

Communications

Complexation of Anionic Conjugated Polyelectrolyte with Cationic Surfactant

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Introduction

In recent years, conjugated polymers have been a target of intensive investigation for application in a variety of areas such as light-emitting diodes, organic transistors, and sensors etc.¹⁻⁸ In particular, water-soluble conjugated polyelectrolytes have been widely recognized as biological and chemical sensors for specific targets such as ions, proteins, and nucleic acids.⁹⁻¹⁹ Several studies have shown that the fluorescence of conjugated polyelectrolytes can be efficiently quenched by ionic species such as methyl viologen (MV^{2+}) with extremely high sensitivity. The Stern-Volmer constants (K_{SV}) for MV^{2+} quenching of poly(2,5-methoxypropyloxy sulfonate phenylene vinylene) (MPS-PPV) and sulfonated poly(phenylene ethynylene) (PPE- SO_3^-) in water range from 10^7 to $10^9 M^{-1}$.^{19,20} The mechanism for the efficient quenching was proposed to be due to a combination of efficient exciton migration within the polymer chain and a rapid charge transfer quenching between the polymer and MV^{2+} .^{19,21} The efficient fluorescence quenching of conjugated polyelectrolytes provides a basis for a new class of sensitive biological and chemical sensors.²²

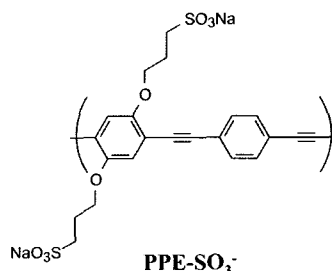
Chen *et al.* demonstrated that optical and chemical properties of the polymer can be controlled by combining the anionic conjugated polyelectrolyte, MPS-PPV, with a cationic surfactant dodecyltrimethyl-ammonium bromide (DTA).^{21,22} They showed, by studying the quenching behavior of MV^{2+} , that the conjugated polymer associated with the surfactant has different geometric conformation from that of the free polymer, which can hinder the self-aggregation of the polymer chain in water.

In this work, based on the fluorescence quenching study, we report on the complexation characteristics of the anionic

conjugated polyelectrolyte, PPE- SO_3^- , with the cationic surfactant, tetraoctylammonium bromide (TOAB).

Results and Discussion

The anionic conjugated polymer, PPE- SO_3^- was prepared based on a literature procedure.²⁰ The M_n value of PPE- SO_3^- was estimated to be 62,000 ($M_w/M_n=1.4$) based on the GPC analysis.



The polymer-surfactant complexes were prepared by adding an aqueous solution of TOAB (10^{-4} - 10^{-5} M) into an aqueous solution of PPE- SO_3^- (10^{-4} - 10^{-5} M in repeating units) at 50 °C.

The absorption and PL spectra of PPE- SO_3^- and the PPE- SO_3^- -TOAB complexes are shown in Figure 1. The absorption maximum of PPE- SO_3^- in aqueous phase in the absence of TOAB appeared at 440 nm, and the emission maximum at 530 nm ($\lambda_{ex} = 440$ nm). The emission spectra of PPE- SO_3^- were not affected by the excitation wavelength. However, the emission spectra of MPS-PPV were strongly dependent on the excitation wavelength due to a heterogeneous distribution of independent emitters, *i.e.* a distribution of conjugation lengths or chain conformations for MPS-PPV in solution.²² This result suggests that the conformation of the PPE- SO_3^- chain is more uniform than that of MPS-PPV.

The PL spectra of the polymer-surfactant complexes were

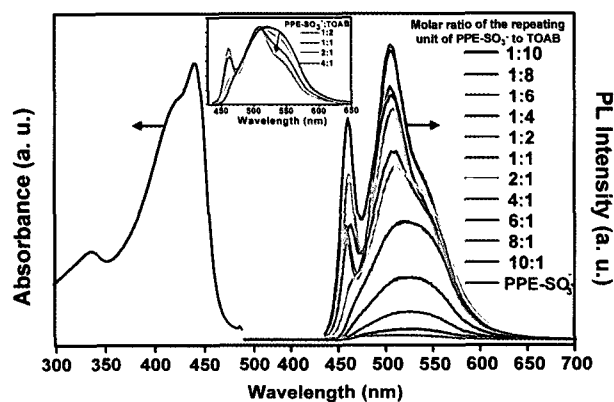


Figure 1. Absorption and PL spectra of PPE- SO_3^- depending on the TOAB concentration.

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highly affected by the concentration of TOAB. Addition of TOAB to an aqueous solution of PPE-SO₃⁻ induced a blue shift with increase of PL intensity. When the molar ratio of the repeating unit of PPE-SO₃⁻ to TOAB, [PPE-SO₃⁻]:[TOAB], was in the range of 10:1-1:1, the emission maximum was blue-shifted from 530 to 510 nm with the increase of PL intensity. When the ratio of [PPE-SO₃⁻]:[TOAB] became 1:2, the blue shift in the emission spectra became saturated, suggesting that the complex formation of polymer-TOAB is in a steady state.^{21,22} The complex at this stage is stable for months without any precipitation. The MPS-PPV-DTA complex forms precipitates when the ratio of MPS-PPV to DTA becomes 3:1.²² These results suggest that PPE-SO₃⁻ forms stable complexes with TOAB. In addition, upon forming the PPE-SO₃⁻-TOAB complex, the surfactant molecules on the polymer chain play an important role in suppressing self-aggregation between the chains of PPE-SO₃⁻ to induce blue shift of the emission spectra, while the chains of PPE-SO₃⁻ without TOAB are strongly aggregated in water.

A cationic surfactant with short alkyl groups such as tetrabutylammonium bromide (TBAB) shows little effects on the fluorescence characteristics of PPE-SO₃⁻ itself in water possibly because butyl moiety is not long enough to wrap the polymer chain. Therefore, the aggregated chains of PPE-SO₃⁻ could not be dissociated even in the presence of TBAB.

In addition to hindering self-aggregation of PPE-SO₃⁻ chains in aqueous solution, the complex formation of PPE-SO₃⁻ with TOAB can protect the polymer chain from the penetration of quencher MV²⁺, so that the PPE-SO₃⁻-TOAB complexes suppress the fluorescence quenching of PPE-SO₃⁻ by MV²⁺. The fluorescence intensity of PPE-SO₃⁻ in water decreases with increasing the concentration of MV²⁺ as shown in Figure 2 indicating that the fluorescence of the PPE-SO₃⁻, in the absence of TOAB, can be efficiently quenched by MV²⁺.²⁰ The Stern-Volmer constant (K_{SV}) for

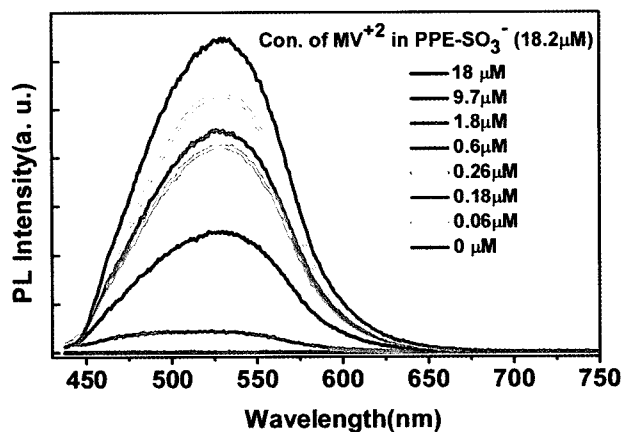


Figure 2. PL spectra of PPE-SO₃⁻ (18.2 μM) depending on concentration of MV²⁺.

MV²⁺ quenching of PPE-SO₃⁻ (18.2 μM) was $3.4 \times 10^6 \text{ M}^{-1}$. The efficient quenching is due to a combination of efficient exciton migration within the polymer chain and electron transfer from the polymer to MV²⁺.¹⁹⁻²² However, Figure 3 (a) and (b) show that the MV²⁺ quenching of PPE-SO₃⁻ is remarkably suppressed when the PPE-SO₃⁻-TOAB complexes are formed. Compared with the MV²⁺ quenching of PPE-SO₃⁻ in the absence of TOAB as shown in Figure 2, the fluorescence of the complexes with [PPE-SO₃⁻]:[TOAB] ratio of 1:2 (Figure 3(a)) and 1:1 (Figure 3(b)) was much less quenched by MV²⁺. The quenching constant ($K_{SV} \sim 3.4 \times 10^6 \text{ M}^{-1}$) of PPE-SO₃⁻/MV²⁺ is decreased to $1 \times 10^5 \text{ M}^{-1}$ and $8 \times 10^4 \text{ M}^{-1}$, respectively with [PPE-SO₃⁻]:[TOAB] ratio of 1:1 and 1:2. These results indicate that the polymer chain of PPE-SO₃⁻ becomes more effectively wrapped by TOAB with increase of TOAB concentration, so that the penetration of MV²⁺ to the chain of PPE-SO₃⁻ would be hindered. Therefore, a remarkable decrease of the fluorescence quenching is observed as the concentration of TOAB increased, which indicates that the optical and chemical properties of the conjugated polyelectrolyte can be controlled with suitable surfactants.

We also observed that the quenched fluorescence of PPE-SO₃⁻ by MV²⁺ in water was entirely recovered when TOAB was added into the solution of PPE-SO₃⁻ and MV²⁺ in which the quenching was pronounced as shown in Figure 2. Figure 3(c) and (d) show that the quenched fluorescence of PPE-SO₃⁻ was recovered by adding TOAB, and the degree of recovery was more pronounced with increasing the concentration of TOAB. In addition, the recovered fluorescence has similar spectral structure and intensity of PPE-SO₃⁻-TOAB complexes with MV²⁺ shown in Figure 3(a) and (b), respectively. These results suggest that the formation of the PPE-SO₃⁻-TOAB complex is much more favorable than that of PPE-SO₃⁻-MV²⁺.

In summary, the anionic conjugated polyelectrolyte, PPE-SO₃⁻, forms stable complexes with a cationic surfactant, TOAB. Upon forming the polymer-surfactant complex in water, the surfactant molecules on the polymer chain play an important role in suppressing the self-aggregation between the chains of conjugated polymers, while PPE-SO₃⁻ chains are self-aggregated in the absence of TOAB. In addition, the formation of polymer-surfactant complex protects the conjugated polymers from the fluorescence quenching by a cationic quencher (MV²⁺) in aqueous solution because the surfactant molecules wrap the chain of PPE-SO₃⁻ and the polymer-surfactant complex is stable. When TOAB was added into the aqueous solution of PPE-SO₃⁻ and MV²⁺, the fluorescence of the polymer was entirely recovered due to a strong preference for forming the polymer-surfactant complex. The interaction of conjugated polyelectrolytes with surfactant molecules remarkably affects the photonic characteristics of the conjugated polymers in aqueous phase. This approach is expected to provide a unique route to a

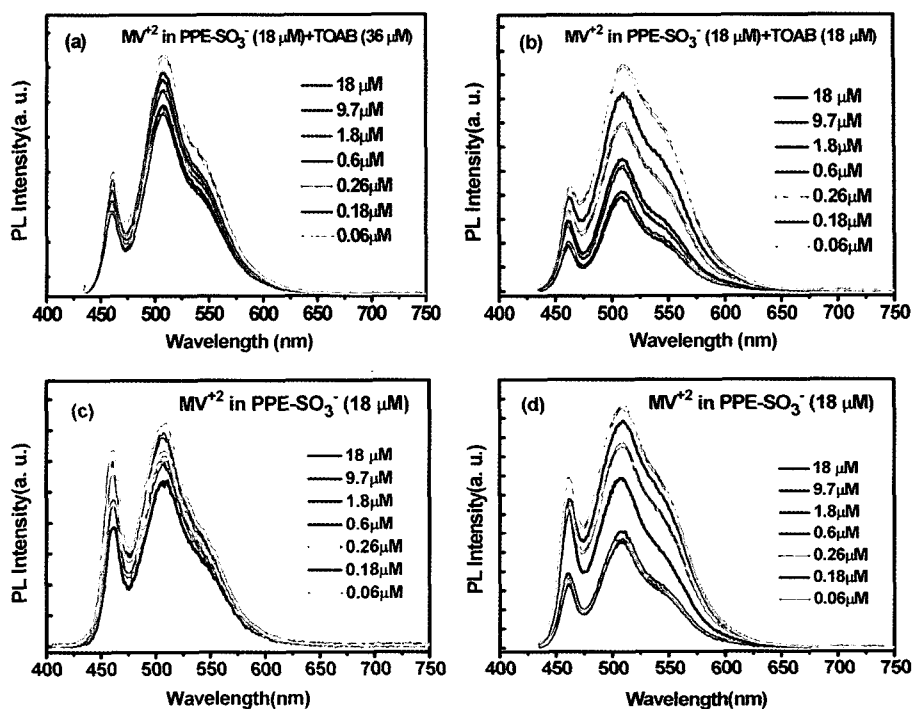


Figure 3. PL spectra of PPE-SO₃⁻ TOAB complexes in water after adding MV²⁺. Molar ratio of repeating unit of PPE-SO₃⁻ to TOAB was (a) 1:2 and (b) 1:1. PL spectra of PPE-SO₃⁻/MV²⁺ in water after adding TOAB. Molar ratio of repeating unit of PPE-SO₃⁻ to TOAB was (c) 1:2 and (d) 1:1 concentration.

new class of biological or chemical sensor application.

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References

- (1) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).
- (2) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).
- (3) F. Hide, M. A. Díaz-Gracia, B. J. Schwartz, and A. J. Heeger, *Acc. Chem. Res.*, **30**, 430 (1997).
- (4) A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.*, **37**, 402 (1998).
- (5) K. M. Coakley and M. D. McGehee, *Chem. Mater.*, **16**, 4533 (2004).
- (6) H. E. Katz, Z. Bao, and S. L. Gilat, *Acc. Chem. Res.*, **34**, 359 (2001).
- (7) D. T. McQuade, A. E. Pullen, and T. M. Swager, *Chem. Rev.*, **100**, 2537 (2000).
- (8) B. Liu, and G. C. Bazan, *Chem. Mater.*, **16**, 4467 (2004).
- (9) N. DiCesare, M. R. Pinto, K. S. Schanze, and J. R. Lakowicz, *Langmuir*, **18**, 7785 (2002).
- (10) S. A. Kushon, K. D. Ley, K. Bradford, R. M. Jones, D. McBranch, and D. Whitten, *Langmuir*, **18**, 7245 (2002).
- (11) D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan, and A. J. Heeger, *Proc. Natl. Acad. Sci.*, **99**, 49 (2002).
- (12) S. Kumaraswamy, T. Bergstedt, X. Shi, F. Rininsland, S. Kushon, W. Xia, K. Ley, K. Achyuthan, D. McBranch, and D. Whitten, *Proc. Natl. Acad. Sci.*, **101**, 7511 (2004).
- (13) M. R. Pinto and K. S. Schanze, *Proc. Natl. Acad. Sci.*, **101**, 7505 (2004).
- (14) P. S. Heeger and A. J. Heeger, *Proc. Natl. Acad. Sci.*, **96**, 12287 (2000).
- (15) R. M. Jones, T. S. Bergstedt, D. W. McBranch, and D. G. Whitten, *J. Am. Chem. Soc.*, **123**, 6726 (2001).
- (16) S. A. Kushon, K. Bradford, V. Marin, C. Suhrada, B. A. Armitage, D. McBranch, and D. Whitten, *Langmuir*, **19**, 6456 (2003).
- (17) H.-A. Ho and M. Leclerc, *J. Am. Chem. Soc.*, **126**, 1384 (2004).
- (18) D. T. McQuade, A. H. Hegedus, and T. M. Swager, *J. Am. Chem. Soc.*, **122**, 12389 (2000).
- (19) L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson, F. Wudl, and D. G. Whitten, *Proc. Natl. Acad. Sci.*, **96**, 12287 (1999).
- (20) C. Tan, M. R. Pinto, and K. S. Schanze, *Chem. Commun.*, 446 (2002).
- (21) L. Chen, D. McBranch, R. Wang, and D. Whitten, *Chem. Phys. Lett.*, **330**, 27 (2000).
- (22) L. Chen, S. Xu, D. McBranch, and D. Whitten, *J. Am. Chem. Soc.*, **122**, 9302 (2000).