Enhanced Conjugated Polymer Fluorescence Quenching by Dipyridinium-Based Quenchers in the Presence of Surfactant

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Poly[(2-methoxy-5-propyloxysulfonate)phenylene vinylene] (MPS-PPV) was synthesized directly from its bischloromethylated monomer, considerably reducing the total number of steps involved in the polymer preparation. For the first time, a simple technique of ultracentrifugation was employed for final purification of the polymer. The interactions among the polymer, surfactant, and quencher molecules, as well as amplified fluorescence quenching and fluorescence enhancement associated with the interactions, were investigated and discussed. When compared with methyl viologen $[MV]^{2+}$, higher values of Stern−Volmer constant K_{SV} values on the order of $\geq 10^7$ M^{-1} were observed for the newly synthesized *N*-(2-carboxyhexadecanoyl)-*N*′-methyl-4,4′-bipyridinium iodide bromide ($[CHMB]^{2+}$) quencher in the presence of 1,2-dioleoyl-3- trimethylammonium propane (DOTAP) surfactant. Comparisons of surfactants demonstrated that the K_{SV} of $[CHMB]^{2+}$ was 10-fold higher in the presence of dodecyltrimethylammonium bromide (DTAB) surfactant than with DOTAP. Polymer fluorescence was totally recovered upon addition of DOTAP surfactant to a MV-quenched polymer system, whereas only 50% of fluorescence was recovered upon addition of DOTAP surfactant to the CHMB-quenched polymer solution. In contrast, no fluorescence was recovered when DTAB was added to either the MV- or CHMB-quenched polymer systems. Thus, fluorescence enhancement was observed for the polymer complex with DOTAP, whereas fluorescence quenching was predominant in the polymer complex with DTAB. Such studies will not only help to better understand the intrinsic properties of the ionic conjugated polymer and amplified fluorescence quenching and enhancement but also provide guidelines to develop the next generation of ionic conjugated-polymer-based biosensors.

Introduction

Fluorescence quenching involves deactivation of an excited molecule at an excited singlet state by long- or short-range interaction of the molecule with a quencher molecule.[1] The quenching efficiency is determined by a variety of factors including, for example, orientational and interactive (electron transfer, dipole−dipole, etc.) parameters. A quantitative measure of the fluorescence quenching can be achieved by determining the Stern−Volmer constant, K_{SV}:

$$I_0/I = 1 + K_{SV}[\text{quencher}]$$

where I_0 is the intensity of fluorescence in the absence of the quencher and I is the intensity of fluorescence in the presence of the quencher. The equation reveals that I_0/I increases in direct proportion to the concentration of the quenching moiety, and the constant K_{SV} defines the efficiency of quenching. When all other variables are held constant, the higher the K_{SV}, the lower the concentration of quencher required to quench the fluorescence.

Amplified fluorescence quenching is a phenomenon associated with conjugated polymers whose mechanism was first investigated by Zhou and Swager.[2] Upon photoexcitation of a conjugated polymer, the electrons from the valence band are excited to the conducting band, thus generating charge-separated electrons and holes. The fluorescence of a conjugated polymer comes from the radiative decay that results from recombination of the electrons and holes. Due to the conjugated nature of the polymer, the electrons can migrate along the polymer chains. Consequently, one quenching site can affect multiple excitation sites of the polymer, which leads to amplified fluorescence quenching.

Recently, Whitten and co-workers[3], Heeger and co-workers,[4] and several other groups[5] including our own[6] extended amplified fluorescence quenching to ionic conjugated polymers. By using oppositely charged quencher molecules, a Stern−Volmer constant (K_{SV}) as high as 10^8−10^{10} M^{-1} for quenching the fluorescence of an ionic conjugated polymer can be achieved. Virtually one quencher molecule was able to quench the fluorescence of an entire polymer chain.[6b] Although the mechanism remains under investigation, such an aggressively amplified fluorescence quenching (AAFQ) is believed to arise due to (i) quench-induced conformational change of the ionic conjugated polymer and (ii) extremely rapid exciton diffusion along the conjugated polymer chain to the quencher "trap site". Removing the quencher molecule from a quenched ionic conjugated polymer chain will result in resuming the fluorescence of the entire polymer chain. Such an amplification process has led to the development of a novel biosensor platform. Such sensors have the potential to detect targeted biomolecules (such as proteins, viruses, bacteria, spores, cells, microorganisms, antibodies, antibody fragments, nucleic acids and toxins) at subpicomolar range.[7]

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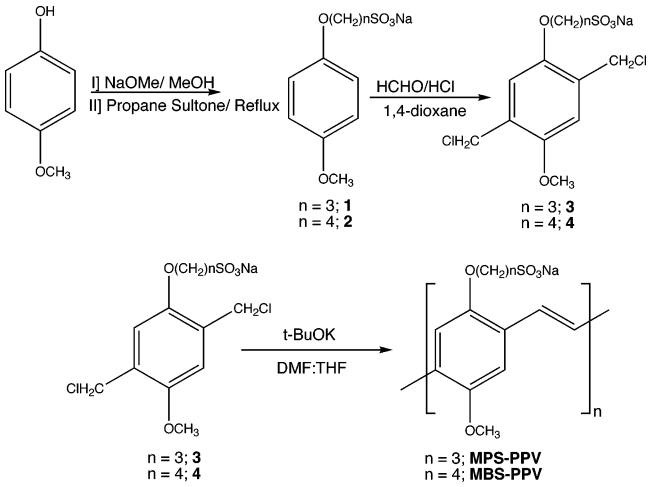
SCHEME 1: Synthesis of Polymer from the Bischloromethylated Monomer



On the other hand, it also has been demonstrated that the fluorescence of ionic conjugated polymers can be enhanced by interaction with certain surfactants[6a] and polyelectrolytes.[8] For example, the addition of small amounts of certain surfactant molecules (∼1−10 surfactant molecules/polymer chain) can enhance the fluorescence of an ionic conjugated polymer up to 10-fold.[6a] It is believed that the fluorescence enhancement is due to the formation of polymer−surfactant complexes, in which the polymer adapts an ordered conformation in the presence of surfactant, resulting in enhancement in the fluorescence intensity.[6a]

In this work, we explore the simultaneous interaction of ionic conjugated polymers with both quencher molecules and surfactant molecules and study the two competing processes of the polymer associated with fluorescence quenching (by quencher molecules) and fluorescence enhancement (by surfactant molecules). The ionic conjugated polymer used is MPS-PPV. For surfactants, we used DOTAP, which is well-known to retain its tendency to assemble in bilayers in solution, and DTAB, which has a tendency to aggregate in the micelle format. For quenching molecules, we used both a conventional quencher molecule, $[MV]^{2+}$, and a newly synthesized quencher, $[CHMB]^{2+}$ (Scheme 2). Key results include our demonstration that fluorescence quenching is predominant in the mixture of polymer, quencher, and DTAB, whereas the fluorescence enhancement is dominant in the mixture of polymer, quencher, and DOTAP. A possible mechanism associated with the observations has been discussed. Since amplified fluorescence quenching and enhancement is the key component for signal transduction, this study opens new avenues for designing the next generation of ionic conjugated-polymer-based biosensors.

Results

Synthesis of MPS-PPV. As indicated in Scheme 1, the MPS-PPV derivative was prepared in an anhydrous mixture of solvents *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) (1:1) via dehydrohalogenation of the corresponding bischloromethylated monomer **3** at 45 °C. Our initial attempts at using t-BuLi as a base led to the formation of oligomers. Polymerization was successfully carried out in the presence of an excess of t-BuOK for 2 days. The reaction was carried out in the absence of light to avoid any oxidation. After removal of the solvents, the crude product was first dialyzed against water by use of a Slide-A-Lyzer dialysis membrane with 10K molecular weight cutoff (MWCO) and then purified by crystallization (methanol). The purification was also carried out by using an ultracentrifuge operated at 100 000 rpm (435000*g*) for 2 h. The purified polymer was characterized by dynamic light scattering, capillary electrophoresis, and different spectroscopic techniques such as NMR, UV−vis, and fluorescence. Light scattering experiments revealed an average polymer mass of 21 kDa (Scheme 1).

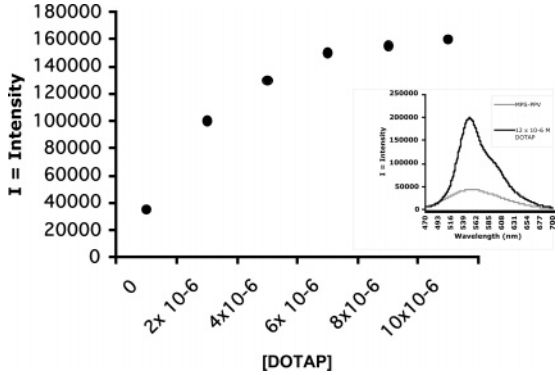
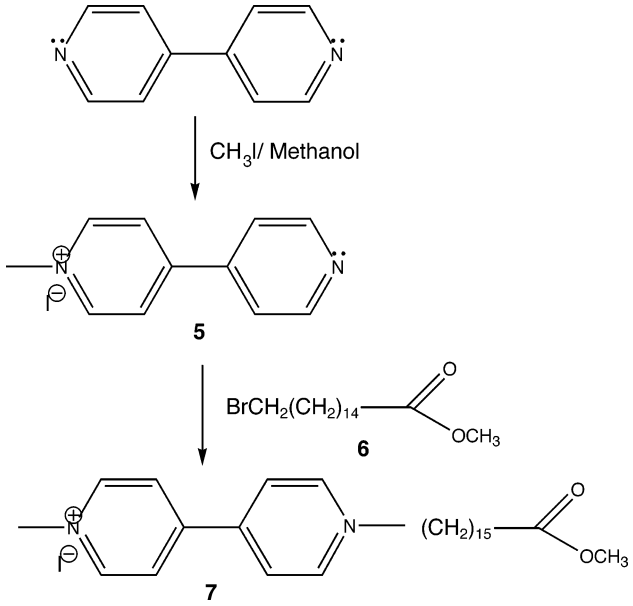


Figure 1. Fluorescence intensity of the polymer [MPS-PPV] = 10^{-5} M (in monomer repeat units) (excited at 450 nm) as a function of DOTAP concentration [2 μM, 4 μM, 6 μM, 8 μM, and 1 × 10^{-5} M]. Inset: Emission spectra of MPS-PPV in water and as its DOTAP complex.

SCHEME 2: Synthesis of Dipyridine-Based Quencher Molecule CHMB 7



Fluorescence of MPS-PPV in the Presence of Surfactant Molecules. MPS-PPV synthesized as described above is a reddish powder and is totally soluble in water. The UV−visible spectrum of the polymer in aqueous solution showed one major broad peak with maximum absorption around 470 nm. The emission spectra of an aqueous solution of MPS-PPV (λ_{em} = 569 nM) is shown in Figure 1 (inset). In contrast to previous reports,[6b] the fluorescence of MPS-PPV was independent of the excitation wavelength.

The addition of DOTAP to the MPS-PPV solution caused an enhancement in MPS-PPV fluorescence. Figure 1 demonstrates the increase in fluorescence intensity of MPS-PPV as the DOTAP concentration was increased. The enhancement effect was saturated when the polymer−DOTAP ratio reached 1:0.6, at which point the emission intensity of MPS-PPV was enhanced 5-fold. The inset of Figure 1 shows the emission

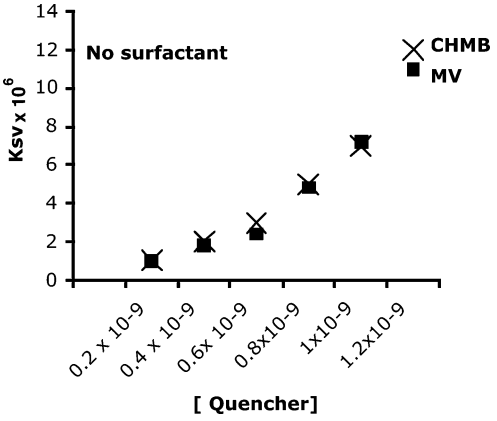


Figure 2. Stern−Volmer plots for quenching of the fluorescence (λ_{ex} = 450 nm) of MPS-PPV in aqueous solution without surfactant ([MPS-PPV] = 10^{-5} M). These measurements were used to calculate K_{SV} values.

spectra from a polymer solution with and without added surfactant (1:0.8 polymer surfactant ratio). A sharper peak with increased intensity and a slight blue shift was observed upon addition of surfactant. In addition, the presence of a shoulder at ~604 nm was noted when DOTAP was employed.

Fluorescence of MPS-PPV in the Presence of Quencher Molecules. The fluorescence of MPS-PPV can be quenched efficiently by both $[MV]^{2+}$ quencher and $[CHMB]^{2+}$quencher. As shown in Figure 2, the ratio of fluorescence intensities without quencher to the intensity with quencher [I_0/I] increased linearly with quencher concentration. The linear (static quenching) Stern−Volmer constant (K_{SV}) values obtained from the slopes of the fitted lines are 4.5×10^{10} for $[CHMB]^{2+}$ and 1.5×10^{10} for $[MV]^{2+}$. Results demonstrate that, in the absence of surfactant, $[CHMB]^{2+}$ is a slightly stronger quenching molecule than $[MV]^{2+}$, and both of them have similar K_{SV} within the same order of magnitude.

Fluorescence of MPS-PPV in the Presence of Surfactant and Quencher Molecules. To investigate the interactions among the polymer, quencher, and surfactant molecules, two sets of experiments were carried out. In the first set, the surfactant was added to the polymer solution to form the polymer−surfactant complex first, and then the behavior of the quencher against the complex was examined. In the second set, the fluorescence of the polymer was first quenched by quencher molecules, and then the surfactant was added to the quenched polymer solution. The behavior of surfactant against quenched polymer was examined.

i. Fluorescence Quenching for MPS-PPV−Surfactant Complex. Experiments were conducted where fluorescence quenching constants of quencher molecule against MPS-PPV−surfactant complex were measured as a function of surfactant concentration. In brief, DOTAP was added to the MPS-PPV solution (1×10^{-5} M). The resulting solution exhibited enhanced fluorescence compared to MPS-PPV itself due to the formation of the MPS-PPV−DOTAP complex (Figure 2). To this complex solution were added quencher molecules (2×10^{-9} to 1×10^{-8} M), and the Stern−Volmer quenching constant was determined. By varying the surfactant concentration, a quenching constant at each surfactant concentration was calculated. As demonstrated in Figure 3A, the quenching constants of both quencher molecules (CHMB and MV) against the polymer−DOTAP complex were plotted vs the concentration of DOTAP. Results show that $[CHMB]^{2+}$ quenched the fluorescence of the MPS-PPV−DOTAP complex with an average K_{SV} value of 2.5×10^7 M^{-1} with variations between 1.5×10^7 and 3.1×10^7 M^{-1}, while the average K_{SV} value for $[MV]^{2+}$ was 5×10^6 M^{-1} (Figure 3A). This implies that $[CHMB]^{2+}$ quenches the fluorescence of MPS-PPV−surfactant complex more efficiently compared to $[MV]^{2+}$. Similar experiments were also conducted with DTAB surfactant. As showed in Figure 3B, both $[MV]^{2+}$ and $[CHMB]^{2+}$ quenched the fluorescence of the MPS-PPV−DTAB complex with a similar K_{SV} value of 2×10^8 M^{-1}. It should be noted that the quenching constants obtained in the DTAB system were significantly higher (10-fold) than those for the DOTAP system, demonstrating a greater quenching efficiency of $[CHMB]^{2+}$ with DTAB than DOTAP.

ii. Fluorescence Enhancement for Quenched MPS-PPV. To further explore the interactions among the polymer, surfactant, and quencher molecules, a second set of complementary experiments were conducted. In this study, the fluorescence of MPS-PPV was first quenched by quencher molecules, and then the fluorescence enhancement of quenched MPS-PPV with different surfactants was determined. As shown in Figure 4B, no fluorescence enhancement was observed when DTAB was added to the CHMB-quenched polymer solution. In contrast, fluorescence of the CHMB-quenched polymer was enhanced about 50% when only 10^{-8} M DOTAP was added to the quenched polymer solution (Figure 4A). In the case where $[MV]^{2+}$ was used as the quencher molecule, no fluorescence enhancement was observed when DTAB was added to the MV-quenched polymer solution (Figure 4D). However, fluorescence was fully recovered when the same concentration of DOTAP (10^{-8} M) was added to the MV-quenched polymer solution (Figure 4C).

Discussion

Various substituted PPV derivatives have been produced either via a processible precursor polymer[9] or directly from the respective monomers.[10] In this work, we reduced the total number of steps involved in the synthesis of PPV derivatives to three by using sultones as a source of ionic side chain (Scheme 1). For polymer isolation and purification, we applied several protein purification methods, including dialysis and ultracentrifugation.

Although MPS-PPV has been used by many groups, to the best our knowledge, there is no detailed discussion about its synthesis directly from the monomer. Polymers obtained from polymer precursor routes may not be ideal, owing to the difficulties in achieving complete elimination of the labile groups, and also to the larger number of parameters affecting the conversion of the precursor to the conjugated material (pressure, duration, rate of temperature increase/decrease). Here the Gilch route[11] was adapted for synthesis of the polymer directly from its monomer. Results provided a simplified procedure for producing polymer with distinguished spectral characteristics.

So far, ultracentrifugation has been used mainly for the separation of proteins of different molecular mass, but for the first time we report the use of ultracentrifugation for the final purification of conjugated polymers, in place of crystallization. Based on the principle of molecular size, the ultracentrifugation technique offers separation for short times at very high speeds. At the end of 2 h of ultracentrifugation at 100K rpm, a purified polymer was conveniently obtained.

The interaction of MPS-PPV with counterionic surfactant DTAB has been studied previously. It was demonstrated that the interaction can make the polymer backbone ordered, eliminate the interchain interactions, and enhance the polymer fluorescence. As expected, fluorescence enhancement was also

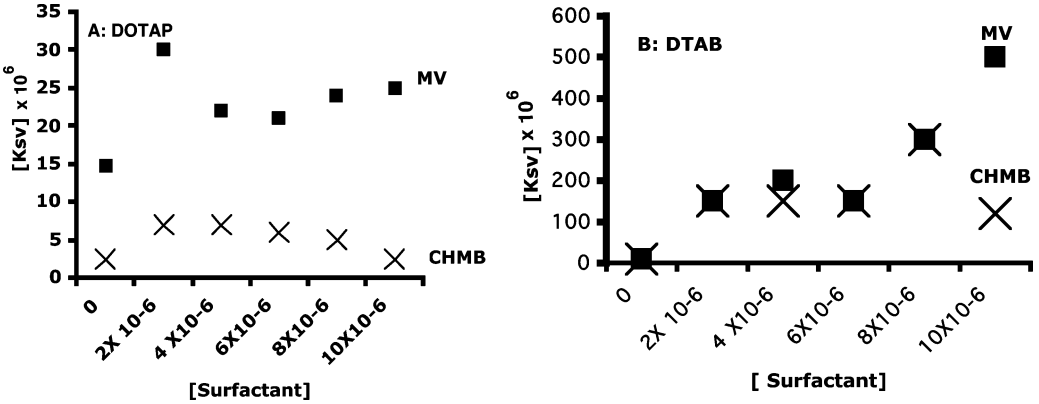


Figure 3. Quenching constant (K_{SV}) of $CHMB^{2+}$ and of MV^{2+} to MPS-PPV as a function of surfactant concentration ($\lambda_{ex} = 450$ nm): [MPS-PPV] $= 10^{-5}$ M; [quencher] $= (2-10) \times 10^{-9}$ M; (A) with DOTAP; (B) with DTAB.

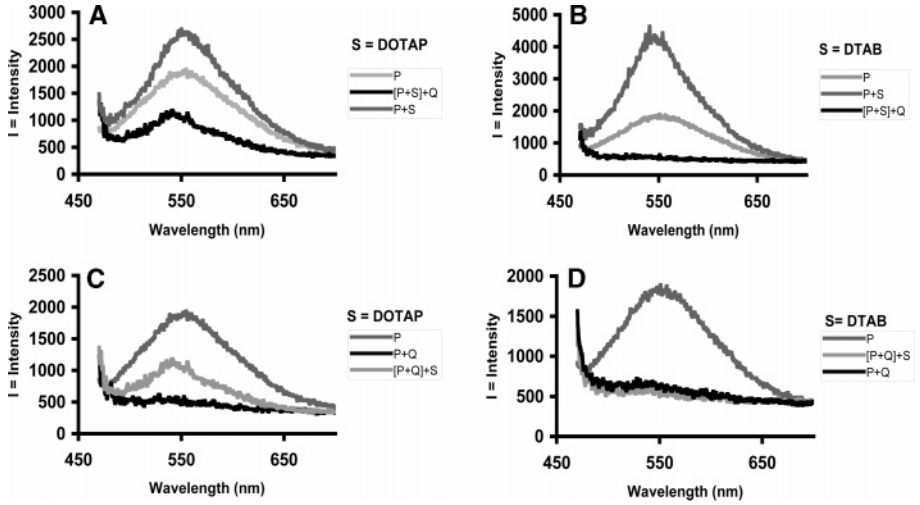


Figure 4. (A, B) Emission spectra of quenched MPS-PPV at different sequence of addition of surfactant (excited at 450 nm): [MPS-PPV) $= 10^{-5}$ M; [CHMB] $= 10^{-9}$ M; (A) [DOTAP] $= 10^{-8}$ M; (B) [DTAB] $= 10^{-8}$ M). (C, D) Emission spectra of quenched MPS-PPV at different sequences of addition of surfactant: [MPS-PPV] $= 10^{-5}$ M; [MV] $= 10^{-9}$ M; (C) [DOTAP] $= 10^{-8}$ M; (D) [DTAB] $= 10^{-8}$ M.

observed when DOTAP surfactant interacts with MPS-PPV (Figure 1). The formation of MPS-PPV−DOTAP complex serves to extend the MPS-PPV chains and inhibit the folding of the polymer chains, reducing the conformational disorder and increasing the fluorescence efficiency. This was confirmed by several spectral features, including a narrowed and slightly blue-shifted fluorescence spectrum, together with the emergence of vibronic structure (presence of a shoulder peak) in emission.

Although DOTAP and DTAB share the same ionic headgroup, the major difference between the two surfactants is that the critical micelle concentration (cmc) of DOTAP is significantly lower (7×10^{-5} M)[12] than the cmc of DTAB (3.8×10^{-3} M).[13] Thus, DOTAP has a much stronger tendency for self-assembling. DOTAP has been a popular transinfectant reagent for cross-membrane delivery of DNA molecules due to its ability to complex with polyanionic DNA and form self-assemblies around the DNA chain. Although the bulk surfactant concentrations were below the critical micelle concentration under the experimental conditions, due to the coulombic interaction between the polymer and surfactant, the local surfactant concentration near the polymer might be higher than the cmc, resulting in self-assembling of surfactant around the polymer chains. This would be especially true for the DOTAP molecules, and it may play an important role in the rationale for the interactions of polymer, surfactant, and quencher molecules.

The amplified fluorescence quenching of ionic conjugated polymers is believed to occur through two major mechanisms: (1) efficient energy or electron transfer between the polymer and quencher and within the polymer chain and (2) quencher-induced polymer conformational change, inducing interchain interactions and thus quenching of the polymer fluorescence. In both cases, the attachment of the quencher molecule to the polymer backbone is critical for polymer fluorescence quenching. Since $[CHMB]^{2+}$ shares the same electron donation core as $[MV]^{2+}$, comparable quenching efficiencies were observed in the absence of surfactant (Figure 2). In this case, both quenchers can attach to the polymer backbone via attractive electrostatic interactions. The trend for enhanced quenching efficiency of $[CHMB]^{2+}$ over $[MV]^{2+}$ in the presence of DOTAP (Figure 3) supports the hypothesis that DOTAP forms self-assembling structures that facilitate the interaction of $[CHMB]^{2+}$ with the polymer backbone due to hydrophobic interactions between the long aliphatic carbon tail of $[CHMB]^{2+}$ and the surfactant assemblies. This hydrophobic interaction would help $[CHMB]^{2+}$ to penetrate well through surfactant chains to reach the polymer chains. However, the situation for DTAB was quite different. Due to its high cmc, no obvious self-assembling of DTAB was observed. DTAB may spread more sparsely along the MPS-PPV polymer chain, explaining why both $[MV]^{2+}$ and $[CHMB]^{2+}$ showed similar quenching behavior against the MPS-PPV−DTAB complex. (Figure 3). This interpretation would also explain why the average quench-

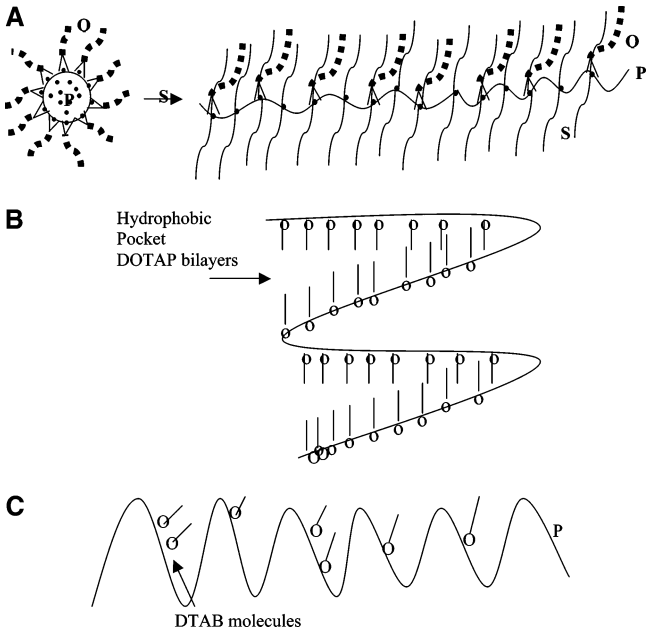


Figure 5. (A) Surfactant-induced conformational change (random coiled to an ordered form) associated with the polymer: Polymer partially covered by quencher in the presence of surfactant. (B) Polymer-bound DOTAP bilayers. (C) Randomly spread DTAB molecules along polymer chain.

ing constant values for both quenchers were 10-fold higher when DTAB surfactant was used compared to DOTAP surfactant. The self-assembling of DOTAP apparently shielded the interaction of quencher molecules with polymer.

Second, supportive data to indicate the self-assembly of DOTAP around the polymer chain came from the experiment in which surfactant was added to a quenched polymer solution. When the polymer fluorescence was quenched by $[MV]^{2+}$ or $[CHMB]^{2+}$, the addition of DTAB did not enhance the polymer fluorescence at all. On the other hand, DOTAP significantly enhanced the quenched polymer fluorescence in both cases (Figure 4). Since the DOTAP concentration used was very low (10^{-8} M), it is unlikely that the quenched molecules were detached from the polymer backbone. Thus, fluorescence quenching was predominant in the mixture of polymer, quencher molecule, and DTAB, while fluorescence enhancement played an important role in the mixture of polymer, quencher molecule, and DOTAP. As mentioned above, charge transfer between the polymer and quencher and quencher-induced conformational change are the two main fluorescence quenching pathways, and the surfactant-induced conformational change is the major fluorescence enhancement pathway. We propose that a change in polymer conformation due to the self-assembly of DOTAP, which leads to fluorescence enhancement, overwhelms the fluorescence quenching in the polymer−quencher−DOTAP system; whereas more efficient interactions of polymer and quencher molecules enable the dominates of polymer fluorescence quenching due to the lack of self-assembly of DTAB in low surfactant concentration conditions. A diagram depicting the proposed model of polymer−quencher−surfactant interactions is illustrated in Figure 5.

It should be noted that the MPS-PPV−DOTAP complex was very stable up to 70 °C. This property is supported by an experiment in which the quenching constant (K_{SV}) of $[CHMB]^{2+}$ to MPS-PPV (10^{-5} M) was determined as a function of temperature in the presence of DOTAP (10^{-7} M). K_{SV} values remained constant as the temperature was increased from 35 to 70 °C. The trend for temperature insensitivity of quencher action on the polymer−surfactant complex indicates that the electrostatic interaction between polymer and quencher, with surfactant present, remains unchanged over a wide range of temperature. This behavior clearly shows that no temperature-induced structural changes occur in the quenched polymer−surfactant complex and that the interaction of quencher with the polymer−surfactant complex is stable even at elevated temperatures.

Conclusion

MPS-PPV was successfully synthesized directly from its bischloromethylated monomer, considerably reducing the total number of steps involved in the polymer preparation. For the first time, a simple technique of ultracentrifugation was employed for final purification of the polymer. The interactions among the polymer, surfactant, and quencher molecules, as well as amplified fluorescence quenching and fluorescence enhancement associated with the interactions, were investigated and discussed. When compared with $[MV]^{2+}$, higher K_{SV} values ($\geq 10^7$ M^{-1}) were observed for the carboxylate ester $[CHMB]^{2+}$ **7** in the presence of DOTAP surfactant. Comparisons of surfactants demonstrated that the quenching constant of $[CHMB]^{2+}$ was 10-fold higher in the presence of DTAB surfactant than with DOTAP. Polymer fluorescence was totally recovered upon addition of DOTAP surfactant to a MV-quenched polymer system, whereas only 50% of fluorescence was recovered upon addition of DOTAP surfactant to the CHMB-quenched polymer solution. In contrast, no fluorescence was recovered when DTAB was added to either the MV- or CHMB-quenched polymer systems. Thus, in the competition between fluorescence enhancement (surfactant-induced conformational change associated with MPS-PPV) and fluorescence quenching (electrostatic interaction between polymer−quencher complex), fluorescence enhancement played a major role for the polymer complex with DOTAP, whereas fluorescence quenching was predominant in the polymer complex with DTAB.

Experimental Section

Materials. Chemicals were purchased from Aldrich and used as received. Fluorescence spectra were measured on a Photon Technology International fluorescence PTI system. ^{1}H NMR spectra were recorded on a Bruker (300 MHz) spectrometer. Electropherograms were run on a Beckman P/ACE system 5000.

Procedures: *Sodium 4-Methoxyphenoxypropane Sulfonate* (**1**). To a solution of methoxyphenol [2 g, 0.016 mol] in dry methanol [10 mL] was added NaOMe [0.87 g, 0.016 mol]. The mixture was allowed to stir for 2 h at 45 °C under N_2. Propane sultone [2 g, 0.0164 mol] was added to the mixture, which was then refluxed under an inert atmosphere for 2−3 h. After cooling, methanol was removed under reduced pressure. The product was recrystallized in methanol. Yield = 85%. ^{1}H NMR (D_2O): 1.9−2.00 (q, 2H), 2.4−2.6 (t, 2H), 3.6 (s, 3H), 3.9 (t, 2H), 6.78 (s, 4H).

Sodium 4-Methoxyphenoxybutane Sulfonate (**2**). A mixture of methoxyphenol (2 g, 0.016 mol) and NaOMe (0.87 g, 0.016 mol) was taken in 10 mL of dry methanol. After in situ generation of phenoxide ion as mentioned for **1**, butane sultone (1.5 mL, 0.015 mol) was added dropwise over 20 min. The reaction mixture was then refluxed for 2−3 h. After removal of solvent under reduced pressure, the product was then purified by recrystallization in methanol. Yield = 81%. ^{1}H NMR (D_2O): 1.87−1.89 (m, 4H), 2.97 (t, 2H), 3.8 (s, 3H), 4.1 (t, 2H), 7.00 (bifurcated s, 4H).

General Procedure Followed for Chloromethylation.[14] To dry 1,4-dioxane (5 mL) was added **1** (1 g, 3.73 mmol) or **2** (1 g, 3.54 mmol), followed by addition of concentrated HCl (0.5 mL). A slow stream of HCl(g) was allowed to pass through the reaction mixture. An aqueous formalin solution (40%) was added at 30 min intervals (3 × 0.3 mL), during which HCl(g) was allowed to pass. After completion of formalin addition, reaction mixture was stirred for another 3 h under HCl(g) atmosphere. Concentrated HCl (2 mL) was added into the ice-cooled reaction mixture. It was then allowed to stand overnight at room temperature, and the precipitated product was dried over KOH pellets in a vacuum desiccator. Chloromethylated product was used for polymerization without any further purification.

Sodium 2,5-Bis(chloromethyl)-4-methoxyphenoxypropane Sulfonate (**3**). Yield = 78%. ^{1}H NMR (D_2O): 2.15−2.25 (q, 2H), 3.1 (t, 2H), 3.82 (s, 3H), 4.1−4.2 (t, 2H), 4.62 (s, 4H), 7.3 (bifurcated s, 2H).

Sodium 2,5-Bis(chloromethyl)-4-methoxyphenoxybutane Sulfonate (**4**). Yield = 72%. ^{1}H NMR (D_2O): 1.8−2.0 (m, 4H), 3.00−3.1 (t, 2H), 3.88 (s, 3H), 4.1 (t, 2H), 7.15 (s, 2H).

General Procedure for Polymerization. The corresponding bischloromethylated monomer (**3** or **4**, 5 mmol) was taken into a 10 mL mixture of anhydrous DMF and THF (1:1). After vigorous shaking, THF solution of t-BuOK (0.05 mol) was added dropwise into the reaction mixture. It was allowed to stir for 2 days at 45 °C under an inert atmosphere. Precipitated polymer was purified by dialysis (10K MWCO). Average yield of purified polymers was found be 55%.

Poly([2-methoxy-5-propyloxy sulfonate]phenylene vinylene), MPS-PPV, and Poly([2-methoxy-5-butyloxy sulfonate]phenylene vinylene), MBS-PPV: λ_{em} = 565 nm when excited at 450 and 500 nm; 8.4 min retention time on capillary electrophoresis (borate buffer, pH 9.2, pressure injection 5 s, 20 kV] when compared with reference polymer, poly(sodium 4-styrene sulfonate) (∼70 K), with 9.1 min retention time, 22K molecular weight shown from light scattering experiment.

N-Methyl-4-(4′-pyridyl)pyridinium iodide (**5**) was synthesized according to the reported procedure.[15] Yield = 79%.^{1}H NMR (D_2O): 4.4 (s, 3H), 7.9 (d, 2H), 8.4 (d, 2H), 8.6−8.9 (m, 4H).

16-Bromohexadecanoic Acid Methyl Ester (**6**). To a solution of bromohexadecanoic acid (1 g) in methanol (22 mL) was added concentrated HCl (0.25 mL). The reaction mixture was refluxed for 4 h. After cooling, methanol was evaporated under reduced pressure. The DCM (20 mL) solution of obtained oil was three times washed with saturated Na_2CO_3solution. The organic layer was dried over $MgSO_4$ and then evaporated under pressure. The obtained colorless oil was dried under vacuum to give a solid, which was used without any further purification. NMR showed the absence of an acid peak. Yield = 81%.

N-(2-Carboxyhexadecanoyl)-N′-methyl-4,4′-bipyridinium Iodide Bromide (**7**). The mixture of *N*-methyl-4-(4′-pyridyl)-pyridinium iodide (0.46 g, 1.55 mmol) and 16-bromohexadecanoic acid methyl ester (0.5 g, 1.86 mmol) was taken in dry DMF (10 mL). It was heated under an inert atmosphere for 2 days at 95 °C. The obtained carboxylate ester was crystallized in methanol. Yield = 69%. ^{1}H NMR (D_2O): 1.25 (s, 3H), 2.3 (t, 2H), 2.75 (t, 7H), 2.92 (d, 6H), 3.45 (s, 3H), 3.62 (s, 3H), 4.85 (s, 3H), 9.00−9.1 (m, 4H), 9.6 (d, 2H), 9.7 (d, 2H).

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