing water-soluble PPE derivative. This WSCP presented minor aggregation in aqueous solution, probably due to the less planar and 'zigzag-like' shape of the main chain and enhanced hydrophilic property. Moreover, this polymer emitted intense blue fluorescence and exhibited high quenching efficiency. All of these make it attractive as a fluorescent sensory material and confirm that introducing the structure unit of PFE into water-soluble conjugated polymers is an effective way to develop improved sensory materials.

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2006.04.038.

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