

Recovery of PET-quenched Fluorescent Conjugated Polymers with Aza-15-crown-5 as Pendant Groups on Interaction with Ions^{*}

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Abstract Novel conjugated polymers with aza-15-crown-5 as pendant groups, **P1** were synthesized by the Sonogashira coupling reaction. The polymer **P1** was found to show fluorescence enhancement response towards Ba²⁺. The gradual recovery and turning-point of emission intensity of polymers appeared in the addition of Ba²⁺, which provided good evidence for the fluorescence amplification mechanism of conjugated polymers.

Keywords: Conjugated polymer; Fluorescence recovery.

INTRODUCTION

Conjugated polymer functional materials have been studied extensively during the past several years due to high photoluminescence and electroluminescence efficiency, good thermal/chemical stability, and good solubility in common organic solvents^[1, 2]. The electronic properties, such as fluorescence emission, of conjugated polymers also provide unique opportunities as chemosensory materials which is of remarkable practical importance in chemical, biological, and pharmaceutical sciences^[3–7]. Conjugated polymer sensory materials usually exhibited a great response to interactions with analytes, few analytes often caused the emission intensity of polymers sharply decreased.

The current mechanism explained that the delocalizable π -electronic conjugated polymer as ‘molecular wire’ could greatly amplify the fluorescence quenching due to the facile energy migration along the polymer backbone upon the light excitations (Fig. 1)^[8]. Thus, many ‘on-off’ fluorescent conjugated polymer sensors have been reported, and ‘off-on’ fluorescent conjugated polymer sensors are rare. Therefore, conjugated polymers are also called as amplifying fluorescent polymers, in fact, fluorescence quenching of the conjugated polymer is amplified.

Based on the above mechanism, we speculated that the amplified fluorescence quenching will happen if pendant groups contain a N atom which connects with the fluorescent conjugated polymer due to photo-induced electron transfer (PET)^[9], that is, the lone pair electrons on N atom may transfer to the main chain of conjugated polymer and may cause the fluorescence of whole polymer chain quenched. Recently, many small molecule PET

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chemosensors were reported, and the fluorescence could be recovered when N atom on chemosensor interacts with analytes, such as metal ions^[10, 11]. Thus, the PET-quenched fluorescence of the conjugated polymer may be recovered when it interacts with some species, however, there are few reports given. We also proposed that the PET-quenched fluorescence of the conjugated polymer will not thoroughly recovered until the last N atom on pendants interacts with analytes (Fig. 2).

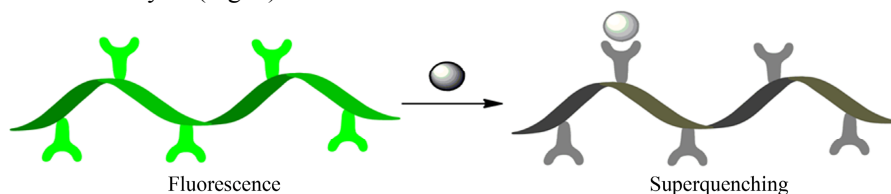


Fig. 1 Fluorescence superquenching mechanism of conjugated polymers

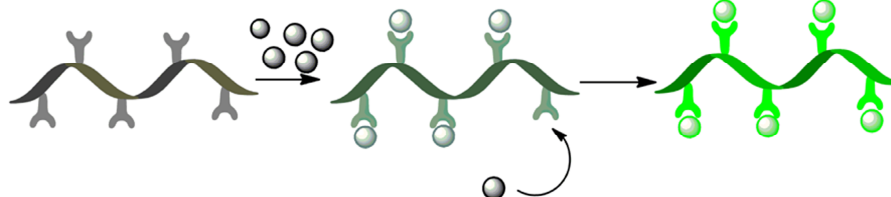
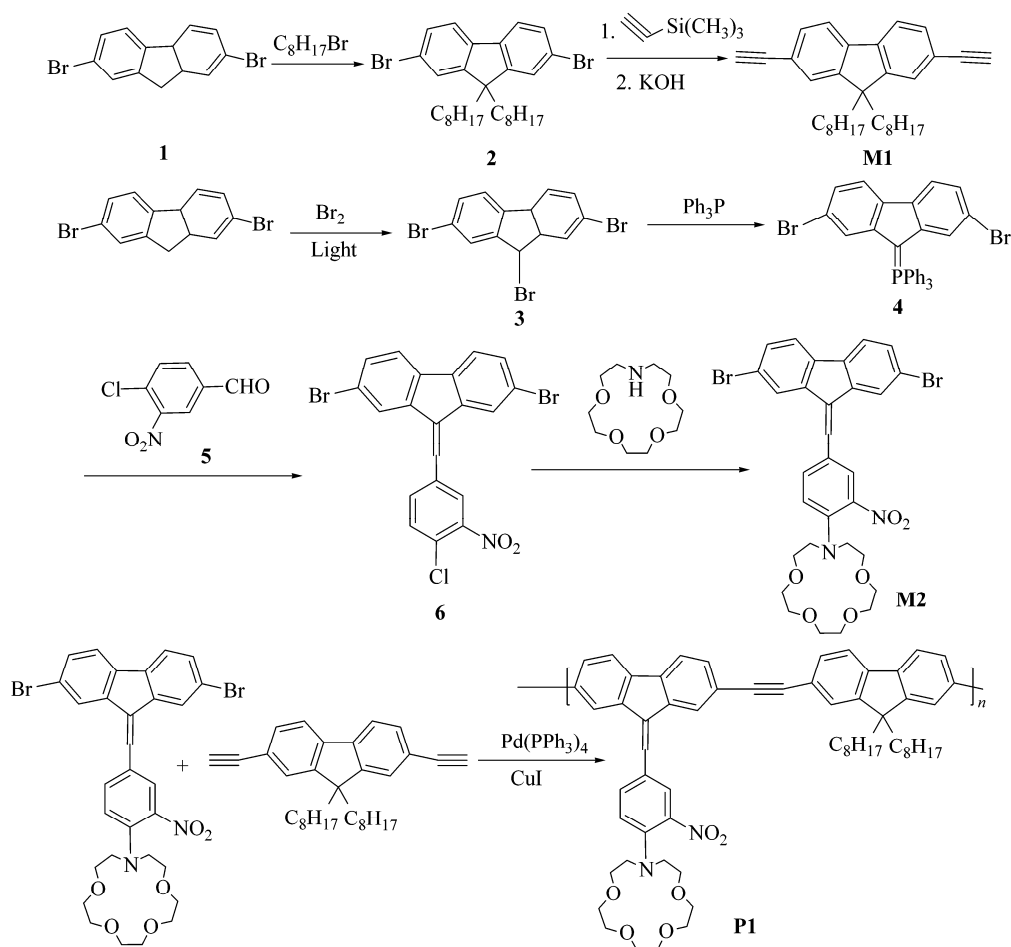


Fig. 2 Fluorescence recovery mechanism of conjugated polymers



Scheme 1 The synthesis procedures of the polymer **P1**

In order to test this idea, a conjugated fluorescent polymer with aza-15-crown-5 as pendant group (**P1**) was designed and synthesized (Scheme 1). The **P1** was found to show selectively and sensitively fluorescence enhancement response towards Ba^{2+} .

EXPERIMENTAL

Solvents and reagents used in the synthesis of chemosensory **P1** were purchased from Acros or Aladdin Reagent Company and used without further purification. All solutions of **P1** were prepared in THF without special efforts to exclude water or air. Both of absorption and fluorescence titrations were carried out with a concomitant addition of small volumes of metal ion aqueous solutions to THF solution of polymers. Analytical grade inorganic salts NaClO_4 , KClO_4 , MgCl_2 , CaCl_2 , $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MnSO_4 , CdCl_2 and $\text{Pb}(\text{NO}_3)_2$ were also purchased from the company.

^1H - and ^{13}C -NMR spectra measurements (all in CDCl_3) were recorded on a 400-Bruker spectrometer with TMS as an internal standard. UV-Vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer LS55 luminescence spectrometer with 10 nm excitation and emission slit widths. Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards.

Each metal ion titration experiment was started with 10.0 mL of polymer in THF solution with a known concentration (1.0×10^{-5} mol/L). Solutions of metal salt (2×10^{-3} mol/L) were used for titration. Polymer-metal complexes were produced by adding aqueous solution of the selected metal salt to a THF solution of the polymer. The mixture was stirred constantly during titration.

Preparation of 2,7,9-Tribromofluorene (**3**)

A mixture of 2,7-dibromofluorene (3.0 g, 9.3 mmol), *N*-bromosuccinimide (NBS) (1.8 g, 9.3 mmol) and CCl_4 (300 mL) was placed in a 1000 mL round bottom flask. The mixture was allowed to reflux and benzoyl peroxide was added as initiator. The mixture was irradiated with IR lamp for 30 min and was continued to reflux for 4 h with stirring. The product mixture was washed twice with dilute sodium bicarbonate, twice with water and once with saturated sodium chloride. The combined organic layer was dried with sodium sulfate, filtered and evaporated to give the crude product^[12]. The crude product was purified by column chromatography with hexane as eluent (56%). ^1H -NMR (CDCl_3 , δ): 5.90 (s, 1H), 7.54 (m, 4H), 7.76 (s, 2H). ^{13}C -NMR (CDCl_3 , δ): 43.6, 121.5, 122.1, 129.6, 132.5, 137.8, 145.8. Anal. Calcd. for $\text{C}_{13}\text{H}_7\text{Br}_3$: C, 38.75; H, 1.75; Br, 59.50. Found: C, 38.51; H, 1.81.

Preparation of 2,7-Dibromofluorene Triphenylphosphine Ylidene (**4**)

A solution of 2,7,9-tribromofluorene (**3**) (4.4 g, 11 mmol) and triphenylphosphine (3 g, 11.4 mmol) in 130 mL of dried toluene was stirred at reflux for 12 h. The reaction mixture was then allowed to cool to room temperature and the white precipitate was collected by filtration, repeatedly washed with dried ether and acetone to get the white solid. The crude product was dissolved in 50 mL ethanol and then refluxed for 10 min, 3.0 mL ammonia was added in and the reaction mixture was continued to reflux for 10 min, it was allowed to cool to room temperature and the white precipitate was collected by filtration and give yellow powder (97.5%)^[10]. ^1H -NMR (CDCl_3 , δ): 8.09 (s, 1H), 7.88 (s, 1H), 7.75 (d, 3H), 7.62–7.52 (m, 5H). ^{13}C -NMR (CDCl_3 , δ): 137.0, 135.7, 133.7, 132.6, 132.3, 132.2, 127.2, 126.2, 124.7, 124, 121.6, 121.4, 121.2. Anal. Calcd. For $\text{C}_{31}\text{H}_{21}\text{Br}_2\text{P}$: C, 63.72; H, 3.62. Found: C, 63.69; H, 3.66.

Preparation of 2,7-Dibromo-9-(4-chloro-3-nitrobenzylidene)-9H-fluorene (**6**)

4-Chloro-3-nitrobenzaldehyde (**5**) (0.7 g, 3.77 mmol) was added into a solution of 2,7-dibromo fluorene triphenylphosphine ylidene (1.9 g 3.24 mmol) in 15 mL of chloroform. After heating the orange solution under reflux for 3 h, the solvent was evaporated on the steam bath. The residual oil was purified by chromatography on silica gel, eluting with EtOAc-petroleum ether (1:1), to afford the orange oil product, yield 45%. ^1H -NMR (CDCl_3 , δ): 8.10 (s, 1H), 7.89 (s, 1H), 7.70 (d, 3H), 7.62–7.53 (m, 5H). ^{13}C -NMR (CDCl_3 , δ): 137.0, 135.7,

133.7, 132.6, 132.3, 132.2, 127.3, 126.2, 124.7, 124.0, 121.6, 121.5, 121.2. Anal. Calcd. for $C_{20}H_{10}Br_2ClNO_2$: C, 48.87; H, 2.05; N, 2.85. Found: C, 48.77; H, 2.09; N, 2.88.

Preparation of 13-(4-((2,7-Dibromo-9H-fluoren-9-ylidene)methyl)-2-nitrophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (M2)

To a stirred hexamethylphosphoramide solution of 2,7-dibromo-9-(4-chloro-3-nitro benzylidene)-9H-fluorene (0.6 g, 1.173 mmol), CuI (33.9 mg), *o*-phenanthroline (28.8 mg) and aza-15-crown-5 (0.71 g, 3.23 mmol) were added in sequence under N_2 protection. The reaction mixture was immersed in a 80 °C oil bath and stirred at this temperature for 24 h. After cooling to room temperature, the reaction mixture was diluted with 60 mL CH_2Cl_2 , washed with water, dried over Na_2SO_4 , and solvent was removed by vacuum. The residue was purified by chromatography on silica gel, eluting with EtOAc-petroleum ether (1:1), to afford 0.75 g yellow solid powder, yield 34%. ^1H -NMR ($CDCl_3$, δ): 7.92–7.41 (m, 10H), 3.81–3.51 (m, 20H). ^{13}C -NMR ($CDCl_3$, δ): 144.5, 141.1, 139.2, 137.7, 136.8, 133.8, 131.6, 131.2, 127.4, 127.1, 123.6, 121.4, 121.3, 121.2, 121.0, 120.0, 77.1, 70.6, 70.4, 69.2. Anal. Calcd. for $C_{30}H_{30}Br_2N_2O_6$: C, 53.43; H, 4.48; N, 4.15. Found: C, 53.48; H, 4.52; N, 4.10.

Polymerization

The synthesis of the copolymer **P1** was carried out using Pd-Cu-catalyzed coupling condensation^[11]. Carefully purified **M2** (1.0 mmol), **M1** (1.0 mmol), $(PPh_3)_4Pd$ (5 mol%) and CuI (5 mol%) were dissolved in a mixture of toluene and triethylamine (1:1). After the reaction mixture was refluxed in nitrogen for 48 h, it was filtered at room temperature to remove triethylammonium bromide precipitate. The salt was rinsed with THF, and the combined filtrates were evaporated till dryness. The residue was dissolved in a minimum amount of $CHCl_3$ and then poured into methanol to give a precipitate. The obtained solid was redissolved in $CHCl_3$ and reprecipitated from methanol, followed by Soxhlet extraction with the same solution for 24 h to give the polymers.

RESULTS AND DISCUSSION

The synthesis procedures of the monomers **M1**, **M2** and the conjugated polymers are outlined in Scheme 1. The monomer **M1**, 2,7-diethynyl-9,9-dioctylfluorene, could be synthesized from 2,7-dibromofluorene by a three-step reaction according to reported literature. 2,7,9-Tribromofluorene was obtained through bromination of 2,7-dibromofluorene with Br_2 under the radiation of IR lamp, which reacted with triphenylphosphine and treated with ammonia to afford 2,7-dibromofluorenetriphenylphosphineylidene. 2,7-Dibromo-9-(4-chloro-3-nitrobenzylidene)-9H-fluorene was obtained *via* Wittig reaction of the ylide with 4-chloro-3-nitrobenzaldehyde, and next it was treated with aza-15-crown-5 in the presence of catalyst CuI and *o*-phenanthroline to give monomer 13-(4-((2,7-dibromo-9H-fluoren-9-ylidene)methyl)-2-nitrophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**M2**) according to the literature. Compounds **M1**, **M2** could be served as the monomers for the synthesis of the conjugated polymers. In this article, a typical Sonogashira reaction condition was applied to the synthesis of the polymers. The polymerization was easily carried out by the monomers **M2** with **M1** in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI with Et_3N under N_2 , yield 76%, $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.74$.

We choose 13-(4-((9H-fluoren-9-ylidene)methyl)-2-nitrophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2H-M2**) as a monomer unit for the synthesis of **P1** because in our previous work: (1) **2H-M2** exhibits weak emission in acetonitrile solution, which should be attributed to PET process of N atom on aza-crown ether. Thus, the designed polymer, of course, will not give strong emission (fluorescence “OFF”) due to super-quenching. (2) It shows special capability of recognising for the divalent alkaline earths such as Sr^{2+} and Ba^{2+} and causes a great increase in the fluorescence intensity (fluorescence “ON”)^[15, 16]. The properties of **2H-M2** meet the requirements of designed polymer.

The UV-Vis absorption spectrum of the polymer is illustrated in Fig. 3. UV-Vis absorption of **P1** showed two absorption ($\lambda_{max1} = 276$ nm, $\lambda_{max2} = 378$ nm) at the region from 250 to 500 nm, the former was strong and the latter was broad, which could be attributed to the effective $\pi-\pi^*$ transition of conjugated structure of the polymers.

Fluorescence spectrum of **P1** is shown in Fig. 4 when excited at 378 nm. The polymer **P1** exhibited main emission band ($\lambda_{\text{max}} = 425$ nm) due to the extended π -electronic structure in the main chain backbone. As we expected, **P1** exhibits weak emission because the receptors of this polymer contains a relatively high-energy nonbonding electron pair of tert amino groups, which quench the fluorescence of the fluorophore by rapid intramolecular electron transfer (ICT) from the pendant to the excited main chain in the absence of coordinating analytes.

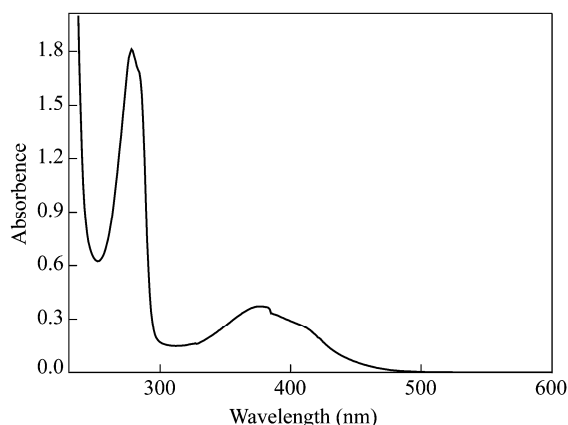


Fig. 3 UV-Vis absorption spectra of **P1**

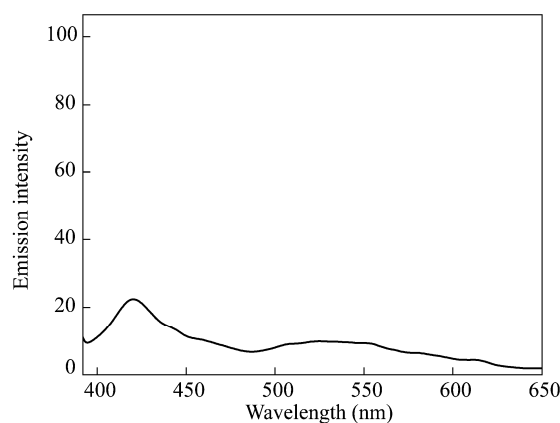


Fig. 4 Fluorescence spectra of **P1**

The fluorescence response behaviors of the polymer on various metal ions were examined, nearly no fluorescence intensity changes were observed in emission spectra with Na^+ , K^+ , Cd^{2+} , Mg^{2+} , Mn^{2+} , Hg^{2+} , Li^+ , Ca^{2+} and Sr^{2+} (100 eq.). However, under identical conditions, the fluorescence intensity of **P1** was all remarkably enhanced in the presence of Ba^{2+} (Fig. 5). The observed variations in the emission spectrum of **P1** with cations were believed to be due to the complexation of aza-crown pendant with metal cations. However, when the ionophores (aza-crown) of polymers were bound to cations (Ba^{2+}), the charge transfer of ICT process was not energetically favored, and thus, fluorescence was “switched on”.

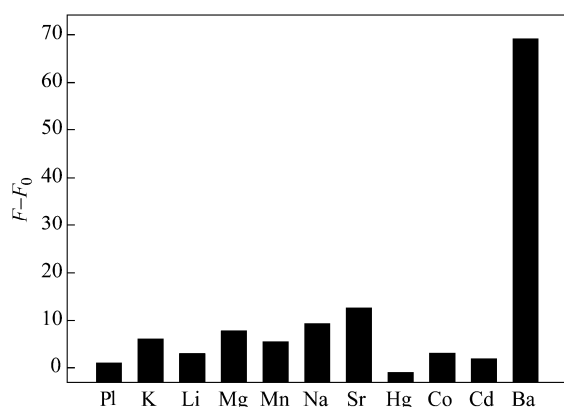


Fig. 5 Selectivity of **P1** to metal ions

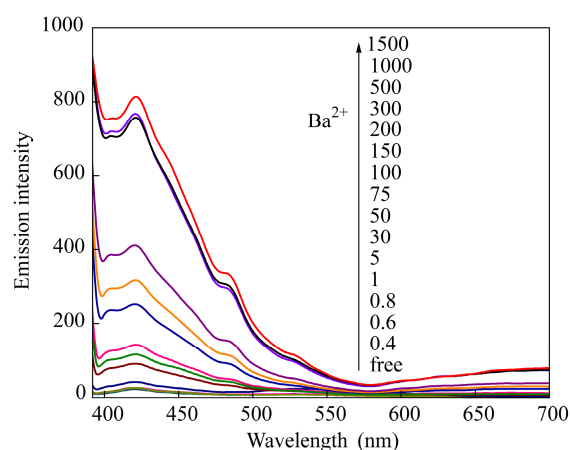


Fig. 6 Fluorescence titration of **P1** with Ba^{2+}

Figure 6 shows the results of fluorescence titration of **P1** with Ba^{2+} . When excited at 376 nm, the fluorescence emission intensity of **P1** around 450 nm was quite weak in the absence of Ba^{2+} ion (Off-state). However, emission intensity created a remarkable enhancement (On-state) on changing the concentration of Ba^{2+} from 0 to 1500 eq. The emission intensity was gradually increased with the addition of Ba^{2+} , a turning-point

appeared and emission intensity of **P1** was sharply increased to two times upon addition of Ba^{2+} from 300 to 500 eq., but there was little change observed over 500 eq. We could see there was a slight red shift of emission peak with the addition of Ba^{2+} . The detection limit of this sensor for Ba^{2+} was about 10^{-5} mol/L estimated from Fig. 6. The given results provided a good evidence for our assumption: the few uncomplexed recognition moieties on the polymers would not bring the complete recovery of fluorescence until all interact with Ba^{2+} , because PET process would be favored and extended to whole polymer chain from nitrogen atom of aza-15-crown-5.

CONCLUSIONS

The conjugated polymer **P1** with aza-15-crown-5 as pendant was synthesized by Pd-catalyzed Sonogashira reaction. The responsive properties of these polymers on various metal ions were investigated by fluorescence spectra. Compared with other cations, Ba^{2+} could produce pronounced fluorescence enhancement of these polymers, **P1** showed an obvious turning-point of fluorescence enhancement upon addition of Ba^{2+} and gave evidence for our assumption that the PET-quenched fluorescence of the conjugated polymer will not be thoroughly recovered until the last N atom on pendants interacts with analytes, which also affords a proof for the fluorescence amplification mechanism of conjugated polymers.

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