

Quenching of Water Soluble Conjugated Polymer by Electrostatic Interaction

Youngeup Jin

Department of Industrial Chemistry, Pukyong National University, Busan 608-739, Korea. E-mail: yjin@pknu.ac.kr
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The water-soluble conjugated polymer with fluorescence quenching as a result of electrostatic interaction and aggregation was synthesized through Suzuki polymerization. The absorption and emission of anionic polymer (**a-PFP**) is blue shifted as compared with cationic polymer (**c-PFP**) although getting same backbone, and the absolute PL quantum efficiency of **a-PFP** in water is over 90% due to good solubility in aqueous solution. We anticipate that the fluorescence quenching of anionic and cationic polymers, with same conjugated backbone, could be shown in aqueous solution.

Key Words : Anionic polymer, Quenching, Water soluble

Introduction

Fluorescent conjugated polymer (CPs) have emerged as an important class of sensory materials for chemical and biochemical targets.^{1,2} The high quenching sensitivity is attributed to a combination of energy and exciton migration within the excited polymer such that nonradiative decay at one or more trap sites can effectively compete with photoluminescence.^{3,4} Energy migration along this backbone is facile,^{5,6} allowing photoexcitations to ultimately reside in low-energy sites; for example, near an ionically bound acceptor molecule. Under these circumstances, very high quenching efficiencies can result from the efficient electron transfer from the excited state of the conjugated polymer to the lowest unoccupied molecular orbital of the acceptor.^{7,8} And, high quenching efficiencies also result from the interaction inside same backbone in ionic binding of cationic and anionic polymer.

The fundamental scientific discovery by Chen *et al.* is that the photoluminescence (PL) of a negatively charged PPV derivative in aqueous solution is quenched *via* photoinduced electron transfer,⁹ and it has been reported that dramatic enhancement of quenching when conjugated polyelectrolytes in solution are exposed to oppositely charged electron or energy acceptors.¹⁰⁻¹² In comparison to ionic polymer counterparts, the electronic structure of the conjugated polymer coordinates the action of a large number of absorbing units. The excitation energy along the whole backbone of the conjugated polymer transferring to the polymer with counter ion results in the amplified fluorescence quenching.^{13,14} We have conducted quenching studies using induced electrostatic interaction and aggregation by fluorescence quenching techniques with anionic and cationic polymer of same backbone in aqueous solution.

Several questions remain on how the polymer structure affects the photophysical processes of interest. In particular, addition of surfactant results in increased fluorescence quantum yields, but a reduced fluorescence quenching efficiency.¹⁵ It is not clear at this stage to what extent the enhan-

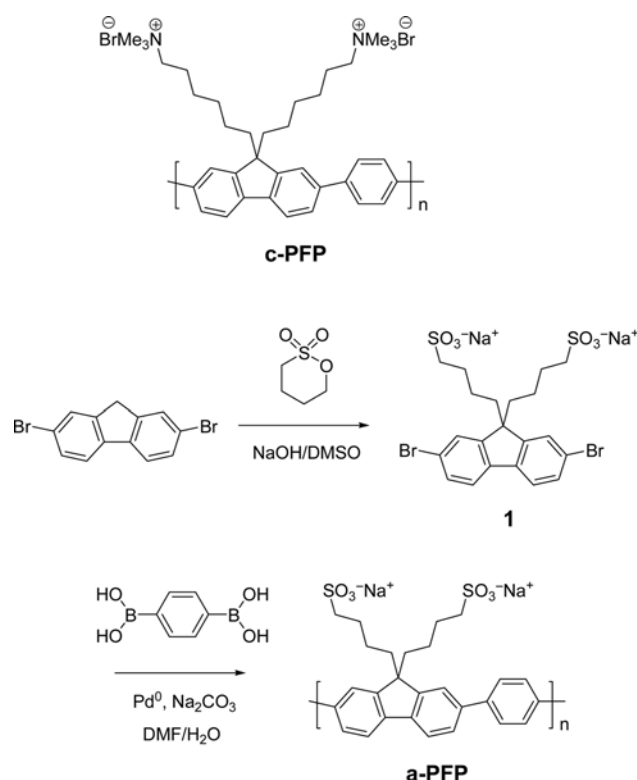
cement is due to changes in polymer coil dimensions or to aggregate polymer breakup. The contributions of intrachain energy transfer, interchain aggregation and association constants to K_{SV} with each polymer have yet to be fully deconvoluted. Furthermore, the statistical distribution of polymer chains, coupled to batch-to-batch variability, make a detailed correlation between polymer structure and optical performance difficult to obtain.

In this study, we report that water-soluble conjugated polymers, anionic poly(fluorene-*co-alt*-phenylene) (**a-PFP**) and cationic poly(fluorene-*co-alt*-phenylene) (**c-PFP**) having the conjugated polymer backbone of same structure, provides the basis to modify PL quenching by electron or energy transfer conditions. The induced **a-PFP** with Ca^{2+} cation by adding $Ca(OH)_2$ in **H-PFP** show fluorescence quenching like aggregation by electrostatic interaction of anionic and cationic polymer.

Results and Discussion

The anionic polymer, **a-PFP** was synthesized according to the procedures reported in Scheme 1. The monomer, 2,7-dibromo-9,9-bis(4-sulfonatobutyl)-fluorene disodium salt, was prepared by alkylation reaction of 2,7-dibromofluorene with 1,4-butane sultone in DMSO at 60 °C. The pure compound was collected by recrystallization from acetone/ H_2O twice in 44% yield. The final polymer was prepared by Suzuki polymerization of the monomer with 1,4-phenylene-bisboronic acid using $Pd(OAc)_2$ and sodium carbonate in DMF/water at 80 °C for 2 days. The reaction mixture was precipitated into acetone, re-dissolved in deionized water, and the resulting mixture was purified by dialysis (M_w 10,000 cut-off) for 3 days.

To test quenching efficiencies between anionic polymer and cationic polymer of same backbone, we introduced a cationic poly(fluorene-*co-alt*-phenylene) (**c-PFP**)¹⁶ and a anionic poly(fluorene-*co-alt*-phenylene) (**a-PFP**). In deionized water, at concentrations below 1×10^{-6} M (in repeat units, RUs), **a-PFP** and **c-PFP** get absorption maximum peaks



Scheme 1. Synthesis of the **a-PFP** and structure of the **c-PFP**.

predominantly in the 350–400 nm region and emit blue color. The absorption and emission of **a-PFP** is blue shifted as compared with **c-PFP** although getting same backbone. We propose that this blue shift should be concerned with solubility and PL quantum efficiency in water. The absolute PL quantum efficiency of **a-PFP** in water is over 90%, and this shows each **a-PFP** polymer backbone is not aggregated as polymer bundle like **c-PFP** due to good water solubility. Although the whole solubility of anionic polymer in water was increased due to good water solubility of side chain with metal cation, the backbone of aromatic structure having bad water solubility should be more twisted in water than in organic solvent, and the absorption and emission are blue shifted.

Aggregation induced in the mixture of **a-PFP** and **c-PFP** having the same conjugated polymer backbone to modify PL quenching by electron or energy transfer conditions. On the basis of well-known interpolymer interactions between oppositely charged polyelectrolytes,^{17–19} we anticipate that complexation of **a-PFP** and **c-PFP** in water would lead to contraction and aggregation of polymer chains, a concomitant reduction of intersegment distances, and more efficient electron or energy transfer between polymer chains. Figure 1 shows the absorption and emission from the mixture of **a-PFP** and **c-PFP** ([RU] is 1×10^{-6} M). Two kinds of polymer with same backbone get electrostatic interaction and fluorescence quenching is observed. Fluorescence quenching by aggregation between polymer backbone in the mixture of **a-PFP** and **c-PFP** isn't recovered although added HCl in order to take off electrostatic interaction.

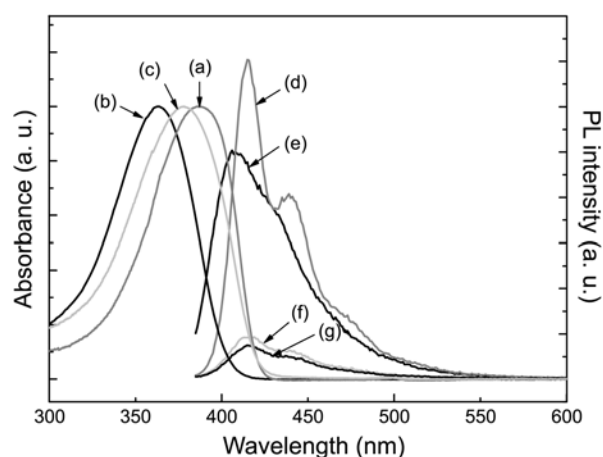


Figure 1. The absorption of (a) **c-PFP**, (b) **a-PFP** (c) mixture of **c-PFP** and **a-PFP** in water. Fluorescence emission spectra ($\lambda_{\text{exc}} = 380$ nm) of (d) **c-PFP**, (e) **a-PFP**, (f) mixture of **c-PFP** and **a-PFP**, (g) adding HCl in mixture of **c-PFP** and **a-PFP** in water.

The mixture of **c-PFP** and **H-PFP** (Na^+ of **a-PFP** exchange to H^+) has increased PL intensity because of non-electrostatic interaction. In this polymer mixture, if NaOH is added to have electrostatic interaction due to changing from **H-PFP** to **a-PFP**, fluorescence quenching is observed again. This also suggests that aggregation by induced electrostatic interaction should derive fluorescence quenching although having same polymer backbone.

Figure 2 shows the absorption and emission from **H-PFP** ([RU] = 2×10^{-5} M) solutions upon addition of $\text{Ca}(\text{OH})_2$ ($[\text{Ca}^{2+}]$ varies from 0 M to 8×10^{-6} M) in order to improve fluorescence quenching of same polymer backbone efficiently. The PL spectra of **H-PFP** as neutral polymer turn to fluorescence quenching after adding $\text{Ca}(\text{OH})_2$, because **H-PFP** turn to **a-PFP** due to OH^- ion and electrostatic interaction is induced by Ca^{2+} cation of dyad. The absorption, after adding $\text{Ca}(\text{OH})_2$ in **H-PFP**, is not changed because the precipitation by mixture of anionic polymer and Ca^{2+} cation of dyad is not produced. The PL spectra, after adding $\text{Ca}(\text{OH})_2$ in **H-PFP**, show decreasing just blue emission of 420 nm by induced aggregation in water. So, we postulate that induced electrostatic interaction in a kind of polymer make fluorescence quenching like aggregation by electrostatic interaction of anionic and cationic polymer.

To investigate the quenching ability of same backbone, the fluorescence quenching of **a-PFP** and **c-PFP** (1×10^{-6} M in repeat units (RUs)) was thus examined by induced electrostatic interaction in mixture. The quenching efficiency is related to the Stern-Volmer constant, K_{SV} , and is determined by monitoring measurable changes in the fluorescence *via* the Stern-Volmer equation. The Stern-Volmer plots of **a-PFP** and **c-PFP** are shown in Figure 3. By the way, K_{SV} in this quenching efficiency is not formed. The quenching efficiency should be proportioned to aggregation and aggregation could be related to electrostatic interaction by geometric progression. The aggregative interaction of **a-PFP** and **c-PFP** is induced after getting electrostatic interaction. We

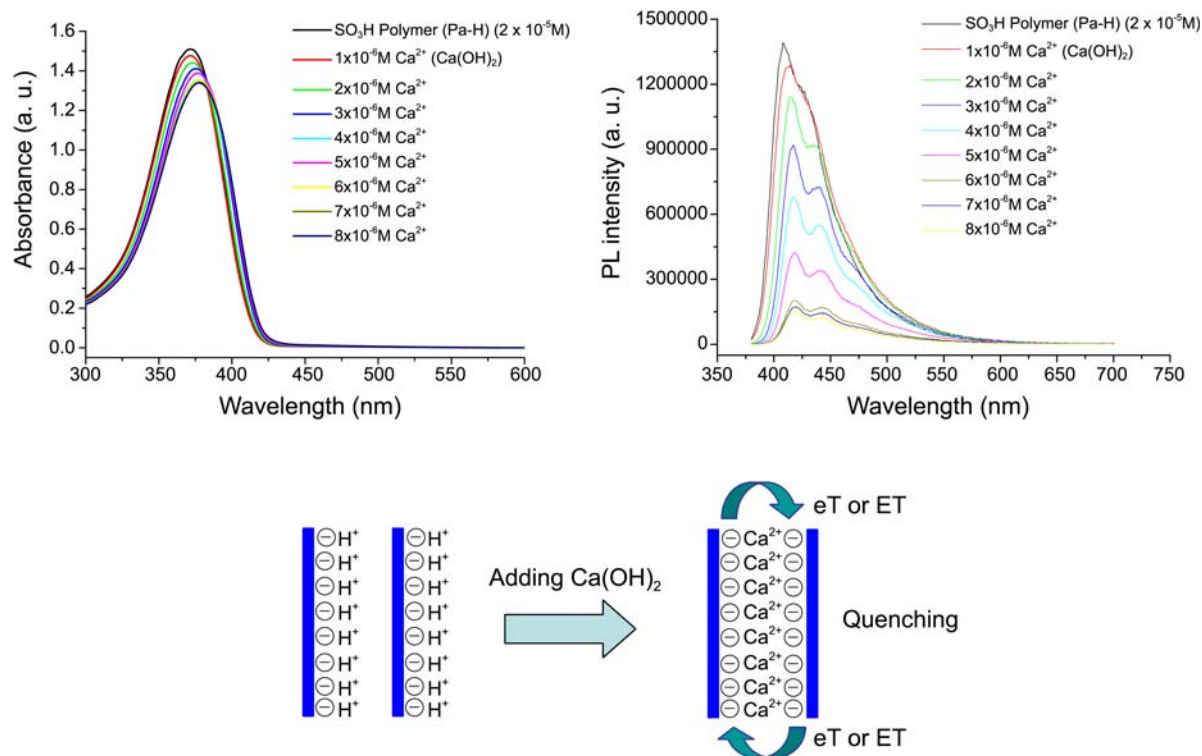


Figure 2. (a) Absorption and (b) Fluorescence spectra ($\lambda_{exc} = 380 \text{ nm}$) of adding $\text{Ca}(\text{OH})_2$ ($[\text{Ca}^{2+}]$ varies from 0 M to $8 \times 10^{-6} \text{ M}$) in **H-PFP** ($[\text{RU}] = 2 \times 10^{-5} \text{ M}$). (c) Fluorescence quenching assay of anionic polymer with Ca^{2+} ion.

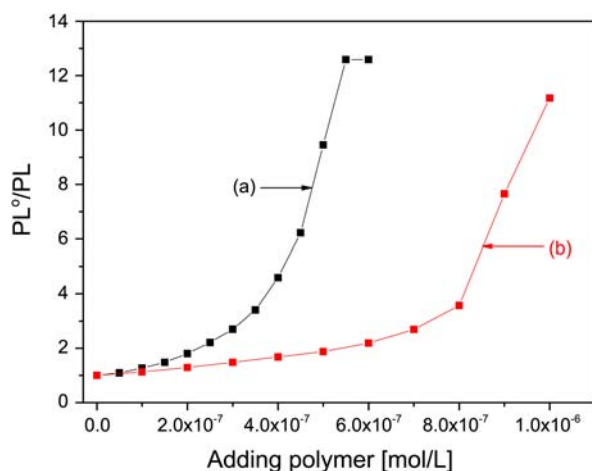


Figure 3. K_{sv} plot of **a-PFP** and **c-PFP** (a) Adding **a-PFP** ($1 \times 10^{-7} \text{ M}$) in the presence of **c-PFP** ($1 \times 10^{-6} \text{ M}$) (b) Adding **c-PFP** ($1 \times 10^{-7} \text{ M}$) in the presence of **a-PFP** ($1 \times 10^{-6} \text{ M}$).

postulate that **a-PFP** could get more electrostatic interaction with opposite charge than **c-PFP** although **a-PFP** and **c-PFP** possess same repeating units because each **a-PFP** polymer backbone is not aggregated as polymer bundle like **c-PFP** due to good water solubility. In case of adding **a-PFP** to bundles of **c-PFP**, fluorescence quenching increases more fast because many bundles of **c-PFP** could get electrostatic interaction with a chain of **a-PFP**. Adding a half of **a-PFP** can get aggregation with almost **c-PFP** and shows the maximum quenching efficiency, and adding another half of **a-PFP** keeps the maximum quenching efficiency. In case of

adding **c-PFP** to **a-PFP**, a small number of **a-PFP** could get electrostatic interaction with adding **c-PFP** because many cation is hidden inside a bundle of **c-PFP**, and fluorescence quenching increases more slowly.

Conclusion

We report that water-soluble conjugated polymer with fluorescence quenching as a result of electrostatic interaction and aggregation. The absorption and emission of **a-PFP** is blue shifted as compared with **c-PFP** although getting same backbone, and the PL quantum efficiency of **a-PFP** in water is over 90% due to good solubility in aqueous solution. Aggregation by induced electrostatic interaction of **a-PFP** and **c-PFP** having the conjugated polymer backbone of same structure provides the basis to modify PL quenching by electron or energy transfer conditions, and changing from **H-PFP** to **a-PFP** by adding NaOH should derive fluorescence quenching although having same polymer backbone. The induced **a-PFP** with Ca^{2+} cation by adding $\text{Ca}(\text{OH})_2$ in **H-PFP** show fluorescence quenching like aggregation by electrostatic interaction of anionic and cationic polymer. The amplified fluorescence quenching of anionic PFP and cationic PFP was employed with Stern-Volmer plots by geometric progression. Therefore, we anticipate that the fluorescence quenching of same conjugated backbone polymers could be shown in aqueous solution. Using this fluorescence quenching could lead to high efficient of the fluorescence amplification characteristic of conjugated polymers about same backbone in aqueous solution.

Experimental

Synthesis of 2,7-Dibromo-9,9-bis(4-sulfonatobutyl)-fluorene Disodium Salt (1). To a stirred mixture of 2,7-dibromofluorene (4 g, 12 mmol) and 60 mL of dimethylsulfoxide (DMSO) under nitrogen were added tetrabutylammonium bromide (80 mg) and 8 mL of a 50 wt % aqueous solution of sodium hydroxide. 20 mL DMSO solution of 1,4-butane sultone (4 g, 29 mmol) was added dropwise to the mixture. The reaction mixture was stirred at room temperature for 3 h and then the reaction mixture was precipitated into 500 mL of acetone. The resulting product was collected by filtration, washed with ethanol, and recrystallized twice from acetone/H₂O to yield (1) 4.3 g (58.6%) after drying in vacuum at 100 °C for 24 h. ¹H NMR (400 MHz, D₂O) δ 0.48-0.45 (m, 4H), 1.40-1.32 (m, 4H), 1.86-1.82 (m, 4H), 2.50-2.46 (m, 4H), 7.33-7.31 (d, 2H), 7.51-7.50 (d, 2H), 7.55 (s, 2H). ¹³C NMR (100 MHz, D₂O) δ 22.49, 24.33, 38.62, 50.85, 55.26, 121.30, 121.54, 126.55, 130.39, 138.91, 152.24.

Synthesis of Anionic Poly(fluorene-co-alt-phenylene) (a-PFP). To the mixture of 2,7-dibromo-9,9-bis(4-sulfonatobutyl)-fluorene disodium salt (1) (1.224 g, 1.81 mmol), 1,4-phenylenebisboronic acid (0.3 g, 1.81 mmol) and Pd(OAc)₂ (12 mg) was added a degassed mixture of 80 mL aqueous buffer (pH 10.0) and 30 mL DMF. The mixture was vigorously stirred at 80 °C for 48 h under argon atmosphere. After the mixture was cooled down to room temperature, it was poured into 1 L of acetone. The resulting precipitate was separated and re-dissolved in deionized water and dialyzed using a membrane with a 10,000-12,000 cutoff for 3 days. The final product was obtained after drying in vacuum at 110 °C for 24 h, yielding 0.46 g (44%) after dialysis. ¹H NMR (400 MHz, DMSO-*d*₆) δ 0.61 (m, 4H), 1.38 (m, 4H), 2.07-2.03 (m, 4H), 2.25-2.18 (m, 4H), 7.88-7.37 (m, 10H).

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