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Electrochemical Fluorescence Switching from Anthracene Polymer Films

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Electrochemical fluorescence switching of electroactive fluorescent anthracene polymer films was studied using an electro active quencher. The fluorescence of a methylene anthracene polymer (PMAn) was intact under redox reaction in the absence of an electroactive quencher. Interestingly the fluorescence of a methylene bridged anthracene polymer (PMAn) film could be modulated by adjusting the redox state of the PMAn and redox reaction of the quencher. The electrochemical fluorescence switching from the PMAn film with a quencher was reversible and the cyclability was longer than 1,000 cycles with an ON/OFF ratio of 3.86 under the applied potential step of +2 V for 4 second. A multi state fluorescent switch was fabricated with a double layered two electrode cell that was consisting of the PMAn layer doped with a quencher and a solid polymer electrolyte layer (SPE).

Keywords Fluorescence switching; iodide ion; iodine; methylene anthracne polymer; redox reaction

Introduction

Fluorescence switching of organic molecules and polymers has been widely applied to sensor, tag, imaging devices, and many other potential opto-electronic applications, since fluorescence detection is highly sensitive down to the single molecule, with submicron visualization and submillisecond temporal resolution [1–9]. As the fluorescence of materials is highly sensitive to environment around the materials, the switching could be conveniently attained by external stimuli such as light, acid, electrochemical potential. Among those, redox switchable fluorescent systems have been attracted for electro-optical switching, electrochemical in situ fluorescence spectroscopy, electronic logic gates, and other ion sensor applications [2–9]. The another way to achieve electro-fluorescence switching utilizes a mixture of a fluorophore and metal centered redox couples, which are operating through redox reaction of the metal centred redox quencher [5]. Very recently fully reversible three-state blue/red/off emission from bis-thiaxanthylidenes has been reported [6]. The blue luminescence of the most stable conformer of thiaxanthylidenes can be switched off by

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photochemical conversion to the meta-stable conformer and switched on again by thermal reversion. The red luminescence of the bis-thiaxanthylium dication can be switched on by oxidation and switched off or to blue by reduction.

Though most of the electro-fluorescence switching system mainly have been reported in solution condition by far, a solid-phase device could be more attractive for practical device fabrication. In our previous report [7(a)], we showed a redox switchable fluorescence cell in which a highly fluorescent and electrochemically stable tetrazine doped polymer gel was in contact to a solid polymer electrolyte layer [7(a),10].

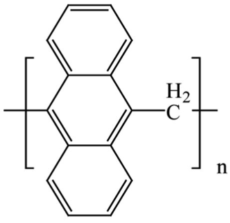
Such redox switching in a SPE contained cell could be extended to a fluorophore coupled electroactive dopant system. Recently, we also showed a redox switchable fluorescence switching of a copolymer of triazine bridged *p*-phenylenevinylene by using external dopant such as iodine and iodide [11]. In this cell, as the electroactive dopant undergoes redox reaction, the resultant oxidized or reduced species of the dopant quenches the luminescence of the fluorescent polymer, as reported for a fluorescence quenching by a redox couple in solution. When the redox reaction of the dopant is reversible, such fluorescence switches should be operated reversibly. Furthermore if the dopant undergoes multi-state redox process, the luminescence intensity from the cell can be modulated in a multi-level, depending upon the redox state of the dopant.

In this report, we report a reversible multi-state fluorescence switching both by the redox state of the fluorescent anthracene polymer (PMAn) itself and by the redox reaction of I^-/I_3^- couple in a solid polymer electrolyte cell.

Experimental

Materials

Methylene bridged anthracene polymer (PMAn) with a weight-average molecular weights of 4,950 was synthesized through Friedel-Crafts alkylation reaction as reported before [12(a)]. Methoxy poly (ethylene glycol) monomethacrylate (MPEGM) (Mn 1000) was purchased from Polyscience, Inc. Poly (ethylene glycol) dimethacrylate (PEGDMe) ($M_n = 550$) and triallyl-1,3,5-triazine-(1H, 3H, 5H)-trione (TATT) were obtained from Aldrich. Lithium trifluoromethanesulfonate (LiTFS) was purchased from Merck. Solvents such as acetone, chloroform tetrahydrofuran (THF), and methanol were purchased from Duksan and purified according to the reported procedures.



PMAn

Preparation of Electrofluorescent Cell

A polymer electrolyte composition was prepared by mixing MPEGM (0.3 g), PEGDMe (0.6 g), TATT (0.072 g), Darocure 1173 (0.06 g), Irgacure 784 (0.003 g),

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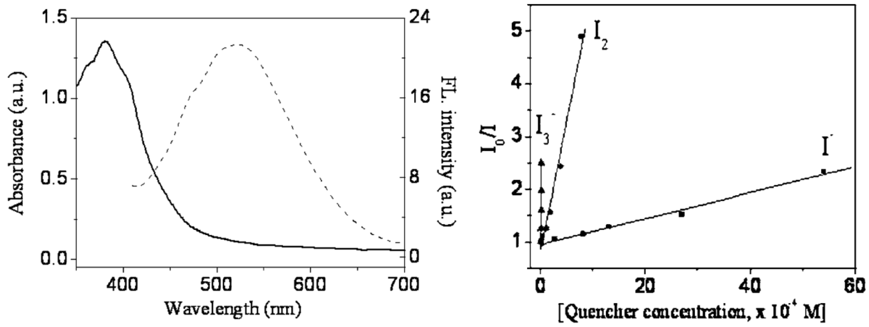
and LiTFS (0.06 g) according to the method reported in literature [10]. One ITO plate was then coated with the above mentioned polymer solution, after which the layer was cured for 10 min under a short UV light. For a two-electrode device containing PMAn with a quencher, a fluorescent solution was prepared by adding PMAn to the solution of polymer electrolyte containing tetrabutylammonium iodide (TBAI) and iodine with a ratio of 9:1. The content of PMAn in the polymer electrolyte solution was 5 wt %. The solution was then used to coat a second ITO plate. A solid-type sandwitched device was prepared by inserting the PMAn – polymer electrolyte mixture solution between a bare ITO electrode and a solid polymer electrolyte-coated ITO electrode. The device was sealed with epoxy resin. For a two-electrode device containing PMAn without a quencher, a fluorescent solution was prepared by only adding PMAn to the solution of polymer electrolyte without TBAI and iodine couple.

Results and Discussion

The PMAn polymer was soluble in common organic solvent such as THF, chloroform, acetone, ethyl acetate, etc. The chloroform solution of PMAn showed absorption peaks maximized at 380 nm and emission peaks at 415 nm when excited at 350 nm [12(a)]. Figure 1(a) shows the absorption and emission spectrum (at 390 nm excitation) of the two electrode device containing PMAn. This two electrode device showed blue fluorescence upon excitation with a UV light. Figure 1(b) shows the Stern-Volmer plot for the fluorescence quenching of the polymer by I^-, I_2, and I_3^- in chloroform. The emission intensity of the polymer solution was decreased drastically as I^-, I_2, and I_3^- were added to the PMAn solution. The equilibrium constant for quenching (K_{sv}) could be determined from the Stern-Volmer equation (1), where I_0 and I represent the fluorescence intensity in the absence and presence of quencher (Q), respectively. [Q] is the concentration of a quencher.

$$I_0/I = 1 + K_{sv}[Q] \tag{1}$$



(a) (b)

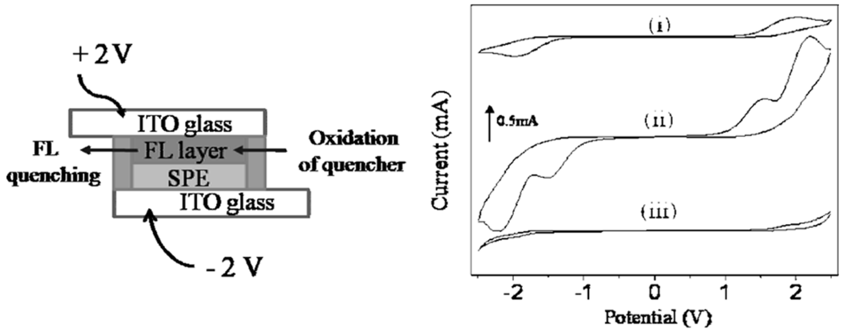
Figure 1. (a) UV-Vis absorption and fluorescence spectrum (excited at 390 nm) of a two electrode device containing PMAn. (b) Stern-Volmer plot for the fluorescence quenching of PMAn in chloroform solution ($[PMAn] = 1 \times 10^{-5}$ M) by I^-, I_2, and I_3^- ($\lambda_{exc} = 352$ nm, monitored at 435 nm).

The quenching constant, K_{sv}, was determined from the slope of the plot of I_0/I versus $[I^-]$. In the presence of TBAI, the K_{sv} of PMAn was determined as 250 M^{-1} from the plot in Figure 1(b) with a correlation constant (R) of 0.9955. The equilibrium constant for quenching by I_3^- was 74,400 M^{-1} from the plot against the quencher concentration (correlation constant, $R = 0.991$).

The quenching effect of I_3^- was ~300 times higher than that of iodide, possibly due to the larger anion size in I_3^-. The K_{sv} in the presence of I_2 was 5,100 M^{-1}. From the above results, it is concluded that the fluorescence quenching of the polymer by iodine derivatives (I^-, I_2 and I_3) is strongly dependent on the redox state of them.

Figure 2(a) shows the schematic structure of the fluorescent device. The fluorescence layer is sandwiched between the top electrode and solid polymer electrolyte layer. The thickness of the fluorescence layer is less than 1 μm, however, that of solid polymer electrolyte layer is 60 μm. In this structure with a SPE layer, it is unlikely that PMAn or quenchers diffuse to the bottom electrode through the thick solid polymer electrolyte. Thus the fluorescence quenching at the top layer could be controlled by the applied potential.

In order to determine the redox potentials of the fluorescent polymer and quencher, cyclic voltammograms (CV) of PMAn in solid electrolyte system were examined. Figure 2(b) shows CV of the two-electrode device containing different content. This result indicates that the redox process in the fluorescent layer occurs at a potential higher than 1.0 V and the cell showed large current in the presence of I_3^-/I^- couple in solid electrolyte system. The anodic current increases above 1.2 V could be attributed to the oxidation of iodide to tri-iodide, and further oxidation at higher potential to that of tri-iodide to iodine at the top ITO electrode contacted with fluorescence layer as shown Figure 2(a) [13]. Thus one can expect that the fluorescence intensity of PMAn become weak at a positive potential since iodide is converted to I_3^- then to I_2, which are strong quenchers. The cathodic current increases below −1.2 V could be attributed to the reduction of iodine followed by that of tri-iodide to iodide at the top ITO electrode contacted with fluorescence layer. Thus fluorescence intensity of PMAn become strong at a negative potential since iodine is converted to I^-, which is weak quencher. Also, a two



(a) (b)

Figure 2. (a) Schematic structure of the fluorescent device. The thickness of the fluorescence layer (FL) is ~1 μm and that of the solid polymer electrolyte (SPE) layer is 60 um. (b) Cyclic voltammogram of two-electrode devices containing (i) TBAI (0.1 mol) and I_2 (0.01 mol), (ii) PMAn, TBAI, and I_2, (iii) PMAn in contact to SPE. Scan rates of 100 mV/s.

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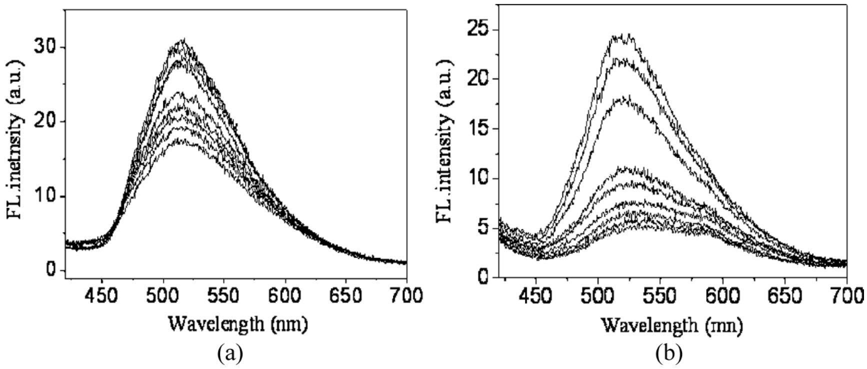
electrode device containing only PMAn without quencher showed redox process at a potential higher than 1.5 V. The CV showed no indication of decompositions during the potential cycles between −2 and +2 V. From ^{1}H-NMR study of a mixture of the copolymer with I_2, we could not observe any decomposed product formation even after 3 days.

The fluorescence intensity of the device having PMAn without an electroactive quencher or with an electroactive quencher was highly dependent on the applied electrochemical potentials. The device became dark with weaker luminescence when a positive potential was applied. Its emission was almost extinguished when +2 V was applied. However, it recovered to a highly fluorescent state upon application of −2 V.

The fluorescence spectra clearly show such fluorescence intensity change by the external potential application. The two-electrode device containing PMAn without iodide and iodine couple showed reversible electro-fluorescence switching originated from the redox state of PMAn as shown in Figure 3(a). Although it showed electrochemical fluorescence switching, the switching was more efficient in the presence of electroactive quencher (Fig. 3(b)).

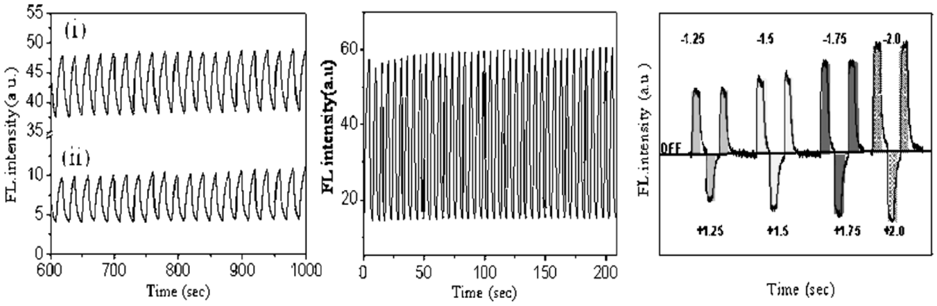
The fluorescence of the device containing electroactive quencher was weak but switching was visibly observed upon application of step potential from −2 V and +2 V for 10 sec. The electrofluorescence switching in Figure 3(b) could be ascribed to the redox reaction of iodide and iodine couple, which showed different degree of quenching for the emission of PMAn (Fig. 1(b)). The fluorescence intensity was controlled by the external potential and almost reversibly extinct upon potential scanning toward positive values.

Figures 4(a) and (b) show that an electro-fluorescence switching was reversible upon repetitive cycling between +2 V and −2 V step with a step duration of 10 sec. and 4 sec. at each potential after >1000 cycles, respectively. The electrochemical fluorescent switching was longer than 1,000 cycles with ON/OFF ratio of 3.86 under the applied potential step of 4 sec. This result indicates that the redox reaction of PMAn as well as electro-active quencher was reversible and stable under the experimental condition.



(a) (b)

Figure 3. (a) Fluorescence change of a two-electrode device containing (a) PMAn and (b) PMAn with TBAI and I_2 at different applied potentials: From top to bottom, −2.0, −1.75, −1.5, −1.25, 0, +1.25, +1.5, +1.75, and +2.0 V.



(a) (b) (c)

Figure 4. (a) Electrofluorescence switching of a two-electrode device containing (i) PMAn, (ii) PMAn, TBAI, and I_2 from -2 V and $+2$ V with 10 sec for each step ($\lambda_{exc} = 390$ nm, monitored at 520 nm). (b) Cyclability of the redox-fluorescence switching of a two-electrode device containing PMAn, TBAI, and I_2 with 4 sec of step time at $+2$ V. (c) A multi-state fluorescence switching of a two-electrode device containing PMAn, TBAI, and I_2 at different potentials, -1.25 V, $+1.25$ V, -1.5 V, $+1.5$ V, neutral (0 V), -1.75 V, $+1.75$ V, -2 V, and $+2$ V for cell under the rest time of longer than 2 min. at each potential.

Such a fluorescence intensity change at different redox states in a solid electrolyte system could be applied to a multi-state polymer fluorescence switch. Figure 4 (c) shows fluorescence intensity at different potentials from -2 to $+2$ V, under the rest time of longer than 2 min. at each potential. The multi-states with distinct fluorescence intensities at different potentials were stable and reversible by the potential application.

The redox-switching in this system is unique in that we utilize iodine redox chemistry for the fluorescence switching of the fluorescent polymer. The multi-state polymeric switch based on electro-fluorescence with SPE as shown in this study provided several advantaging prospects: (1) the starting materials are easily available and the polymer was easily synthesized with one-pot reaction, (2) it can be switched simply by electricity (low voltage), (3) the states are stable, reversible and modulated by applied potential, and (4) it can be applied to a flexible organic device or a bio-inspired device when the ITO glass is substituted to a flexible conductive substrate such as an ITO film or PEDOT film.

Conclusion

We have shown a multi state electro-fluorescence switching of a solid polymer electrolyte cell containing fluorescent polymer and redox couple. This polymer showed high fluorescence in solution with a good processibility for an organic device. Fluorescence of the PMAn was electrochemically controlled as the fluorescent layer was subjected to the redox reaction of the quencher within ±2 V in a two electrode thin film device. Fluorescence quenching of the PMAn was more effective in the presence of an electroactive quencher (I_3), indicating that the PMAn could be utilized as a fluorescence switch. Electrochemical fluorescent switches were fabricated using the polymers, which showed visible ON and OFF switching as a function of applied potential with a cyclability longer than 1,000 cycle.

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References

[1] (a) Tan, W., Shi, Z. Y., Smith, S., Birnbaum, D., & Kopelman, R. (2003). *Science*, *258*, 778; (b) Jörg, D., Martin, B., Andreas, K., & Hubert, S. (1996). *Pure Appl. Chem.*, *68*, 1399; (c) Guilbault, G. G. (1990). *Practical Fluorescence*, 2nd ed., Dekker: New York; (d) Jeong, Y. C., Yang, S. I., Kim, E., & Ahn, K. H. (2006). *Macromol. Rapid Commun.*, *27*, 1769; (e) Copeland, G. T. & Miller, S. J. (1999). *J. Am. Chem. Soc.*, *121*, 4306; (f) Bernhard, D. D., Mall, S., & Pantano, P. (2001). *Anal. Chem.*, *73*, 2484; (g) Dixon, A. J. & Benham, G. S. (1988). *Symp. Soc. Gen. Microbiol.*, *4*, 417; (h) Irie, M., Fukaminato, T., Sasaki, T., Tamai, N., & Kawai, T. (2002). *Nature*, *420*, 759; (i) Lewis, A. & Lieberman, K. (1991). *Anal. Chem.*, *63*, 625A; (j) Foyer, C. H. & Noctor, G. (1999). *Science*, *284*, 599.

[2] (a) Balaei, S., Aaron, J. J., Desbenemonvernay, A., & Lacaze, P. C. (1992). *Synth. Met.*, *53*, 95; (b) Hennrich, G., Sonnenschein, H., & Genger, U. R. (1999). *J. Am. Chem. Soc.*, *121*, 5073; (c) Zhang, G., Zhang, D., Guo, X., & Zhu, Z. (2004). *Org. Lett.*, *6*, 1209; (d) Montilla, F., Pastor, I., Mateo, C. R., Morallón, E., & Mallavia, R. (2006). *J. Phys. Chem. B.*, *110*, 5914; (e) Martínez, R., Ratera, I., Tárraga, A., Molina, P., & Veciana, J. (2006). *Chem. Commun.*, *36*, 3809; (f) Do, J., Huh, J., & Kim, E. (2009). *Langmuir*, *25*, 9405.

[3] (a) Silva, A. P., Nimal Gunaratne, H. Q., Gunnlaugsson, T., Huxley, A. M., McCoy, C. P., Rademacher, J. T., & Rice, T. E. (1997). *Chem. Rev.*, *97*, 1515; (b) Cho, D., Yang, G., Lee, S., & Bang, D. (2005). *Macromolecular Research*, *13*, 273; (c) Yang, S., & Lee, C. (2002). *J. Ind. Eng. Chem.*, *8*, 557.

[4] Becker, K., Lupton, J. M., Máller, J., Rogach, A. L., Talapin, D. T., Weller, H., & Feldmann, J. (2006). *Nature Materials*, *5*, 777.

[5] (a) Pflug, J. S., Faulkner, L. R., & Seitz, W. R. (1983). *J. Am. Chem. Soc.*, *105*, 4890; (b) De Santis, G., Fabbrizzi, L., Licchelli, M., Sardone, N., & Velders, A. H. (1996). *Chem. Eur. J.*, *2*, 1243; (c) Martínez, R., Ratera, I., Tárraga, A., Molina, P., & Veciana, J. (2006). *Chem. Commun.*, *36*, 3809.

[6] Browne, W. R., Pollard, M. M., de Lange, B., Meetsma, A., & Feringa, B. L. (2006). *J. Am. Chem. Soc.*, *128*, 12412.

[7] (a) Kim, Y., Kim, E., Clavier, G., & Audebert, P. (2006). *Chem. Commun.*, *34*, 3612; (b) Kim, Y., Do, J., Kim, E., Clavier, G., Galmiche, L., & Audebert, P. (2009). *Journal of Electroanalytical Chemistry*, *632*, 201; (c) Lee, W. R., Kim, Y., Kim, J. Y., Kim, T. H., Ahn, K.-D., & Kim, E. (2008). *Journal of Nanoscience and Nanotechnology*, *8*, 4630; (d) Oh, H., Kim, J., & Kim, E. (2008). *Macromolecules*, *41*, 7160.

[8] (a) Barltrop, J. A. & Coyle, J. D. (1975). *Excited states in organic chemistry*, Wiley: London; (b) de Silva, A. P., Gunaratne, H. Q. N., Gunnlaugsson, T., Huxley, A. J. M., McCoy, C. P., Rademacher, J. T., & Rice, T. E. (1997). *Chem. Rev.*, *97*, 1515.

[9] (a) Miller, A. E. W., Bian, S. X., & Chang, C. J. (2007). *J. Am. Chem. Soc.*, *129*, 3458; (b) Dwight, S., Gaylord, B. S., Hong, J. W., & Bazan, G. C. (2004). *J. Am. Chem. Soc.*, *126*, 16850.

[10] Kim, E. & Jung, S. (2005). *Chem. Mater.*, *17*, 6381.

[11] (a) Yoo, J., Kwon, T., Sarwade, B., Kim, Y., & Kim, E. (2007). *Applied Physics Letters*, *91*, 241107; (b) Yoo, J., Jadhav, P., & Kim, E. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 114.

(c) Kwon, T., Sarwade, B. D., Kim, Y., Yoo, J., & Kim, E. (2008). *Mol. Cryst. Liq. Cryst.*, *486*, 101.

[12] (a) Rameshbabu, K., Kim, Y., Kwon, T., Yoo, J., & Kim, E. (2007). *Tetrahedron Lett.*, *48*, 4755; (b) Kim, J., Oh, H., Yoo, J., Rameshbabu, K., & Kim, E. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 67.

[13] Popov, A. I. & Geske, D. H. (1958). *J. Am. Chem. Soc.*, *80*, 1340.

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