

AGGREGATION-INDUCED EMISSION ENHANCEMENT IN POLY(PHENYLENE-ETHYNYLENE)S BEARING ANILINE GROUPS*

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Abstract Poly(phenylene ethynylene)s (**P1**) with 4-vinylaniline pendant groups were successfully prepared by the Sonogashira coupling polymerization between 1,4-diethynyl-2,5-bis(pentyloxy)benzene and 4-[2-(2,5-dibromophenyl)vinyl]-aniline. In comparison with its analogue **P2** without amino group, the emission of **P1** is only enhanced by aggregation when adding *n*-hexane into its THF solution, exhibiting an aggregation-induced emission enhancement (AIEE) effect. When methanol or water instead of hexane was added into THF solution, **P1**, however, didn't show AIEE. The results indicated that amino groups strengthen the inter-chain and intra-chain interactions in **P1** and restrict the non-radiative energy transition. This strategy can provide a platform for developing highly sensitive and efficient bio- and chemosensors.

Keywords: Conjugated polymer; Poly(phenylene ethynylene)s; Aggregation-induced emission enhancement; Amino group.

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INTRODUCTION

In recent decades, much effort has been devoted to designing and exploring conjugated polymers (CPs) and oligomers due to their combination of fascinating optoelectronic properties with mechanical properties, processing advantages of plastics and wide potential applications in optoelectronics, microelectronics and chemical and biological sensors^[1–9]. Morphologies and supramolecular ordering, which usually determined by the inter-chain interactions, are main factors governing the performance of these conjugated materials devices in the aggregation or solid state. It has often been the rule that aggregation of polymer chains results in the undesirable side effect of self-quenching to the detriment of fluorescence efficiencies^[10, 11]. Many attempts, such as introducing bulk side groups and improving fabrication techniques, have been made to overcome this aggregation-caused quenching (ACQ) effect^[12–14]. However, there are still remaining challenges in finding a more efficient and widespread approach to prevent fluorophore from aggregating.

Aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) have been recently discovered as an intriguing phenomenon to solve these notorious ACQ problems in small molecules: a series of nonemissive or low-emissive molecules such as tetraphenylethene, hexaphenylsilole and pentaphenylpyrrole as well as their derivatives are induced to emit efficiently by aggregating formation^[15–23].

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The restriction of intramolecular rotation (RIR) is often accounted for such greatly boosting of fluorescence quantum yields in the aggregation state^[24–27]. However, due to their synthetic difficulties, there is few example of conjugated polymers, whose fluorescence mainly originated from the appending AIE small molecules at the side chains, presenting such AIE(E) effect in aggregation state^[28–33].

In our previous research, we synthesized a series of DOPO-containing derivatives or polymers and found that the emission of luminophores could be affected by hydrogen bonding interactions between intramolecular or intermolecular side groups^[34–36]. With this contribution, we tried to make a better understanding of the relationship between the molecular packing/interaction and optical properties of the conjugated polymers in the aggregation state. We prepared poly(phenylene-ethynylene)s (PPEs) with 4-vinylaniline pendant group (**P1** shown in Scheme 4) and found that it demonstrated AIEE phenomenon. But analogue **P2** without amino group just shows conventional conjugated PPE property-quenching in the aggregating state. By comparing the photoluminescence (PL) behaviors of **P1** and **P2** in different aggregating state, we supposed that inter-chain and intra-chain interactions in **P1** strengthen because of the introduction of amino groups as the pendant groups and have made a significant effort to widen the distance between the backbones, and thus avoid nonradiative decay process caused by π - π stacking. Such attractive fluorescence behavior may provide a way to develop effective conjugated polymer optoelectronic devices and chemosensor.

EXPERIMENTAL

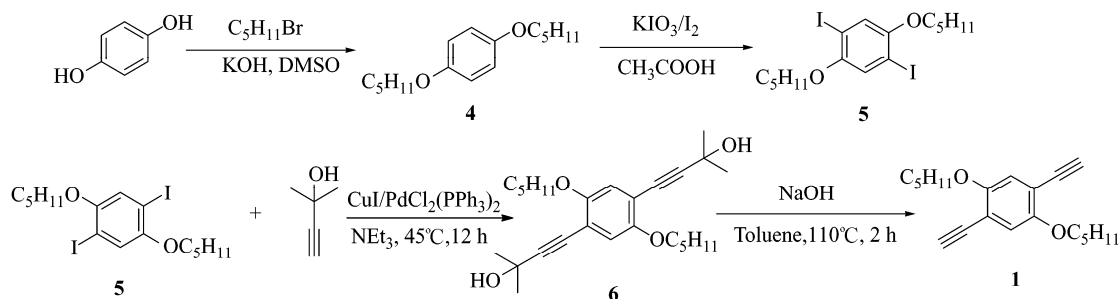
General Procedures

All solvents were additionally purified and dried by standard techniques. 2,5-Dibromobenzyltriphenylphosphonium bromide **8** were synthesized according to the literature procedures^[37]. All other reagents were obtained from Acros or Alfa Aesar and used without further purification. ¹H-NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer at room temperature using chloroform-d or DMSO-d₆ as the solvent and tetramethylsilane (TMS) as the internal standard. Gel permeation chromatographic (GPC) measurements were carried out at 35°C on a Waters 2410 instrument using THF as the eluent at a flow rate of 1.0 mL/min. All of the GPC data were calibrated with polystyrene (PS) standards. UV-Vis absorption spectra were recorded on a Hitachi U-2800 spectrophotometer. Photoluminescence (PL) spectra were collected on a Cary Eclipse spectrofluorometer at room temperature. PL quantum yields were measured using quinine sulfate as the standard, with a quantum yield of 57.7% in H₂SO₄ (0.1 mol/L)^[38]. Mass spectra were recorded on a Finnigan TSQ7000 spectrometer operating in electron ionization (EI) mode.

Monomer Synthesis

1,4-Diethynyl-2,5-bis(pentyloxy)benzene (**1**)

It was prepared according to the synthetic route as described in Scheme 1. ¹H-NMR (400 MHz, CDCl₃), δ = 6.95 (s, 2H), 3.97 (t, 4H), 3.33 (s, 2H), 1.89–1.71 (m, 4H), 1.51–1.29 (m, 8H), 0.93 (t, 6H).



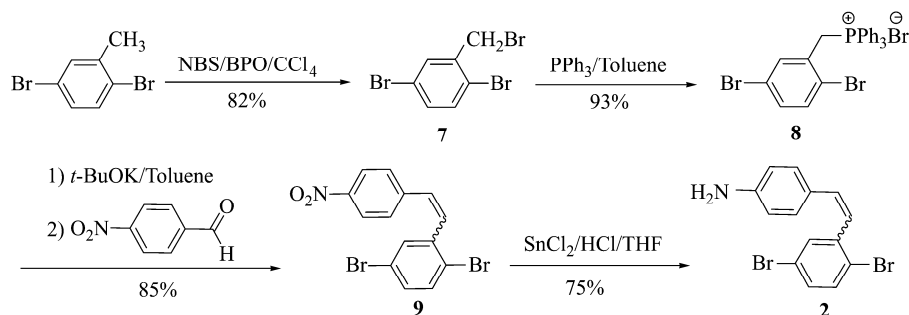
Scheme 1 Synthetic route of **1**

1,4-Dibromo-2-(4-nitrostyryl)benzene (9)

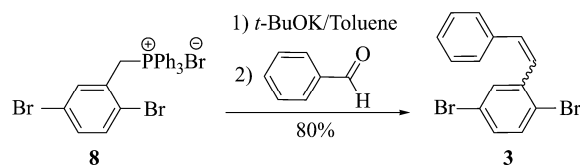
Synthetic routes of **9** and **2** are shown in Scheme 2. 2,5-Dibromobenzyltriphenylphosphonium bromide (**8**) (2.36 g, 4 mmol) was dissolved in dry toluene (30 mL) and stirred at 0°C under argon atmosphere. Potassium *tert*-butoxide (0.89 g, 8 mmol) was then added and stirred for 1 h. A solution of *p*-nitrobenzaldehyde (0.91 g, 6 mmol) in dry toluene (20 mL) was added dropwise over a period of 30 min and stirred for 1 h at 0°C, and then allowed to warm to room temperature overnight. After solvent evaporation, the yellow solid was dissolved in CH₂Cl₂ and washed with aqueous solutions of ammonium chloride and potassium carbonate. The organic layer was dried over MgSO₄ and filtered. The crude product was passed through a column with silica gel (200–300 mesh) eluted with a mixture of CH₂Cl₂-hexane (3:7). 1,4-Dibromo-2-(4-nitrostyryl)benzene **9** was obtained as a mixture of *Z*- and *E*-isomers as a yellow solid. The yield is 85%. MS: *m/z*: calcd for C₁₄H₉Br₂NO₂: 383.03 [M]⁺; found 383.

4-(2,5-Dibromostyryl)aniline (2)

9 (0.61 g, 1.5 mmol) was dissolved in THF (20 mL) and stirred. A solution of SnCl₂·2H₂O (1.03 g, 4.5 mmol) in concentrated HCl (20 mL) was immediately added with stirring. Vigorous exothermic reaction accompanied by a refluxing of the solvent was observed. When **9** was no longer detected by TLC, the reaction mixture was treated with 50% aqueous NaOH to adjust pH to about 13. The phases were then separated. The aqueous phase was extracted with ether (30 mL × 3) and discarded. The extracts were combined with the organic phase, washed with brine, water, and dried over MgSO₄. Concentration in vacuo afforded crude product as a yellow solid, which was recrystallized from methanol-water mixture to give 0.42 g (75%) of 4-(2,5-dibromostyryl)aniline **2** as a light-brown crystalline material. The reaction gave the anti isomer as the major product, with syn/anti ratio 1:3 according to ¹H-NMR spectra. MS: *m/z*: calcd for C₁₄H₁₁Br₂N: 353.05 [M]⁺; found 353.

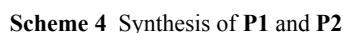
**Scheme 2** Synthetic route of **2****1,4-Dibromo-2-styrylbenzene (3)**

This compound was prepared in 80% yield as essentially in the same manner as described for **9** using benzaldehyde instead of *p*-nitrobenzaldehyde as shown in Scheme 3. The reaction gave the anti isomer as the major product, and the syn/anti ratio was 1:2. MS: *m/z*: calcd for C₁₄H₁₀Br₂: 338.04 [M]⁺; found 338.

**Scheme 3** Synthetic route of **3****Polymer Synthesis**

Polymers were synthesized *via* Sonogashira cross-coupling reaction as shown in Scheme 4.

1 (149 mg, 0.5 mmol), **2** (194 mg, 0.55 mmol), 10 mg Pd(PPh₃)₂Cl₂ (3 mol%) and 5 mg CuI (5 mol%) were added to an oven-dried 50 mL round-bottom flask containing a magnetic stir bar. The vessel was sealed, evacuated and backfilled with nitrogen repeatedly for three times. A degassed mixture of 15 mL of toluene and 10 mL diisopropylamine was added and the flask was heated to 70°C for 12 h. Upon cooling, the solvent was evaporated and the residue was extracted into dichloromethane. The organic layer was washed with aqueous ammonium chloride, dilute hydrochloric acid and brine. The organic layer was dried over MgSO₄ and removed. The crude polymer was dissolved in a minimal amount of dichloromethane and precipitated into a rapidly stirring excess of methanol and the solid was collected by filtration. This process was repeated twice to obtain a dark yellow solid **P1** in 62% yield.



This polymer was prepared essentially in the same manner as described for **P1** just using **3** (185 mg, 0.55 mmol) instead of **2** for polymerization. A yellow powder was obtained by repeating precipitation from methanol in 55% yield.

The preparation of 1,4-diethynyl-2,5-bis(pentyloxy)benzene (**1**) was performed in four steps according to literature procedures^[39, 40], as shown in Scheme 1. The syntheses of 4-(2,5-dibromostyryl)aniline (**2**) and 1,4-dibromo-2-styrylbenzene (**3**) were outlined in Scheme 2 and Scheme 3, respectively. An isomeric mixture of 1,4-dibromo-[2-(4-nitrophenyl) vinyl]benzene (**9**) with *E*- and *Z*-conformations was prepared by Wittig reaction of **7** and 4-nitrobenzaldehyde (**8**), and then **9** was treated with stannous chloride to afford 4-[2-(2,5-dibromophenyl)vinyl]aniline (**2**). The reaction gave the *trans*-isomer as the major product, with *cis*-/*trans*- ratio 1:3 according to ¹H-NMR spectrum (Fig. S1). 1,4-dibromo-2-styrylbenzene (**3**) was prepared according to the similar synthetic procedures to **2** and the *cis*-/*trans*- ratio was 1:2 (Fig. S2). The conjugated polymers, **P1** and **P2**, were synthesized through the palladium-catalyzed Sonogashia coupling of **1** to **2** or **3**, respectively, in a mixture of toluene and diisopropylamine, as shown in Scheme 4. The yields of **P1** and **P2** were found to be 62% and 55%, respectively. Both polymers have high solubilities in THF and CHCl₃, which result from the attachment of long alkyl groups to the linear, rigid PPE backbones. The structures and photochemical behaviors of **P1** and **P2** were characterized by various spectroscopic measurements.

We characterized them by ^1H -NMR spectroscopy and infrared spectra. Figure S3 shows the ^1H -NMR spectrum of **P1** along with that of its diyne monomer **1**. The ethynyl protons of **1** resonate at δ 3.33, which are absent in the spectrum of **P1**, indicative of the coupling of monomers. Additionally, in comparison with the infrared spectra of the monomers, the peaks of that for **P1** at 1020 and 3268 cm^{-1} , respectively attributed to the vibrational bands of Ar-Br and acetylenic hydrogen were weakened, which also confirmed the formation of polymers (Fig. S4). Gel permeation chromatography (GPC) analyses show that the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of polymer **P1** were 11800 and 5600, respectively, with a polydispersity index (PDI) of 2.1. The degrees of polymerization (DP) of **P1** and **P2** are only 10 and 5

according to GPC measurements. The difference between two polymers is because amino groups increase the solubility of monomer and product in polymerization system, which is propitious to the propagation of chains. Such low values of DP and wide molecular weight distributions may be attributed to the low reactivity of brominated monomers and inaccuracy values determined by GPC measurements using flexible coiled polystyrene as standard^[41].

As shown in Fig. 1, the absorption spectra of the two polymers are almost the same and exhibit a maximum peak at 385 nm, which can be attributed to the π - π^* transition of polymer backbone. Both of the diluted THF solutions of **P1** and **P2** showed high intensities in the PL spectra; that is, the polymer is virtually luminescent when molecularly dissolved in its good solvent. The emission profile of **P1** is, however, wider than that of **P2** at *ca.* 525 nm, which is the result from the contribution of 4-vinylaniline as the pendant group to non-planarity with main chain. Okamoto *et al.* found that the intensity of emission of alkyl-substituted poly(*p*-phenyleneethynylene)s was strongly associated with the size and geometry of the side chain, which affected the torsion angle and the relative movement of the phenyl rings^[42].

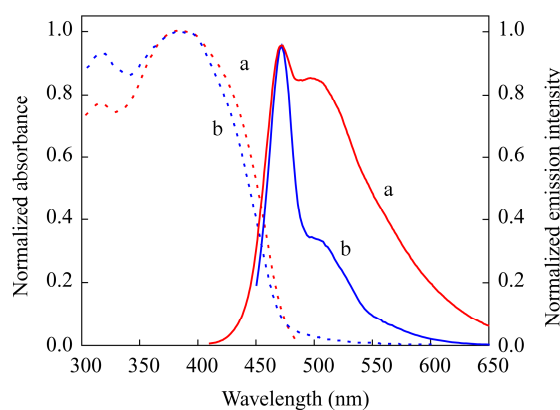


Fig. 1 Absorption (dotted line) and emission (solid line) spectra of **P1** (a) and **P2** (b) in THF

The PL behaviors of **P1** and **P2** were also investigated in the aggregate states. When large amounts of hexane were added into the solutions, **P1** and **P2** exhibited completely different behaviors under identical measurement conditions, as shown in Fig. 2. The fluorescence of **P2** was decreased while increasing the hexane fractions in the hexane/THF mixtures; in the meanwhile, the fluorescence of **P1** was astonishingly increased by up to 3 times magnitude (Fig. 2c). Because of the rigid molecular structures of both **P1** and **P2**, the polymer chains must have aggregated in the solvent mixtures even when only 10% of hexane is added. **P1** is thus enhanced of emission by aggregation while the emission of **P2** is quenched by aggregation; in other words, **P1** is AIEE active and **P2** is ACQ active. Compared with the analogue **P2** without amino group, the PL experimental results in THF reveal that 4-vinylaniline as the pendant group isn't co-planar with PPE main chain due to the existence of amino group. Adams reported that the amino group is only conjugated to be coplanar with aromatic ring containing a very strongly π -electron withdrawing centre^[43]. In our work, vinyl group at the para-position of aniline isn't a π -electron withdrawing group and can't induce the co-planarity between aniline pendant group and main chains, which increases the distance and restrains the π - π interactions between PPE chains. Moreover, the hydrogen bonds, which are about half normal strength, generated from interactions between the centre of a benzene ring and amino groups, play an important role in stabilizing protein structures^[44]. Therefore, we assume that the distance between the backbones of **P1** in the aggregation state is widened by the H-bonding interactions between amino groups at the side chains or between amino groups and the aromatic rings in the backbones. Consequently, the rotations of vinyl groups are restricted just like the phenyl groups in the backbones. Thus, the nonradiative decay pathways of both π - π interactions and intramolecular rotations in the aggregation state of **P1** have been suppressed, resulting in the appearance of AIEE behavior of **P1** in hexane/THF mixtures. Indeed, the

PL quantum yields for **P1** in the mixture of hexane/THF increased with increasing ratio of hexane/THF, as shown in Fig. 3, while the PL quantum yields for **P2** in the mixture of hexane/THF decreased with increasing ratio of hexane/THF. When hexane fraction reached ninety percent in the mixtures, the quantum yield of **P1** decreased a little due to disappearance of shoulder peak at 500 nm.

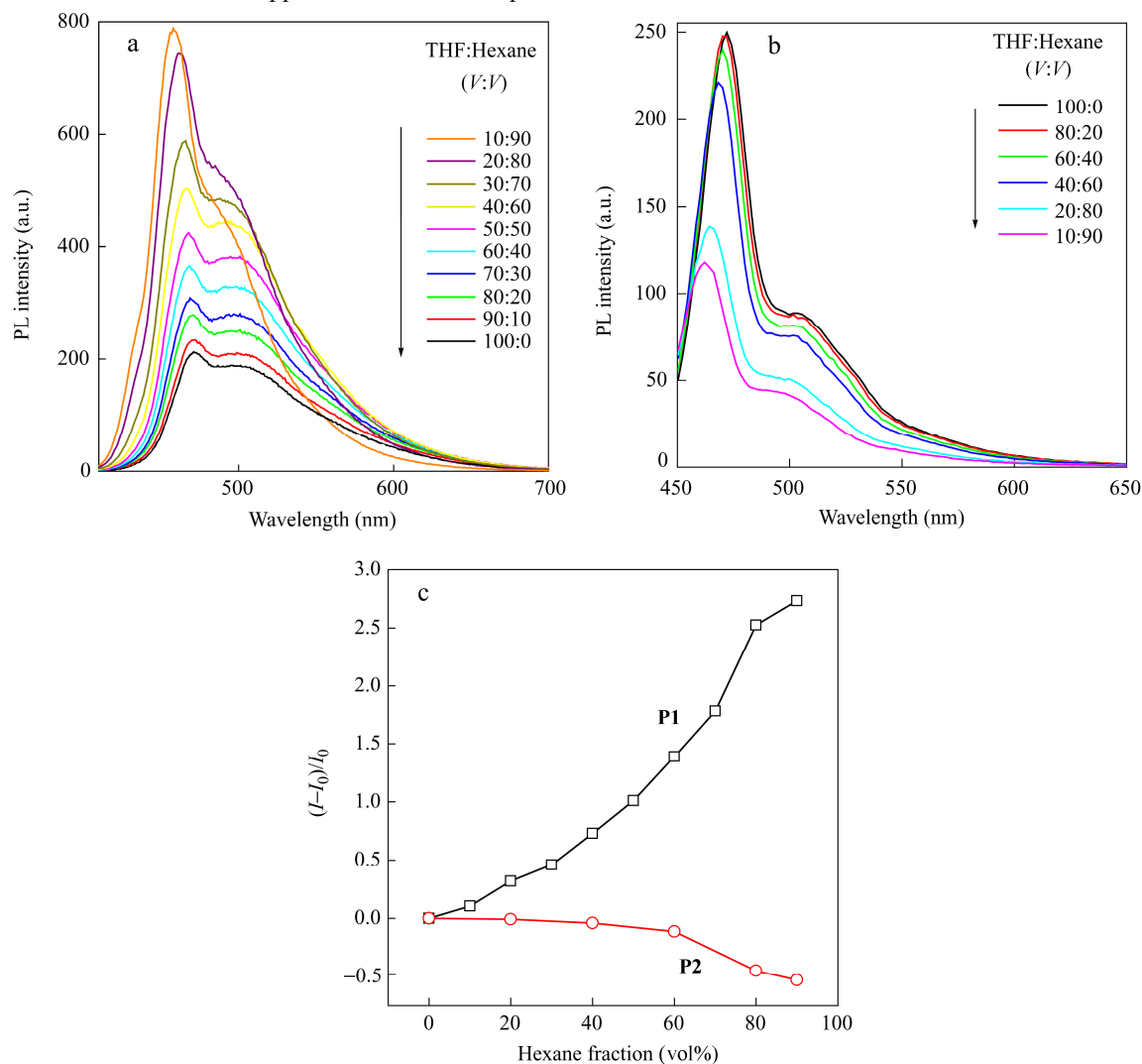


Fig. 2 PL spectra of (a) **P1** and (b) **P2** in THF/hexane mixtures and (c) their variation tendency line in PL intensity $[(I-I_0)/I_0]$
Polymer concentration: 1.0×10^{-5} mol/L; Excitation wavelength: 400 nm

To further confirm our assumptions, we studied the PL of **P1** in aggregation state by means of replacing of hexane by water or methanol. Similar to hexane, both water and methanol are non-solvents for **P1**, which cause aggregation of **P1** chains in the water/THF or methanol/THF mixtures, too. However, the solvent effect of water or methanol to **P1** chains is much stronger than that of hexane because the H-bonding interaction between water (or methanol) and amino group exists. Furthermore, the strength of $O-H \cdots N$ is more than two times stronger than that of $N-H \cdots \text{central benzene}$; in the meantime, the numbers of solvent molecules are much more than that of amino groups in **P1**, it is prospected that the amino groups will form H-bond with solvents molecules in both solvent and aggregation state^[45]. Thus, water or methanol molecules participate in the aggregation of **P1** chains during the precipitating process, which destroyed the H-bonding interactions between amino groups at the side chains or between amino groups and the aromatic rings in the backbones. Therefore, the moving ability of

main and side chains strengthened and the thermal-radiative efficiency of intramolecular rotations in the aggregation state of **P1** have been enhanced, resulting in the disappearance of AIEE behavior of **P1** in water/THF or methanol/THF mixtures, as shown in Fig. 4. So the formation of H-bonds between intermolecules or intramolecules is favorable for enhancing emission of PPEs.

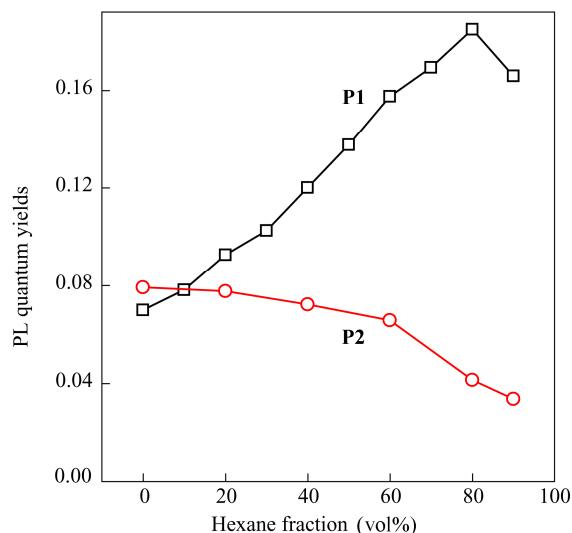


Fig. 3 PL quantum yields for **P1** and **P2** in THF/hexane mixtures using quinine sulfate in 0.1 mol/L H_2SO_4 (QY = 0.577) as the standard

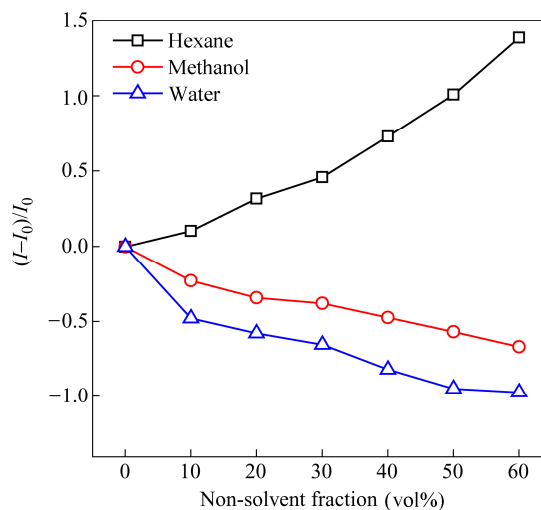


Fig. 4 Variation tendency line in PL intensity $[(I-I_0)/I_0]$ with increasing non-solvent fractions in the THF solution of **P1**
Polymer concentration: 1.0×10^{-5} mol/L

In summary, we have successfully prepared PPEs with 4-vinylaniline or styrene at the side chains by the Sonogashira coupling polymerization. By investigating the PL behaviors of polymers in both solution and aggregation state, we found that the formation of H-bond can effectively avoid the ACQ obstacle in the aggregation state of PPEs. It may offer a way to construct high performance optoelectronic devices. Further studies are under way in our research group.

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