

Synthesis of a New Conjugated Polymer Based on Benzimidazole and Its Sensory Properties Using the Fluorescence-Quenching Effect

Ho Wook Choi,¹ Youn Suk Kim,¹ Nam Choul Yang,^{2,*} Dong Hack Suh¹

¹School of Chemical Engineering, Hanyang University, Haengdang-1-Dong, Seongdong-Ku, Seoul 133-791, Korea

²Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 400-600, Korea

Received 3 February 2003; accepted 21 June 2003

ABSTRACT: A new anionic conjugated polymer containing a fluorene group in the main chain was designed and synthesized from poly(2,7-(9,9'-dihexylfluorene)-5,5'-bibenzimidazole) (PFBI). The polymer showed strong blue emission with high quantum efficiency (0.64) at 450 nm in MeOH and the dramatic quenching effect by Methyl Viologen (MV²⁺). The fluorescence-quenching effect results from the weak complex formation between an anionic polymer and

electron acceptors such as bipyridinium derivatives. The linear Stern–Volmer constant (K_{sv}) was $3.7 \times 10^5 \text{ M}^{-1}$ for MV²⁺. The newly synthesized polymer is expected to show the applicability for biological and chemical sensors. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 900–904, 2004

Key words: conjugated polymer; polybenzimidazole; fluorene; fluorescence; sensors

INTRODUCTION

Fluorescent conjugated polymers have been one of the most attractive research fields for their varieties of applications such as light-emitting displays, laser diodes, fluorescent polarizers, and sensors.^{1–4} Nowadays, they are attracting great interest as sensory materials due to their high sensing efficiency and thermal stability, facile processibility based on small molecules.⁵ Remarkable advance in researches in biological and chemical sensors have been achieved recently, Chen et al.⁶ proposed a novel biosensor system using the quenching effect of fluorescent conjugated polymers. They demonstrated that the fluorescence of water soluble polymers such as PPV derivatives is quenched by *N,N'*-dimethyl-4,4'-bipyridinium (MV²⁺, Methyl Viologen) via the photoinduced electron transfer. Due to the weak complex formation between the anionic polymer and the cationic quencher, when the quencher is linked to a specific ligand such as biotin, the quenched fluorescence can be fully recovered by using a quencher-recognition protein such as avidin. This can be applied to highly sensitive biosensors in fields such as toxicology, medical diagnostics, etc.

Although many PPV derivatives have been studied and have shown great development in fluorescence-based sensors, they still have several problems and

limitations such as low fluorescence and quenching efficiencies. For application of the sensors to detect small quantities of biomolecules—in monitoring diseases like cancers and blood analytes with real time—new highly sensitive materials having improved optical properties were beginning to make their necessity felt. Hence, to fulfill these requirements, the fluorene group was introduced into benzimidazole. Polyfluorenes represent the major class of highly blue-light-emitting conjugated polymers. Its 9-position offers the improved solubility and processibility.⁷ To our knowledge, the sensors using polybenzimidazoles have been rarely reported.

In this work, a new sulfonated polybenzimidazole having a fluorene group in the main chain (PFBI-SO₃⁻) was designed and synthesized by the direct sulfonation of the polymer poly(2,7-(9,9'-dihexylfluorene)-5,5'-bibenzimidazole) (PFBI). The synthesized polymer will be expected to exhibit improved optical properties such as a good emission color, high fluorescence quantum efficiency, and thermal stability. Details of the characteristics, optical and sensory properties of the polymer will also be discussed.

EXPERIMENTAL

Materials

9,9-Dihexylfluorene-2,7-dicarboxylic acid was prepared according to the previously reported procedure.^{8,9} All chemical reagents were supplied by Aldrich (USA), TCI (Japan), Acros (Belgium), Junsei (Japan), and Samjun (Korea). They were used without

*Present address: Samsung SDI LTD. 482-5, Gongse-Ri, Kiheung-Eup, Yongin-City, Gyeonggi-Do 449-902, Korea.

Correspondence to: D. H. Suh dhsuh@hanyang.ac.kr)

further purification. For the NMR measurement, methyl sulfoxide- d_6 (DMSO- d_6 , Aldrich, 99.9%), formic- d acid (DCO₂H, Aldrich, 98%) and methyl- d_3 alcohol- d (CD₃OD, Aldrich, 99.8%) were used as received.

Synthesis

Synthesis of PFBI

3,3'-Diaminobenzidine tetrahydrochloride (0.18 g, 0.5 mmol) was dehydrochlorinated in phosphorus pentoxide/methanesulfonic acid (PPMA) (5 mL) at 110°C for 2 h under a dry nitrogen flux. Then 9,9-dihexylfluorene-2,7-dicarboxylic acid (0.21 g, 0.5 mmol) was added and the solution was heated to 130°C for 3 h under a positive nitrogen flow with stirring. The resultant viscous solution was poured into a diluted NaOH solution, filtered off, and washed with water and methanol several times. For further purification, the precipitation was carried out from a formic acid solution into methanol/triethylamine several times and then dried at 80°C in a vacuum. Yield, 0.27 g (98%); IR (KBr, cm^{-1}), 3,500–3,000 (broad, N—H in imidazole), 2,919 and 2,850 (aliphatic C—H), 1,616 (C=N in imidazole); ¹H-NMR (DCO₂H, ppm), δ 8.08–8.60 (12 H), 2.42 (4 H), 1.14 (16 H), 0.78 (6 H).

Synthesis of PFBI-SO₃⁻

PFBI (0.0594 g, 0.1 mmol) was dissolved in purified *N*-methyl-2-pyrrolidinone (NMP) (9 mL) and allowed to stir at room temperature for 10 min. In an argon filled glovebox, NaH (0.04 g, 1 mmol) was slowly and carefully added to the solution and then, the mixture was stirred at room temperature for 3 h under a positive nitrogen flow. Purified 1,3-propane-sultone was added to the solution and the solution was stirred at room temperature for 6 h under a positive nitrogen

flow. The resulting polymer was precipitated by pouring it into an excess of distilled diethyl ether. Then the precipitate was filtered and washed with acetone and diethyl ether several times and dried at 100°C in a vacuum. Yield, 0.059 g (>70%); IR (KBr, cm^{-1}), 3,500–3,000 (broad, N—H in imidazole), 2,925 and 2,854 (aliphatic C—H), 1,615 (C=N in imidazole), 1,046 (S=O in N-alkyl chain); ¹H-NMR (CD₃OD, ppm), δ 7.80–8.38 (12 H), 3.64 (4 H), 3.49 (4 H), 2.42 (4 H), 2.01 (4 H), 1.14 (16 H), 0.78 (6 H).

Measurements

¹H-NMR spectra were obtained using a Varian VXR-300 FT-NMR spectrometer, referenced to tetramethylsilane (TMS, Acros, 99.9+%) as an internal standard.

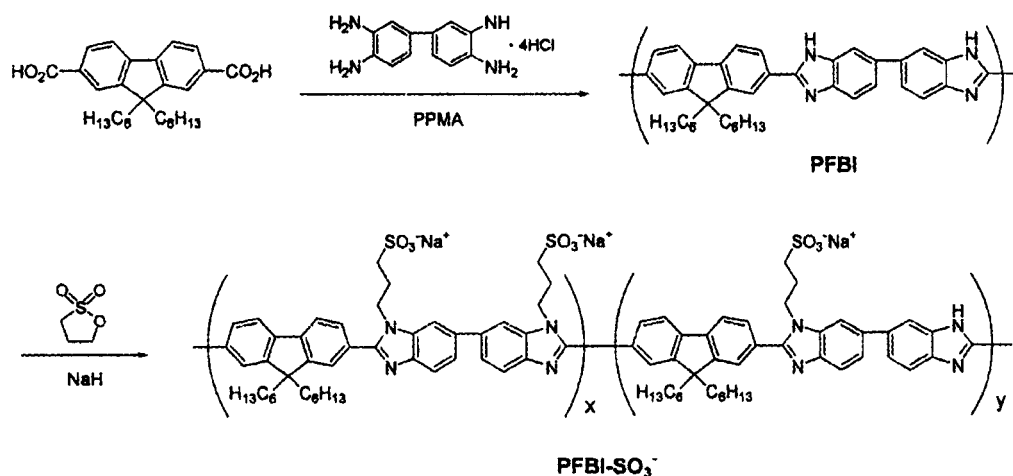
FT-IR spectra were recorded on Nicolet 360 FT-IR on KBr (BDH Laboratory Supplies, UK, Spectrosol) pellets.

UV-visible absorption (Abs) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2101PC UV-VIS scanning spectrophotometer and a Shimadzu RF 5301PC Spectro fluorophotometer with a xenon lamp as a light source, respectively, at room temperature.

The fluorescence quantum efficiency was calculated with 9,10-diphenylanthracene in cyclohexane as a reference using the equation (1)

$$\Phi_{\text{PLs}} = \Phi_{\text{PLr}} \left(\frac{A_r}{A_s} \right) \cdot \left(\frac{F_s}{F_r} \right) \cdot \left(\frac{n_s}{n_r} \right)^2 \quad (1)$$

where Φ_{PL} , A , F , and n are the fluorescence quantum efficiency, the absorbance at the excitation wavelength, the integral over the fluorescence spectrum, and the refractive index of the solvent, respectively,



Scheme 1 Synthesis of PFBI-SO₃⁻.

and the subscripts of s and r refer to the sample and the reference solution specimens, respectively.¹⁰

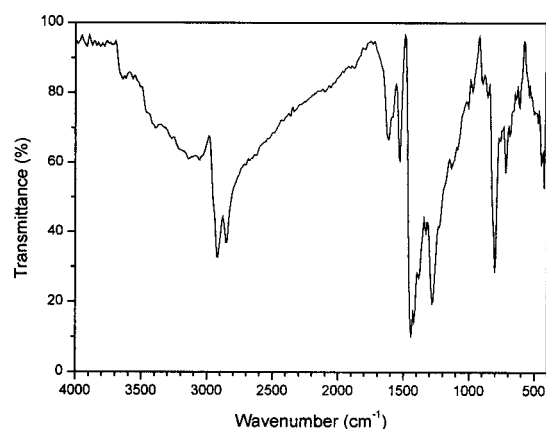
RESULTS AND DISCUSSION

Synthesis and characterization

The dicarboxylic acid monomer of 9,9-dihexylfluorene-2,7-dicarboxylic acid was prepared according to the previously reported procedure.^{8,9}

As shown in Scheme 1, PFBI was prepared from 9,9-dihexylfluorene-2,7-dicarboxylic acid and 3,3'-diaminobenzidine tetrahydrochloride *via* conventional direct condensation in PPMA as both a condensation agent and a polymerization solvent.^{11,12,13} In Figure

(a)



(b)

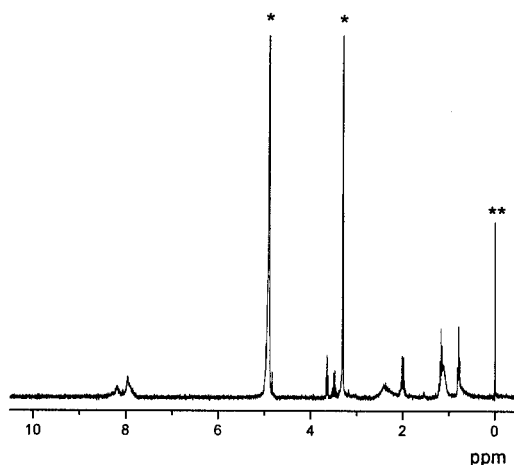


Figure 1 (a) The IR spectrum of poly(2,7-(9,9'-dihexylfluorene)-5,5'-bibenzimidazole) (PFBI) and (b) the ¹H-NMR spectrum of PFBI-SO₃⁻. The single and double asterisks (*) and (**) indicate the solvent (CD₃OD) and tetramethylsilane (TMS), respectively.

1(a), the IR spectrum of PFBI exhibits characteristic imidazole absorption bands at 3,500–3,000 cm⁻¹ and 1,616 cm⁻¹ corresponding to N—H and C=N stretching, respectively,^{12,13} while there is no carboxylic acid absorption band at 1,682 cm⁻¹ as shown in that of the dicarboxylic acid monomer. This IR result indicates that polymerization has been successfully carried out. Greenish brown fibrous PFBI showed poor solubility in common organic solvents except for polar aprotic solvents such as NMP, DMSO, and *N,N*-dimethylformamide (DMF). The polymer was also soluble in an acidic solvent such as formic acid and trifluoroacetic acid.

PFBI-SO₃⁻ was synthesized from PFBI by direct sulfonation with 1,3-propane-sultone in NMP. Sodium hydride in NMP caused deprotonation of the NH group of the imidazole rings to give a polyanion.^{14–16} Subsequent treatment of the polyanion with 1,3-propane-sultone gave the sulfonated polybenzimidazole. The IR spectrum of PFBI exhibits characteristic imidazole absorption bands at 3,500–3,000 cm⁻¹ and 1,046 cm⁻¹ corresponding to S=O stretching. The peaks of C—H in the side chain appeared at 2,925 and 2,854 cm⁻¹. In Figure 1(b), the ¹H-NMR spectrum of PFBI-SO₃⁻ exhibits new peaks due to the —NCH₂, —CH₂, —CH₂SO₃Na at δ 3.49, 2.01, and 3.64 (ppm), respectively. The degree of sulfonation was calculated as 60% from the peaks integral ratio between hydrogen atoms of —NCH₂ alkyls in the imine group and those of two alkyl groups in a fluorene group. Yellowish brown fibrous PFBI-SO₃⁻ showed better solubility in polar aprotic solvents such as DMAc and DMSO than PFBI due to higher polarity by sulfonated long alkyl chains in a benzimidazole group. The polymer also showed good solubility in MeOH, but showed poor solubility in water.

Optical characterization

PFBI-SO₃⁻ showed the maximum absorption wavelength at 345 nm and the emission maximum at 450 nm in MeOH with a concentration of 1 × 10⁻⁵ M. In MeOH, the polymer showed strong blue fluorescence with the high quantum efficiency (Φ_{PL} = 0.64). To determine the fluorescence quantum efficiency, 9,10-diphenylanthracene was used as a standard material.^{17,18} The standard quantum efficiency of 9,10-diphenylanthracene in cyclohexane is 0.90 at the excitation wavelength of 350 nm. Refractive indices of cyclohexane and methanol are 1.4262 and 1.3290 at 20°C. In the measurement of PL quantum efficiency, the excitation wavelength was fixed to 350 nm and the integration region of a PL spectrum was chosen between 360 and 690 nm.

Figure 2(a) shows the quencher-concentration dependence of the fluorescence spectrum of the polymer in MeOH. The addition of low concentration of MV²⁺

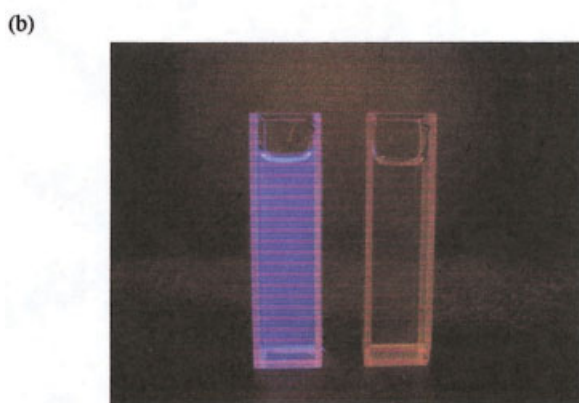
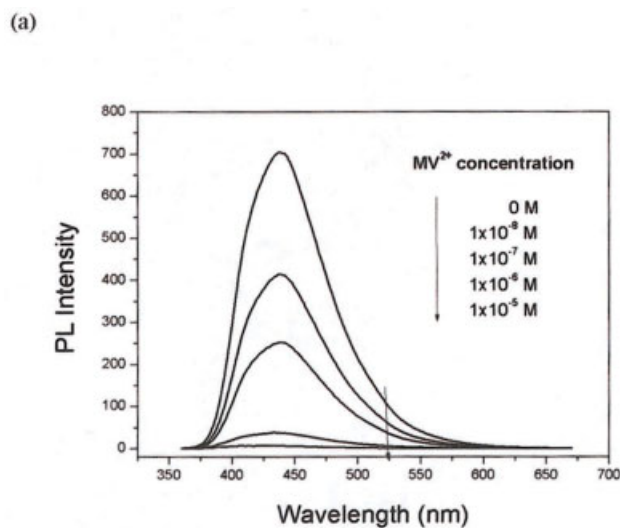


Figure 2 (a) PL spectra changes of $1 \times 10^{-5} \text{ M}$ PFBI-SO₃⁻ in MeOH upon the addition of MV²⁺ and (b) the picture shows the strong blue emissive and quenched solution.

leads to noticeable changes in the PL spectrum. It is reported that many intermolecular photophysical processes usually result in the fluorescence quenching or other similar effects corresponding to quenching. PFBI-SO₃⁻ showed the dramatic quenching effect with the addition of MV²⁺. When one equivalent of MV²⁺ was added, the fluorescence was almost quenched without a large change in the PL spectrum shape. Figure 2(b) exhibits the strong blue emissive and quenched solution after MV²⁺ was added.

The efficiency of fluorescence-quenching is quantified through the Stern-Volmer constant, K_{sv} :

$$\frac{\Phi^0}{\Phi} = 1 + K_{sv}[Q] \quad (2)$$

where Φ^0 and Φ are the fluorescence quantum efficiencies in the absence and presence of the quencher, and $[Q]$ is the concentration of quencher ions. The Stern-Volmer analysis of fluorescence quenching with

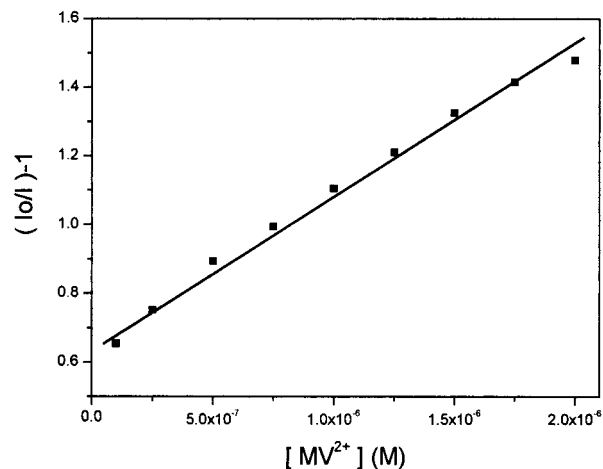


Figure 3 The Stern-Volmer plot for quenching of the fluorescence of $1 \times 10^{-5} \text{ M}$ PFBI-SO₃⁻ by MV²⁺ in MeOH.

MV²⁺ under the dilute condition gave a linear plot and the quenching constant, $K_{sv} = 3.7 \times 10^5 \text{ M}^{-1}$ was obtained from Figure 3. So the new anionic conjugated polymer exhibited remarkable and high sensitivity to cationic quencher of MV²⁺. The efficiency of fluorescence-quenching is promoted with the increase in K_{sv} . It is also reported that K_{sv} can be increased with increase in the charge of the quenchers.¹⁹ The quenching mechanism is not explained exactly, but it is believed that the quenching is caused by the electron transfer from the singlet excited state of the polymer to quencher MV²⁺.²⁰⁻²²

Figure 4 exhibits the PL spectra of PFBI-SO₃⁻ in MeOH, MeOH-H₂O (2:1), MeOH-H₂O (1:1), and MeOH-H₂O (1:2). The absorption spectra showed the small amount of red-shift with increase in the volume fraction of H₂O (345–355 nm). The polymer exhibited the good emission in MeOH, but the fluorescence was

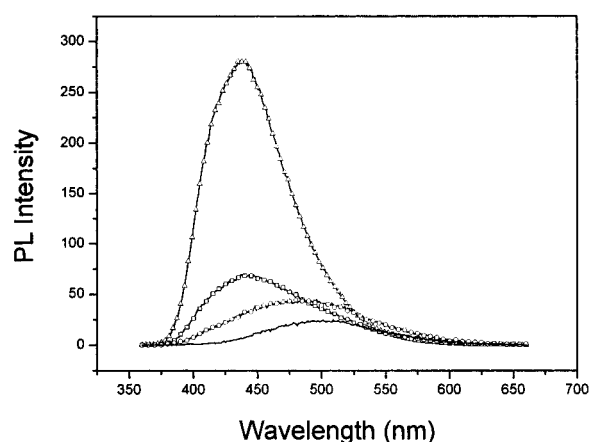


Figure 4 Figures 4 PL spectra of $1.2 \times 10^{-6} \text{ M}$ PFBI-SO₃⁻ in MeOH (Δ), (2:1) MeOH-H₂O (\square), (1:1) MeOH-H₂O (\circ), and (1:2) MeOH-H₂O ($-$).

noticeably quenched with the addition of H₂O. The changes in the spectroscopic properties with the solvent suggest that the polymer is strongly aggregated in H₂O, but it exists in a monomeric and non-aggregated state in MeOH.²⁰

CONCLUSIONS

We synthesized and characterized a new anionic conjugated polymer based on bezimidazole containing a fluorene group. The polymer (PFBI-SO₃⁻) was synthesized by direct sulfonation of PFBI. The polymer showed the strong blue emission with high quantum efficiency (0.64) at 450 nm in MeOH and the dramatic quenching effect by MV²⁺. PFBI-SO₃⁻ was gradually quenched with the addition of MV²⁺ and the linear Stern-Volmer constant (K_{sv}) was obtained as $3.7 \times 10^5 M^{-1}$ for MV²⁺. This new anionic conjugated polymer showed promise in application of biological and chemical sensors.

This paper was supported by the IMT-2000 Program of Advanced Backbone IT technology development project supported by Ministry of Information & Communication in republic of Korea.

References

1. Leclerc, M. *J Polym Sci: Part A: Polym Chem* 2001, 39, 2867.
2. Neher, D. *Macromol Rapid Commun* 2001, 22, 1365.
3. Montali, A.; Bastiaansen, G.; Smith, P.; Weder, C. *Nature* 1998, 392, 261.
4. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem Rev* 2000, 100, 2537.
5. Swager, T. M. *Acc Chem Res* 1998, 31, 201.
6. Chen, L.; McBranch, D. W.; Wang, H. L.; Hegelson, R.; Wdul, F.; Whitten, D. G. *Proc Natl Acad Sci* 1999, 96, 12287.
7. Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv Mater* 2000, 12, 1737.
8. Yang, N. C.; Ph.D. Thesis, Hanyang University, 2002.
9. Yang, N. C.; Lee, S. M.; Suh, D. H. *Polym Bull* 2003, 49, 371.
10. Eaton, D. F. *Pure Appl Chem* 1988, 60, 1107.
11. Ueda, M.; Sugita, H. *J Polym Sci Polym Chem (A)* 1989, 27, 2815.
12. Ueda, M.; Sato, M.; Mochizuki, A. *Macromolecules* 1985, 18, 2723.
13. Saegusa, Y.; Horikiri, M.; Nakamura, S. *Macromol Chem Phys* 1997, 198, 619.
14. Glipa, X.; Haddad, M. E.; Jones, D. J.; Roziere, J. *Solid State Ionics* 1997, 97, 323.
15. Kawahara, M.; Rikukawa, M.; Sanui, K.; Ogata, N. *Solid State Ionics* 2000, 136, 1193.
16. Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Macromolecules* 1997, 30, 4288.
17. Eaton, D. F. *Pure Appl Chem* 1988, 60, 1107.
18. Hamai, S.; Hirayama, F. *J Phys Chem* 1983, 87, 83.
19. Wang, D.; Wang, J.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Synth Met* 2001, 119, 587.
20. Tan, C.; Pinto, M. R.; Schanze, K. S. *Chem Comm* 2002, 446.
21. Gaylord, B. S.; Wang, S.; Heeger, A. J.; Bazan, G. C. *J Am Chem Soc* 2001, 123, 6417.
22. Wang, D.; Wang, J.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Langmuir* 2001, 17, 1262.