

# Applications of Ionic Liquids for the Development of Optical Chemical Sensors and Biosensors

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This paper reviews the primary literature reporting the use of ionic liquids (ILs) in optical sensing technologies. The optical chemical sensors that have been developed with the assistance of ILs are classified according to the type of resultant material. Key aspects of applying ILs in such sensors are revealed and discussed. They include using ILs as solvents for the synthesis of sensor matrix materials; additives in polymer matrices; matrix materials; modifiers of the surfaces; and multifunctional sensor components. The operational principles, design, texture, and analytical characteristics of the offered sensors for determining CO<sub>2</sub>, O<sub>2</sub>, metal ions, CN<sup>-</sup>, and various organic compounds are critically discussed. The key advantages and disadvantages of using ILs in optical sensing technologies are defined. Finally, the applicability of the described materials for chemical analysis is evaluated, and possibilities for their further modernization are outlined.

**Keywords** Ionic liquids, task-specific ionic liquids, poly(ionic) liquids, optical chemical sensors, optical sensing materials, ionogels, ionic liquid-coated materials, polymer/ionic liquid materials, pH indicator strips

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## 1 Introduction

The application areas of ILs in chemical analysis, industry and biotechnology are continually expanding. Those areas of application have benefited from the improved synthesis of ILs and methods of their cleaning for reuse,<sup>1,2</sup> the developed designer's ILs for solving special tasks,<sup>3-5</sup> and accumulated extensive experimental data on physicochemical characteristics,<sup>6,7</sup> electrochemical,<sup>8</sup> optical,<sup>9,10</sup> and extraction<sup>11-14</sup> properties of ILs and their features as fluids (nanoheterogeneity and essential regularity).<sup>15,16</sup> Moreover, mathematical models for estimating the solvent power<sup>17-19</sup> and ecotoxicity<sup>20</sup> of ILs, and novel approaches to predict their biodegradation<sup>21</sup> allowed miniaturization of experimental investigations that saves time and resources. The accumulated experimental data and achievements served a good basis for using ILs in sensing technologies.

Unique physicochemical properties (high conductivity, excellent thermal and chemical stability, wide electrochemical window, and negligible evaporation) along with extraction and plasticizing properties of ILs have proved to be intrinsic to the development of electrochemical sensors and biosensors.<sup>22-26</sup> The electrochemical sensing materials prepared using ILs have been discussed in detail in the reviews.<sup>22-26</sup>

The ability of some ILs to dissolve a broad range of substances gave rise to studying the possibilities of ILs in optical sensing technologies. ILs can dissolve inorganic gases (O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>2</sub>, H<sub>2</sub>S, *etc.*),<sup>24,27</sup> silicon alkoxides (tetramethoxysilane, TMOS; triethoxysilane, TEOS; methyltrimethoxysilane, MTMOS),<sup>28</sup> mono- and polysaccharides (carbohydrates, starch, cellulose, chitin, chitosan, guar gum, and xanthan gum),<sup>10,29-32</sup> natural organic materials (silk<sup>17</sup> and wood<sup>29,33,34</sup>), some synthetic polymers,<sup>35,36</sup> enzymes,<sup>37-39</sup> *etc.* The listed substances can serve either as matrix materials (natural and synthetic polymers) or recognition elements (dyes, complexes, and biocatalysts), and target compounds (gases) for optical sensing platforms. The developed optical sensors prepared using ILs are still inferior to known electrochemical sensors in the range of sensing materials and analytes. Nevertheless, according to the database Scopus, the number of publications between 2005 and 2016, that are devoted to the optical sensors under discussion, has increased by at least six times. Despite the achieved progress and the wealth of the literature on the considered topic, a comprehensive review highlighting the various roles of ILs in optical chemical sensors and evaluation of their potential to yield the novel materials for chemical analysis is still needed. To our knowledge, the previous reviews either cover briefly such optical sensors<sup>25,40-42</sup> or focus on the classification and methods

of the preparation of the IL-based materials.<sup>25,28,43</sup> Warner *et al.*<sup>44</sup> reported the IL functions while producing photonic IL sensors. Kadokawa<sup>10</sup> used the imidazolium-type polymerizable ILs as components in polymeric IL films to carry various combinations of fluorescent dye moieties and exhibit tunable color emissions. The potential of using ILs in optical sensors has only been highlighted for CO<sub>2</sub> detection<sup>45,46</sup> and monitoring biological liquids.<sup>47</sup>

The aim of this review is to disclose, systemize, and critically discuss various aspects of current and future applications of ILs for the development of optical chemical sensing materials.

## 2 Types of Optical Sensing Materials and Sensors Prepared Using Ionic Liquids

### 2.1 Ionic liquids used in optical sensing materials

The chemical structures of cations and anions of ILs mentioned in this review are presented in Figs. S1 and S2 (Supporting Information), respectively. In optical sensing technologies, researchers give priority to commercially available and well-studied imidazolium ILs. Hydrophilic 1-alkyl-3-methylimidazolium ILs in combination with anions Cl<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, Ac<sup>-</sup>, and BF<sub>4</sub><sup>-</sup> are used more frequently than hydrophobic ILs, *e.g.*, hexafluorophosphates of 1-butyl-3-methylimidazolium, [BMIm]<sup>+</sup>, and 1-octyl-3-methylimidazolium, [OMIm]<sup>+</sup>, though the latter are practically nontoxic, especially compared to the conventional organic solvents, such as acetone, acetonitrile, DMSO, *etc.*<sup>20</sup> Besides imidazolium ILs, some tetraalkylphosphonium ILs are applied, on the basis of tetrabutylphosphonium, [P<sub>4,4,4,4</sub>]<sup>+</sup>, and trihexyl(tetradecyl)phosphonium, [P<sub>6,6,6,14</sub>]<sup>+</sup> (Fig. S1), in particular. The large, unreactive, and low symmetric cation [P<sub>6,6,6,14</sub>]<sup>+</sup> is called an "universal liquifier" owing to its ability in combination with relatively large anions (*e.g.*, dyes' anions) to introduce hydrophobicity to ILs.<sup>44,48,49</sup> Being viscous, the resultant IL is a free flowing liquid.<sup>48</sup> Recently, some "task-specific" or "functionalized" ILs, for instance, carboxylated,<sup>50</sup> carbamate,<sup>51,52</sup> amidine,<sup>53</sup> and polydiacetylene-imidazolium<sup>54</sup> ILs are used for CO<sub>2</sub> detection. As a rule, functionalized ILs bear functional groups in their cations<sup>50-54</sup> and more rarely in their anions (8-hydroxyperene-1,3,6-trisulfonate (pyranine), HPTS<sup>3-</sup> in [P<sub>6,6,6,14</sub>]<sub>3</sub>HPTS;<sup>49</sup> glycine and  $\beta$ -alanine in [P<sub>4,4,4,4</sub>]<sup>+</sup>-based ILs,<sup>55</sup> Fig. S2) that are responsible for the accomplishment of chemical functions.<sup>56</sup> More recently, the scientific interest in poly(ionic liquid)s or polymerized ILs (PILs) for pH sensing<sup>57,58</sup> and CO<sub>2</sub> separation<sup>59-62</sup> has grown. Imidazolium-based PILs (*e.g.*, poly[1-cyanomethyl-3-vinylimidazolium] bis(trifluoromethane sulfonyl)imide, P[CMVIm]Tf<sub>2</sub>N; poly[1-(*p*-vinylbenzyl)-3-butylimidazolium]



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Among different awards, she has received the title of Emeritus Professor of MSU (2008). Her research interests include basic studies and applications of enzymatic and spectroscopic methods of analysis.

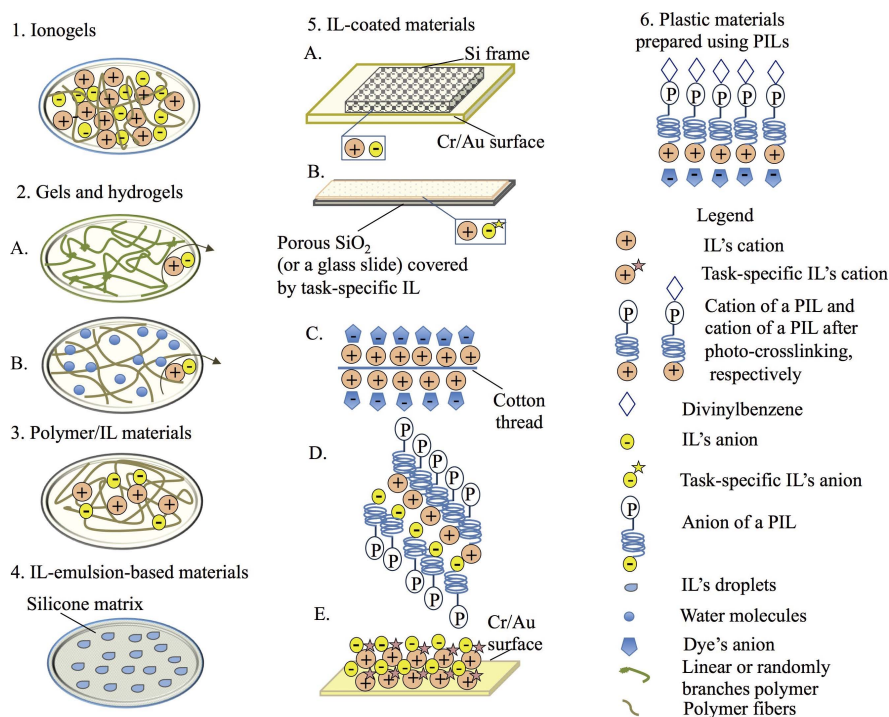


Fig. 1 Schematic images of main types of optical sensing materials made using ILs. For simplicity, the recognition elements are not shown in material images 1 – 4.

tetrafluoroborate,  $P[VBBIm]BF_4$ , and bis(trifluoromethane sulfonyl)imide,  $P[VBBIm]Tf_2N$ ; and poly[1-(2-methacryloyloxy)-ethyl-3-butylimidazolium] tetrafluoroborate,  $P[MABIm]BF_4$  and ammonium-based PILs (e.g., poly[*p*-vinylbenzyltrimethylammonium] tetrafluoroborate,  $P[VBtMA]BF_4$ , and poly[2-(methacryloyloxy)ethyltrimethylammonium] tetrafluoroborate,  $P[MATMA]BF_4$ ) (Figs. S1 and S2) are the polymerization products of the corresponding IL monomers.<sup>58–61</sup> Polybenzimidazole-based PILs are obtained by anion exchange of  $Br^-$  on  $Tf_2N^-$ ,  $BF_4^-$ , and  $Ac^-$  of partly quaternized polybenzimidazole,  $PBI-BuI$  (Fig. S1).<sup>62</sup>

## 2.2 Material varieties and preparation methods

Figure 1 shows the schematic images of the most common types of optical sensing materials that are obtained using ILs and applied to some degree in chemical analysis. They include (1) ionogels, (2) gels and hydrogels, (3) polymer/IL materials, (4) IL-emulsion-based materials, (5) IL-coated materials, and (6) plastic materials prepared using PILs.

The first type of the optical sensing materials belongs to a class of materials often referred to as *ionogels* (or ion gels) in the literature. The term *ionogel* expresses that a material represents a gel that contains ions of an IL (Fig. 1.1).<sup>16,63</sup> Ionogel materials offer “a symbiosis between the dispersed IL phase and solid continuous phase”.<sup>43</sup> Thus, they combine the properties of both solid and liquid components.<sup>25,43,63</sup> Moreover, the ILs dispersed/trapped/incorporated inside solids keep the main physicochemical properties of ILs except for outflow.<sup>28,43</sup> Ionogels are IL-based materials because the content of IL in them can reach 80 vol%.<sup>64–66</sup>

Several methods that have been developed for preparing IL-based electrolytes for electrochemical devices are commonly used to fabricate an ionogel as an optical sensor platform. These approaches include (1) doping polymer with ILs, (2) *in situ* polymerization or crosslinking of monomers in ILs, and (3)

synthesis of PILs.<sup>36</sup> The ionogels intended for optical sensing materials represent flexible, transparent solid monoliths, films, and membranes. Depending on the nature of the solid-like network, organic (typically polymers), inorganic (silica-based matrices), and hybrid (inorganic-organic composites) ionogels are commonly distinguished.<sup>28</sup> It is worth highlighting here that the silica-based materials are ionogels when they are prepared by a non-hydrolytic sol-gel processing route with an assistance of a water immiscible IL (e.g.,  $[BMIm]Tf_2N$ <sup>64,67</sup> and 1-hexyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide,  $[HMI]Tf_2N$ <sup>65,66</sup>), pure or mixed with formic acid.

However, a final sensing material can contain no IL though it has been prepared using IL.<sup>68,69</sup> For example, the water miscible ILs,  $[BMIm]Cl$  and  $[BMIm]BF_4$ , are exploited as solvents for silicon alkoxides in an aqueous sol-gel synthesis with or without alcohols but then the ILs are removed from the obtained polymer gels using calcination.<sup>70,71</sup> In this context, the resulting solid materials are *gels* (Fig. 1.2.A) but not ionogels.

The materials made by dissolution/regeneration of the natural polymers (cellulose, chitin, and chitosan) in ILs and followed by washing with an appropriate coagulant (in other words, anti-solvent)<sup>30</sup> for removing ILs are called *hydrogels*, stressing their capability of absorbing large amounts of water and swelling (Fig. 1.2.B).<sup>72</sup> However, small amounts of ILs may be entrapped in the hydrogels.<sup>73</sup> The residual imidazolium ILs should be taken into account because they could be crucial for the mechanical and optical properties of the resulting materials.<sup>9,69,73</sup>

The major component of *polymer/IL materials* is a synthetic polymer (5 – 50 wt%)<sup>78</sup> such as ethyl cellulose (EC), poly(methyl methacrylate) (PMMA), and polyvinyl chloride (PVC) (Fig. 1.3).<sup>74–80</sup> Polymer/IL composites are obtained either by a simple casting of the liquid sensing cocktail on an appropriate support (commonly a polyester or glass slide) or by electrospinning. The resultant materials are continuous thin and bulk films (the thickness is several and 200  $\mu m$ , respectively)

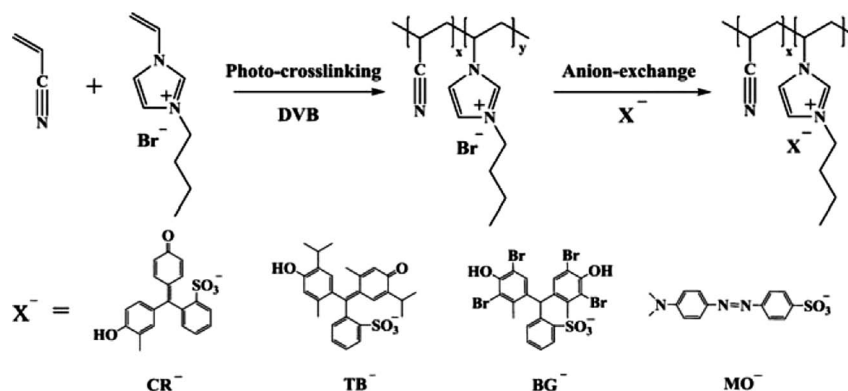


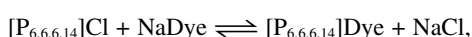
Fig. 2 Reaction scheme for the preparation of plastic pH-responsive membranes. Reproduced from Ref. 57 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/c2py21076b>.

or electrospun nanofibers.

*IL-emulsion-based materials* represent one more type of optical sensing materials. The dispersed phase of the emulsion is a buffer solution containing a pH indicator (thymol blue, TB; or bromothymol blue, BTB; or trisodium salt of HPTS dissolved in a hydrophilic IL, [BMIm]BF<sub>4</sub> or [BMIm]Tos (Tos, tosylate), and the base (tetrabutylammonium hydroxide, TBAOH, or NaHCO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub>). The continuous phase is a hydrophobic polydimethylsiloxane-based silicone “cocktail”.<sup>81</sup> Thus, the droplets of IL-containing buffer solution appear to be buried within the silicone matrix (Fig. 1.4). After vacuuming the emulsions on the polyester support, films (the thickness is 60 μm) that are sensitive toward gaseous CO<sub>2</sub>, are formed.<sup>81</sup>

ILs are also used for fabricating several kinds of *IL-coated materials* (Fig. 1.5). For monitoring gaseous CO<sub>2</sub>, droplets of 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIm]BF<sub>4</sub> (an absorbent) are encapsulated in a Si frame that was placed on the surface of a Au-coated glass prism of a SPR sensor<sup>82</sup> (Fig. 1.5.A) or the task-specific IL, [P<sub>4,4,4,4</sub>]amino acid (a trap for the analyte), is spread on porous SiO<sub>2</sub> (Fig. 1.5.B).<sup>55</sup> To determine various amine vapors, the [P<sub>6,6,6,14</sub>]<sub>3</sub>HPTS film are fabricated by spin casting on the surface of glass slides made hydrophobic by derivatization with propyltrichlorosilane.<sup>49</sup> Note that in the latter two materials, the anions of the used task-specific ILs interact with analytes.

For estimating the pH values of aqueous solutions and detecting acidic and basic vapors, disposable photonic IL-based sensors are applied.<sup>83</sup> Such sensing materials include silica and alumina TLC plates, filter paper, and cotton thread matrices (Fig. 1.5.C) with noncovalently immobilized [P<sub>6,6,6,14</sub>]<sup>+</sup>-based task-specific ILs. Deprotonated forms of the 12 different pH indicators serve as anions of the ILs. The preparation of the sensing materials includes (a) a synthesis of [P<sub>6,6,6,14</sub>]<sup>+</sup>-based task-specific IL using anion exchange procedure according to the reaction:



and (b) an immobilization of the obtained IL on an appropriate support. The technique of the IL immobilization (spotting of the IL solution on the surface of the matrix or dip coating in the IL solution) depends on the type of the support.<sup>83</sup>

The optical fibers coated by porous polyelectrolyte membranes (PPMs) is an example of the use of PILs in the IL-coated materials for pH monitoring (Fig. 1.5.D).<sup>58</sup> The PPMs are obtained *via* ionic bonding between [P[CMVIm]Tf<sub>2</sub>N, a

hydrophobic cationic PIL, and deprotonated poly(acrylic) acid (Figs. S1 and S2). Membranes gained a hierarchical nanopore structure and charge during a simple immersion/activation procedure using an NH<sub>3</sub> or NaOH aqueous solution.

One more kind of the IL-coated materials includes the IL self-assembled monolayers (IL-SAMs) with immobilized molecular receptors on gold surfaces of SPR sensors (Fig. 1.5.E).<sup>50</sup> To prepare IL-SAMs that are capable of chemical binding to gold surfaces as molecular receptors, the task-specific ILs (bromides of 1-((+)-biotin)pentanamido)propyl-3-12-mercaptododecyl-imidazolium, IL-biotin, and 1-(carboxymethyl)-3-(mercaptododecyl)imidazolium, IL-COOH, (Fig. S1) were synthesized. Nowadays such materials have been developed to construct streptavidin-based and human immunoglobulin G biosensors.

The optical sensors of a different type represent *plastic materials prepared using PILs*, for instance, pH indicator strips (Fig. 1.6). They can be obtained *via* photo-crosslinking of an IL monomer, 1-butyl-3-vinylimidazolium bromide, with acrylonitrile in the presence of divinylbenzene (DVB), and followed by anion-exchange with anionic dyes, such as cresol red (CR), TB, bromocresol green (BG), and methyl orange (MO) (Fig. 2).<sup>57</sup> The described example demonstrates one of the possible ways<sup>10</sup> of the application of PILs in optical sensing technologies.

### 2.3 Optical methods for the registration of the analytical signal

Table S1 (Supporting Information) displays the developed optical sensors prepared using ILs and compares their analytical characteristics.<sup>49-51,74-94</sup> As shown in Table S1, the overwhelming majority of the developed optical sensors are either colorimetric, spectrophotometric or fluorescent. Such sensors involve a sensing platform in the form of one of the aforementioned materials that contain a chemically active sensing agent (a recognition element). Depending on the analyte, ligands, complexes, chromo-responsive agents (Fig. 3), indicators, and enzymes can serve as recognition elements. Typically, the recognition element incorporated into a sensor matrix or immobilized on its surface changes the optical properties (UV-Vis absorbance or fluorescence intensity) as a result of the chemical reaction with the desired analyte proportionally to the concentration of the last. Thus, the sensor's response is measured indirectly. After contact with an analyzed liquid sample, a sensing material, which is kept by adhesive forces onto an optically transparent glass or a polyester slide, is placed into the cell holder of a spectrophotometer or a fluorimeter.<sup>38,85,88,89</sup>



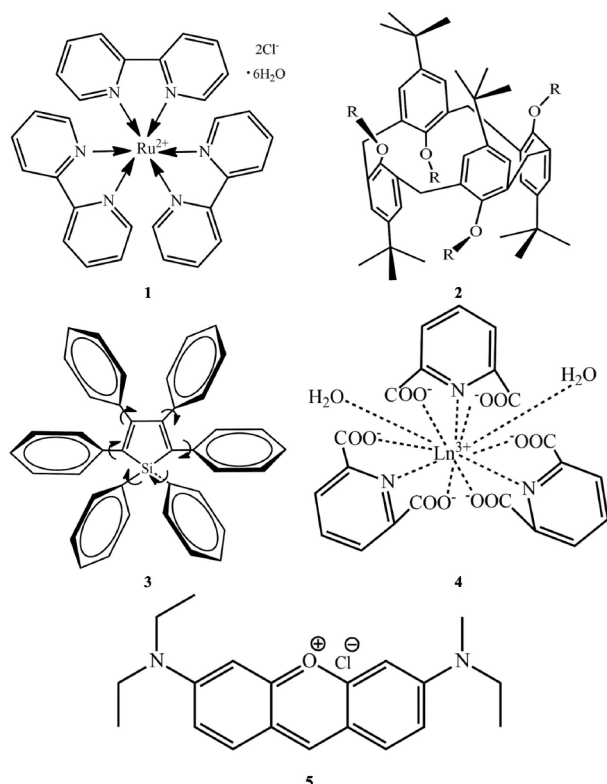


Fig. 3 Chemical structures of the recognizing reagents: **1**, [Ru(bipy)<sub>3</sub>]Cl<sub>2</sub> · 6H<sub>2</sub>O; **2**, calix[4]arenes: calix 1 (R = (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>) and calix 2 (R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>); **3**, 1,1,2,3,4,5-hexaphenylsilole, HPS; **4**, Ln(DPA)<sub>3</sub> · 2H<sub>2</sub>O; **5**, pyronin B, in the optical sensing materials prepared using ILs for the determination of **1**, O<sub>2</sub>; **2**, NO<sub>x</sub>; **3**, CO<sub>2</sub>; **4**, Cu(II); **5**, artemisinin.

When a gas analysis is carried out, a sensing material is placed into a flow-cell, where a gas mixture (*e.g.*, analyte CO<sub>2</sub> with a regeneration agent N<sub>2</sub>) is introduced *via* a diffuser needle under ambient conditions either directly or after humidification of the gas by bubbling through water.<sup>76</sup> The intensity of fluorescence in the absence and presence of a gaseous analyte is often measured and referenced against the luminescence intensity (or decay time) of a second inert and spectrally compatible luminophore (*e.g.*, 4-dicyanomethylene-2-methyl-6-(4-(dimethylamino)styryl)-4H-pyran, DCM,<sup>75,81</sup> a fluorogenic IL (as in [P<sub>6,6,6,14</sub>]<sub>3</sub>HPTS),<sup>49</sup> a special excimer-forming fluorescent microviscosity probe (*e.g.*, 1,3-bis(1-pyrenyl)propane, 1,3-bis(1-pyrenyl)decane, *etc.*)<sup>52</sup> In the literature, such kind of fluorescent sensing is termed ratiometric sensing.

To quantify the analytical information contained on colorimetric sensors, test materials (silica and alumina TLC plates, filter paper, cotton threads, and cellulose films) have been scanned using a simple flatbed scanner after their exposure to the analytes and drying.<sup>83,86</sup> Then the scanned images are divided into color-uniform parts, which are processed using image analysis software, to calculate the mean values of the color components, R, G, B (red, green, blue) and H, S, V (hue, saturation, value) along with their dispersions.<sup>83,86</sup>

The miniature devices based on microfluidic and centrifugal platforms with incorporated ionogels are worth a special mention. One kind of device, a wearable chemical barcode micro-fluid platform, allows monitoring of the pH of sweat in real-time by comparison of the observed color of an ionogel with a standard color chart or using photo and video analysis of

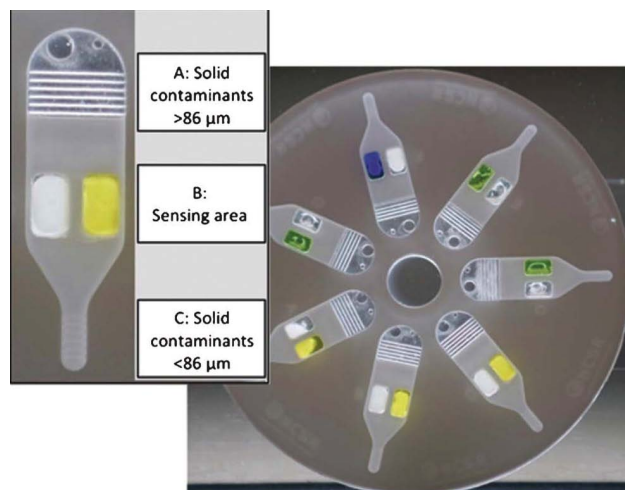


Fig. 4 Picture of the lab-on-a-disc device for water quality analysis (on the right) with a magnification of the fluidic channel with the sensing area (on the left), white (reference region) and yellow (ionogel sensor). The liquid and solid contaminants of the water samples are transported through the microfluidic channel from the top to the bottom chamber during disc rotation. Reproduced in part from Ref. 96 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/c2lc40781g>.

the color changes.<sup>95</sup> Another device in a form of a centrifugal disc with a dye-ionogel sensing area provides an opportunity to monitor water *in situ* (Fig. 4).<sup>96</sup> Such a device consists of two light emitting diodes, one serving as the light source and the other, in reverse bias mode, as the light detector.<sup>96</sup> Note that both types of the ionogels were prepared by cross-linking of the corresponding monomers in [P<sub>6,6,6,14</sub>]DCA and [P<sub>4,4,4,4</sub>]DCA (DCA — diacetylamide).

Only a few articles reported surface plasmon resonance (SPR)-based sensors for detecting CO<sub>2</sub><sup>82</sup> and binding streptavidin and immunoglobulin G.<sup>50</sup> A conventional Kretschmann-type<sup>97</sup> and a high-resolution<sup>98</sup> SPR sensing schemes using glass and dove prisms, respectively, are applied for detecting changes in a reflective index occurring near a gold thin film in the presence of the target compounds.

### 3 Different Roles of ILs in Optical Sensors and Systems

For illustration purposes, Fig. 5 shows the roles of ILs in optical sensing materials, which have been revealed by the analysis of the literature data published over the last 15 years along with the statistical information on the frequency of using ILs in each role. The role of IL is not always obvious or unique. Moreover, it will be demonstrated further, that in some optical sensing materials, ILs can play several major and minor roles. For instance, IL can serve as a solvent for a silicon alkoxide and a protein stabilizer.<sup>70</sup> IL can concurrently play three different roles, as a plasticizer, a ligand, and a dye transducer.<sup>92</sup> In gas analysis systems, the role of an IL depends on an affinity and a permeability of IL toward the gases and its ability to dissolve gaseous analytes. Additionally, we have found out some contradictions in interpretation of a role of IL in the process of fabricating CO<sub>2</sub> sensing EC-based electrospun nanofibers. Aydogdu *et al.*<sup>76</sup> considered [EMIm]BF<sub>4</sub> as a polymer electrolyte though the IL more likely served as a plasticizer that was

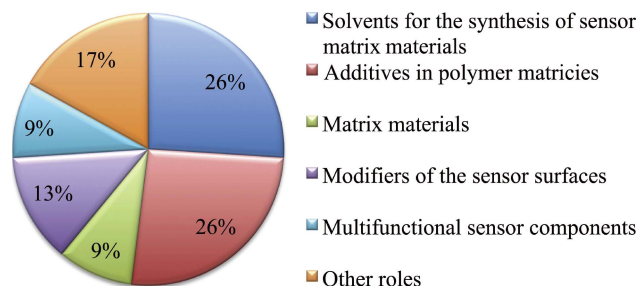


Fig. 5 Different roles of ILs for optical sensing materials and statistical data on the frequency of their application in the respective role.

additional to the classic plasticizer dioctyl phthalate. Sometimes it is difficult to distinguish the roles of ILs as solvents and chemical additives to methanol or ethanol in the course of the preparation of sol-gel materials.<sup>71</sup> Thus, the offered classification of the functions of ILs provides our point of view on the considered subject and, consequently, is disputable.

### 3-1 Ionic liquids as solvents for the synthesis of sensor matrix materials

#### 3-1-1 Ionic liquids in sol-gel transition

Liu *et al.*<sup>70</sup> replaced ethanol in the aqueous acid-catalyzed hydrolysis of TEOS on [BMIm]BF<sub>4</sub> to obtain a sol-gel with highly active and thermally stable noncovalently immobilized horseradish peroxidase. The resulting material represented a transparent and crack-free monolith with numerous worm-like interconnected channels and pores around 3 nm.<sup>70</sup> A bulky porous structure facilitated the internal diffusion of the substrate and, as a consequence, the catalytic activity of the immobilized enzyme in guaiacol oxidation by H<sub>2</sub>O<sub>2</sub> increased by a factor of >30 compared with an IL-free material. In the authors' opinion, [BMIm]BF<sub>4</sub> covered the enzyme and protected it from the destructive effect of ethanol, which is commonly used as a co-solvent in hydrolysis of silicon alkoxides. Moreover, the enzyme that was encapsulated by IL exhibited a high thermostability. A great number of hydroxyl groups in sol-gels produced strong electrostatic interaction and hydrogen bonds to form a high kinetic barrier for unfolding the enzyme.<sup>70</sup> As a result, the structure of the biocatalyst became more rigid and stable.

To obtain a porous and crack-free TEOS-based sol-gel matrix for the fluorescent O<sub>2</sub> sensor, Oter *et al.*<sup>84</sup> used [EMIm]BF<sub>4</sub> not only as a solvent but also as a charged surfactant additionally to Triton X-100 in the classical acid-catalyzed sol-gel technique. This approach provides the preparation of more uniform, optically transparent, thin, and crack-free sol-gel films compared to the IL-free composites.<sup>84,99</sup> The addition of an IL reduced the interfacial energy and thereby decreased the capillary pressure in the "walls" of the gel pores exerted by the liquid inside the capillaries when drying.<sup>84,99</sup> Due to the reduced risk of a fracture, the sensor stability increased. The sol-gels with the embedded ruthenium complex tris(2,2'-bipyridyl)ruthenium(II) chloride, [Ru(bipy)<sub>3</sub>]Cl<sub>2</sub> × 6H<sub>2</sub>O (Fig. 3.1), exhibited the enhanced sensitivity to gaseous O<sub>2</sub> (Table S1), larger Stern-Volmer constants, and linear Stern-Volmer plots with respect to an IL-free sol-gel procedure.<sup>99</sup> The optimized sol pH and IL content provided the enhancing O<sub>2</sub> sensitivity along with a faster sol-gel process. Klingshirn *et al.*<sup>71</sup> found that the higher volume of [BMIm]Cl in sol was used, the more ordered, transparent, flexible, and highly porous TMOS-based sol-gel might be

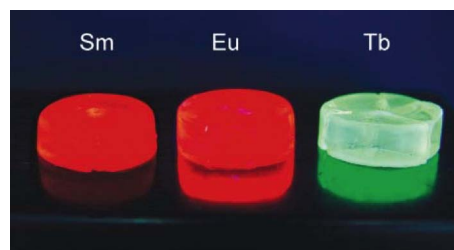


Fig. 6 Luminescence of the monolithic ionogel samples doped with the Sm(III), Eu(III), and Tb(III) complexes ( $\lambda_{\text{ex}} = 345 \text{ nm}$ ). Reproduced from Ref. 66 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/b812292j>.

obtained.

The strongly fluorescent TMOS/MTMOS-based ionogels with immobilized lanthanide complexes<sup>65,66</sup> (Fig. 6) and phenylene-ethynylene polyelectrolytes<sup>64</sup> are the most promising hybrid material for chemical analysis. The incorporation of imidazolium functions to phenylene-ethynylene compounds allowed their solubilizing in [BMIm]Tf<sub>2</sub>N, and, finally, fluorescent materials were achieved through a simple one-step synthesis.<sup>64</sup>

#### 3-1-2 Ionic liquids in cellulose dissolution/regeneration

*Cellulose materials with embedded low-molecular weight analytical reagents.* Cellulose, a biocompatible, biodegradable, nontoxic, and inexpensive natural material, is well soluble in [BMIm]Cl and other ILs with melting points below 100°C.<sup>100</sup> Theoretical aspects of the interaction of cellulose and some cellulose-based materials with ILs have been discussed in previous reviews.<sup>29-32,101</sup> The solubility of cellulose in ILs depends on the origin, extent of polymerization, temperature of the dissolution, and water content in the system, in particular.<sup>30-32,102</sup> Cellulose can be regenerated from the cellulose-IL solutions in a variety of forms (films, fibers, beads, sponges, *etc.*) by adding an anti-solvent, as a rule, water.<sup>31,32</sup>

To date, the [BMIm]Cl-reconstituted cellulose films with the embedded low-molecular weight analytical reagents are the most popular optical sensing platforms. The mass ratio of cellulose to IL in such films varied from 1.5 – 2.0 to 20% w/w. Note that [BMIm]Cl served as a solvent for both cellulose and a sensing agent. In the sensors for determination of metal ions, colorimetric signal (an appearance of a defined color) appeared as a result of adsorption of the target metal ions (Hg(II);<sup>85</sup> Zn(II), Mn(II), Ni(II), and Cu(II))<sup>86</sup> from the aqueous solutions by cellulose films modified by organic ligands, 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolylazo)-2-naphthol (TAN). Note that the PAN(TAN)-in-cellulose sensors were flexible but opaque. The determination of Cu(II) was based on quenching fluorescence of binary rare-earth complexes, Eu(DPA)<sub>3</sub> × 2H<sub>2</sub>O or Tb(DPA)<sub>3</sub> × 2H<sub>2</sub>O (DPA — dipicolinic acid) (Fig. 3.4), embedded into transparent cellulose films. Due to the protection by a cellulose matrix, the lanthanide complexes, which were unstable in aqueous solution, had strong fluorescence (visible even by naked eye) and enhanced thermal stability in the immobilized state.<sup>87</sup>

Hines *et al.*<sup>103</sup> demonstrated the fundamental possibility to use the cellulose films for colorimetric detection of NO<sub>x</sub> gases, *i.e.*, the sum of NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> (NO × NO<sub>2</sub>), N<sub>2</sub>O<sub>4</sub> (NO<sub>2</sub> × NO<sub>2</sub>), and N<sub>2</sub>O<sub>5</sub>. Calix 1 and Calix 2 (Fig. 3.2) immobilized in the films reacted quickly with NO<sub>x</sub> gases forming the colored calix[4]arene-NO<sup>+</sup> complexes. The films were exposed to NO<sub>x</sub> gases directly with a reversal in water or air and indirectly, in a solution of chloroform containing trifluoroacetic acid and

a Lewis acid,  $\text{SnCl}_4$ , as a stabilizer of the arene-nitrosonium charge-transfer complexes. Both flexibility and durability of the final calix films depended on their storage conditions, the way of the regeneration, and acidity of the external solution.<sup>110</sup> Unfortunately, both cellulose films were opaque due to the hydrophobicity of the used calix[4]arenes.

**Cellulose materials with immobilized enzymes.** The cellulose films reconstituted from imidazolium ILs were also explored as a platform for noncovalent and covalent immobilization of several enzymes.<sup>38,88,104–106</sup> The procedures for producing enzyme-containing films differed from each other by the cellulose content, conditions of its dissolution in ILs, and the features of adding biocatalysts into the matrix. Laccase from *Rhus vernicifera* was the first enzyme, immobilized into cellulose films.<sup>38</sup> Laccase preserved the highest enzymatic activity (29% of its initial value) in the films prepared from the supercooled solution cellulose-[BMIm]Cl with adding the enzyme solution in [BMIm]Tf<sub>2</sub>N. The films with [BMIm]Tf<sub>2</sub>N-coated laccase were colorless, flexible and transparent. The catalytic activity of the films was determined by the absorbance of syringaldazine or the pink product of its oxidation by oxygen. Probably, the hydrophobic [BMIm]Tf<sub>2</sub>N protected the laccase hydration shell from the denaturing effect of Cl<sup>−</sup> present in its high concentrations.<sup>38</sup> Thanks to the modification of the cellulose film surface by different polyamines with high concentrations of primary amino groups<sup>104</sup> and biocompatible polyamidoamine dendrimers,<sup>105</sup> covalently immobilized laccase retained at least 50% of its initial catalytic activity. The improvement of the specific enzyme activity was attributable to multiple branching sites with free amino groups on the surface for the further covalent attachment of the enzyme<sup>105</sup> but not the presence of [BMIm]Cl.

The use of both well-dried [BMIm]Cl and cellulose allowed us to obtain optically transparent, strong, flexible, and catalytically active for at least 35 days of storage cellulose films with noncovalently immobilized horseradish and soybean peroxidases.<sup>88</sup> Such films differed advantageously from the cellulose films with the noncovalently immobilized laccase<sup>38</sup> in 1.7 times higher residual catalytic activity and, as a result, higher rate of the substrate transformation (the indicator reactions proceeded within 1–2 min rather than 12 h or more). This finding seemed to be an indicator of the “friendliness” of [BMIm]Cl with respect to the plant peroxidases. Moreover, since the time of dissolution of plant peroxidases in the solution cellulose-[BMIm]Cl increased with an increase in pI values of the enzyme, the immobilization of cationic horseradish peroxidase into cellulose films seemed to be preferable compared to the immobilization of anionic soybean and peanut peroxidases.<sup>88</sup>

The cellulose-supported peroxidase sensors were successfully tested in the reactions of aryldiamines (3,3',5,5'-tetramethylbenzidine, *o*-dianisidine, and *o*-phenylenediamine) and catecholamines (dopamine, adrenaline,  $\alpha$ -methyl dopa, and dobutamine) oxidation by  $\text{H}_2\text{O}_2$ . The performed tests showed that the substrate specificity of the plant peroxidases, immobilized into the cellulose films and native enzymes, was the same. This finding is valuable for the further development of optical biosensors for detecting aryldiamines and catecholamines. The developed cellulose film with co-immobilized pyronin B and Mn(II)-sodium dodecyl sulfate (a peroxidase mimic) for the fluorescent determination of a natural antimalarial endoperoxide artemisinin (Fig. 3.5, Table S1) is another contribution demonstrating that the cellulose films can be very useful for chemical analysis.<sup>89</sup>

Klein *et al.*<sup>106</sup> developed highly catalytically active and durable

films based on cellulose acetate (polymer:IL = 500% w/w) with covalently immobilized  $\beta$ -galactosidase that preserved 60% of its initial catalytic activity in the reaction of *o*-nitrophenyl- $\beta$ -D-galactopyranoside hydrolysis. The use of water immiscible [BMIm]Tf<sub>2</sub>N with acetone increased the formability and flexibility of the films due to enhanced separation between the cellulose macromolecules.

### 3.2 Ionic liquids as additives in polymer matrices

ILs were widely used as additives to EC and PMMA for the development of the fluorescence quenching-based sensors for gaseous  $\text{CO}_2$ ,  $\text{O}_2$ , and metal ions.<sup>74–79</sup> The continuous thin films and electrospun nanofibers were fabricated using water miscible ILs ([EMIm]BF<sub>4</sub>, [BMIm]BF<sub>4</sub>, and [BMIm]SCN) and water immiscible ILs ([EMIm]PF<sub>6</sub>, [EMIm]Tf<sub>2</sub>N, and [BMIm]PF<sub>6</sub>) with a traditional plasticizer dioctyl phthalate.<sup>74–80</sup>

Owing to the use of [EMIm]BF<sub>4</sub> in EC and PMMA thin films, the sensitivity of the  $\text{CO}_2$  sensor increased, the hyperbolic response of the recognition element (HPTS)/(TOA)<sub>4</sub> in the working concentration range of  $\text{CO}_2$  straightened, HPTS photostability was enhanced and the sensor lifetime was prolonged up to 95 days under ambient conditions.<sup>75</sup> Note that IL-free sensors completely lost their sensing capability within 3 days. The  $\text{CO}_2$ -sensitive EC and PMMA electrospun fibers provided high porosity, large surface area, and high gas permeability compared to the same parameters of continuous thin films along with high stability (7 months).<sup>76</sup>

The electrospinning technique was used for the development of the  $\text{O}_2$ -sensitive fibers of EC and PMMA modified by [Ru(bipy)<sub>3</sub>]<sup>2+</sup> (Fig. 3.1).<sup>74</sup> PMMA materials with 25% w/w of [EMIm]BF<sub>4</sub> showed the highest relative signal change and sensitivity toward  $\text{O}_2$ . Moreover, the sensor competed favorably with other IL-free  $\text{O}_2$  sensors due to its extraordinary long-term stability of more than 3 years. Importantly, the values of the Stern-Volmer constant  $\text{O}_2$  in fiber forms prepared from the fluorine-containing imidazolium ILs (*i.e.*, [EMIm]BF<sub>4</sub>, [BMIm]BF<sub>4</sub>, and [BMIm]PF<sub>6</sub>), in which oxygen was readily soluble, were higher than those in the materials made with an addition of [BMIm]SCN. The pressure of an electron-withdrawing cyano group in thiocyanate anion can contribute to the delocalization of the  $\pi^*$  orbitals of the bipyridyl ligand and decrease the lifetime of the ruthenium complex.<sup>74</sup>

[EMIm]BF<sub>4</sub> served as an additive to EC and PMMA for fabricating the continuous thin films and the electrospun nanofibers for the sensitive, rapid, and reproducible fluorescent determination of metal ions.<sup>77–79</sup> In the course of Fe(III) determination, [EMIm]BF<sub>4</sub> in the EC matrix provided a highly stable, spectroscopically available microenvironment for the immobilized recognition element *N'*-(4-cyanobenzylidene)-isonicotinohydrazide (CBINH).<sup>77</sup> The fluorophores 1,2-bis(4-methoxybenzylidene)hydrazine (M-AZM) and 2-(9-methyl-9H-carbazol-3-yl)-5-(pyridine-4-yl)-1,3,4-oxadiazole (ODC-3) that were doped into modified EC and PMMA matrices along with the anionic additive (potassium tetrakis-(4-chlorophenyl) borate) extracted Ag(I) and Hg(II) ions, respectively, because of the ion-exchange mechanism.<sup>78,79</sup> Meanwhile, potassium ions diffused from the membrane into the aqueous phase. Acting as a sink for acidic or basic species from the ambient air of the laboratory, [EMIm]BF<sub>4</sub> enhanced the photostability of M-AZM and ODC-3 in the polymer matrices by up to 7 and 5 months, respectively.<sup>78,79</sup>

The hydrophobic [EMIm]Tf<sub>2</sub>N and [EMIm]PF<sub>6</sub> served as additives to EC and PVC matrices for obtaining pH-sensitive fluorescent thin films.<sup>80</sup> Different zinc phthalocyanines whose spectroscopic properties significantly depended on pH were exploited as the recognition elements. The ILs in the sensing

cocktails enhanced the proton responses, and, as a result of that, improved the linearity of the relative signal on pH compared with that for IL-free materials. In the authors' opinion, the pH-sensitivity of zinc phthalocyanines embedded in the resulting materials was mainly defined by the effectiveness of competition between two bases, the anions of ILs,  $\text{Tf}_2\text{N}^-$  and  $\text{PF}_6^-$ , and zinc phthalocyanines, for protons. The protonated and non-protonated forms of the ILs anions acted as a buffer system. The buffer effect was more distinct in the case of PVC matrix, which had more pronounced intrinsic acid-base characteristics compared to EC.<sup>80</sup>

The use of hydrophobic  $[\text{HMIm}]\text{Tf}_2\text{N}$  as a plasticizer for Eu(III)-doped PMMA/IL bulk films significantly improved their flexibility and enhanced the solubility of fluorescent Eu(III) complexes in the polymer matrix.<sup>107</sup> Owing to a more homogeneous distribution of the fluorophores in the PMMA polymer, the fluorescence quenching caused by undissolved aggregates was reduced.

### 3-3 Ionic liquids as matrix materials

PILs provide an excellent way to obtain reusable, transparent, flexible, and freestanding pH-sensitive membranes that can be adjusted in size and shape.<sup>57,108</sup> In  $\text{CO}_2$  sensors, solid imidazolium PILs served both the attractive membrane materials and effective absorbents with a higher absorption capacity compared with room temperature ILs, *e.g.*,  $[\text{BMIm}]\text{BF}_4$ .<sup>59,61</sup> Importantly, the type of cation in PILs influenced the  $\text{CO}_2$  absorption capability to a much greater degree than the nature of the anion.<sup>61</sup> This finding contradicted the results obtained for room temperature imidazolium-based ILs, in which the nature of the anion primarily affected the  $\text{CO}_2$  solubility in ILs.<sup>109,110</sup> So, tetraalkylammonium-based PILs (*i.e.*,  $[\text{VBtMA}]\text{BF}_4$  and  $[\text{MATMA}]\text{BF}_4$ ) seemed to be the better absorbents than imidazolium-based PILs (*i.e.*,  $[\text{VBBIm}]\text{BF}_4$ ,  $[\text{VBBIm}]\text{Tf}_2\text{N}$ , and  $[\text{MABIm}]\text{BF}_4$ ). Besides, the polymers with polystyrene backbone had a higher absorption capacity than those with polymethylmethacrylate backbone.<sup>61</sup> A notable effect of the anion on the  $\text{CO}_2$  gas permeability was found for the film forming PILs based on polybenzimidazoles.<sup>62</sup> PILs with  $\text{BF}_4^-$  anion had a high  $\text{CO}_2$  permeability coefficient and  $\text{CO}_2$  permselectivity over  $\text{N}_2$  and  $\text{CH}_4$ ; at the same time, PILs with the bulk  $\text{Tf}_2\text{N}^-$  anion were preferable for sorption of non-interacting gases, such as He,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ .

### 3-4 Ionic liquids as modifiers of the surfaces

Absalan *et al.*<sup>90,91</sup> constructed spectrophotometric sensors for  $\text{CN}^-$  and ascorbic acid by using ILs ( $[\text{BMIm}]\text{Br}$ ,  $[\text{BMIm}]\text{PF}_6$ , and  $[\text{OMIm}]\text{PF}_6$ ) as the modifiers for the transparent triacetylcellulose membranes. Besides the ILs, the sensor membranes for  $\text{CN}^-$  and ascorbic acid determination contained  $[N,N'\text{-bis}(\text{salicylidene})\text{-2,3-diaminopyridine}]\text{tributylphosphorin}$  cobalt(III) perchlorate monohydrate (Co(III) Shift base complex)<sup>90</sup> and Cu(II)-neocuproine reagent,<sup>91</sup> respectively. The sensitivity (the slopes of the calibration graphs, in particular) of the offered  $\text{CN}^-$  and ascorbic acid sensors was better in the case of using water immiscible  $[\text{BMIm}]\text{PF}_6$  and  $[\text{OMIm}]\text{PF}_6$ , correspondingly. Due to the presence of  $[\text{BMIm}]\text{PF}_6$  in the  $\text{CN}^-$  sensor, the molar absorptivity and the slope of the calibration graph increased by a factor of five and eight, respectively, compared with those for IL-free materials.<sup>90</sup> Moreover,  $[\text{BMIm}]\text{PF}_6$  as the modifier provided a more uniform surface of membranes than chitosan and surfactants.<sup>111</sup> Homogeneous spreading of the modifiers resulted in the improvement of the reproducibility of both sensors.

High chemical stability of the sensors during their use and

storage was explained by electrostatic interactions (*e.g.*, Van der Waals interactions) between the imidazolium ring of IL and triacetylcellulose molecules.<sup>112</sup> Moreover, a reagent with amino groups, neocuproine, could be linked chemically with triacetylcellulose.<sup>113</sup> There was no evidence of leakage of the reagents from the membranes and no drifts in the signal were observed for 7 and 5 h for  $\text{CN}^-$  and ascorbic acid sensors, respectively.<sup>90,91</sup>

The application of imidazolium ILs in the SAMs on gold surfaces in SPR sensors provided the native conformation of the proteins/enzymes in the course of their chemical immobilization to be maintained that resulted in greater catalytic activity than those for other surfaces.<sup>50</sup> Moreover, the use of a binary monolayer of the IL-biotin and 11-mercaptopundecanol significantly reduced the nonspecific adsorption of streptavidin and, consequently, improved the selectivity of its binding by the sensor's surface.

Exploiting PPMs as modifiers of the surface of optical fibers provided successful coupling of the high pH sensitivity with a fast response time that was unachievable when other types of polymer-coated fiber-optic sensors were used.<sup>58</sup> Thus, the common "trade-off" rule in sensor application was overcome. The hydrophobicity of the employed PIL, which depended on the nature of PIL's counteranion, was the necessary prerequisite for the creation of the membrane with hierarchical pore architectures.

The pairing of  $[\text{P}_{6,6,6,14}]^+$  cation with dye anions provided considerable hydrophobicity to the ILs as modifiers of the cotton threads, silica-, alumina-, and paper-based matrices to be obtained.<sup>83</sup> The resultant pH sensitive IL-coated materials could work in aqueous solutions without leaching IL.

### 3-5 Ionic liquids in multiple roles

Kavanagh *et al.*<sup>92</sup> developed a very simple two-component chemical sensor based on a PVC membrane and task-specific IL,  $[\text{P}_{6,6,6,14}]\text{DCA}$ , for the determination of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{2+}$ . The IL served concurrently as an ion-complexing ligand, a transducer dye, and a plasticizer.<sup>92</sup> Note that the content of IL in the sensing cocktail (66 wt%)<sup>92</sup> corresponded to the content of the traditional plasticizers for PVC such as dioctyl phthalate, dioctyl sebacate, and trioctyl phosphate.<sup>114</sup> As usual, the solvent for PVC was THF. Earlier, the capacity of phosphonium-based ILs to plasticize and bring the ion-sensing ability to PVC and PMMA membranes was used for preparing ion-selective electrodes.<sup>115</sup> The PVC- $[\text{P}_{6,6,6,14}]\text{DCA}$  membranes represented transparent, homogeneous and thin (thickness approximately 10  $\mu\text{m}$ ) discs. The color of the membranes was generated during their exposure to the respective metal ion salt solutions (Fig. 7). The target metal ion and its counterion from aqueous solution were simultaneously extracted into the membrane phase to preserve charge balance; consequently, the co-extraction mechanism but not the ion-exchange mechanism occurred.<sup>92</sup>

Yung *et al.*<sup>49</sup> used  $[\text{P}_{6,6,6,14}]\text{HPTS}$  for the development of a fluorescent sensor for monitoring gaseous  $\text{NH}_3$  and various alkylamines (Table S1). This task-specific IL served as both the matrix material for the sensing spin-cast thin film and the fluorescent pH-responsive agent, which was responsible for the generation of the analytical signal and sensitive to changing gas-phase basicity (Fig. 8). The anion of the IL (Fig. S2) played a key role in the chemosensing scheme. Since the optical signal was visible even to the naked eye, the developed material can be applied in smart sensing technologies like liquid logic gas, electronic noses, and sensory inks.<sup>49</sup>



### 3-6 Other functions

ILs can serve as *absorbents or chemical traps for a target gas*, i.e., CO<sub>2</sub>. Ishizu *et al.*<sup>82</sup> used [EMIm]BF<sub>4</sub> as the selective CO<sub>2</sub> absorbent in an SPR sensor. The change in average molecular weight and anion-cation intermolecular force caused by the chemical reaction between IL included in an Si frame (Fig. 1.5.A) and the absorbed CO<sub>2</sub> resulted in increasing the IL's permittivity.<sup>82</sup> The developed SPR sensor allowed detection of both low and high concentrations of gaseous CO<sub>2</sub> (Table S1) and was chemically stable for a long time. Phosphonium-based ILs with amino acids as anions supported on porous SiO<sub>2</sub> (Fig. 1.5.B) fast and reversibly absorbed CO<sub>2</sub> because of the interaction between CO<sub>2</sub> and anions of ILs.<sup>55</sup> Liu *et al.*<sup>51</sup> and Tian *et al.*<sup>53</sup> developed specially designed CO<sub>2</sub> chemosensors based on a novel photophysical effect aggregation-induced emission. Carbamate and amidine ILs that were the products of the reactions between CO<sub>2</sub> and dipropylamine<sup>51</sup> or amidine-based compounds<sup>53</sup> increased viscosity and polarity of the reaction media. The change of the media properties resulted in the formation of the highly emissive aggregates of 1,1,2,3,4,5-hexaphenylsilole, HPS (Fig. 3.3)<sup>51</sup> and tetraphenylethylene<sup>53</sup> from their non-fluorescent molecules. The amidine-based fluorescent chemosensor had an extraordinarily high water-resistant property and was free of CO-interference problems.<sup>53</sup> To detect CO<sub>2</sub>, Pandey *et al.*<sup>52</sup> used a completely reversible and highly reproducible fluorescent response of 6-(1-pyrenyl)hexyl-11-(1-pyrenyl)undecanoate to detect changes in microviscosity introduced by the formation of carbamate IL as a result of the

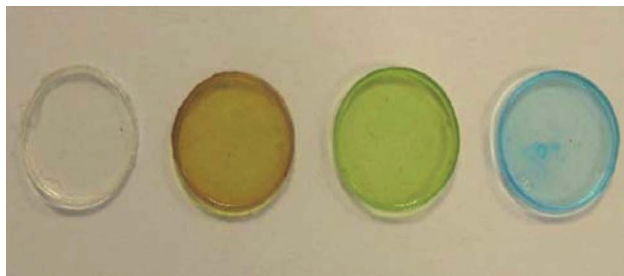


Fig. 7 Two-component IL-PVC polymeric membranes before (colorless membrane) and after exposure to Cu(NO<sub>3</sub>)<sub>2</sub> solution (yellow membrane), equimolar mixture of Cu(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> solutions (green membrane), and Co(NO<sub>3</sub>)<sub>2</sub> solution (blue membrane). Reproduced from Ref. 92 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/c0an00770f>.

capture of CO<sub>2</sub> by dipropylamine.

Li *et al.*<sup>116</sup> used a task-specific IL 3-(5-carboxypropyl)-1-methylimidazolium bromide as the solvent for Eu<sub>2</sub>O<sub>3</sub> and the organic ligands (2-trenoyltrifluoroacetone and 1,10-phenanthroline) to prepare a soft, transparent, and highly luminescent material. The IL dissolved the Eu(III) oxide because the carboxylic acid from the IL reacted with Eu<sub>2</sub>O<sub>3</sub> to form carboxylate complexes.

Water miscible ILs ([BMIm]BF<sub>4</sub>, [BMIm]Tos, and [BMIm]Br) were exploited as solvents for both recognition elements (pH indicators such as TB, BTB, and HPTS) and the determined gas (CO<sub>2</sub>) in IL-emulsion-based (Fig. 1.4)<sup>81</sup> and reservoir-type sensors.<sup>93,94</sup> Unlike the CO<sub>2</sub> sensors described above,<sup>75,76,81</sup> the reservoir-type optical systems had no polymeric matrix. They included a cuvette that was filled with a sensing cocktail IL-BTB (or IL-HPTS) with the additive of a base (NaHCO<sub>3</sub> or TBAOH). The solubility of CO<sub>2</sub> in the used ILs was at least 10–20 times higher than its solubility in the conventional solvents, polymer matrices or water,<sup>27</sup> that could be a result of the formation of weak acid-base complexes between CO<sub>2</sub> (the electron-pair acceptor) and the IL anion (the electron-pair donor).<sup>109,116–118</sup> Additionally, the hydrophobic polydimethylsiloxane-based silicone matrix exhibited excellent permeability to CO<sub>2</sub>.<sup>81</sup> The sensitivity of the CO<sub>2</sub> sensors depended on the indicator pK<sub>a</sub>, the nature of the counterion of IL, and the nature of the base used in the internal buffer solution.<sup>81,93,94</sup> So, in colorimetric IL-emulsion-based sensors, the range of CO<sub>2</sub> content was wider when TB but not BTB was used (Table S1). A significantly higher fluorescent response of HPTS toward CO<sub>2</sub> in the same type of CO<sub>2</sub>-sensor with [BMIm]Tos compared to [BMIm]BF<sub>4</sub> was attributable to higher gas solubility in the IL with a more bulky anion, Tos<sup>−</sup>.<sup>81</sup> The use of [BMIm]Br in the reservoir-type fluorescent sensor provided a wider dynamic range of gaseous CO<sub>2</sub> than [BMIm]BF<sub>4</sub> (Table S1). The lower limits of detection for the dissolved CO<sub>2</sub> was 100-fold lower when the [BMIm]BF<sub>4</sub>-based sensing cocktail was used. This fact was explained by the catalytic effect of fluoride ion from BF<sub>4</sub><sup>−</sup> on bicarbonate formation.<sup>94</sup>

## 4 Application of the Developed Optical Sensors in Chemical Analysis

The analytical applicability of the developed optical materials was demonstrated using examples of inorganic and organic gases, heavy and transition metal ions, cyanide ion, and some organic substances (Table S1).

Table S1 shows that ILs are more often used for the

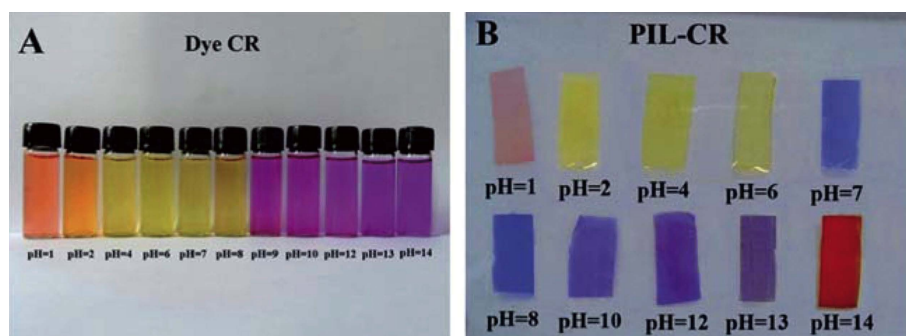


Fig. 8 The dye CR (A) and PIL-CR membranes (B) in aqueous solutions with varied pH values. Reproduced from Ref. 57 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/c2py21076b>.

development of CO<sub>2</sub> sensors. The determination of CO<sub>2</sub> dissolved in blood and seawater as well as the gas level in zones of volcanic and seismic activity, greenhouses, food-packaging technology, and the expired air in tray packing are of significant interest. Monitoring high concentrations of CO<sub>2</sub> (60 – 100%) is a rather trivial analytical task, but the determination of small amounts is a challenging goal. The use of ILs provides both high and low CO<sub>2</sub> concentration determination.<sup>51,75,76,81,82,94</sup> The colorimetric sensor with [BMIm]BF<sub>4</sub> and pH-indicator BT in a silicone matrix allows the semi-quantitative determining of 2% CO<sub>2</sub> and lower concentrations in the gas phase.<sup>81</sup> The sensor based on the same matrix, but with the fluorescent indicator HPTS dissolved in [BMIm]Tos allows detecting up to 20% gaseous CO<sub>2</sub>.<sup>81</sup> The reversible and stable fluorescent CO<sub>2</sub> sensor based on EC and PMMA matrices with the embedded dye HPTS and [EMIm]BF<sub>4</sub> as a specific additive makes it possible to determine up to 30% gaseous CO<sub>2</sub>.<sup>76</sup> Moreover, this sensor has the shortest response time (15 – 30 s) among all the described CO<sub>2</sub>-sensors in the review (Table S1). Finally, the reservoir-type design sensing system, in which IL serves as a solvent for both recognition element and analyte, provides the sensitive determination of both gaseous and dissolved CO<sub>2</sub> over a period longer than 7 months.<sup>94</sup> The developed SPR sensor for CO<sub>2</sub> determination with its miniature gas detection scheme is extremely useful for environmental analysis.<sup>82</sup>

Three O<sub>2</sub>-sensors, which serve the purpose of environmental and biomedical analysis are fabricated with IL addition to TEOS sol-gel, EC and PMMA matrices (Table S1). These sensors based on quenching of ruthenium 2,2'-bipyridyl complex fluorescence by O<sub>2</sub> molecules have the same wide linearity ranges and similar response time.<sup>74,84</sup> The stability of EC and PMMA sensors with the addition of [EMIm]BF<sub>4</sub> is incredibly high—44 months without a significant decrease in fluorescence intensity.<sup>74</sup>

A large number of sensors have been developed for metal ions determination (Table S1). The most sensitive of them are based on EC and PMMA electrospun nanofibers, in which ILs play the role of the specific additives. The developed sensors allow determining of Ag(I) and Hg(II) at sub-nanomolar levels,<sup>78,79</sup> which are comparable (and even lower) with their threshold limit values for drinking water, according to US requirements.<sup>119</sup> The unique sensitivity of these sensors and the short response time (30 s) in the case of Fe(III) favorably distinguishes them from other optical sensors developed so far.<sup>120,121</sup> PMMA- and EC-based nanofibers are capable of determining 10<sup>-3</sup> mol dm<sup>-3</sup> of Ag(I) and Hg(II) ions with high selectivity in the presence of different cations and inorganic anions at their comparable concentrations with the analytes. Only Sn<sup>2+</sup> ions (10<sup>-3</sup> mol dm<sup>-3</sup>) interfered with Ag(I) determination. The response of the used ODC-based sensor for Hg(II) markedly changed in the presence of Fe<sup>3+</sup>, Ag<sup>+</sup>, Pb<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and OH<sup>-</sup>.<sup>79</sup> However, the fact that the sensor outclasses even innovative nanomaterial-based optical sensors in terms of sensitivity for the determination of Hg(II) compensates the mentioned drawback.<sup>122</sup> Besides Fe(III) ions, OH<sup>-</sup> and Al<sup>3+</sup> ions significantly quenched the fluorescence of the CBINH-based sensor.<sup>77</sup>

Another Hg(II)-sensor based on [BMIm]Cl-reconstituted cellulose films with encapsulated PAN could be used up to five times after their regeneration by soaking in 2 mol dm<sup>-3</sup> CH<sub>3</sub>COOH. Further regeneration became impossible because the reagent was leached from the cellulose matrix.<sup>85</sup> The comparable concentrations of Cu(II) and Zn(II) interfered with Hg(II) determination. Practically the same principle was used for the development of cellulose films for transition metal ions determination.<sup>86</sup> Such sensors can be applied at least twice.

The high selectivity along with optical transparency, good flexibility, and thermal stability are the attractive properties of the cellulose-based films with immobilized lanthanide complexes for Cu(II) determination.<sup>87</sup>

Though the sensitivity of the determination of metal ions using the PVC-IL membranes was not high (Table S1), both the simplicity of the membrane preparation procedure and the possibility to recognize Cu(II) and Co(II) in a single measurement were excellent (Fig. 7).<sup>92</sup> Besides, there was no leaching of the components from the self-indicating thin membranes.

Spectrophotometric sensors based on the triacetylcellulose membranes modified with ILs were successfully used for the determination of CN<sup>-</sup> and ascorbic acid in drinking water and orange juice, respectively.<sup>90,91</sup> The offered CN<sup>-</sup> sensor can determine 4.2 μmol dm<sup>-3</sup> concentrations of this anion that is almost 100 times less than its lethal dose to humans: 40 – 200 μmol dm<sup>-3</sup>.<sup>123</sup> Moreover, unlike the disposable sensor for ascorbic acid, the CN<sup>-</sup> optode can be regenerated with HNO<sub>3</sub>.

The success in the development of enzyme sensors is not so obvious compared to the sensors for the determination of inorganic gases and metal ions. Conditions of noncovalently and covalently immobilizing an enzyme into/on the cellulose films are under detailed investigation. Although there have been some attempts to determine the enzyme substrates (syringaldazine,<sup>38,104,105</sup> guaiacol,<sup>70</sup> aryldiamines,<sup>88</sup> catecholamines,<sup>88</sup> and *o*-nitrophenyl-β-D-galactopyranoside),<sup>106</sup> the practical use of such kinds of biosensing materials seems to be a future goal. Currently, there exists only one cellulose-based film sensor with a noncovalently immobilized catalytic indicator system of pyronin B-Mn(II)-sodium dodecyl sulfate for fluorescent determination of artemisinin in pharmaceuticals.<sup>89</sup>

SPR sensors based on imidazolium IL-SAMs are extremely useful for medical applications. Strong affinity of biotin in IL-biotin-SAM to streptavidin allows use of the streptavidin/biotin pair in biosensors for the highly sensitive and selective detection of some antibiotics, viruses, and cancer.<sup>50</sup> The IL-COOH-modified SPR sensors based on a principle of immune analysis demonstrate the high potential impact of human immunoglobulin G sensing. The procedure for immobilization of human dihydrofolate reductase on the IL-COOH SAM-modified with *N,N'*-bis(carboxymethyl)-L-lysine opens up the feasibility of detection of the widely administrated chemotherapy drug, methotrexate, in clinical samples of patients undergoing chemotherapy.<sup>50</sup>

The portable sensing systems for *in situ* monitoring of pH are of particular interest for real-time sweat analysis<sup>95</sup> and water testing (Fig. 4).<sup>96</sup> The developed chemical barcode microfluidic platforms that incorporate IL are capable of defining the pH of sweat with an accuracy of ~0.49 pH units.<sup>95</sup> The paired emitter detector diode platform for lab-on-disc water quality analysis has a great potential for samples with a relatively high level of solid particles.<sup>96</sup> Plastic reusable pH indicator strips prepared using PILs were found to be stable in both aqueous and organic solutions.<sup>57</sup> The attractive features of the developed pH indicator strips are their reusability, enhanced pH-responsive color changes, and pH-response reversibility in aqueous and organic solutions (Fig. 8).<sup>57</sup>

Chromogenic agents (*i.e.*, different acid-base indicators and HPTS) embedded into IL-coated materials<sup>83</sup> and [P<sub>6,6,6,14</sub>]<sub>3</sub>HPTS-based films<sup>49</sup> changed their optical characteristics in the presence of vapors of various acids and bases, including organic compounds (Fig. 9). The selectivity of the detection of acidic/basic vapors using disposal photonic IL-coated materials

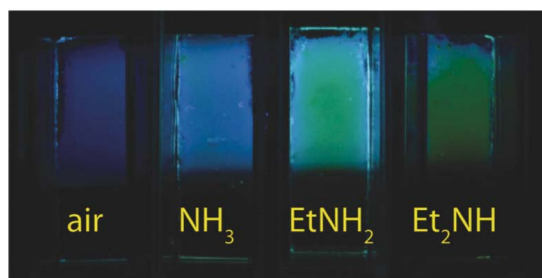


Fig. 9 Spin-cast thin films showing the visible response of  $[P_{6,6,6,14}]_3\text{HPTS}$  to amine vapor exposure under UV lamp excitation at 365 nm. Reproduced in part from Ref. 49 with permission of the Royal Society of Chemistry. <http://dx.doi.org/10.1039/c1cc00065a>.

depended on the nature of the used matrix (a cotton thread, a filter paper, silica or alumina TLC plate).<sup>83</sup> This finding seemed to be very useful for the chemical detection of a variety of vapors that had been demonstrated on the example of analysis of aqueous solutions of cigarette's smoke.<sup>83</sup> The wearable sensors in the form of cotton threads have a great potential for military applications.

Thus, there are various analytes that can be currently determined with the use of the discussed optical materials. However, we can already predict their further expansion due to the development of the new gas target materials,  $\pi$ -conjugated silica ionogels, and Eu(III)-doped PMMA films for potential determination of  $\text{CO}_2$ ,<sup>53,59,62</sup> 2,4-dinitrotoluene and 2,4,6-trinitrotoluene;<sup>64</sup> and biologically active organic and inorganic compounds,<sup>107</sup> respectively.

## 5 Advantages and Drawbacks of Using ILs in Optical Sensing Technologies

The advantages of using ILs in optical sensing technologies include the following:

- (1) Fabrication of various sensing materials in the different forms (gels, hydrogels, films, and membranes) due to the unique solvent ability of ILs with respect to different matrix materials (TEOS,<sup>70,84</sup> cellulose,<sup>85–89</sup> EC, PMMA, and PVC<sup>74–80</sup>), recognition elements (ligands,<sup>77–79,85,86,103</sup> indicators,<sup>81,93,94</sup> chromo-responsive dyes,<sup>89</sup> complexes,<sup>74–76,80,84,87,90,91</sup> and enzymes<sup>70,88</sup>), and gaseous analytes (in particular,  $\text{CO}_2$ <sup>82</sup>).
- (2) Simplified sensor design due to using task-specific<sup>49,83,92</sup> and PILs<sup>10</sup> as multifunctional components.
- (3) Stable pH-response in the aqueous and organic medium due to using sensitive nanoporous poly(ionic liquid)s membranes.<sup>58</sup>
- (4) Improved sensor sensitivity, selectivity, and response time owing to increased affinity and accessibility of task-specific ILs to  $\text{CO}_2$ ,<sup>74</sup> acidic/basic vapors,<sup>49,83</sup> and metal ions.<sup>92</sup>
- (5) Regulation of mechanical properties, porosity, and surface quality of optical sensing materials due to the application of ILs as solvents for synthesis sensor matrix materials<sup>70,72,84</sup> or specific additives to polymers.<sup>74–79</sup>
- (6) Improved storage stability and lifetime compared to IL-free prototypes due to the non-volatile behavior of ILs,<sup>78,79</sup> and similar (and even longer) storage life of the developed sensors compared to the lifetime of IL-based ion-selective electrodes.<sup>22,124</sup>

- (7) Reusable  $\text{CO}_2$  sensors due to a reversible sorption/desorption of the gas by PILs.<sup>61</sup>
- (8) Recovery of imidazolium-based ILs, mainly  $[\text{BMIm}]\text{Cl}$ , used for the preparation of cellulose hydrogels after separation of ILs from water.<sup>125</sup>

We summarize some drawbacks, which could limit wider application of ILs in the optical sensors. These include:

- (1) The high cost of commercial ILs, a necessity in a synthesis of task-specific and polymeric ILs.
- (2) Changing physicochemical properties of ILs with the different temperature of the sensing cocktails can affect the optical properties of the final materials.
- (3) The need to account for the effect of ILs (solvatochromic shifts<sup>9,84,126</sup> and an inactivating action,<sup>127</sup> respectively) on optical and catalytic properties of the recognition reagents.

## 6 Conclusions and Outlook

To conclude, the role of ILs in optical sensors is determined by (i) the type of the final sensing material; (ii) the desired properties and shape; and (iii) the nature of the analytes. The role of ILs can be tuned by the appropriate choice of cations and anions to determine their properties. Due to the use of ILs, the performance characteristics of the sensing materials such as sensitivity, response time, flexibility, affinity, and permeability toward analytes can be improved. Even now the advantages of the application of ILs in optical sensing technologies surpass the shortcomings. Owing to the use of ILs, the greatest progress and advancements have been achieved in optical  $\text{CO}_2$  and  $\text{O}_2$  sensing. The sensors have a bright future, based on the attained results in optical sensing technologies using ILs and the great interest of researchers in this “hot-topic”.

In our view, future investigations will be focused on (i) improving the specific functionality in ILs by synthesis of new task-specific and polymeric ILs, (ii) an in-depth study into the mechanisms of the sensing processes, and (iii) development of novel chemical-based strategies for determining various analytes. The further advancement of the PIL-based approach to creating PPMs might compete with the electrostatic layer-by-layer method due to the simplicity and speed of the membrane preparation procedure. New techniques for the synthesis of IL-SAMs and biochemical approaches providing a strong affinity to target compounds will be of great benefit to biochemical and medical analysis. Short-term goals should include investigating the behavior of enzymes in ILs, necessary for the broader applicability of the environmentally friendly cellulose-based biomaterials. These developments open the door to new portable, sensitive, selective, and recyclable optical sensors and biosensors with applications for chemical analysis.

## 7 Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

## 8 Acknowledgements

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## 9 Supporting Information

Figures S1 and S2 display the structures of cations and anions of the ILs mentioned in the review. Table S1 summarizes the optical chemical sensors developed by the use of ILs. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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