Fluorescence Quantum Yield of Poly(3-octylthiophene) upon Electrochemical Doping

T. Danno,[1] K. Kobayashi,[2] A. Tanioka[2]

[1]Department of Lifestyle Design, Kochi Prefectural University, Eikokuji-cho, Kochi 780-8515, Japan
[2]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ABSTRACT: The in situ optical absorption and fluorescence of poly(3-octylthiophene) (POT) upon electrochemical doping were studied. Fluorescence from the undoped POT was observed in the acetonitrile electrolyte. It was quenched by the electrochemical doping. The effect of a dopant molecule on the intensity change of the fluorescence is 7.5 times greater than the one for the optical absorption. Thus, the fluorescence quantum yield decreased after electrochemical doping. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3111–3115, 2006

Key words: poly(3-octylthiophene); electrochemical doping; absorption; fluorescence; quantum yield; Nernst equation

INTRODUCTION

Conducting polymers can become soluble and processable by introducing long side chains onto the molecular main segments.[1,2] Poly(3-alkylthiophene)s have attracted much interest as good examples because they exhibit a thermochromic phase transition.[3]

In our previous studies, the optical absorption and Raman scattering from doped poly(3-octylthiophene) (POT) were investigated.[4,5] Electrochemical doping of POT was studied by in situ optical absorption and in situ resonance Raman scattering. The absorption of polarons and, at higher doping levels, of bipolarons were observed. A strong quenching of the fluorescence and main Raman lines was particularly found for the initial part of the doping process.[5] Hayashi et al. reported that the quenching of the photoluminescence in poly(thiophene) and poly(3-methylthiophene) films by electrochemical doping is due to the formation of a metallic state.[6] Luzatti et al. studied the strong anisotropy of the emission spectra in the POT–polyethylene blend fiber.[7] Linton et al. studied the fluorescence of poly(3-hexylthiophene) in solution and calculated the kinetic energy of fluorescence from the temperature dependence.[8] The kinetics of fluorescence from the solid state poly(alkylthiophene) is, however, still not clear, especially corresponding to the optical absorption.

In this article, we discuss the fluorescence from POT by the in situ electrochemical doping. The in situ change in the optical absorption is simultaneously discussed from the standpoint of the quantum yield.

EXPERIMENTAL

POT was synthesized by the oxidative coupling method.[3] About 80-nm thick films were formed on indium–tin oxide glass or platinum substrates from a 2 wt % toluene solution using spin-coating.

The electrochemical doping was carried out using a laboratory-made electrooptical cell with an electrolyte of $0.1M$ $AgClO_4$ in acetonitrile. The potential was controlled with a potentiostat(HOKUTO HA-301). Ag/Ag^+ was used as the reference electrode.

The optical absorption was measured in situ in the same electrooptical cell using a HITACH U-2000 spectrophotometer. The in situ fluorescence spectra were measured using a JASCO FP-750 fluorescence spectrophotometer excited at 500 nm. The excitation spectrum was also measured in the electrolyte at 645 nm.

Chronoamperometry was carried out for the coated film on the platinum substrate using the same system as the electrochemical measurement combined with a HP2458A multimeter to measure the current.

RESULTS

Optical absorption

Figure 1 shows the optical absorption of POT at different applied potentials. When no potential was applied, the absorption maximum was observed at 500
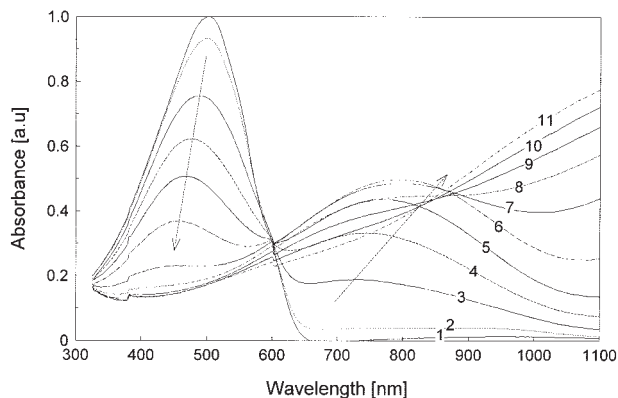
Figure 1 In situ absorption spectra of POT recorded in $0.1M$ AgClO$_4$ in acetonitrile at various applied potentials in Volts (versus Ag/Ag$^+$): (1) 0.0; (2) 0.1; (3) 0.2; (4) 0.3; (5) 0.4; (6) 0.5; (7) 0.6; (8) 0.7; (9) 0.8; (10) 0.9; (11) 1.0.

nm. The peak intensity decreased with the increasing applied potential and an additional peak around 750 nm appeared. The peak at 750 nm is assigned to the antibonding orbital of the bipolarons.[5] The peak at 500 nm, which is assigned to the interband transition (HOMO–LUMO), shifted towards a shorter wavelength, while the bipolaron peak at 750 nm shifted towards a longer wavelength with the increasing applied potential.

Figure 2 shows the intensity change in the absorption maximum as a function of the applied potential during doping. The intensity began to continuously decrease with the applied potential and leveled off at 0.7 V versus Ag/Ag$^+$, while the oscillator strength for the bipolaron increased until 0.5 V versus Ag/Ag$^+$ and afterwards drastically shifted towards a longer wavelength. As shown in Figure 2, the intensity reverted back to the original value after releasing the potential.

Fluorescence spectrum

Figure 3 shows the fluorescence spectra of POT at different applied potentials with a 500 nm excitation.
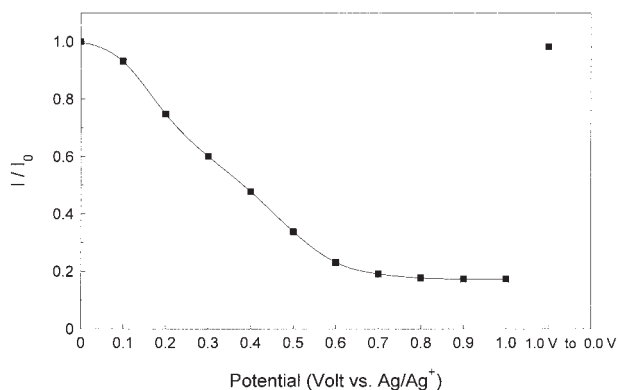

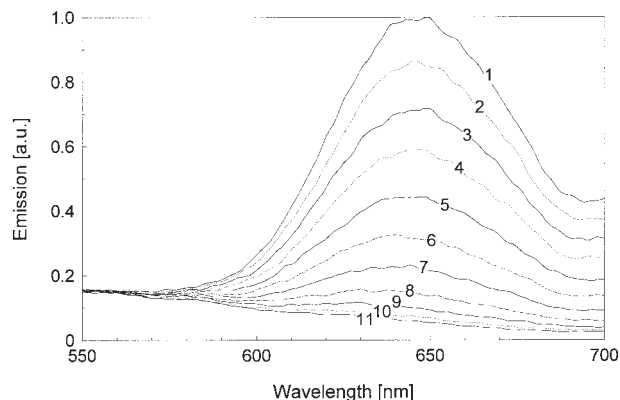**Figure 2** Change in the absorption maximum as a function of the applied potential.

Figure 3 In situ fluorescence spectra of POT recorded in $0.1M$ AgClO$_4$ in acetonitrile at various applied potentials in Volts (versus Ag/Ag$^+$):(1) 0.00; (2) 0.01; (3) 0.02; (4) 0.03; (5) 0.04; (6) 0.05; (7) 0.06; (8)0.07; (9) 0.08; (10) 0.09; (11) 0.10.

The undoped POT shows a fluorescence maximum around 650 nm. The maximum decreased with the increasing applied potential accompanied by a blue shift.

Figure 4 shows the intensity change in the fluorescence maximum as a function of the applied potential during doping. The intensity began to spontaneously decrease after applying the potential.

It decreased to about 10% of that for the undoped POT at 0.1 V versus Ag/Ag$^+$. The range of the applied potential to change the fluorescence spectrum was about 1/10 when compared with that for the optical absorption. Similar to the optical absorption, the fluorescence returned to that for the undoped state after releasing the potential, as shown in Figure 4.

Excitation spectrum

Figure 5 shows the excitation spectrum of the undoped POT in the electrolyte. A similar optical absorption is also shown in Figure 5. Both spectra showed similar shapes with the maxima at ~500 nm.
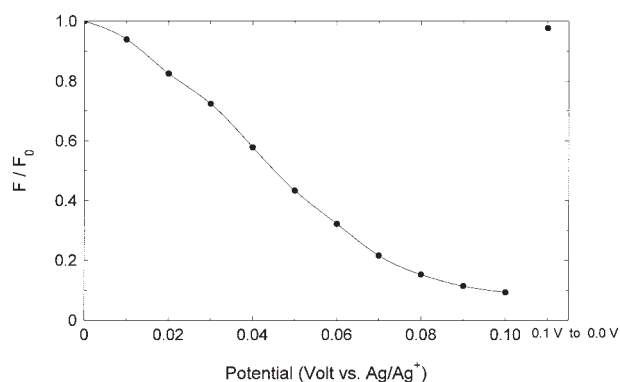

Figure 4 Change in fluorescence maximum as a function of the applied potential.
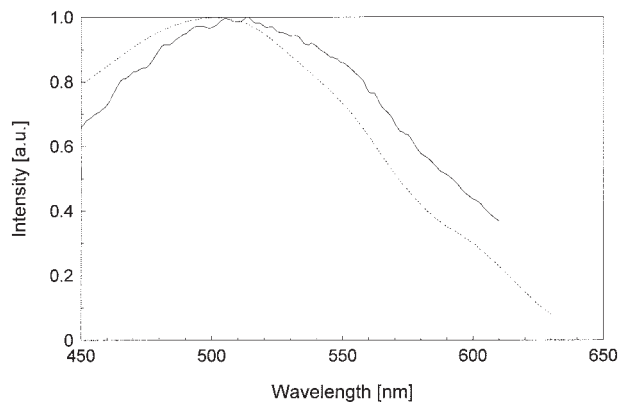
Figure 5 Excitation spectrum of undoped POT in $0.1M$ $AgClO_4$/acetonitrile electrolyte.

Chronoamperometry

Figure 6 shows the total charge quantity by integrating the current measured at different applied potentials. The curve has a sigmoid shape.

DISCUSSION

The interband transition decreases and simultaneously shifts towards a shorter wavelength. This means that the intragap transitions take their oscillator strength from the interband transition between the HOMO and LUMO regimes. The loss of oscillator strength is concentrated near the band edges and thus causes the shift towards the shorter wavelength with doping. The shift in the bipolaron peak is similarly explained. The asymmetry and apparent decrease in the higher bipolaron transition for the high doping state originates from a strong broadening of the latter.[2] The reversible change in the absorption maximum by releasing the potential means that the doping and undoping process reversibly occurs.

The shape of the excitation spectrum of the undoped POT corresponds to the optical absorption. Thus, the observed fluorescence originates from POT itself in the electrochemical doping system. The fluorescence maximum decreases and shifts simultaneously towards a shorter wavelength. No additional structure was formed in the fluorescence spectrum during doping. This means that the polaron and bipolaron species are nonradiative. The intensity change and shift in the fluorescence maximum are similarly explained like that for the absorption maximum, where the increase in the interband gap directly affected the gap for quenching. Similar as that mentioned earlier, the fluorescence was reversible after releasing the potential. Both phenomena from the optical absorption and fluorescence convinced us that the electrochemical doping of POT is reversible.

The fluorescence intensity is represented as

$$F = I \times \phi, \tag{1}$$

where I is the intensity of the absorbed excitation light, and ϕ is the fluorescence quantum yield. In the present results, the fluorescence decreased very rapidly upon doping when compared with the optical absorption. The fluorescent decreases until 0.1 V versus Ag/Ag^+, while the optical absorption decreases just 10% in this potential range. This strongly suggests that the fluorescence quantum yield of POT decreases upon doping. Therefore, the estimation of the fluorescence quantum yield is carried out based on the results of the chronoamperometry as discussed later:

When the charge transfer from the undoped POT to dopant molecules forms bipolarons, it is necessary to also form polarons. This scheme is written as follows,

$$u \leftarrow n_1 \rightarrow p \leftarrow n_2 \rightarrow b, \tag{2}$$
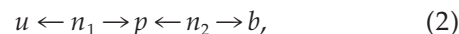
where u, p, and b represent the undoped, polaron, and bipolaron, and n_1 and n_2 are the number of electrons consumed per OT monomer unit at each charge transfer. From the Nernst equation,

$$E = E_1^0 + \left(\frac{RT}{n_1F}\right)\ln\left(\frac{p}{u}\right) \tag{3}$$

$$E = E_2^0 + \left(\frac{RT}{n_2F}\right)\ln\left(\frac{b}{p}\right), \tag{4}$$

where E is the applied potential, E_1^0 and E_2^0 are the standard potentials of the polaron and bipolaron, respectively, and R and F are the gas and Faraday constants, respectively. The charge derived from faradic current, Q_f, and its maximum charge, Q_{fmax}, are written
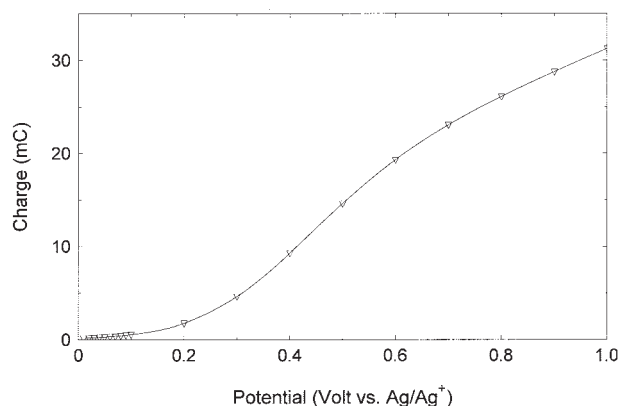
$$Q_f = nFp + 2nFb \tag{5}$$

Figure 6 Total charge quantity of POT during electrochemical doping as a function of the applied potentials. Triangle: observed value; solid line: curve fit from eq. (11).

TABLE I
Parameters from eq. (11)

	Value
n_1	0.27
E_1^0	0.30 V
n_2	0.25
E_2^0	0.47 V
$1/n_1$	3.67
$1/n_2$	3.96

$$Q_{fmax} = 2nF(u + p + b). \qquad (6)$$

The total amount of molecules are normalized as

$$1 = u + p + b. \qquad (7)$$

The charge derived from the non-Faradaic current, Q_c, is written as

$$Q_c = s(E - E_{pzc})Q_f, \qquad (8)$$

and measured charge, Q, is written as

$$Q = Q_c + Q_f = s(E - E_{pzc})Q_f + Q_f, \qquad (9)$$

where s is a constant and E_{pzc} is the potential of zero charge. Thus, the relation between the applied potential and the charge is written as

$$Q = \frac{Q_{fmax}[1 + s(E - E_{pzc})]}{\dfrac{1 + 2\exp\left[\dfrac{-n_1F(E - E_1^0)}{RT}\right]}{1 + 2\exp\left[\dfrac{n_2F(E - E_2^0)}{RT}\right]} + 1} \qquad (10)$$

After replacing $k_1 = sQ_{fmax}$, $k_2 = Q_{fmax}(1 - sE_{pzc})$, $k_3 = n_1/RT$, $k_4 = E_1^0$, $k_5 = n_2/RT$, and $k_6 = E_2^0$, Q is represented by[9,10]

$$Q = \frac{k_1E + k_2}{\dfrac{1 + 2\exp[-k_3(E - k_4)]}{1 + 2\exp[k_5(E - k_6)]} + 1}. \qquad (11)$$

In Figure 6, the solid line shows the curve fitting result with the six parameters in eq. (11).

Furthermore n_1, n_2, E_1^0, E_2^0, $1/n_1$, $1/n_2$ are shown in Table I. These values are similar to the one for poly-(thiophene).[10]

The number of thiophene units involved in the change of optical absorption at 500 nm was calculated as follows:

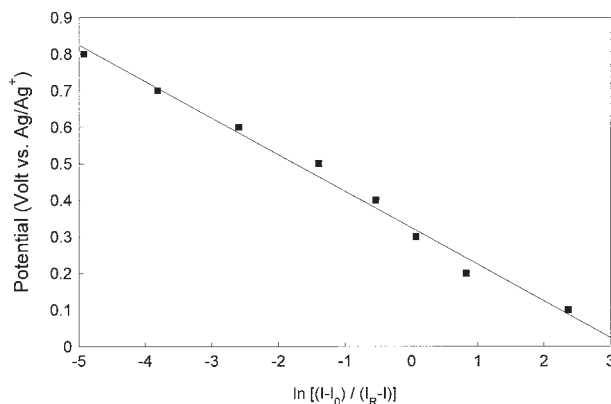The redox reaction of doping is written as

$$R = O + n_a e, \qquad (12)$$

Figure 7 Nernst equation plots for optical absorption of POT during electrochemical doping. Solid line shows the least squares estimation.

where R and O are the thiophene units that absorb and do not absorb 500 nm light, respectively. n_a is the nominal number of electrons contributing to the redox reaction. If the applied potential is assumed to yield only the faradic current, the applied potential equals the electromotive force (EMF).

Thus, the EMF and/or applied potential is written by the Nernst equation as follows:

$$E = E^0 - \frac{RT}{n_aF} \ln\frac{[R]}{[O]}, \qquad (13)$$

where $[R]/[O]$ is the molecular ratio of the oxidized and reduced states. E^0 is the standard potential of the system. In the absorption spectra, I_R is the absorption maximum for the reduced state, I is for a given potential and I_o is for oxidation state. Thus, the molecular ratio is written as[11,12]

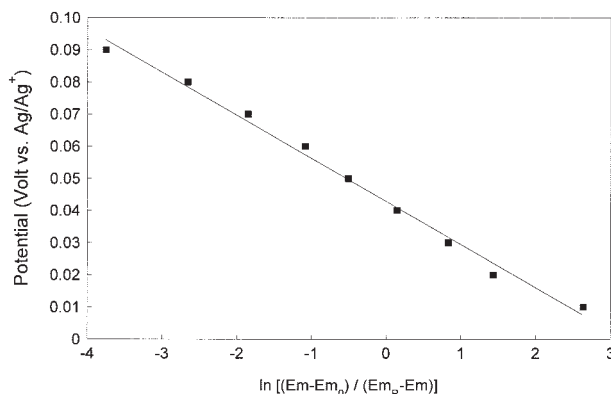$$\frac{[R]}{[O]} = \frac{I - I_o}{I_R - I} \qquad (14)$$

Figure 8 Nernst equation plots for the fluorescence intensity of POT during electrochemical doping. Solid line shows the least squares estimation.

TABLE II
Parameters from eqs. (15) and (16)

	Value
n_a	0.26
E^0	0.32 V
n_k	1.93
$E_k{}^0$	0.043 V
$1/n_a$	3.87
$1/n_k$	0.52

By combination with the Nernst equation, we obtain the relation between the applied potential and optical absorption as follows:

$$E = E^0 - \frac{RT}{n_a F} \ln \frac{I - I_o}{I_R - I}. \tag{15}$$

Figure 7 shows the applied potential as a function of $\ln[(I-I_o)/(I_R-I)]$ (Nernst equation plots). From the slope and the ordinate intercept, n_a and E^0 are obtained, respectively.

A similar argument is applied to the relation between the applied potential and the fluorescence intensity as follows:

$$E = E_k{}^0 - \frac{RT}{n_k F} \ln \frac{Em - Em_o}{Em_R - Em}, \tag{16}$$

where n_k is the nominal number of electrons contributing to the redox reaction, Em_R is the emission intensity for the reduced state, Em is for a given potential, and Em_o is for the oxidation state from fluorescence spectra, respectively. Figure 8 shows the applied potential as a function of $\ln[(Em-Em_o)/(Em_R-Em)]$. From the slope and the ordinate intercept, n_k and $E_k{}^0$ are obtained, respectively.

Table II shows the n_a, E^0, n_k, $E_k{}^0$, and $1/n_a$, $1/n_k$ values obtained from these arguments. n_a is similar to n_1. n_1 means that 0.27 electrons are removed from a thiophene unit by a dopant molecule, and $1/n_1$ means that a polaron is distributed around 3.7 thiophene units for the case of optical absorption.

n_k means that the number of nominal electrons removed from the thiophene units by a dopant molecule. Actually, however, a dopant removes n_1 electrons; thus, from n_k/n_1 (=7.5) thiophene units, 0.27 electrons are removed in the case of fluorescence.

Therefore, a dopant molecule affects 3.7 thiophene units for the absorption and affects 7.5 units for the fluorescence. This means that the fluorescence quantum yields decrease depending on the difference in the numbers of units.

CONCLUSIONS

Fluorescence from the undoped POT was observed in the acetonitrile electrolyte. It was quenched by electrochemical doping. The effect of a dopant molecule on the intensity change in the fluorescence is 7.5 times greater than the one for the optical absorption. Thus, the fluorescence quantum yield decreased with electrochemical doping.

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