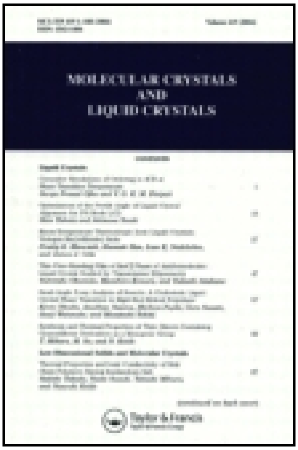

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Fluorescence Switching of a Copolymer of s-Triazine and p-Phenylene Vinylene by Redox Reaction of Iodide Ions

Jungmok Yoo [a], Parashuram Jadhav [a] & Eunkyoung Kim [a]

[a] Department of Chemical Engineering, Yonsei University, Seodaemun-gu, Seoul, South Korea

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Fluorescence Switching of a Copolymer of s-Triazine and *p*-Phenylene Vinylene by Redox Reaction of Iodide Ions

Jungmok Yoo, Parashuram Jadhav, and Eunkyoung Kim
Department of Chemical Engineering, Yonsei University,
Seodaemun-gu, Seoul, South Korea

A fluorescence switching property of a copolymer of piperidinyl s-triazine (PT) and p-(trimethylsilyl) phenylene vinylene (TPV) was investigated by utilizing redox reaction of electroactive iodides. A polymer having high fluorescence quantum yield was synthesized by Wittig polycondensation reaction with 4, 6-bis (4-formylphenoxy)-2-piperidinyl-s-triazine and 2, 5-bis (triphenylphosphonionmethyl)-1, 4-bis (trimethylsilyl) benzene dibromide, to make a copolymer of PT and TPV (PTTPV). The fluorescence of the polymer was easily modulated by external potential in a two electrode cell consisting fluorescent layer and polymer electrolyte layer. When the fluorescent polymer layer was doped with iodide ions, the cell showed reversible switching property by applied potentials within ±3 V.

Keywords: fluorescence switching; iodide ion; iodine; *p*-phenylene vinylene; redox reaction; s-triazine

INTRODUCTION

Organic materials showing fluorescent switching through external stimuli such as light and application of electrochemical potential have been attracted for opto-electronic applications and sensors [1–9]. In particular, electrochemical fluorescence and emission switching could afford sensors that detect electrochemical change around the probe by oxidation and/or reduction, or a display that is modulated through

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Address correspondence to Eunkyoung Kim, Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea. E.mail: eunkim@yonsei.ac.kr

color filter. The sensitivity of fluorescence is extremely high thus fluorescence switching can be further applied to a human-molecule communication. Several molecules such as thiadiazole/iminoylthiourea [2(b)] and a triad with tetrathiafulvalene and anthracene units [2(c)] have been reported as redox fluorescent switching materials. In our previous report [7], we showed a redox switchable fluorescence device in which a highly fluorescent and electrochemically stable tetrazine doped polymer gel was in contact to a solid polymer electrolyte layer [7]. The fluorescence from the tetrazine contained device was almost disappeared when the device was applied to a negative potential at which tetrazine was reduced to form an anion radical. The device showed reversible fluorescence modulation with a working voltage less than 3 V. This solid phase device containing a solid polymer electrolyte which prohibited diffusion of fluorescent polymer toward counter electrode could be extensively applied to practical device fabrication compared to that of solution phase.

The redox fluorescence switching systems could be also accomplished by a mixture of a fluorophore coupled electroactive redox materials, which undergoes redox reaction. The resultant oxidized or reduced materials change the luminescence of the fluorescent polymer. If the redox material undergoes reversible redox process, the fluorescence switching also can be reversible. Indeed recently we showed that the fluorescence of a copolymer of diphenylamino s-triazine (DT) and PPV (DTPPV) could be switched by the external dopant such as iodine and iodide [10]. As the s-triazine and PPV units can be modified to improve electro-fluorescence switching, we explore new polymers based on s-triazine and PPV. In this report, we report the synthesis and reversible fluorescence switching of a copolymer of piperidinyl s-triazine and *p*-(trimethylsilyl) phenylene vinylene (PTTPV) by the redox reaction of iodide and iodine couple in a solid polymer electrolyte device.

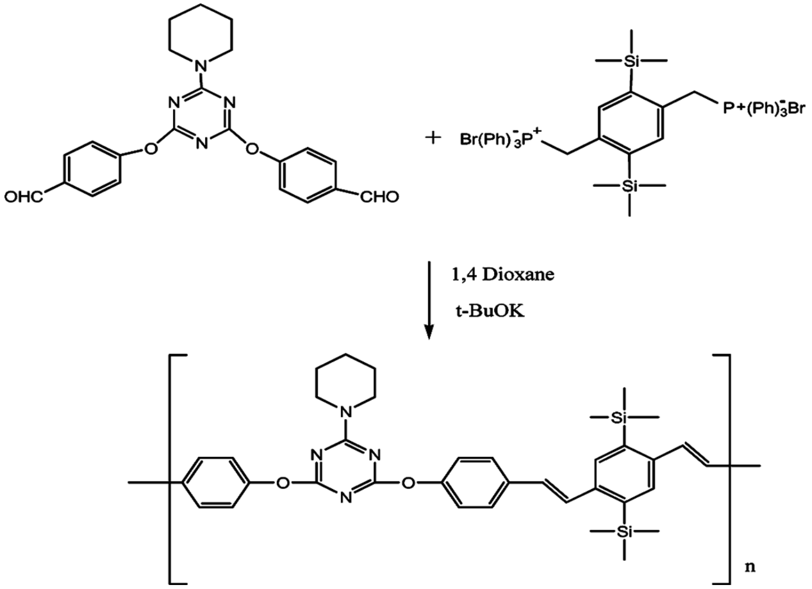
EXPERIMENTAL

Materials

Cyanuric chloride, 4-hydroxybenzaldehyde (HBD) and piperidine, potassium-tert-butoxide, triphenylphosphine were obtained from Aldrich and used without purification. 4, 6-bis (4-formylphenoxy)-2-piperidinyl-s-triazine was prepared according to the reported procedure [11]. Methoxy poly (ethylene glycol) monomethacrylate (MPEGM) (Mn 1000) was purchased from Polyscience, Inc. Poly (ethylene glycol) dimethacrylate (PEGDMe) (Mn 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 purified using reported procedures.

Synthesis of PTTPV

The Wittig poly-condensation reaction was used for the polymerization as summarized in Scheme 1 [12]. To a stirred 1,4-dioxane (anhydrous) (50 ml) solution of 2, 5-bis (bromo triphenylphosphonionmethyl)-1, 4-bis (trimethylsilyl) benzene (1.17 g, 1.34 mmol) was added the 1, 4-dioxane (20 ml) solution of potassium tert-butoxide (0.32 g, 2.85 mmol) dropwise at 40°C. The reaction mixture color changes to red. After 2 hrs, the 1, 4-dioxane (5 ml) solution of 4, 6-bis (4-formylphenoxy)-2- piperidinyl-s-triazine (0.5 g, 1.34 mmol) added to reaction mixture. The color of reaction mixture gradually changes to yellow. The reaction was continued for 32 hrs at same temperature. After 1, 4-dioxane was removed on rotary evaporator, the resulting crude polymer was precipitated using methanol to give yellow colored materials (15% of isolation yield). The weight average molecular weight (M_w) was 3900 (PDI = 1.17): FT-IR (cm^{-1}/solid): 1575 (-C=N, triazine), 1201 (C-O-C) and 966



SCHEME 1 Synthesis of PTTPV.

(trans-vinylene). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.8 (s, aromatic protons), 7.6 and 7.4 (d, vinylene protons), 7.2-6.84 (m, aromatic protons), 3.8 and 3.6 (t, -N-CH_2 protons of piperidine), 1.5 and 1.3 (m, -CH_2 protons of piperidine), 0.56 (s, 18 H, -Si $(CH_3)_3$).

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), and LiTFS (0.06 g) according to the method reported in literature [13]. One ITO plate was then coated with the above mentioned polymer solution, after which the layer was cured for 10 min under a 210 nm UV light. A fluorescent solution was prepared by adding PTTPV to the solution of polymer electrolyte containing tetrabutylammonium iodide (TBAI) and iodine with a ratio of 9:1. The content of PTTPV 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 PTTPV – polymer electrolyte mixture solution between a bare ITO electrode and a solid polymer electrolyte-coated ITO electrode. The device was sealed with epoxy resin.

RESULTS AND DISCUSSION

The Wittig poly-condensation of 4, 6-bis (4-formylphenoxy)-2-piperidinyl-s-triazine with 2, 5-bis (bromo triphenylphosphoniummethyl)-1, 4-bis (trimethylsilyl) benzene produced a copolymer of piperidinyl s-triazine and *p*-(trimethylsilyl) phenylene vinylene (PTTPV). The resultant polymer was soluble in common organic solvents such as chloroform, THF, acetone, ethyl acetate, etc. The structure of the polymer was confirmed with FT-IR and proton NMR analysis. The chloroform solution of the polymer showed strong fluorescence at 430 nm when excited at 340 nm. Figure 1(a) shows the absorption and emission spectra of the polymer in the chloroform solution. Compared to DTPPV [10], the absorption band of PTTPV was blue shifted. The polymer showed high fluorescence with a fluorescent quantum yield as 0.57 (referenced to quinine sulfate). Figure1(b) shows the cyclic voltammogram (CV) curve from the two electrode cell, which indicates that the redox process in the fluorescent layer occurs at a potential higher than ± 131.25 V.

Figures 2(a) shows the fluorescence intensity change dependent on the external potential. This fluorescence intensity was almost reversibly increased on potential scanning toward negative values.

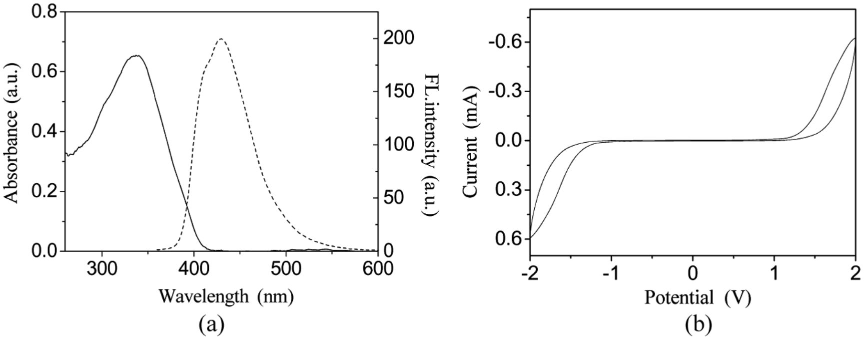


FIGURE 1 (a) UV-Vis absorption (solid) and Emission (dashed) spectra of PTTPV in chloroform solution (1×10^{-4} M), (b) Cyclic voltammogram of two electrode device (scan rates: 100 mV/s).

Interestingly, the device without iodide and iodine couple did not show reversible electro-fluorescence switching. This indicates that the electro-fluorescence switching from the cell could be ascribed to the redox reaction of iodide and iodine couple. When external bias is applied, a redox active material is oxidized (p-type doping) at the anode and reduced at the cathode (n-type doping) in such two-electrode system. Thus, the anodic current increases above 1.25 V in Figure 1(b) from the two-electrode fluorescence device could be attributed to the oxidation of iodide to tri-iodide, and further oxidation at higher potential to that of tri-iodide to iodine [14]. Similarly the

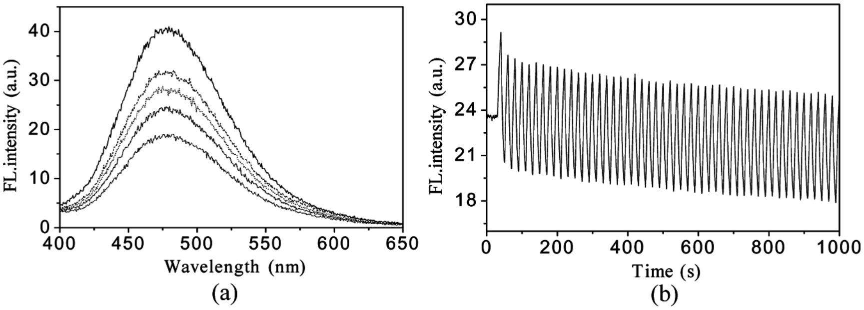


FIGURE 2 (a) Fluorescence spectra of a two electrode device at different applied potentials: From top to bottom, −1.5 V, −1.25 V, 0, +1.25 V, +1.5 V (Excited at 380 nm), (b) Cyclability of the fluorescence switching from −1.5 V and +1.5 V with 10 sec for each step ($\lambda_{exc} = 380$ nm, monitored at 460 nm).

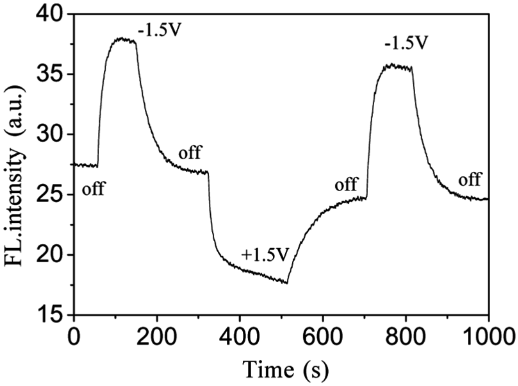


FIGURE 3 A three state fluorescence switching at bias potential of -1.5 V, 0, $+1.5$ V for PTTPV device ($\lambda_{exc} = 380$ nm, monitored at 460 nm).

cathodic current increases below -1.25 V could be attributed to the reduction of iodine followed by that of tri-iodide to iodide. As the device is highly fluorescent at negative potential, it is concluded that the fluorescence of PTTPV is quenched by the electrochemically generated tri-iodide and iodine at > 1.25 V. On the other hands, at negative potential (< -1.25 V), where the content of iodide should be high, the quenching is very low to give high fluorescence intensity.

Figure 2(b) shows that such an electro-fluorescence switching was stable upon repetitive cycling between -1.5 V and $+1.5$ V with a residual time at each potential of 10 s. This result indicates that the reversible redox and quenching reaction of the electro-active quencher in the fluorescent device are quite fast and efficient.

Figure 3 shows a three state fluorescence switching at three different potentials of -1.5 V, 0, $+1.5$ V for 90 sec at each potential. Importantly, the three states having different fluorescence intensities at -1.5 V, 0, $+1.5$ V were stable and reversible under a given bias potential. The fluorescence switching of PTTPV by iodine is comparable to that of DTPPV [10]. Therefore redox-fluorescence switching of s-triazine and PPV derivatives could be generalized and extended to the other couple of fluorophores and electroactive dopants, which opens up new method for fluorescence control.

CONCLUSION

A new copolymer of piperidinyl s-triazine and *p*-(trimethylsilyl) phenylene vinylene was synthesized through the Wittig polycondensation reaction. This polymer showed a high fluorescence in a solution and a good processibility. The fluorescence of new polymer was electrochemically modulated with an electroactive quencher. The fluorescence switching including a three state fluorescence switching was reversible and stable under low voltage of 1.5 V.

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