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# Ionic Liquids as Components in Fluorescent Functional Materials

Jun-ichi Kadokawa

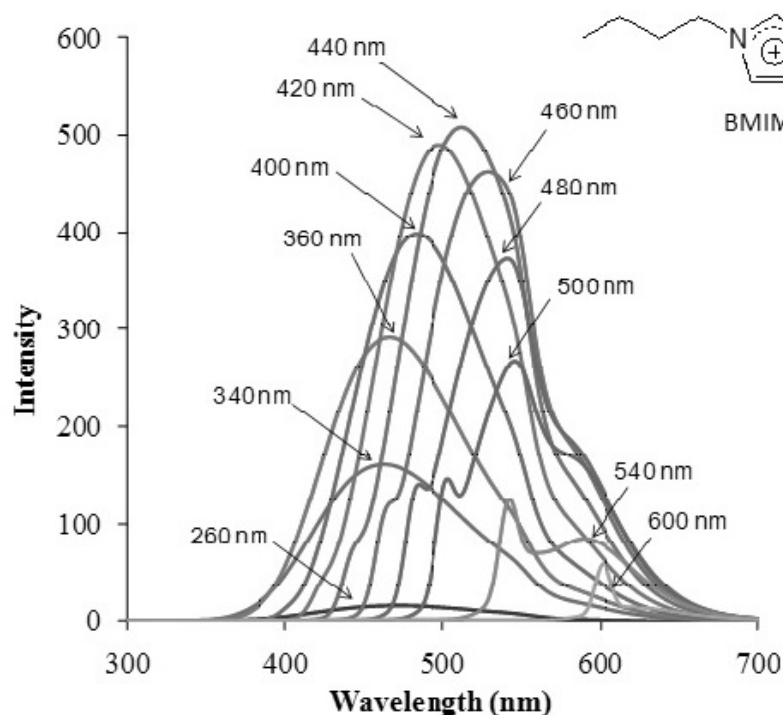
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## 1. Introduction

In recent years, photo functional materials have been increasing much attention because of their attractive characteristics such as good specificity, excellent sensitivity, and easy handling [1]. Fluorescent-emitting materials are one of the most practically used photo functional materials in the many application fields such as color sensors and probes in biological science, key elements in color devices and displays, organic light-emitting diodes, and organic field-effect transistors [2]. Furthermore, a variety of polymers bearing covalently linked fluorescent dye moieties, exemplifying polymethacrylate, polyacrylamide, and conjugated polymer, have been synthesized to provide novel polymeric fluorescent materials [3-5]. To develop new fluorescent functional materials, the author has noted ionic liquids (ILs) as material components. ILs are low-melting-point molten salts, defined as which form liquids at room temperature or even at temperatures lower than a boiling point of water. The property is owing to that the liquid state is thermodynamically favorable due to the large size and conformational flexibility of the ions, in which these behaviors lead to small lattice enthalpies and large entropy changes that favor the liquid state [6]. In the past more than a decade, ILs have attracted much attention due to their specific characteristics such as a negligible vapor pressure, excellent thermal stabilities, and controllable physical and chemical properties [7]. Beyond these traditional properties of ILs, recently, interests and applications on ILs have been extended to the researches related to functional materials as designer substrates with controllable physical and chemical properties or even specific functions [8], so-called 'task-specific ILs' [9,10]. As one of the unique and specific properties of ILs, it has been reported that imidazolium-type ILs exhibit excitation-wavelength-dependent fluorescent behavior due to the presence of energetically different associated species [11-14]. For example, 1-butyl-3-methylimidazolium chloride (BMIMCl) typically

exhibits emissions maxima at around 450-600 nm depending on the excitation wavelengths (Figure 1). The imidazolium-type ILs which form such different species have potential as components to contribute to developing new fluorescent functional materials.



**Figure 1.** Fluorescence spectra of a liquid BMIMCl by excitation at 260-600 nm.

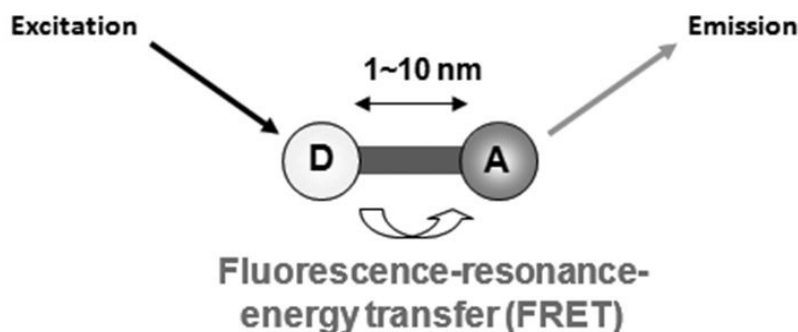
In this chapter, the author describes the use of the imidazolium-type ILs as components to prepare new fluorescent functional materials. A first topic deals with the appearance of fluorescent resonance-energy-transfer (FRET) in solutions of fluorescent dyes with BMIMCl. As a second topic, on the basis of this unique FRET system, the preparation and FRET functions of polymeric IL (PIL) films carrying fluorescent dye moieties are disclosed. Furthermore, a third topic deals with the preparation of ion gel materials from BMIMCl which exhibit the FRET function and other unique fluorescent properties.

## 2. Fluorescent Properties in Solutions of Rhodamine 6G with Ionic Liquid

### 2.1. FRET

Besides exhibiting emission by excitation at a characteristic wavelength of each fluorescent dye, the fluorescent materials in practical applications are often required to exhibit fluorescent emissions by excitation at different wavelength areas. For the purpose to develop such dye materials, the author has noted the FRET technique [15], which has been used in de-

signed fluorescent materials to obtain a large shift of the excitation wavelength from that the dyes natively show. FRET is an interaction between the electronic excited states of two fluorescent substrates, a donor and an acceptor, in which excitation energy is transferred from the former to the latter without emission of a photon (Figure 2) [16]. By means of FRET, new high performance biosensors, fluorescence imaging, and quantification systems of selective interaction have been developed for targets of biological molecules, such as proteins and lipids [17,18].

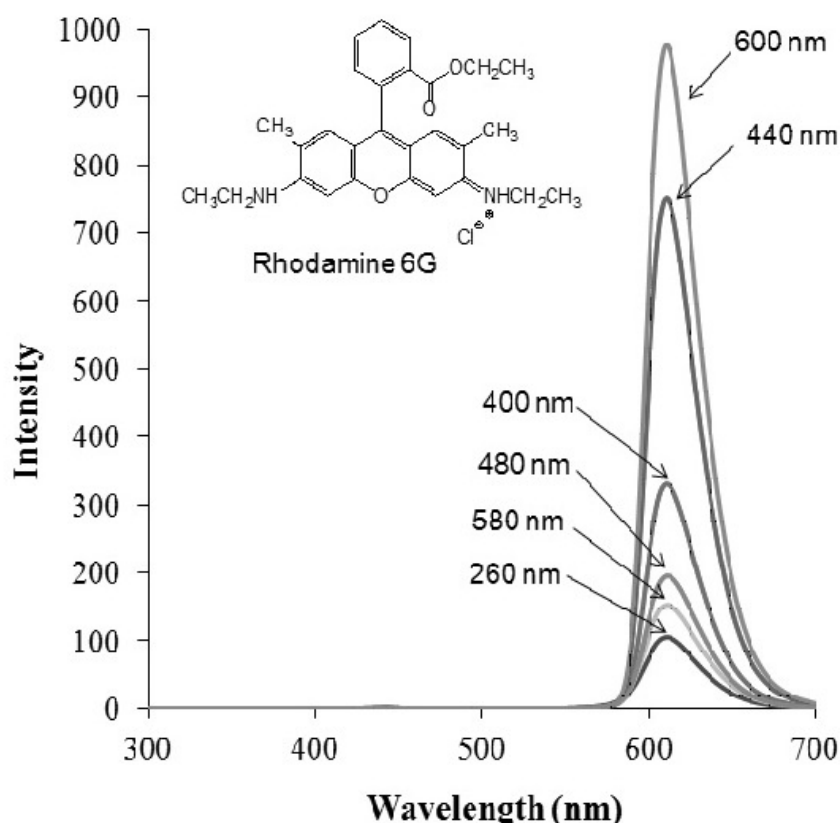


**Figure 2.** Image of FRET from a donor to an acceptor.

## 2.2. FRET in Systems of Rhodamine 6G with BMIMCl

To develop the basic technique for the preparation of new functional fluorescent materials, the author found a unique FRET system in a solution of rhodamine 6G with BMIMCl, where the former and latter acted as an acceptor and a donor, respectively [19]. Rhodamine 6G is a representative red fluorescent dye and exhibits emission maxima at ca. 540-610 nm by excitation at around 520 nm [20]. When the fluorescence spectra of the solution of rhodamine 6G with BMIMCl (2.5 mmol/L) were measured by excitation at 260-600 nm, emissions at ca. 608 nm due to the dye were observed in all the spectra, whereas fluorescence peaks due to BMIMCl were not detected (Figure 3). From these results, the occurrence of FRET from BMIMCl to rhodamine 6G in the solution was supposed. Indeed, all the fluorescence spectra of a sole BMIMCl liquid excited at various wavelengths were overlapped with an absorption peak of rhodamine 6G at 545 nm. The occurrence of FRET in the solution of rhodamine 6G with BMIMCl was confirmed further using the Stern-Volmer relation [21].

On the other hand, the fluorescence spectra of a solution of another fluorescent dye, pyrene, with BMIMCl by excitation at 260-600 nm showed the emissions due to BMIMCl. This was owing to no occurrence of FRET in the solution because an absorption of pyrene was not overlapped with the emissions of BMIMCl. Moreover, when the fluorescence spectra of a solution of a dye with no fluorescent emission, that is, Congo red, were measured by excitation at various wavelengths, the emissions due to BMIMCl were not observed. This result was explained by the energy transfer from BMIMCl to Congo red because an absorption of the dye overlapped with the emissions of BMIMCl.



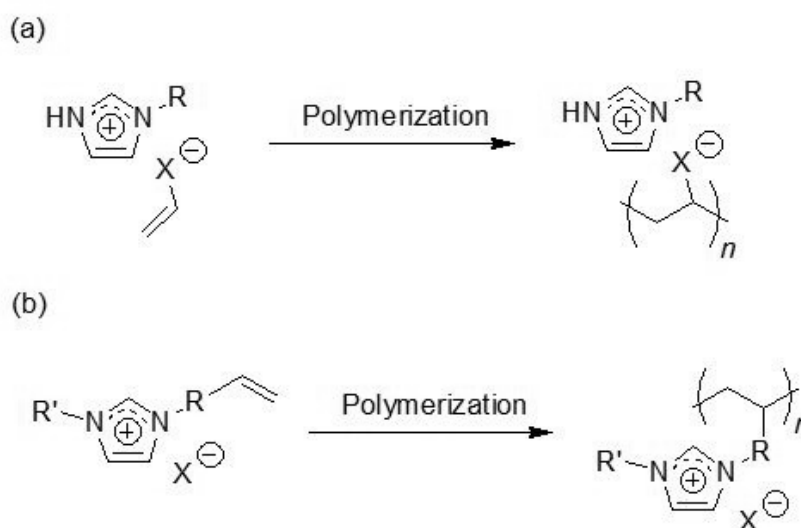
**Figure 3.** Fluorescence spectra of rhodamine 6G/BMIMCl solution by excitation at 260–600 nm.

### 3. Tunable Multicolor Emissions of Polymeric Ionic Liquid Films Carrying Fluorescent Dye Moieties

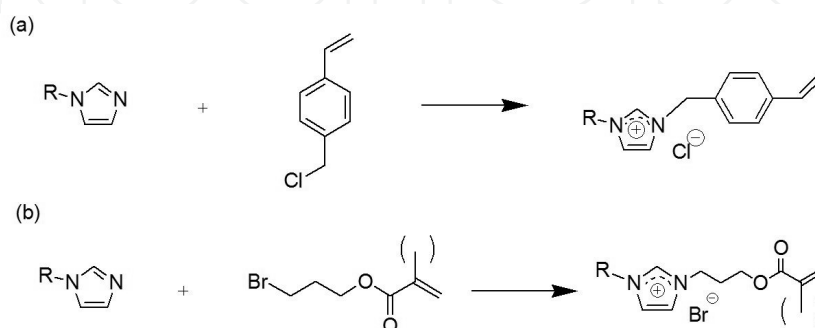
#### 3.1. Polymeric Ionic Liquids

Polymeric ionic liquids (PILs) are defined as the polymers obtained by polymerization of ILs having polymerizable groups (polymerizable ILs) [22,23]. Thus, 'PILs' are termed just the polymeric forms of ILs, but they are not necessary to show liquid forms at room temperature or even at some ambient temperatures. The polymeric ILs, therefore, are often called 'polymerized ILs' too. The major advantages for providing the PILs are to be enhanced stability, and improved processability and feasibility in application as practical materials. Polymerizable ILs as a source of the PILs can be available by incorporating the polymerizable groups at both anionic and cationic sites (Figure 4). In the former case, polymerizable anions are ionically exchanged from some anions of general ILs (Figure 4(a)), giving the polymeriz-

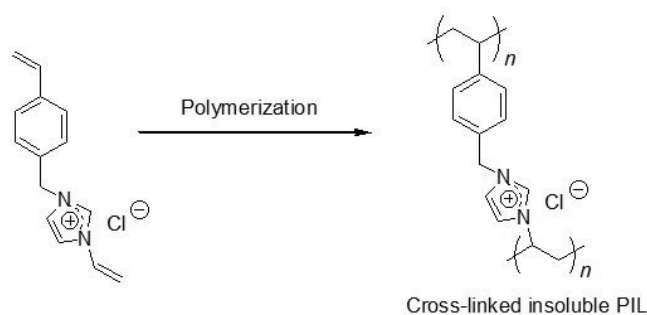
able ILs. In the latter case, vinyl, meth(acryloyl), and vinylbenzyl groups have typically been appeared as the polymerizable group (Figure 4(b)). Because 1-vinylimidazole is a commercially available, the vinylimidazolium-type polymerizable ILs are prepared by quaternization of 1-vinylimidazole with a variety of alkyl halides. The reaction of vinylbenzyl halides or haloalkyl (meth)acrylates with 1-alkylimidazoles gives the corresponding imidazolium-type polymerizable ILs having the vinylbenzyl or (meth)acryloyl polymerizable group (Figure 5). Furthermore, when vinylbenzyl halides or haloalkyl (meth)acrylates are reacted with 1-vinylimidazole, the polymerizable ILs having two polymerizable groups are produced. Because these polymerizable ILs can be converted into insoluble and stable PILs with the cross-linked structure by the radical polymerization (Figure 6), they have a highly potential as the source of the components in the practical materials.



**Figure 4.** Polymerization of polymerizable ILs having a polymerizable group at anionic site (a) and cationic site (b).



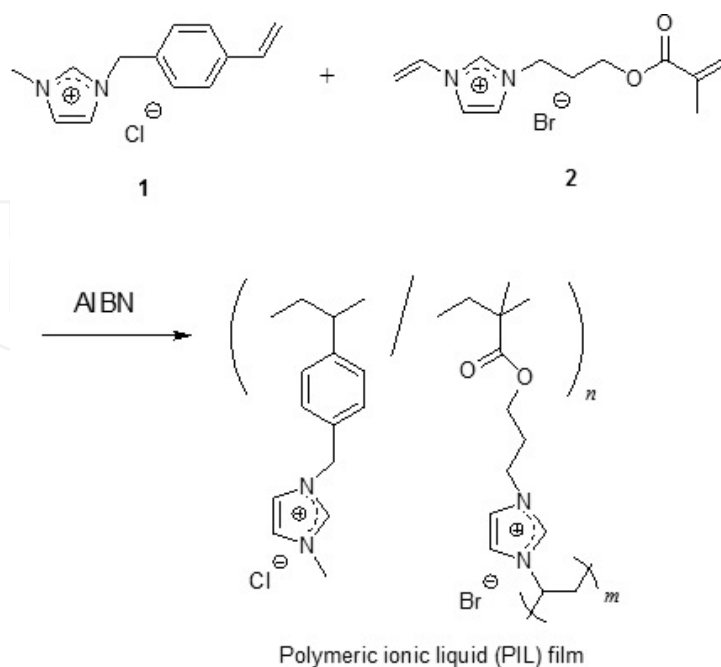
**Figure 5.** Typical synthetic schemes for polymerizable ILs having vinylbenzyl (a) and (meth)acrylate (b) groups.



**Figure 6.** Polymerization of a polymerizable IL having two polymerizable groups to produce a cross-linked insoluble PIL.

### 3.2. Preparation of Transparent Polymeric Ionic Liquid Films

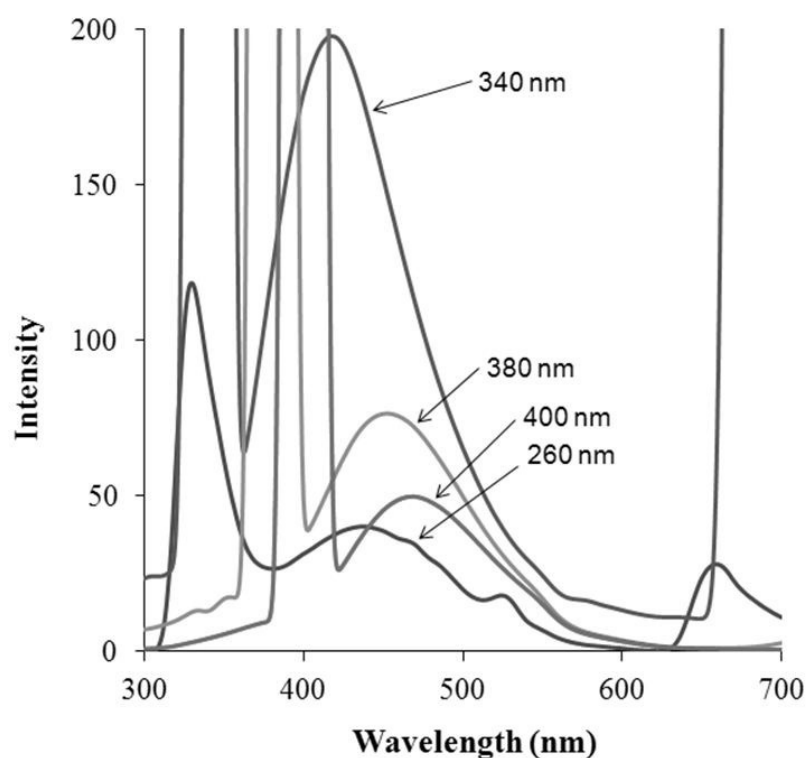
To incorporate the aforementioned unique FRET function into a film material, the preparation of a transparent PIL film was attempted by radical polymerization of the appropriate polymerizable ILs [24]. For this purpose, the two imidazolium-type polymerizable ILs, 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (1) and 1-(3-methacryloyloxypropyl)-3-vinylimidazolium bromide (2) were employed to obtain a cross-linked PIL (Figure 7). For the preparation of the film form of PIL, a solution of 1 and 2 (10:1), and AIBN as a radical initiator (1mol% for 1+2) was sandwiched between two glass plates. Then, the system was heated at 65 °C for 30 min and subsequently at 75 °C for 2 h to occur the copolymerization. The resulting material had the film form with transparent property.



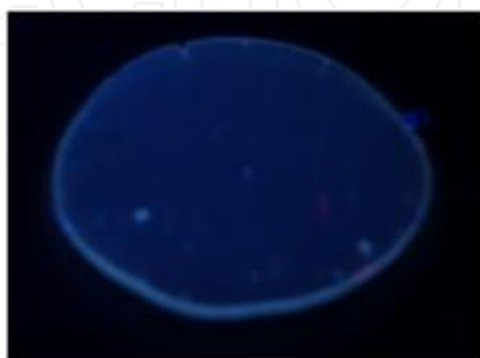
**Figure 7.** Radical copolymerization of 1 with 2 by AIBN to give PIL film.



The UV-vis spectrum of the film showed small absorptions at 280-550 nm, which were probably related to the fluorescent emissions of the imidazolium-type ILs, besides large absorptions at the wavelengths below 280 nm. The fluorescence spectra of the film showed excitation-wavelength-dependent fluorescent emission maxima at around 430-470 nm by excitation at 260-400 nm (Figure 8). Indeed, the film exhibited blue emission by UV light irradiation at 365 nm (Figure 9). The fluorescent behavior of the film was similar as that of the general imidazolium-type IL such as BMIMCl.



**Figure 8.** Fluorescence spectra of PIL film by excitation at 260-400 nm.

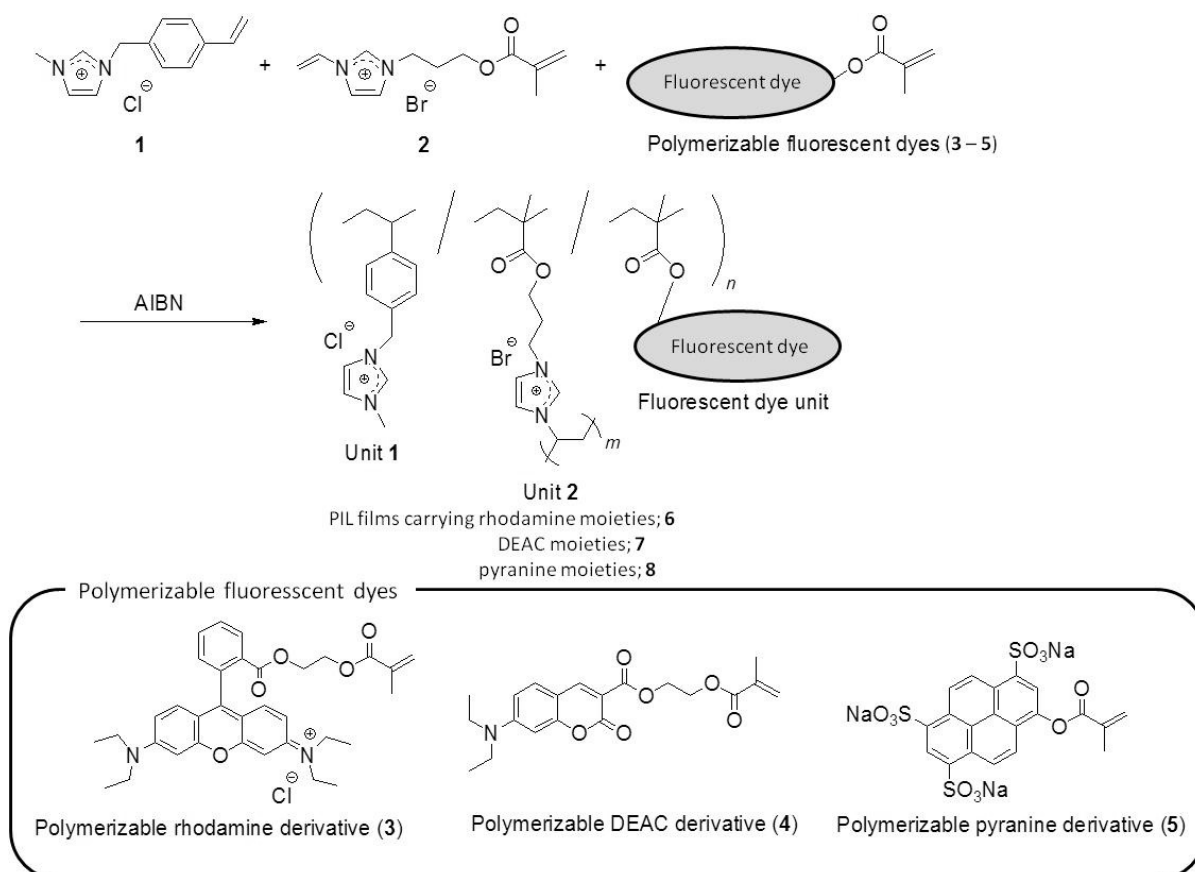


**Figure 9.** Photograph of PIL film under UV light irradiation at 365 nm.



### 3.3. Preparation and Multicolor Emissions of Fluorescent Polymeric Ionic Liquid Films

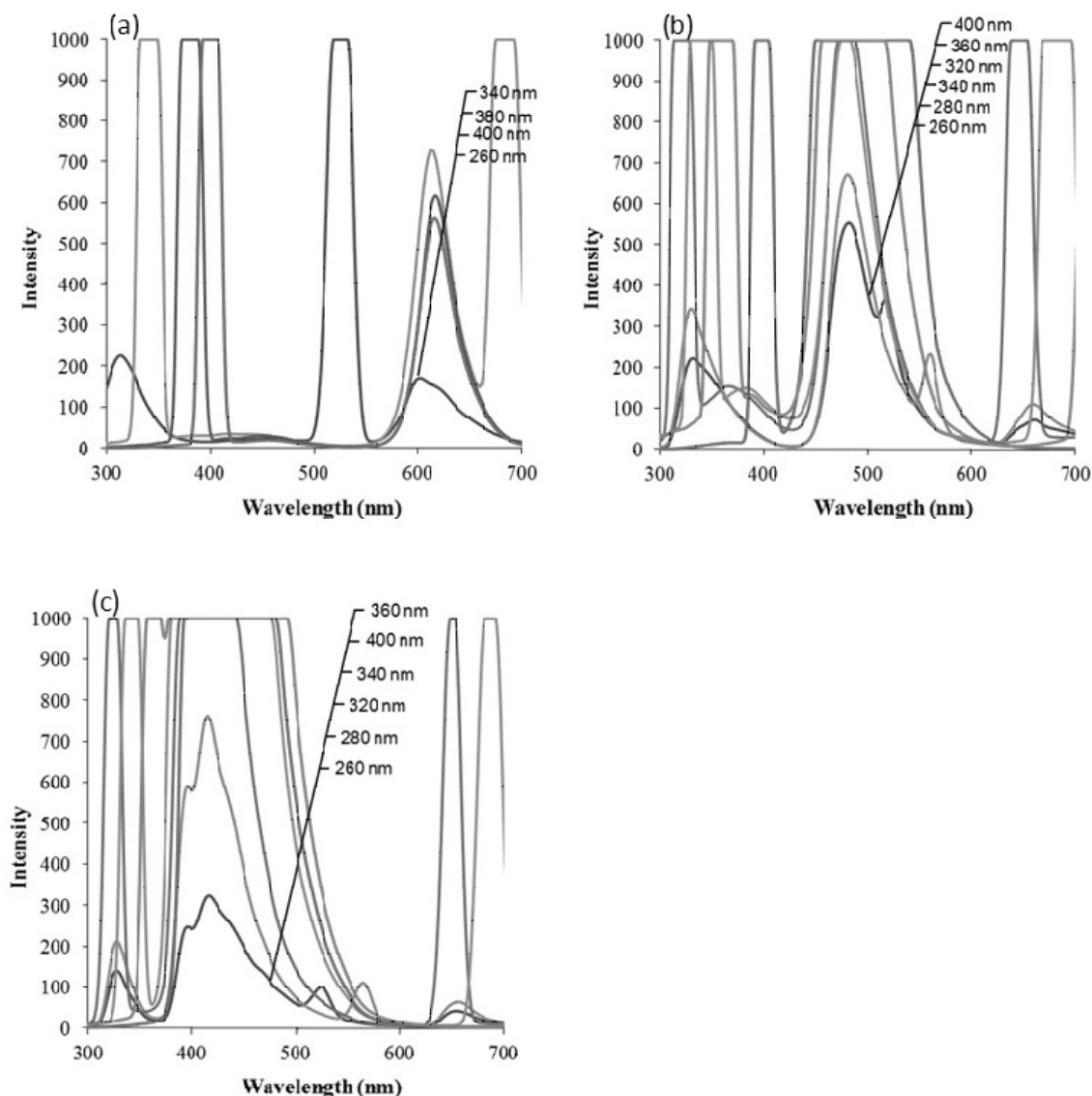
On the basis of the principle of three primary colors, the PIL films which exhibit multicolor emissions depending on combinations of the primary colors have considerably been designed [24,25]. For this purpose, three fluorescent dyes, rhodamine (red emission), 7-(diethylamino)coumarin-3-carboxylic acid (DEAC, green emission), and pyranine (blue emission) were selected, and thus, polymerizable rhodamine, DEAC, and pyranine derivatives (3, 4, and 5) having a methacrylate group were synthesized. Then, radical copolymerization of 1, 2, with 3, 4, or 5 was conducted by a similar procedure as aforementioned for PIL film to produce the PIL films 6, 7, and 8 carrying respective dye moieties (Figure 10).



**Figure 10.** Radical copolymerization of 1, 2, with 3, 4, or 5 to give PIL films carrying primary color fluorescent dye moieties.

When the fluorescence spectra of the film 6 were measured by excitation at 260-400 nm, emissions at ca. 620 nm due to the rhodamine group in addition to scattering peaks of excitation lights were observed in all the spectra (Figure 11(a)). On the other hand, fluorescent emissions at around 430-470 nm due to the units 1 and 2 did not appear. These results suggested the occurrence of FRET from the units 1 and 2 to the rhodamine group in the film. Indeed, all the emissions of the PIL film composed of the units 1 and 2 (without fluorescent dye moieties; hereafter, this film is named the basic PIL film) excited at various wavelengths

were partially overlapped with an absorption peak of the film 6 at wavelength areas of around 450-600 nm.



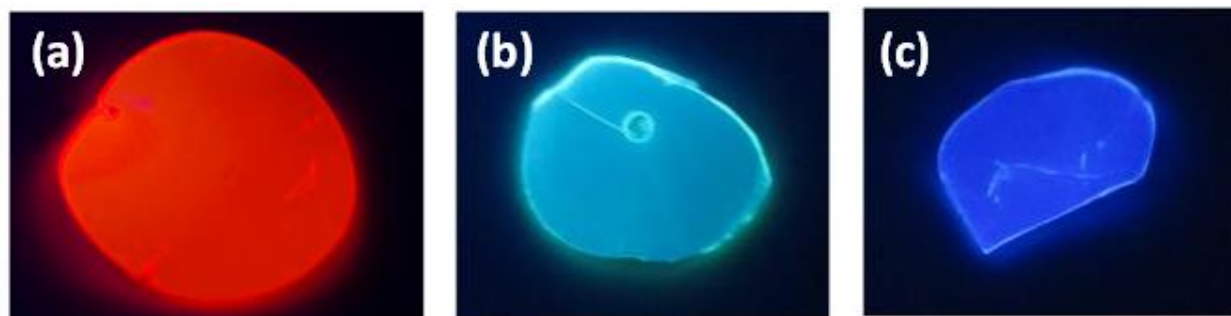
**Figure 11.** Fluorescence spectra of PIL films 6, 7, and 8 ((a)-(c), respectively) by excitation at 260-400 nm.

When the fluorescence spectra of the film 7 were also measured by excitation at 260-400 nm, emissions at ca. 470 nm due to the DEAC group were observed (Figure 11(b)). Furthermore, all the emissions of the basic PIL film excited at various wavelengths were totally or even partially overlapped with absorptions of the film 7. Taking the UV-vis spectrum of the film 7 into consideration, it was also supposed that the DEAC moieties in 7 emitted by excitation at around the wavelengths areas where the absorptions of 7 appeared. Therefore, the above results suggested that the emissions due to the DEAC group in 7 excited at wide wavelength

areas were owing to either direct excitation of the DEAC group or FRET from the units 1 and 2 to the DEAC group in the film.

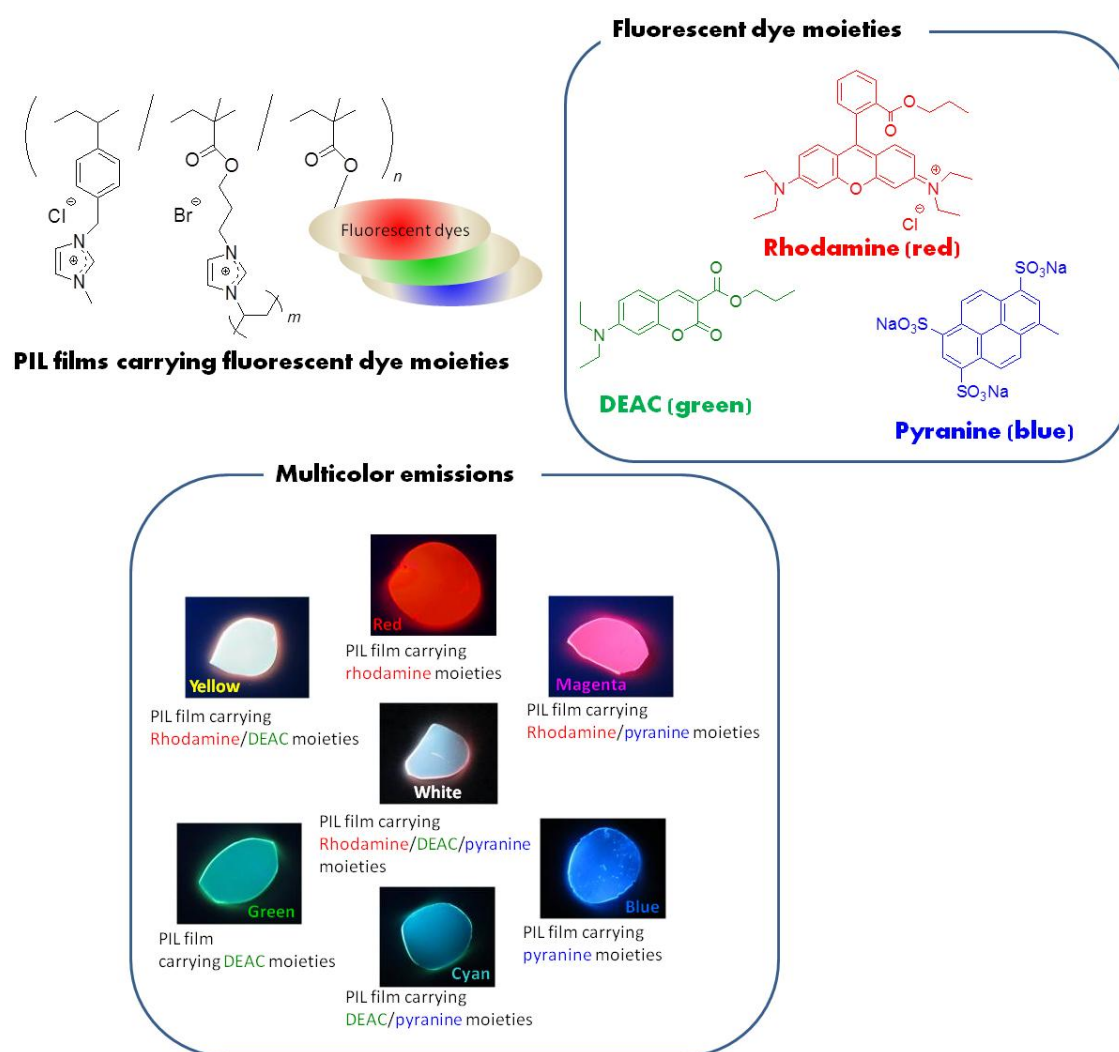
Similarly, emissions due to pyranine moieties were observed at ca. 420 nm in the fluorescence spectra of the film 8 excited at 260–400 nm (Figure 11(c)). The fluorescent emissions of the basic PIL film excited at shorter wavelength areas, i.e., 260–360 nm were partially overlapped with absorptions of the film 8 at around 300–400 nm. On the other hand, the emissions of the basic PIL film by excitation at longer wavelength area such as 380 and 400 nm appeared at wavelengths longer than ca. 400 nm, which were not mostly overlapped with the absorptions of the film 8. Moreover, the pyranine moieties in 8 emitted by excitation at around the wavelength areas where the absorptions of 8 appeared. Therefore, it was supposed that the emissions of the pyranine group in the film 8 by excitation at shorter wavelength area were owing to either direct excitation of the pyranine group or FRET from the units 1 and 2 to the pyranine group, whereas those excited at longer wavelength areas were probably caused by only direct excitation of the pyranine group in the film.

Actually, the film 6, 7, and 8 showed the red, green, and blue emissions, respectively, by the UV-vis light irradiations at 365 nm (Figure 12).



**Figure 12.** Photographs of PIL films 6, 7, and 8 ((a)–(c), respectively) under UV light irradiations at 365 nm.

By means of possible combinations among the rhodamine, DEAC, and pyranine dyes, which emitted the three primary colors, the PIL films exhibiting tunable color emissions were prepared. Three combinations of polymerizable dyes, that is, 3 and 4, 3 and 5, and 4 and 5, were copolymerized with 1 and 2 by AIBN according to the same experimental manner as that for the basic PIL film (Figure 13). The fluorescence spectra of the resulting films showed two kinds of emissions due to the incorporated dye moieties by excitation at 260–400 nm. These data suggested that the respective dye groups in the PIL films were individually emitted by direct excitation or FRET. The PIL film carrying three dye moieties was similarly prepared by copolymerization of 1, 2, with the three polymerizable dyes. The fluorescence spectra of the resulting film also showed three kinds of emissions excited at 260–400 nm. Thus, the resulting films exhibited yellow, magenta, cyan, and white fluorescent emissions, respectively, by UV light irradiation at 365 nm (Figure 13). These results indicated that the PIL films carrying proper fluorescent dye moieties emitted tunable multicolors by excitation at a sole wavelength.



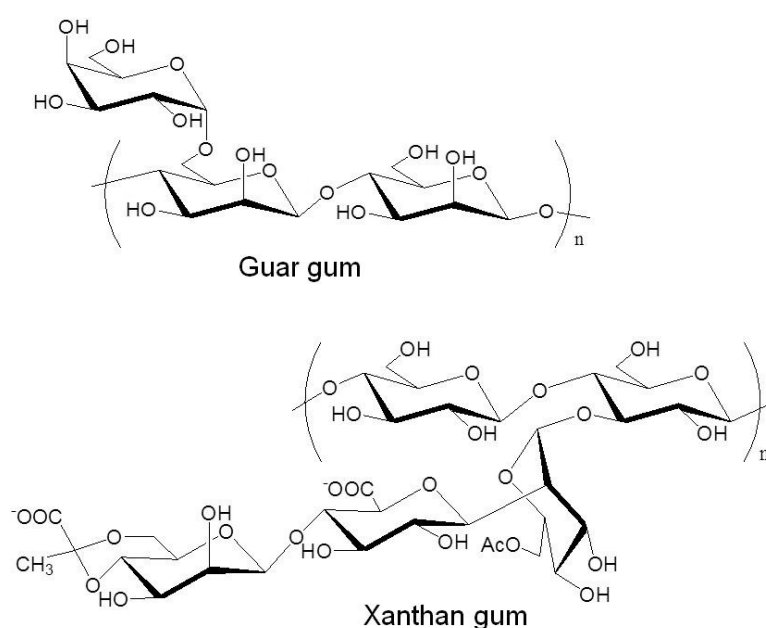
**Figure 13.** Multicolor emissions of PIL films carrying various combinations of fluorescent dye moieties.

## 4. Preparation of Photo Functional Ion Gels of Polysaccharides with an ionic liquid

### 4.1. Ion Gels of Polysaccharides with Ionic Liquids

Because ILs have been found to be used as good solvents for natural polysaccharides such as cellulose [26-29], and accordingly, can be considered to have a specific affinity for polysaccharides, efficient methods to produce new polysaccharide-based materials compatibilized with ILs have the potential to lead to the practical use of natural polysaccharides as the promising biomass resources [30,31]. On the basis of these viewpoints, the author has reported the facile preparation of gel materials of abundant polysaccharides such as cellulose, starch, and chitin, which include ILs as disperse media in the polysaccharide network matrixes, so-called ion gels [32-35]. Besides such abundant polysaccharides, many kinds of nat-

ural polysaccharides from various sources have been known [36]. For example, some polysaccharides such as guar gum and xanthan gum are used as hydrocolloid polysaccharides for a stabilizer, a viscous agent, and a structure provider in food industries [37]. Guar gum is a galactomannan extracted from the seed of the leguminous shrub *Cyamopsis tetragonoloba* and consists of a (1→4)-linked β-D-mannopyranose main-chain with a branched α-D-galactopyranose unit at 6 position (Figure 14). Xanthan gum produced by *Xanthomonas campestris* has a cellulose-type main-chain (β-(1→4)-glucan) with trisaccharide side chains attached to alternate glucose units in the main-chain (Figure 14). The author has reported that functional ion gels of hydrocolloid polysaccharides, e.g., guar gum and xanthan gum, with BMIMCl were obtained when the corresponding solutions of the polysaccharides in BMIMCl in appropriate concentrations were left standing at room temperature [38-42]. These ion gels have been applied to providing functional materials by means of the specific fluorescent behaviors of ILs.



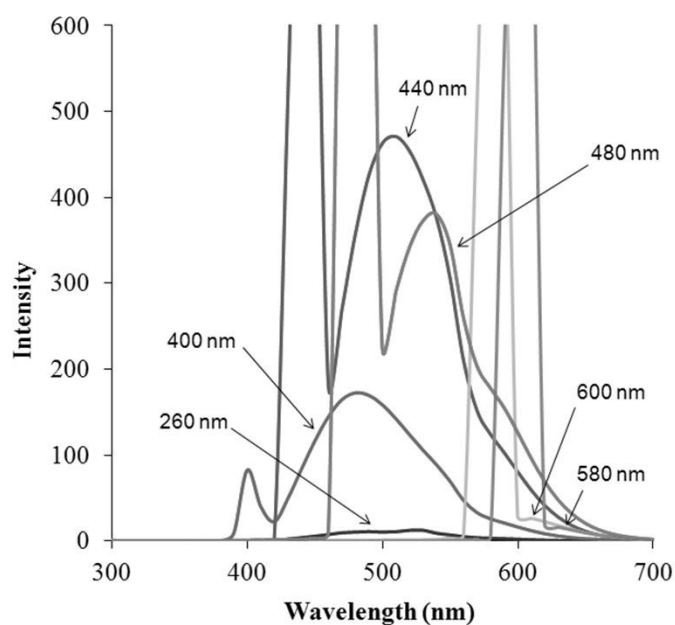
**Figure 14.** Structures of guar and xanthan gums.

#### 4.2. FRET Function of Ion Gel of Guar Gum with an Ionic Liquid

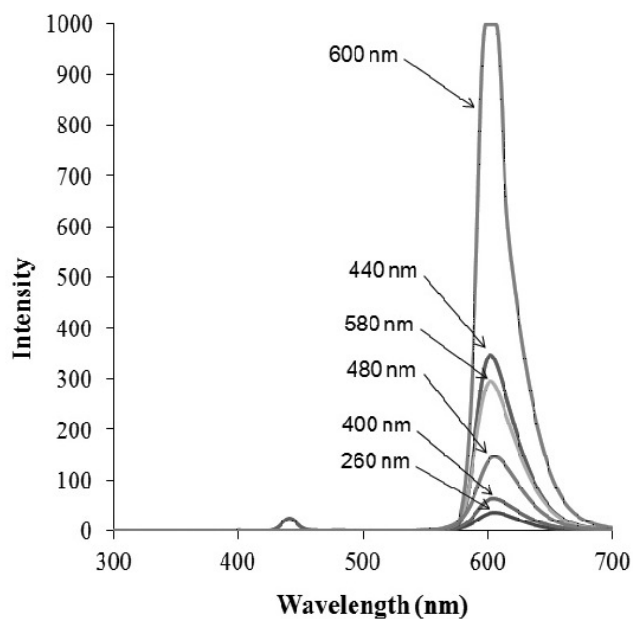
For the preparation of gel materials exhibiting the aforementioned unique FRET function, the gelling system of BMIMCl using guar gum was employed. When the fluorescence spectra of the guar gum/BMIMCl ion gel was measured by excitation at 260-600 nm, the similar excitation-wavelength-dependent fluorescence behavior as that of a sole BMIMCl was appeared (Figure 15). Accordingly, the guar gum/BMIMCl ion gel containing rhodamine 6G (1.5 mmol/L) was prepared from the mixture of rhodamine 6G and guar gum with BMIMCl. The fluorescence spectra of the resulting ion gel exhibited emissions due to rhodamine 6G by excitation at 260-600 nm, whereas no emissions due to BMIMCl were observed (Figure 16). These results indicated the occurrence of FRET from BMIMCl to rhodamine 6G in the



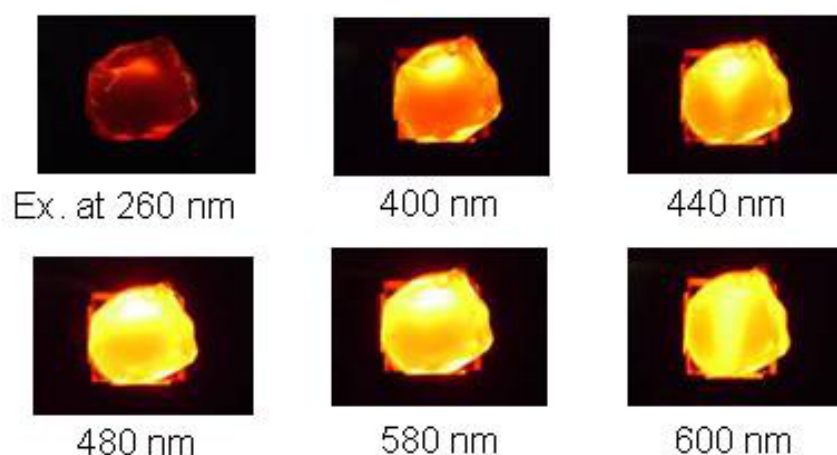
ion gel. Indeed, the gel showed the red emissions by photo irradiation at various wave-  
lengths (Figure 17).



**Figure 15.** Fluorescence spectra of guar gum/BMIMCl ion gel by excitation at 260-600 nm.



**Figure 16.** Fluorescence spectra of guar gum/rhodamine 6G/BMIMCl ion gel by excitation at 260-600 nm.



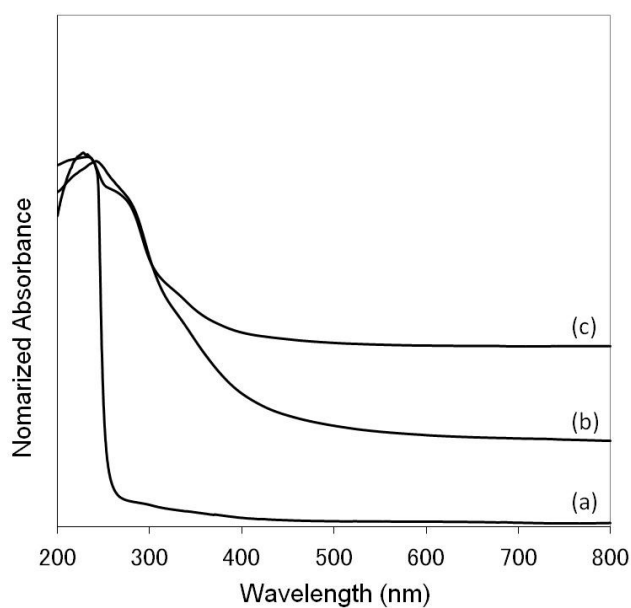
**Figure 17.** Photographs of guar gum/rodamine 6G/BMIMCl ion gel by excitation at 260–600 nm.

#### 4.3. Fluorescent Behaviors of Ion Gel of Xanthan Gum with an Ionic Liquid

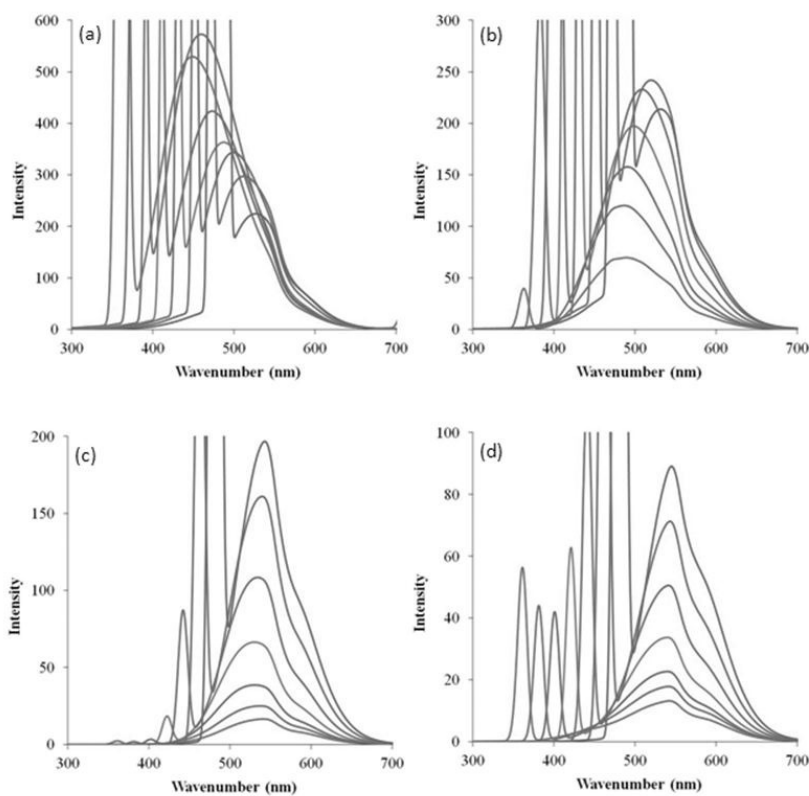
The author has been interested in the association state of BMIMCl in the xanthan gum/BMIMCl ion gels because nano-ordered association of 1-butyl-3-methylimidazolium-type ionic liquids in the liquid state was suggested in previous report [43]. The UV-vis spectra of the ion gels were measured to evaluate the association states of BMIMCl [41]. A liquid BMIMCl showed significant absorptions at wavelengths below 250 nm besides very small absorptions at 250–450 nm (Figure 18(a)). However, the strong absorptions in a wide range from 200 to 450 nm were observed in the UV-vis spectra of the ion gels with different contents (10 and 30% (w/w), Figure 18(b) and (c)). Such strong absorption was not observed in the UV-vis spectrum of guar gum/BMIMCl ion gel. These results suggested the presence of the different association state of BMIMCl in the xanthan gum/BMIMCl ion gel from that in the liquid and the guar gum/BMIMCl ion gel. The presence of the specific association state of BMIMCl in the xanthan gum/BMIMCl ion gel was also confirmed by the  $^1\text{H}$  NMR analysis.

On the basis of the above findings, the fluorescent behaviors of the xanthan gum/BMIMCl ion gels were investigated. Figure 19 shows the fluorescence spectra of the ion gels in the different xanthan gum contents (10, 20, 40, and 60% (w/w)) by excitation at 360–480 nm. Emission maxima were obviously shifted to the longer wavelength areas with increasing xanthan gum contents. Such red-shift was probably due to the presence of the specific association states of BMIMCl depending to the xanthan gum contents in the gels. Actually, the colors of the gels were changed from yellow to red-brown with increasing the xanthan gum contents (Figure 20). These results suggest that the present xanthan gum/BMIMCl ion gels can be applied to the new fluorescent gel materials in the future.

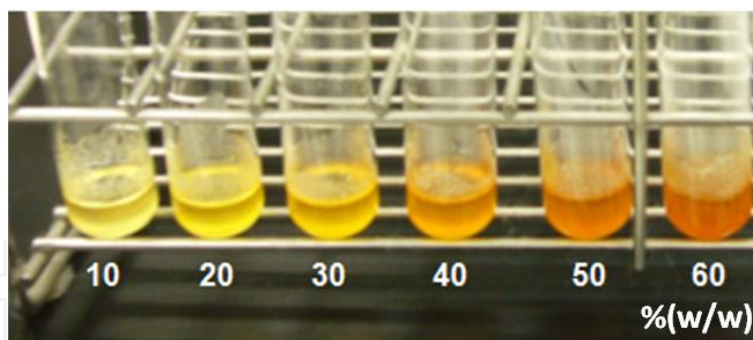




**Figure 18.** UV-vis spectra of a liquid BMIMCl (a), and xanthan gum/BMIMCl ion gels in 10 and 30% (w/w) contents ((b) and (c), respectively).



**Figure 19.** Fluorescence spectra of xanthan gum/BMIMCl ion gels in 10, 20, 40, and 60% (w/w) contents by excitation at 360-480 nm ((a) – (d), respectively).



**Figure 20.** Photographs of xanthan gum/BMIMCl ion gels in 10-60% (w/w) contents.

## 5. Conclusion

This chapter overviewed the preparation of new fluorescent materials composed of the ILs as components which exhibited specific and unique photo functions. The unique FRET system using rhodamine 6G and the imidazolium-type IL, BMIMCl, was successfully appeared. The radical copolymerization of two PILs, which had one and two polymerizable groups, respectively, was carried out with AIBN as an initiator to give the transparent polymeric ionic liquid (PIL) film. The fluorescence spectra of the film exhibited excitation-wavelength-dependence fluorescent emission maxima at around 430 – 470 nm by excitation at 260 – 400 nm. On the basis of the above results, the PIL films carrying fluorescent dye moieties were prepared by radical copolymerization of polymerizable ionic liquids with appropriate polymerizable fluorescent dye derivatives. The films carrying rhodamine, 7-(diethylamino)coumarin-3-carboxylic acid (DEAC), and pyranine moieties exhibited the three primary color emissions, i.e., red, green, and blue, respectively, by excitation at wide wavelength areas. By incorporating possible combinations of the dye moieties in the PIL backbones, furthermore, the PIL films, which emitted tunable multicolors, were successfully obtained.

For the preparation of materials exhibiting the unique fluorescent behaviors, the gelling system of BMIMCl using guar gum of a natural polysaccharide containing rhodamine 6G was employed. The fluorescence spectra of the resulting ion gel showed the emissions due to rhodamine 6G by excitation at 260 – 600 nm, whereas no emissions due to BMIMCl were observed, indicating the occurrence of FRET from BMIMCl to rhodamine 6G in the gel. The fluorescent behaviors of xanthan gum/BMIMCl ion gels were also investigated. The gels exhibited the xanthan gum content-dependent emission changes, probably owing to the presence of specific association states of BMIMCl in the gels.

The specific fluorescent functions of the materials described in this chapter are realized by the unique photo properties of the ILs. The present materials have the potential for the practical applications in the various fields in the future.

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