Photoluminescence Study of Polypyrrole Micelles in Various Solvents

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Abstract

Photoluminescence (PL) was observed from micelles of polypyrrole without substituent groups in various solvents. Chloroform and THF showed a typical fluorescence quenching behavior that can be observed when quencher molecules are added to a micellar solution of fluorescent material. The PL intensity varied depending upon the solvent in the order of DMSO > DMF > NMP > ethanol > toluene > THF. From the results that the LUMO energy level of dopant was below that of polypyrrole in CV experiment and the PL intensity of the same solution did not decreased under photo-excitation at 290 nm, we propose another quenching mechanism for this behavior, photo-induced charge transfer mechanism.

Keywords: Photoluminescence, polypyrrole, micelles, quenching.

1. Introduction

Polypyrrole (PPy) has drawn tremendous interests of researchers due to its high conductivity and thermal stability which are crucial for electronic applications.

Another strategy to obtain high solubility is to dope the polymer with anionic surfactant which enhances the solubility by promoting the compatibility between PPy chain and the solvent. Unlike the method of chemical modification, this approach does not alter the chemical structure of PPy itself but affects the charge on the polymer backbone depending upon the doping level. Among the surfactants, alkylbenzenesulfonate anions have been used widely. However, the polymer solubility obtained with these surfactants does not fulfill the requirements necessary for various applications[1,2]. Recently, Jang and coworkers reported that di(2-ethylhexyl) sulfosuccinate anion is more effective than alkylbenzenesulfonate for promoting the solubility of PPy in various organic solvents[3–5]. Although many researchers have been successful in solubilizing PPy without any substituent group, to the best of our knowledge, photoluminescence (PL) of non-substituted PPy has not been reported yet.

We envisioned that PL could be observed from the micellar dispersion of PPy in which non-radiative quenching by aggregate phase is minimized as the polymer chains are separated from each other. In this communication we report the observation of PL from the micellar dispersion of PPy with no substituent group.
2. Experimental

A mixture of pyrrole (0.4 mol) and sodium di(2-ethylhexyl) sulfosuccinate (DEHSNa) (0.15 mol) in distilled water (900 mL) and a solution of ammonium peroxysulfate (APS) (0.10 mol) in distilled water (100 mL) were cooled to 0 °C. The APS solution was slowly added to the pyrrole mixture for 2 minutes at 0 °C while stirring. The reaction was continued for 20 h at 0 °C. The resulting precipitate was filtered and washed with 2 L of distilled water and dried in vacuum to give the product, \([\text{Py}_n]^+\text{(DEHS)}^-\)_x, where n is known to be 3.[18]

Electronic absorption and PL spectra of the polymer solutions were recorded using Shimadzu UV-3100 and Shimadzu RF-5301PC spectrometers, respectively. The excitation wavelength was set at 380 nm.

Cyclic voltammograms of a Ppy-DEHS or a DEHS solution was recorded using EG&G PAR 362 potentiostat. A Pt wire and a Pt mesh were used as working and counter electrodes, respectively. The potentials were monitored with respect to Ag/AgCl (3 M NaCl(aq)) electrode. The electrolyte solution was 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The electrochemical cells were deaerated by nitrogen bubbling before the experiment.

3. Results and Discussion

Table 1 shows the PL intensity of the polymer in various organic solvents at the same polymer concentration of 4x10⁻³ wt.-%. PL intensity of \([\text{Py}_3]^+\text{(DEHS)}^-\)_x was the highest in DMSO, and decreased in the order of DMF > NMP > ethanol > toluene > THF.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMSO</th>
<th>DMF</th>
<th>NMP</th>
<th>Ethanol</th>
<th>Toluene</th>
<th>THF</th>
<th>Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum PL</td>
<td>8.25</td>
<td>4.92</td>
<td>1.65</td>
<td>1.47</td>
<td>1.46</td>
<td>0.15</td>
<td>not observed</td>
</tr>
</tbody>
</table>

\(^a\) The polymer concentration was 4x10⁻³ wt.-%, the excitation wavelength was 380 nm.

It is noteworthy that no PL was observed in chloroform. Since the polymer solutions in ethanol and toluene show similar magnitudes of PL intensity even though their polarities are somewhat different, there seems to be no clear relationship between the PL intensity and the solvent polarity in this case.

In the case of mixed solvent systems, the PL intensity varied almost linearly with respect to the composition of the co-solvent. Figure 1 shows the variation of PL spectra with the composition of the co-solvent. In co-solvent systems of DMSO/ethanol and DMSO/toluene (Figure 1 insets), as the composition varied from 100 to 0 vol.-% DMSO, the PL intensity changed almost linearly with the composition of the co-solvent.
Figure 1. PL intensity of [(Py$_3$)$^+$ (DEHS)$^-]$ solutions vs. the composition of the co-solvent systems: (A) ethanol/DMSO and (B) toluene/DMSO. The polymer concentration was 4x10$^{-3}$ wt.-% and the excitation wavelength was 380 nm.

Cyclic voltammograms of Ppy–DEHS and DEHSNa solutions in acetonitrile were obtained to investigate the existence of PL quenching site in DEHS moiety. If the quenching site exists, the LUMO energy level of DEHS will be below the LUMO energy level of polyppyrole to transfer the photo-excited electron from the latter to the former level. The CV of DEHSNa exhibited reductive peak in the range of 1.9 and 1.5 V while that of Ppy–DEHS did not exhibit any reduction in the same potential range. The disappearance of reduction peak corresponding to the DEHS moiety in Ppy–DEHS was presumably due to the extraction of the dopant from polyppyrole matrix to the bulk solution during rinsing the Ppy–DEHS coated electrode after dip-coating. From this results, we can confirm that the LUMO energy level of DEHS moiety is lower than that of polyppyrole indicating that the dopant has a pathway for irradiative decay of photo-excited electron.

As a result, we propose one more mechanism for quenching in PL intensity, i.e. charge transfer mechanism (Scheme 1).

Scheme 1. Schematic diagrams of (A) radiative and (B) irradiative decay in photo-excited Ppy–DEHS solutions at 380 nm: (A) DMSO, DMF, and NMP, (B) Chloroform and THF.
When a dopant was photo-excited, the charge transfer from LUMO of the dopant to that of the polypyrrole moiety would not occur because the LUMO of polypyrrole is much higher than that of dopant. The independency of PL intensity on solvent media in Figure 1 is just because of the impossible charge transfer pathway. Meanwhile, when a polypyrrole chain is photo-excited, the charge transfer from the LUMO of the polymer chain to that of a dopant in the vicinity of the chain can occur if the migration is energetically favorable. The energy barrier for charge transfer is the value combined of the energy difference between the LUMO energy levels and the required energy for hopping from the polymer chain to the dopant due to their interaction. When the polymer is dissolved in DMSO, the interaction would be weak because the positive charge of a polypyrrole chain and negative charge in a dopant would solvated in the polar solvent. The weak interaction would make the energy barrier too high for the charge transfer to occur. After small addition of chloroform, the non-polar solvent would interrupt the interaction between the charges and DMSO resulting in the strong interaction between the polymer chain and the dopant. The strong interaction induced low energy barrier for charge transfer. The photo-excited electron in polypyrrole would migrate to the energetically favored LUMO of the dopant. The amount of chloroform was too small for chain conformation change resulting in invariant free-carrier tail as shown in Figure 1A and similar shapes of PL curves in Figure 1B.

4. Conclusion

Photoluminescence was observed from micelles of polypyrrole ([(Py$_3$)$_n$]($^{+}$DEHS$^-$_)$_n$)$_m$ without any substituent group. Di(2-ethylhexyl) sulfosuccinate anion was used as a dopant as well as a surfactant. Among the chlorinated solvents, CHCl$_3$ and CCl$_4$ showed a typical quenching behavior, which can be observed when quencher molecules are added to a micellar solution of fluorescent material. On the other hand, CH$_2$Cl$_2$ did not show such quenching behavior. The PL intensity was the highest in DMSO solvent and decreased in the order of DMF > NMP > ethanol > toluene > THF. In co-solvent systems of DMSO/ethanol and DMSO/toluene, the PL intensity changed almost linearly with the composition of the co-solvent.

Acknowledgements
This work was supported by Seoul National University of Technology.

Reference