

## Acridine Fluorescence Behaviors in Different Polymeric Microenvironments Directed by C2-Proton-Acidity of Imidazolium-Based Ionic Liquids

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A new fluorescent system (acridine/RTIL hybrid gel) confined in the 3D micro-structure of a poly(lactic acid) membrane were prepared from 1-butyl-3-methylimidazolium-based ionic liquids ([bmim]X (X = SbF<sub>6</sub>, NTf<sub>2</sub>, Cl); RTILs), poly(lactic acid) (PLA), and acridine *via* the sol-gel route. SEM images showed that, in the presence of [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub>, 3D-like particulated structures were created inside the PLA membranes and acridine/RTIL hybrid gels were confined in gaps of particulates. However, the use of [bmim]Cl induced the formation of a 3D-like porous structure containing the hybrid gel of acridine/[bmim]Cl in the micro-pores. The three fluorescent systems exhibited different fluorescence behaviors (fluorescence maximum and intensity) depending on the C2-H acidity scale of the RTILs (or their anion type). Acridine gels hybridized with [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub> showed blue fluorescence with relative high intensity, whereas the hybrid gel with [bmim]Cl exhibited almost no fluorescence under dry conditions. However, the acridine/[bmim]Cl hybrid system in the micro-porous PLA membrane started to emit fluorescent light under humid conditions and showed a possible response, indicating that it could be applied as a humidity sensor.

**Key Words :** Acridine/RTIL hybrid gel, Fluorescent system, 3D micro-structured polymer membrane

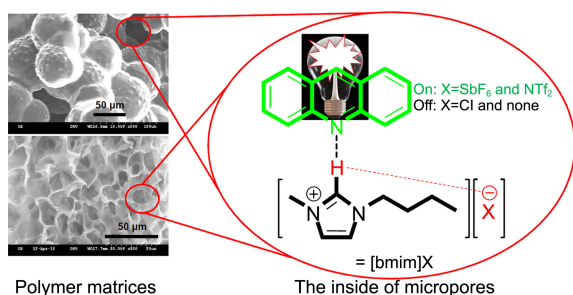
### Introduction

Photoluminescence, including fluorescence and phosphorescence as light emitted by electromagnetic radiation, is often used in a wide variety of purposes including fluorescent labeling,<sup>1,2</sup> semiconductor amplifiers,<sup>3,4</sup> solar cells,<sup>5,6</sup> and saturable absorbers.<sup>7</sup> *N*-Heterocyclic aromatic compounds such as acridine and its derivatives, which have a rigid planar structure and a high quantum yield of fluorescence, have recently generated a great deal of interest because of their use in the production of dyes and some valuable drugs, as well as in fluorescent labeling due to their ability to bind to DNA and RNA.<sup>8-11</sup> Acridine molecules have basic characteristics similar to that of pyridine ( $pK_a \approx 5.4$ ) and are generally characterized by their pH-dependent fluorescence intensity under blue light. Ryan *et al.* recently reported that the fluorescence intensity of acridine molecules is associated closely with the intermolecular hydrogen-bond between the *N*-heterocyclic compound and surrounding protic species.<sup>12</sup>

Room temperature ionic liquids (RTILs), which are organic salts in the liquid state at or close to room temperature, have many fascinating properties.<sup>13</sup> As a result, they have been used as a new medium for organic synthesis,<sup>14</sup> catalyst support<sup>15</sup> and nanostructure construction.<sup>16</sup> Specifically, the utilization of anion-directed properties such as their hydrophilic (or hydrophobic) nature and the acidity scale of the C2-proton (C2-H) of their imidazolium ring have been of special importance in research fields such as surface chemistry and catalysis.<sup>17</sup> The acidity scale of C2-H is highly

dependent on the degree of hydrogen bonding (C2-H $\cdots$ X<sup>-</sup>) between the hydrogen on the electron-deficient C2 carbon atom of the imidazolium ring and the counter anion (X<sup>-</sup>).<sup>18-26</sup> For example, more small and basic anions such as Cl<sup>-</sup> can be strongly coordinated to the C2-H, while large and less basic anions such as SbF<sub>6</sub><sup>-</sup> and NTf<sub>2</sub><sup>-</sup> bind weakly to the proton.

We recently reported the three-dimensional micro-patterning introduced inside poly(lactic acid) by using diverse RTILs bearing different anions, which resulted in an anion effect on the 3D-micropatterning of polymers.<sup>27</sup> During our on-going studies on RTIL-application,<sup>28-31</sup> we considered that the hydrogen bonding strength dependent fluorescence behavior of basic acridine molecules might also be observed in the presence of 1-butyl-3-methylimidazolium-based RTILs bearing different type of anions, because the acidity scale of C2-H of RTILs is variable depending on the anion type (Scheme 1).<sup>32</sup> To avoid possible interference from surrounding conditions (solvent, moisture), the fluorescence system (acridine/RTILs) was brought into polymeric micro pockets such as the three-dimensional honeycomb structure of a polymer membrane created *via* the phase separation between polymer and RTILs.<sup>33,34</sup> However, the use of ionic liquids in polymer matrices has rarely been reported.<sup>35-39</sup> Moreover, the usage of this composite system for determination of the fluorescent behavior of molecules has not yet been considered. In the present study, we reported for the first time the fluorescence behavior of acridine depending on the C2-H acidity (or the anion type) of 1-butyl-3-methylimidazolium-based ionic liquids within the polymeric microenviron-



**Scheme 1.** Schematic demonstration of acridine fluorescence behavior in the presence of 1-butyl-3-methylimidazolium-based ionic liquids within a microporous polymer matrix.

ment.

### Experimental Section

[bmim]X (bmim = 1-butyl-3-methylimidazolium cation; X = SbF<sub>6</sub>, NTf<sub>2</sub>, and Cl; purchased from C-Tri Co., Ltd, Korea) and CH<sub>2</sub>Cl<sub>2</sub> (MC; analytical grade; purchased from Sigma Aldrich Korea) were selected as the room temperature ionic liquid (RTILs) and the organic solvent, respectively. The materials were used without further purification. Acridine (purchased from Sigma Aldrich Korea) was purified by recrystallization from MC in a darkened room. Poly(lactic acid) (PLA, from Boehringer Ingelheim) was used as a polymeric substrate to create an aprotic microenvironment to enable the acridine molecules to effectively interact with the C2-protons of imidazolium-based RTILs.

Micro-patterned PLA-membranes containing complexes of acridine with RTILs were prepared according to the following procedures. Briefly, 0.2 g of PLA, 1.0 g of an ionic liquid, and 3.58 mg of acridine were dissolved in 10 mL of MC to obtain a homogeneously transparent solution. The solution was then spread onto a cover glass support (Mylar™17) to obtain thin films, after which the organic solvent was evaporated under ambient conditions, which left a rubbery yellowish polymer film on the surface of the glass. After the film was additionally dried in vacuum desiccators several days, it was cut to 2.5 × 2.5 cm size and fixed diagonally into the sample cuvette for the measurements. The film thicknesses were measured by scanning electron microscopy (SEM; JEOL and HITACHI S-3000H, Japan) and found to be 0.52 ± 0.01 mm (n = 5).

The absorption spectra were recorded using a Shimadzu 1601PC UV-Visible spectrophotometer at 25 °C. Fluorescence measurements were recorded using a Jasco FP-6500 spectrofluorometer. All measurements were conducted at room temperature (25 °C) under atmospheric pressure. The morphology of the 3D structured PLA membrane and the intermolecular hydrogen-bond interaction between the basic acridine molecule and the C2-proton of the RTILs were examined by scanning electron microscopy (SEM; JEOL and HITACHI S-3000H, Japan) and NMR spectrometry (Varian INOVA 500 MHz), respectively. The samples were sputter-coated with gold prior to scanning electron microscopic analysis. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub>

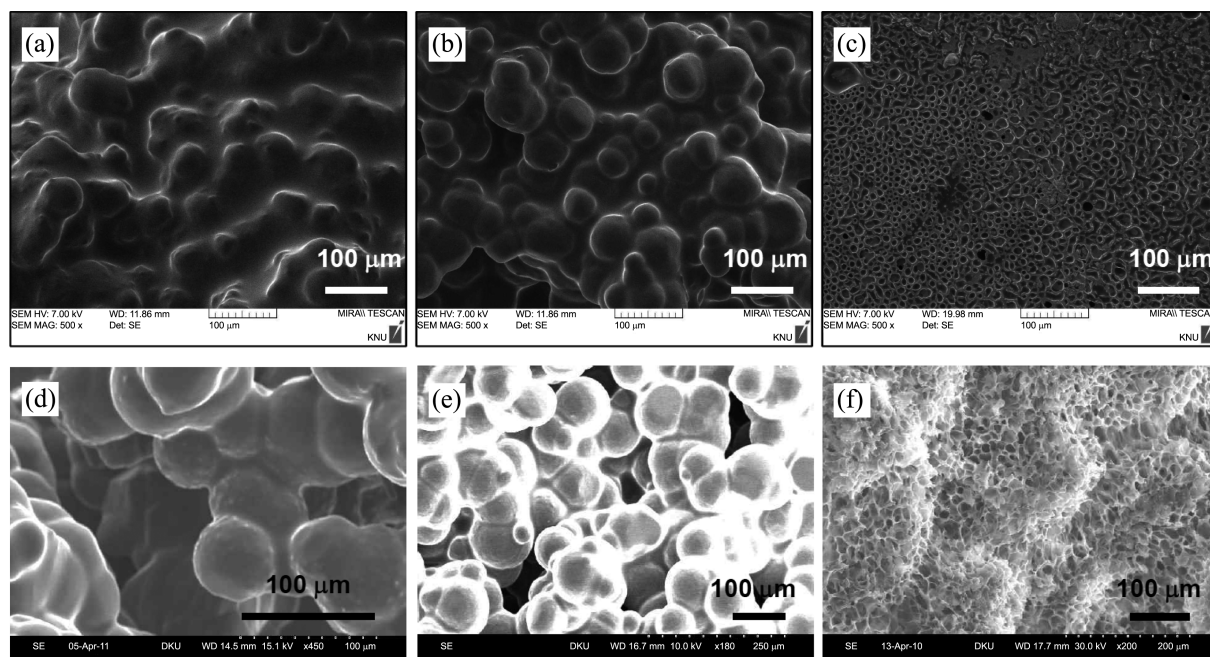
solutions using TMS as an internal reference.

### Results and Discussion

As a way to maximize the intermolecular hydrogen bonding of acridine and RTILs as a fluorescence system while minimizing that of acridine with the surrounding matrix (or protic impurity), we selected a technique to produce a three-dimensionally micro-patterned polymer membrane with micropores that contained a gel type fluorescence system (acridine/RTIL gel) similar to honey in a honeycomb. As mentioned above, we developed a method for the three-dimensional micro-patterning of a polymer (PLA) using bmim-based RTILs, [bmim]X (X = SbF<sub>6</sub>, PF<sub>6</sub>, NTf<sub>2</sub>, OTf, BF<sub>4</sub>, Cl).<sup>25</sup> By varying the counter-anion type of the RTILs, the 3D morphology inside the produced membranes was easily changed from a particulate to a porous structure. Based on the results of previous studies, herein we prepared PLA membranes containing acridine and RTILs ([bmim]X (X = SbF<sub>6</sub>, NTf<sub>2</sub>, or Cl) in their pores or gaps as a fluorescent hybrid gel.

The morphologies of the PLA membranes in the presence and the absence of acridine and RTILs were examined by SEM (Figure 1). The SEM images clearly show the formation of particulates (Figure 1(a), 1(b), 1(d), 1(e)) and pores (Figure 1(c), 1(f)) distributed throughout the polymer film. As discussed in our previous study, this morphological difference was caused by the relative hydrophilicity (or hydrophobicity) of RTILs and the polymer. For example, [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub> exhibit more hydrophobic characteristics than PLA polymer, whereas [bmim]Cl is more hydrophilic. During phase separation induced by removing the solvent from the mixture solution, more hydrophilic material generally tends to form particulate and minimize the surface area within the hydrophobic circumstance. Accordingly, the hydrophilic PLA phase (or [bmim]Cl phase) was separated from the hydrophobic [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub> phase (or PLA phase) to form particulates. Acridine molecules with basic characteristics are generally effectively solvated with bmim-based RTILs *via* intermolecular hydrogen-bonding between the basic nitrogen atom of the acridine and acidic C2-proton of [bmim] cation, whereas the PLA phase as a solid matrix only contains the fluorescence system (acridine/RTILs) without any characteristic interaction with acridine. When the morphologies of the fluorescence system-containing PLA membranes (Figure 1(a), (b), (c)) were compared to that of the fluorescence system-free PLA membranes (Figure 1(d), (e), (f)), it was clear that the well developed particulate and porous structures were filled with a gel type of the fluorescence system as a homogenized mixture in the gaps between the particulates or within the pores. When the fluorescent gel was cleared by washing with ethanol, the particulate and porous structures patterned by the fluorescent ionic liquid gel came into view.

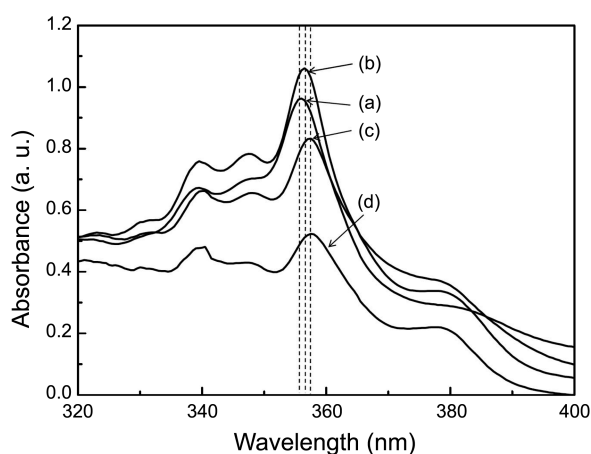
N-Heterocyclic aromatic compounds such as acridine generally undergo two possible electronic transitions,  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$ . It is well known that the presence or absence of



**Figure 1.** SEM images of the surface of the solid matrix before and after washing away the acridine-ionic liquid complexes.

hydrogen bonding between the lone pair of electrons of acridine and surrounding molecules can influence the wavelength of the absorbed UV light *via* stabilization of either the ground state or the excited state.<sup>40</sup> For example, the hydrogen bonding can stabilize the ground state of the  $n \rightarrow \pi^*$  transition, leading to an increase in the transition energies and a blue shift. Conversely, aprotic polar and nonpolar matrices without any intermolecular hydrogen bonding with acridine can stabilize the excited state of the  $\pi \rightarrow \pi^*$  transition, resulting in a decrease of the transition energies and a red shift.

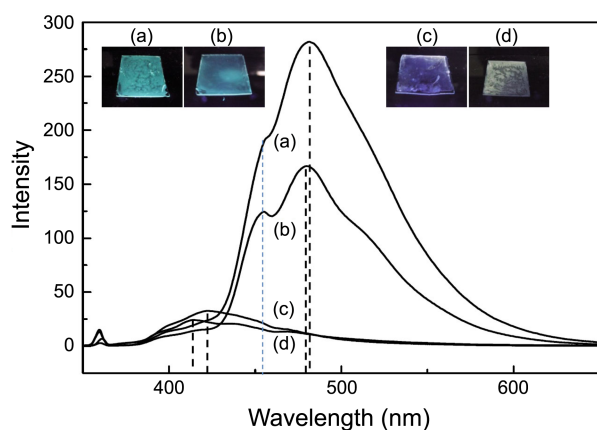
The absorption spectra of the acridine complexes ( $\text{Ac} \cdots \text{H-C2}$ ) coordinated with C2-protons (C2-Hs) of 1-butyl-3-methylimidazolium rings were recorded by UV-vis spectroscopy (Figure 2). The absorption maxima ( $\lambda_{\text{max}}$ ) of Ac and



**Figure 2.** Absorption spectra of acridine complexes with several 1-butyl-3-methylimidazolium-based ionic liquids ([bmim]X) within microstructured poly(lactic acid) matrices: X = (a)  $\text{SbF}_6^-$ , (b)  $\text{NTf}_2^-$ , (c)  $\text{Cl}^-$ , and (d) none.

$\text{Ac} \cdots \text{H-C2}$  appeared in the range of 355–358 nm, with a broad shoulder centered at 378 nm. Herein, the effects of different acidity scales of C2-H of [bmim]X (X =  $\text{SbF}_6^-$ ,  $\text{NTf}_2^-$ ,  $\text{Cl}^-$ ) on electronic transitions were observed. When the acidity of C2-H increased in the order of  $\text{Cl}^- < \text{NTf}_2^- < \text{SbF}_6^-$ , the absorption maxima of  $\text{Ac} \cdots \text{H-C2}$  showed a blue shift from 358 to 355 nm, indicating that this absorption may have originated from the  $n \rightarrow \pi^*$  transition. In this experiment, the polymer (PLA) matrix may be considered to effectively provide an aprotic polar microenvironment to form acridine complexes with bmim-based ionic liquids *via* intermolecular hydrogen bonding,  $\text{Ac} \cdots \text{H-C2}$ .

To study the C2-H acidity directed fluorescence behavior of acridine in the polymeric microenvironment, several combinations of acridine and three types of ionic liquids were subjected to a fluorescence experiment. It is well known that fluorescence intensities of nitrogen heterocycles are sensitive to their hydrogen-bond interaction with neighboring molecules.<sup>41</sup> For example, acridine fluoresce is much stronger in protic media than in aprotic media, because under protic conditions the lowest excited state of an acridine complex ( $(\text{Ac} \cdots \text{H}^+)^*$ ) is the excited state of the  $\pi \rightarrow \pi^*$  transition and a fluorescent state, while under aprotic conditions, the lowest excited state of acridine ( $\text{Ac}^*$ ) is the excited state of the  $n \rightarrow \pi^*$  transition and a nonfluorescent state. According to the results of previous studies,<sup>42</sup> acridine molecules (Ac) in neutral water ( $\text{pK}_a = 5.4$  at 25 °C) are in equilibrium with protonated acridine molecules ( $\text{Ac} \cdots \text{H}^+$ ). Therefore, under electromagnetic radiation, two types of electronic excitations may be possible through  $\pi \rightarrow \pi^*$  electronic transition, for example,  $\text{Ac} \rightarrow \text{Ac}^*$  and  $(\text{Ac} \cdots \text{H}^+) \rightarrow (\text{Ac} \cdots \text{H}^+)^*$ . Herein, the fluorescence maximum produced from the excited state  $(\text{Ac} \cdots \text{H}^+)^*$  of the protonated acridine molecules was observed at 475 nm, while that of  $\text{Ac}^*$  occurred at 430 nm with a

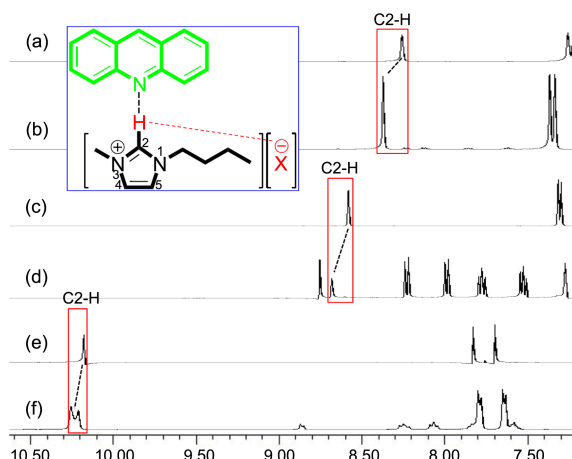


**Figure 3.** Fluorescence spectra of acridine complexes with several 1-butyl-3-methylimidazolium-based ionic liquids ([bmim]X) within microstructured PLA matrices: X = (a) SbF<sub>6</sub>, (b) NTf<sub>2</sub>, (c) Cl, and (d) none.

weak intensity.

In our fluorescence experiments of acridine within quasi-protic RTILs with diverse C2-H acidity scales (Figure 3), similar fluorescence behavior to that found under the aqueous condition was observed. The first acridine hybrid gel of [bmim]SbF<sub>6</sub> with the strongest C2-H acidity among the RTILs used showed characteristic fluorescence peaks at 480 nm with a shoulder at approximately 455 nm. However, the second hybrid gel of [bmim]NTf<sub>2</sub> resulted in a slight blue shift of the peak of 480 nm to 477 nm, whereas the shoulder peak was unchanged. When [bmim]Cl, which has the weakest C2-H acidity among the RTILs, was used, the fluorescence peaks were strongly shifted to about 424 nm. In addition, their fluorescence intensities were clearly distinguished from each other. Additionally, the intensities decreased in parallel in order of increasing C2-H acidity of the ionic liquids, for example, [bmim]X (X = SbF<sub>6</sub> > NTf<sub>2</sub> > Cl). In conclusion, the changes in the fluorescence peak position and intensity should be closely correlated to the acidity scale of the C2-proton of imidazolium RTILs, namely, their intermolecular interaction *via* hydrogen-bonding with the lone pair electrons on the nitrogen atom of the acridine molecule.

In the presence of imidazolium-based RTILs with different acidity scales based on their C2-protons, naked acridine molecules (Ac) may be in equilibrium with RTIL-coordinated acridine molecules (Ac⋯H-C2)\*. In such cases, two types of electronic excitations of acridine molecules under electromagnetic radiation could be considered, for example, Ac\* and (Ac⋯H-C2)\*. When imidazolium-based ionic liquids with relatively acidic C2-protons, such as [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub>, were employed in the system, relatively strong hydrogen-bonding with acridine was predominant, leading to a strong fluorescence maximum from the excited complex (Ac⋯H-C2)\* at approximately 480 nm. However, in the presence of [bmim]Cl with much less acidic C2-protons, hydrogen-bond-free acridine molecules will be predominant and may be excited to the state (Ac\*). The fluorescence peaks at about 424 nm with extremely weak intensity, as shown in Figure 3, may have originated from the excited



**Figure 4.** <sup>1</sup>H-NMR spectra of ionic liquids ((a), (c), and (e) = [bmim]X) and acridine/ionic liquid complexes ((b), (d), and (f) = Ac/[bmim]X) in CDCl<sub>3</sub>: X = SbF<sub>6</sub> for (a) and (b), NTf<sub>2</sub> for (c) and (d), and Cl for (e) and (f).

state (Ac\*). The fluorescence behavior of acridine/[bmim]Cl is quite similar to the case of RTIL-free acridine embedded within PLA microcapsules. However, the acridine/[bmim]Cl hybrid system started to emit fluorescent light under humid conditions, indicating that the system has the potential to be used as a humidity sensor. Assessment of the applicability of this system as a humidity sensor is currently underway. The relative fluorescence intensities of the four samples were also optically confirmed as shown in inset of Figure 3.

The intermolecular hydrogen-bonding (Ac⋯H-C2) of acridine with [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub> was also confirmed by <sup>1</sup>H-NMR spectrometry. As shown in Figures 4(a) and 4(b), there were similar changes in the <sup>1</sup>H-NMR spectra caused by the addition of acridine to CDCl<sub>3</sub> solutions of [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub>, respectively. When 1 equiv of acridine was added into each solution, downfield shifts (about 0.12–0.10 ppm) with broadening in the signal of the C2-H of imidazolium moieties were observed. Further addition of acridine resulted in saturation of the chemical shift changes. These observations clearly suggest that acridine molecules acted as a proton receptor to form stable 1:1 stoichiometric complexes with C2-protons of the RTILs used and to form an intermolecular hydrogen bond, even in chloroform solution. However, the addition of acridine did weakly affect the signal of the C2-H of [bmim]Cl in CDCl<sub>3</sub> solution (about 0.05 ppm). These findings suggest that halide anions (Cl<sup>−</sup>) are stronger C2-proton receptors that are in competition with acridine molecules and can thus be closely associated with the C2-H of [bmim] cation in acridine solution of CDCl<sub>3</sub>.

## Conclusion

Three dimensionally micro-structured RTILs/PLA hybrid films containing acridine were successfully prepared from 1-butyl-3-methylimidazolium-based ionic liquids ([bmim]X (X = SbF<sub>6</sub>, NTf<sub>2</sub>, Cl); RTILs), poly(lactic acid) (PLA) and acridine *via* the sol-gel route. Acridine molecules coordinated with C2-protons of RTILs *via* intermolecular hydro-

gen bonding were located within micro-pores or gaps around micro-particulates induced by the anion types of RTILs in the polymer matrix. Several combinations of acridine/RTILs exhibited different fluorescence behaviors (fluorescence maximum and intensity) depending on the C2-H acidity scale (or the anion type of RTILs). Two types of acridine gels hybridized with [bmim]SbF<sub>6</sub> and [bmim]NTf<sub>2</sub> within micro-particulate PLA membranes showed blue fluorescence with relative high intensity, whereas the system with [bmim]Cl exhibited almost no fluorescence. Finally, the acridine/[bmim]Cl hybrid system in the micro-porous PLA membrane that emitted fluorescent light only under humid conditions had the potential for use as a humidity sensor.

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