Photoluminescence Characteristics of Merocyanine Dyes in Ionic Liquids

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The photoluminescence (PL) characteristics of merocyanine dye molecules in ionic liquids of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) with different purity grades were investigated. The absorption spectra for this dye in all the ionic liquid solvents investigated looked very similar while the PL emission spectra differed markedly depending on the type of ionic liquid and the impurity content. In all purity grades of [BMIM]BF$_4$ and the ultrahigh grade of [BMIM]PF$_6$, the PL spectra of these merocyanine solutions showed a single peak around 480 nm. However, when a lower grade of [BMIM]PF$_6$ was used as the solvent, an additional PL peak appeared around 575 nm. The deprotonation from the hydroxyl group of the merocyanine molecule after photoexcitation is proposed to explain the phenomenon in this unique solvent system.

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I. INTRODUCTION

The merocyanine dye molecule has been extensively studied for applications in many different areas. It is used as an electrochromic molecular probe to measure the membrane potentials with high voltage sensitivity in biological systems [1–3]. Due to the large molecular hyperpolarizability value arising from the intrinsic charge asymmetry, it is extensively exploited as a nonlinear optical material for frequency doublers [4]. Solvatochromism, in which the dye solution changes its color depending on the pH value or the polarity of the solvent, is one of the most well-known properties of the merocyanine dye. An earlier investigation found it to be due to the removal of hydrogen from a hydroxyl group of the merocyanine molecule [5], and many spectroscopic studies followed to investigate the solvent-dependent spectral shift of merocyanine and related compounds [6–12].

Ionic liquids are organic salts composed entirely of anions and cations, and remain in the liquid state at ambient conditions. Recently, ionic liquids have been extensively studied as possible “green substitutes” for volatile organic solvents [13]. Due to their unique chemical and physical properties, such as thermal stability, low vapor pressure, and the surface properties [14,15], ionic liquids have also been used for electrochemical applications [16], solar batteries [17], and biopolymers [18]. Furthermore, many dyes are known to be soluble in different ionic liquids, and the photophysical properties of the dyes in ionic liquids are expected to be interesting. For example, as the solvation of dye molecules in ionic liquids is expected to have the properties different from those in usual solvents, several experimental studies of the dynamical solvation properties of the dye in ionic liquids have been reported [19–22].

In this work, the photophysical properties of the merocyanine dye and its derivative dissolved in ionic liquids of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) and 1-butyl-3-methylimidazolium hexafluoride ([BMIM]PF$_6$) were studied by investigating the steady-state absorption and the photoluminescence (PL) spectra. The absorption and the PL spectral change shown in specific ionic liquids were explained in terms...

II. EXPERIMENTS

\(\beta-(1\text{-Methylpyridin-4-yl})-4\text{-hydroxystyrene}\) (merocyanine) and \(\beta-(1\text{-Methylpyridin-4-yl})-4\text{-methoxystyrene}\) (merocyanine derivative) dyes were synthesized as follows. The chemical structures are shown in Fig. 1. For the: Dry triethylamine(100 ml) was added into the mixture of 4-bromophenol (6.92 g, 40 mmol, for merocyanine) or bromoanisole (7.36 g, 40 mmol, for merocyanine derivative), Palladium acetate (0.09 g, 0.4 mmol), tri-o-tolylphosphine (0.49 g, 1.6 mmol), and 4-vinyl pyridine (5.26 g, 50 mmol) in a round-bottom flask under \(N_2\) at room temperature. The reaction mixture was stirred at 90 \(^\circ\)C for 24 h. Triethylamine was removed by evaporation, and the solid residue was washed with distilled water and dried. The solvent was removed under vacuum, and the product was purified by column chromatography. Purified product (2 g, 10 mmol) was dissolved in \(\text{CH}_3\text{CN}\), and then \(\text{CH}_3\text{I}\) was slowly added into the above solution at room temperature. The reaction mixture was stirred at 70 \(^\circ\)C for 24 h, and solvent was removed. Recrystallization from MeOH/ether yielded the desired compound as orange products.

1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF\(_4\)) and 1-butyl-3-methylimidazolium hexafluoride ([BMIM]PF\(_6\)) of different grades were purchased from C-Tri. The chemical structures of the ionic liquids used are also shown in Fig. 1. The merocyanine solutions for all purity grades were made in \(10^{-4}\) mol concentrations. The steady-state absorption spectra were obtained using an Agilent 5483 UV-VIS spectrophotometer.

For the measurement of the steady-state PL spectra of the molecules in the above solvents, the solutions (\(10^{-4}\) mol) were put into a quartz cuvette with a thickness of 1 cm. The second harmonic pulses of a femtosecond Ti:sapphire laser (Tsunami, Spectra-Physics, 800 nm, 100-fs pulse width, 82-MHz repetition rate) were used to excite the sample. The fluorescence signal was dispersed by using a monochromator (MS3504i, SOLAR TII) and was detected by using a fast photomultiplier tube (PMH-100, Becker & Hickl) [23,24]. All the measurements were done at room temperature (22 \(^\circ\)C).

III. RESULTS AND DISCUSSION

Shown in Fig. 2 are the steady-state absorption and the PL spectra of merocyanine in aqueous solutions with different pH values (waters of different pHs purchased from Jin chemical). The solutions of the merocyanine derivative in which the OH group was replaced by an O-CH\(_3\) methoxy group were compared as control samples for the same set of pH values. The absorption spectra for pH4 and pH7 merocyanine solutions had an absorption peak at 370 nm. At pH10, the absorption peak was redshifted to 440 nm [25]. This change in the absorption spectra also changed the PL spectra, where the PL peak was also redshifted from \(\sim\)500 nm to 575 nm in the basic solution. This redshift of the absorption and the PL emission is well-known solvatochromism and is caused by deprotonation of the hydroxyl group of the merocyanine molecule, as shown in the pictures at Fig. 2(b). On the other hand, the absorption spectra and the PL spectra did not change at all with the pH for the solutions of the merocyanine derivative as deprotonation cannot happen.
Fig. 3. (a) Steady-state absorption of merocyanine in [BMIM]PF$_6$ of ultra high grade (dotted lines) and in lower grade (solid lines), in ultrahigh grade [BMIM]BF$_4$ (dashed lines). (b) PL spectra of merocyanine in [BMIM]PF$_6$ of ultrahigh grade (dotted lines) and of lower grade (solid lines), and in [BMIM]BF$_4$ of ultrahigh grade (dashed lines).

Table 1. The impurity contents and pH values in ionic liquids of [BMIM]PF$_6$ and [BMIM]BF$_4$.

<table>
<thead>
<tr>
<th>Grade</th>
<th>[BMIM]PF$_6$</th>
<th>[BMIM]BF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.58</td>
<td>7.63</td>
</tr>
<tr>
<td>Water content</td>
<td>60 ppm</td>
<td>&lt;0.11 %</td>
</tr>
<tr>
<td>Chloride content</td>
<td>6 ppm</td>
<td>50 ppm</td>
</tr>
<tr>
<td></td>
<td>60 ppm</td>
<td>1200 ppm</td>
</tr>
<tr>
<td></td>
<td>6 ppm</td>
<td>6 ppm</td>
</tr>
<tr>
<td></td>
<td>70 ppm</td>
<td></td>
</tr>
</tbody>
</table>

in the latter case.

The steady-state absorption and the emission spectra for a 10$^{-4}$ mol solution of merocyanine in different grades of ionic liquids of [BMIM]PF$_6$ and [BMIM]BF$_4$ are shown in Fig. 3. Table 1 (provided by the company) shows the impurity contents and the pH values of the ionic liquids used in this experiment. For all the solutions of merocyanine, the absorption peak was at 377 nm, except for the merocyanine solution in a lower (solvent) grade of [BMIM]PF$_6$, where the absorption peak was redshifted a bit to 390 nm. On the other hand, the emission spectra shown in Fig. 3(b) differed markedly for the lower grade of [BMIM]PF$_6$. In all purity grades of [BMIM]BF$_4$ and the ultrahigh grade of [BMIM]PF$_6$, the PL spectra showed a single emission peak around 480 nm, but the merocyanine in a lower grade of [BMIM]PF$_6$ showed dual PL peaks at 480 nm and 575 nm. This additional PL peak at 575 nm is at the same position as the PL peak in Fig. 2(b) for the basic solution and is considered to come from deprotonation of the hydroxyl group. That the merocyanine derivative did not show any changes in the absorption and the PL spectra for any of the ionic liquids of different grades (spectra not shown) supports this mechanism.

There is a notable difference in the solvatochromic behavior in a lower grade of [BMIM]PF$_6$ as compared to the aqueous solution. Both the absorption peak and the PL peak were redshifted for case of merocyanine in a basic solution while only the PL peak was appreciably redshifted in the case of merocyanine in a lower grade of [BMIM]PF$_6$. Since the absorption spectrum represents molecules from the electronic ground state, it can be inferred that the merocyanine molecule in a lower grade of [BMIM]PF$_6$ is in an intact, protonated state in ground state. After the molecule gets photoexcited, the proton can be easily removed from the hydroxyl group, which lowers the energy difference between the excited and the ground electronic states [26,27]. The redshifted part of the PL peak can be explained if the molecule is mainly deexcited from this deprotonated energy state, after which it gets the proton back in the ground state.

Why this phenomenon happens only for the lower grade ionic liquid with PF$_6$ anion needs to be answered. As the lower grade ionic liquids (both [BMIM]BF$_4$ and [BMIM]PF$_6$) contain higher amounts of water and chloride ions, naturally these impurities can be considered as causes of the observed solvatochromism. To check this possibility, first we mixed up to 8.2 % w/w of [BMIM]Cl with an ultrahigh grade of [BMIM]PF$_6$ to increase the chloride content, or up to 1.5 % w/w (near miscibility limit) [28] of water to an ultrahigh grade of [BMIM]PF$_6$, and we measured the PL from the merocyanine in these impurity-rich solvents. As Fig. 4 shows, the fluorescence spectral peak positions in these cases were very similar, all around ~490 nm corresponding to the pro-
tonated case of merocyanine. An enhancement of the photoluminescence intensity in [BMIM][PF₆]/chloride as compared to that in ultrahigh-grade [BMIM][PF₆], and a slight reduction of the red-side shoulder in the PL spectra for the [BMIM][PF₆]/water mixture were observed, but none of these resemble the observed large PL redshift in lower-grade [BMIM][PF₆]. The absorption spectra did not change with the addition of chloride or water to [BMIM][PF₆], nor did it affect the absorption and the PL spectra of [BMIM][BF₄] at all, consistent with our observation in Fig. 3. Thus, the trace amount of chloride ions or water cannot be the cause of the observed redshift of the PL peak. The merocyanine derivative dissolved in these mixtures of solvents did not show any change in the absorption and the emission spectra either, as expected from the absence of solvatochromism in the aqueous solutions.

It should be remembered that solvatochromism in merocyanine is an indicator of the proton concentration (that is, the pH value) of the solution, as shown in Fig. 2. While the above impurities can be excluded as a cause of the observed solvatochromism, this redshift of the PL peak still informs us that the proton can be easily removed from the dye molecule in the excited state. Thus, it is obvious that the lower grade of [BMIM][PF₆] lacks protons as compared to the other ionic liquids. Although the pH values provided by the company (Table 1) are almost the same for all the ionic liquids investigated, these values are misleading, as most pH meters are only suitable for determining the proton concentrations of the aqueous liquids, not those of novel liquids like ionic liquids. What causes the lower-grade ionic liquid with PF₆ anion to be lacking in protons and how to measure the pH values of ionic liquids reliably are issues waiting to be addressed. Studies of the fast dynamics, such as pump-probe transient absorption and PL decay lifetime measurements, can follow the detailed proton transfer process and will be helpful for further understanding of this unique solvatochromic phenomenon.

IV. CONCLUSIONS

The steady-state absorption and the PL from merocyanine and its derivative in different grades of ionic liquid [BMIM][PF₆] and [BMIM][BF₄] were investigated. In all purity grades of [BMIM][BF₄] and the ultrahigh grade of [BMIM][PF₆], the PL spectra showed a single emission peak, but merocyanine in a lower grade of [BMIM][PF₆] showed dual PL peaks while the absorption spectrum remained the same. This additional PL peak is dominantly redshifted, is similar to the one from solvatochromism in basic aqueous solution, and is considered to be from deprotonation of a hydroxyl group in the merocyanine molecule. Water and chloride impurities added to ultrahigh-grade [BMIM][BF₄] were found not to change the PL spectrum. From these results, we concluded that the redshift in the PL peak originated from excited-state proton transfer, and we proposed that the pH value of merocyanine in a lower purity grade of [BMIM][PF₆] might be different from the known value. This result can potentially be used in practical applications of diagnosing the chemical state of ionic liquids.

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