

**MULTIFUNCTIONAL SOFT MATERIALS:
FACILE & MODULAR STRATEGIES
TOWARDS IONIC LIQUID-BASED GELS &
GELATORS**

By

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TOWARDS IONIC LIQUID-BASED GELS &
GELATORS**

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ABSTRACT

The incorporation of a hexadecyl group on imidazolium, pyridinium, and pyrrolidinium scaffolds produces low-molecular-weight ionic organogelators that can gel several types of ionic liquids, deep eutectic solvents, and several molecular organic solvents. On the basis of polarized optical microscopy, differential scanning calorimetry, and X-ray data, the mechanism of gelation is due to crystallization of these salts that produce high-surface-area crystals, which generate sufficiently stable three-dimensional networks that are capable of trapping the solvent molecules. Importantly, the nature of the fluid component of the gel appears to have a profound effect on the morphology of the crystallized organogelators. On the other hand, the organogelators appeared to modulate phase transitions of the liquids.

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INTRODUCTION

The field of supramolecular chemistry considers the synthesis and application of materials and structures that are beyond single, individual molecules. One area of interest for our laboratory is the molecular self-assembly of small molecules in to gels (a phase that is in between a liquid and a solid). When small organic molecules (oligomers, polymers, inorganic materials, etc.) are dissolved in a liquid (typically referred to as a solvent), those same compounds (that are referred to as solutes) upon interactions with each other as well as with the molecules of the solvent, produce complex 3D-arrangements that possess novel, unique properties that are distinct from both solvent and solutes. This supramolecular phenomenon is responsible for gelation of the fluid component; thus, the resulting structure becomes non-fluid and generally immobile at a given temperature (Figure 1).

Importantly, due to the non-covalent nature of the interactions present in gels, exposure of the gel to elevated temperature causes the collapse of supramolecular structure, and as a result the gel returns to the original solution state. The reversible nature of the interactions between the gelator (solute) and liquid (solvent) is responsible for reversible gel-to-sol and sol-to-gel transitions upon heating and cooling cycles, respectively. In general, a suitable, but preferably minimal, amount of the gelator must be added to a solvent (i.e., fluid) to induce gelation, upon dissolution of the gelator upon heating, and the gelation takes place upon cooling to either room temperature or below.¹ The nature of the gelator as well as its amount in the solvent would determine the phase transition temperatures of the gels. The melting temperature of the gel (i.e., gel-to-sol transition) could, in principle, be an indicator of gel strength.¹⁻³

Notably, the specific properties of the gel could be determined by the properties of the gelator as well as the properties of the solvent, which offers a significant degree of tunability.

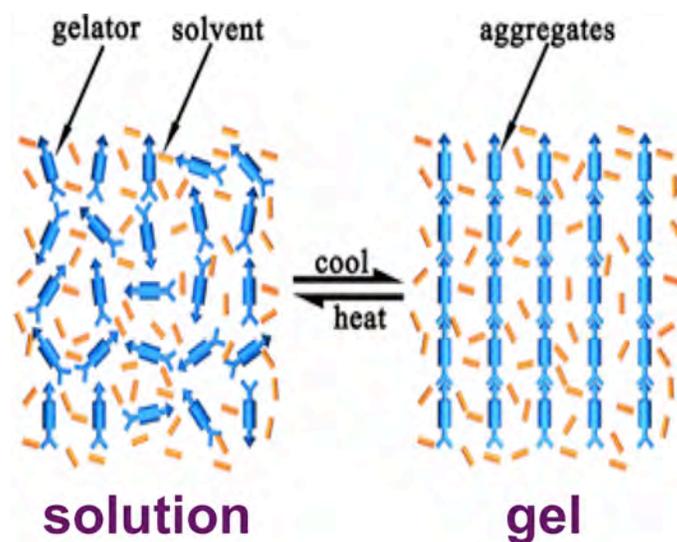


Figure 1. Schematic representation of self-assembly of LMWGs into aggregates and further formation of gelation network. Adopted from ref. 1.

Gels have shown promise in a number of applications due to their various functions in energy-related, catalytic, and environmental processes. For example, certain conducting and luminescent gelators were shown to lead to gels that could be incorporated into products such as LEDs.¹ In addition, gels can be applied to environmental clean-up procedures; environmental disasters such as oil spills can be remedied by applying suitable gelators that induce gelation of spilled oil. This gelation process of the oil, *i.e.*, solidification of liquid oil, facilitates the oil removal from the environment both physically and from a swift timeframe perspective.³ In the same context, it has been shown that ionogels (gels of liquids that are composed of or contain ions) are applicable to wastewater treatment, and they are capable of removing dyes (that serve as model for pollutants) over multiple cycles.⁴ Despite successful existing and potentially useful emerging application of the gels, there are various aspects of the gelation processes that need to be clarified. In particular, how the structure of the gelator is related to the gelation ability is still a

poorly understood topic. In addition, most gelators are discovered serendipitously, and in many cases establishing structure-functional relationships are not feasible. Therefore, studies on establishing how the structural features of a gelator could be translated into (and/or correlated to) gelation processes are of paramount importance from both fundamental and practical stand points of view.

Arguably, the net property of the gel is predominately a consequence of its components. Therefore, increasing the tunability of gel components would provide valuable flexibility in controlling the properties of the gel. This would allow one to produce designer gels made for specific processes as needed.

Although various types of organic molecules (e.g., small organic molecules, oligomeric and polymeric species) have been used to induce the gelation of various types of fluids, it could be argued that the use of low-molecular-weight gelators (LMWGs) provides maximum flexibility in regard to the manipulation of the structures of the gelators and gels as well as the properties of the gels for a better fit for potential applications. Some structures of several classes of LMWGs are shown in Figure 2.^{5,6}

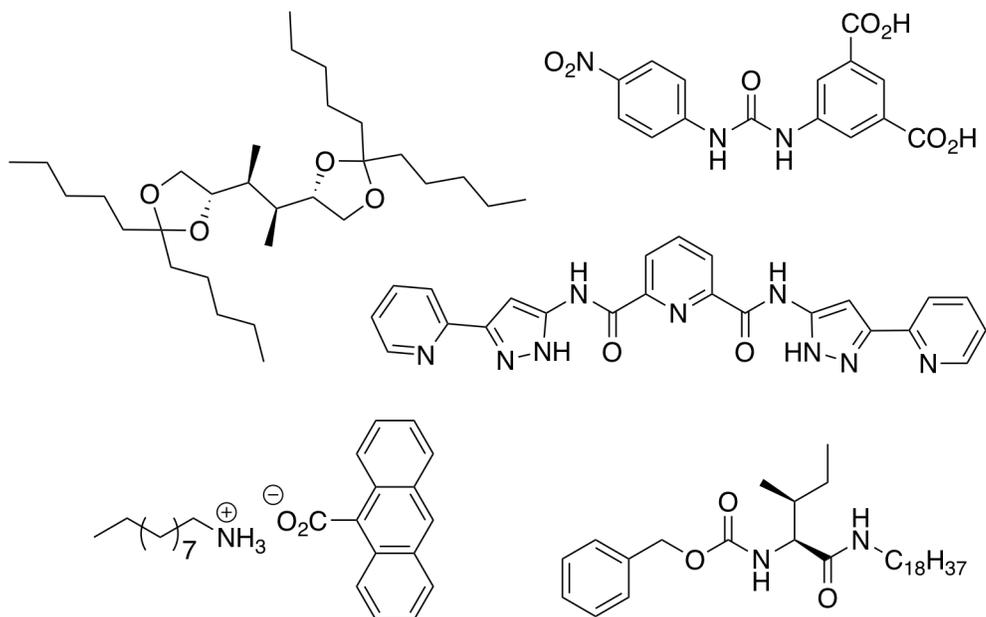


Figure 2. Some examples of LMWG.

In general, the gelation of solvents by LMWG is accomplished by dissolving a small amount of the gelator in the solvent under heating producing a homogenous solution; the subsequent cooling leads to a formation of the gel phase (Figure 3). The gel formation is proven by inverting the vial and observing no fluid floating down the walls. Importantly, the heating/cooling cycles could be repeated many times to produce reversible sol to gel and gel to sol transition.

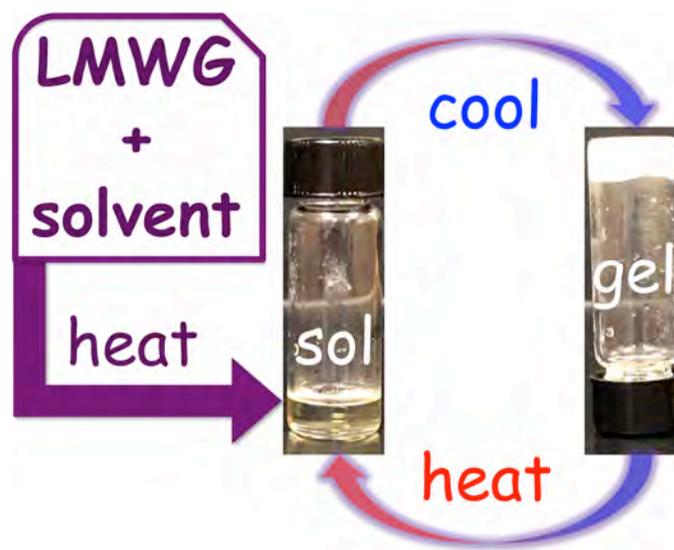


Figure 3. A typical process of sol to gel and gel to sol transition induced by LMWG.

To further promote functional diversity of gels, solvents with tunable properties could also be employed. Ionic liquids and eutectic solvents are two categories of solvents of such interest.

Ionic liquids (ILs) are essentially liquids composed of ions, *i.e.*, cations and anions, and exhibit solid-liquid transitions at or below room temperature.^{7,8} Cations are ions with a positive charge and anions are ions that contain a negative charge. ILs possess a number of interesting and useful properties, such as thermal stability, low volatility, as well as tunable ionic conductivity, polarity, to name a few, that contribute to ever-expanding applications of ILs. In addition, ILs are also heralded as “designer solvents” because of ease of adjusting their properties, using relatively facile synthetic manipulations, towards a particular application.⁸

It is important to mention that imidazolium-based ILs (Figure 4) are among the most versatile and widely used types of ILs, and they have been utilized in a number of gel-based systems.⁹⁻¹⁰ Other types of ILs include pyridinium, pyrrolidinium, ammonium and phosphonium

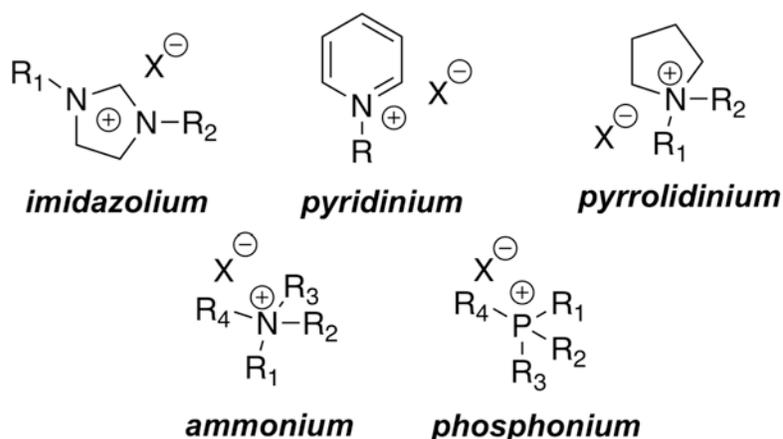


Figure 4. Some representative examples of ILs. R₁, R₂, R₃, R₄ = functional groups; X = anion

(Figure 4) to name a few. Arguably, IL-derived materials should retain these unique and useful attributes and thus they hold a lot of promise and should further expand the range of applications of ILs and the corresponding ionogels.

As an alternative to ILs, deep-eutectic solvents (DESs) have been recently introduced (Figure 5).¹¹ DESs are attractive alternatives to ILs because their cost of synthesis is typically lower than those of ILs and are easier to prepare.^{12,13}

In addition, some DESs are known to be biodegradable as well as nontoxic.¹² Similar to ILs, DES-based gels could lead to novel, interesting and potentially useful soft materials. Due to the structural and functional versatility of these designer solvents (*i.e.*, DES and ILs), a possibility to manipulate the specific structure and thus properties of the gel might be intriguing and potentially useful for a variety of applications.

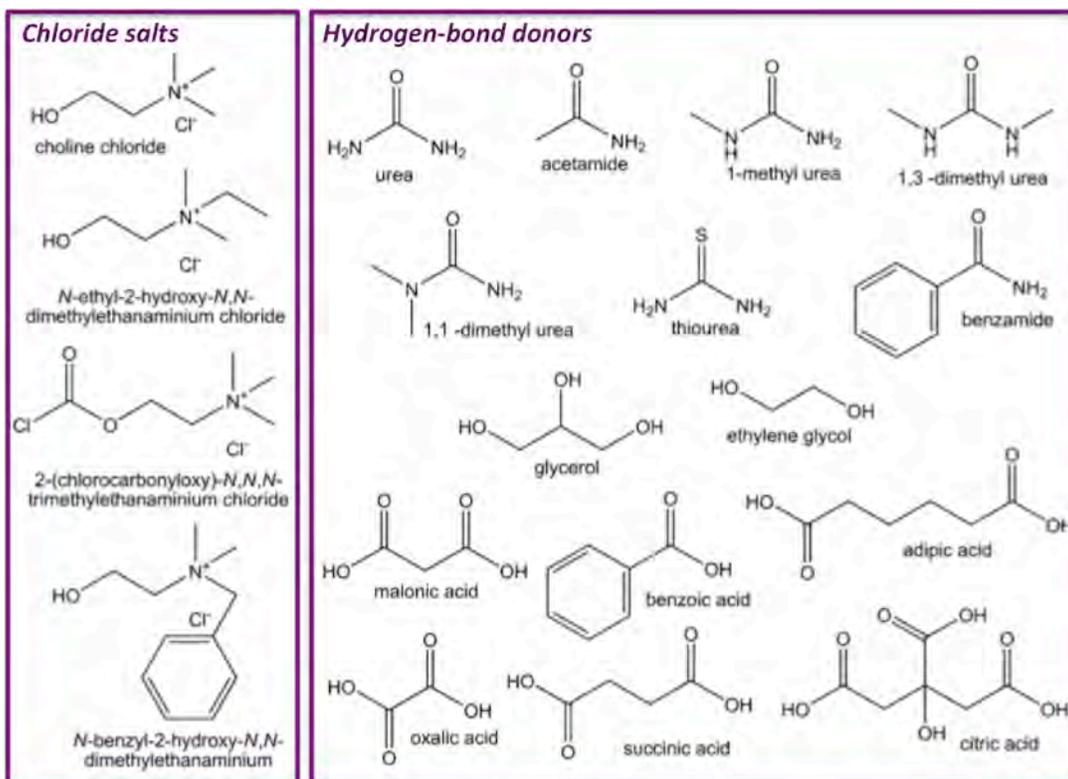


Figure 5. Structures of some representative examples of DESs, where halides of the organic salts is acting as hydrogen bonds acceptor. Adopted from ref. 11.

Several imidazolium-LMWGs that featured either long dialkyl substituents or dicationic moieties have been reported to gel aqueous and organic solvents as well as ILs.^{4,14-20} For example, didodecylimidazolium salts with di- and tricarboxylate-containing anions (Figure 6A) were able to gel dimethylsulfoxide (DMSO) as well as several imidazolium-, pyrrolidinium-, and ammonium-based ILs with a minimum gelator concentration (MGC) of 1.2–5.0% (wt).⁴ In addition, n-octyl- and n-dodecyl-containing bis-imidazolium-based gelators (Figure 6B) were shown to gel not only imidazolium-based ILs but also alcohols (e.g., ethanol, propanol, octanol, and glycerol) with MGC in 2–20% (w/w) range.^{4,14-20}

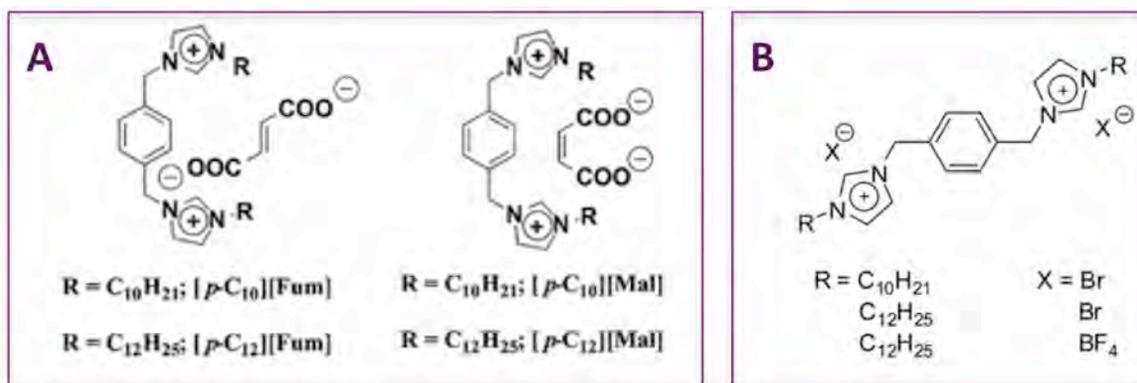


Figure 6. Dicationic imidazolium-based salts as LMWGs. Adopted from refs. 21 and 4.

Notably, the ability of a relatively simple, normal alkyl chain containing 1-alkyl-3-methylimidazolium-based ILs (*i.e.*, $[C_n\text{-mim}]$) to act as LMWGs toward ILs, for example, has been significantly less explored. However, it is plausible that due to straightforward, efficient and modular synthetic approaches towards this class of ILs, their LMWGs potential could be established and/or optimized in a facile manner. In addition, for these $[C_n\text{-mim}]$ -based salts, the ability to generate additional congeners via robust anion metathesis reactions should further increase scope of potential LMWGs. Arguably, by generating libraries of imidazolium-based LMWGs (or other IL-based LMWGs) it might be possible to establishing structure-property relationships and potentially provide a more rational design (as opposed to a trial and error approach that is currently utilized in this field) gelators for various types of fluids.

RESULTS AND DISCUSSION

Ironically, we were prompted to explore rational and hypothesis-driven approaches towards the design of LMWGs, starting with a serendipitous discovery on the ability of 1-hexadecyl-3-methylimidazolium bromide, $[C_{16}\text{-mim}]\text{Br}$ to gel some 1-alkyl-3-methylimidazolium bromides (Figure 7).

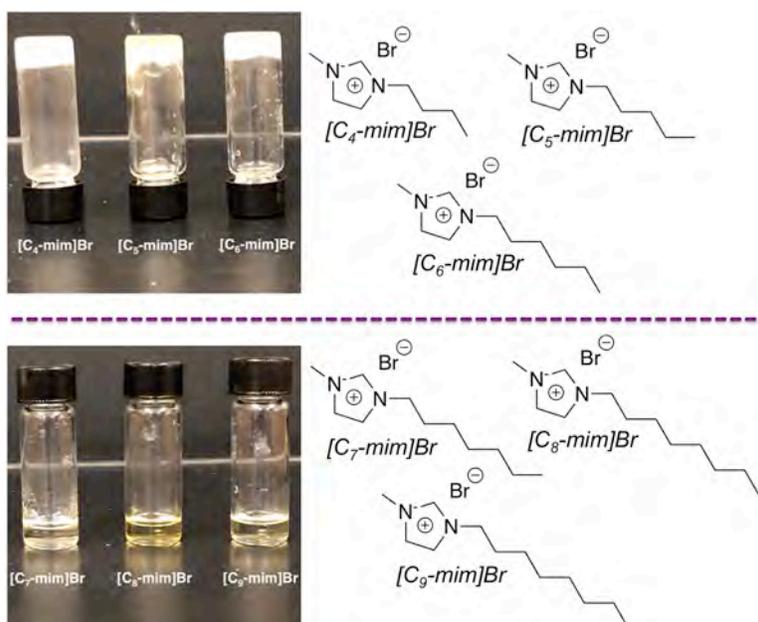


Figure 7. Gelation ability of $[C_{16}\text{-mim}]\text{Br}$ towards $[C_n\text{-mim}]\text{Br}$ ILs; $n = 4-9$; $[C_{16}\text{-mim}]\text{Br} = 10.0\%$ w/v in all cases. Modified from ref. 22.

The efficacy of $[C_{16}\text{-mim}]\text{Br}$ diminished as the length of the 1-alkyl substituent on 1-alkyl-3-methylimidazolium bromides, ($[C_n\text{-mim}]\text{Br}$, where $n = 4-9$) increased, these observations indicated that $[C_{16}\text{-mim}]\text{Br}$ could be used as LMWG. Only $[C_4\text{-mim}]\text{Br}$, $[C_5\text{-mim}]\text{Br}$ and $[C_6\text{-mim}]\text{Br}$ formed gels in the presence of $[C_{16}\text{-mim}]\text{Br}$; whereas other homologous ILs in this series remained fluid even after several days (Figure 7).

In addition, it is worth pointing out that neither $[C_{12}\text{-mim}]\text{Br}$ nor $[C_{10}\text{-mim}]\text{Br}$ appeared to gel $[C_4\text{-mim}]\text{Br}$, which suggested to us that the cetyl substituent (C_{16}) on the imidazolium core (mim) could be a critical element that might be responsible for the gelation.

These results have laid the foundation for this honors research, which focused on a novel ability of cetyl (i.e., $n\text{-}C_{16}$ -group) containing organic salts, namely, 1-hexadecyl-3-methylimidazolium $[C_{16}\text{-mim}]$, N-hexadecylpyridinium $[C_{16}\text{-py}]$, and N-cetyl-N-methylpyrrolidinium $[C_{16}C_1\text{-pyrr}]$ (Figure 8A), to gel several representative classes of ILs

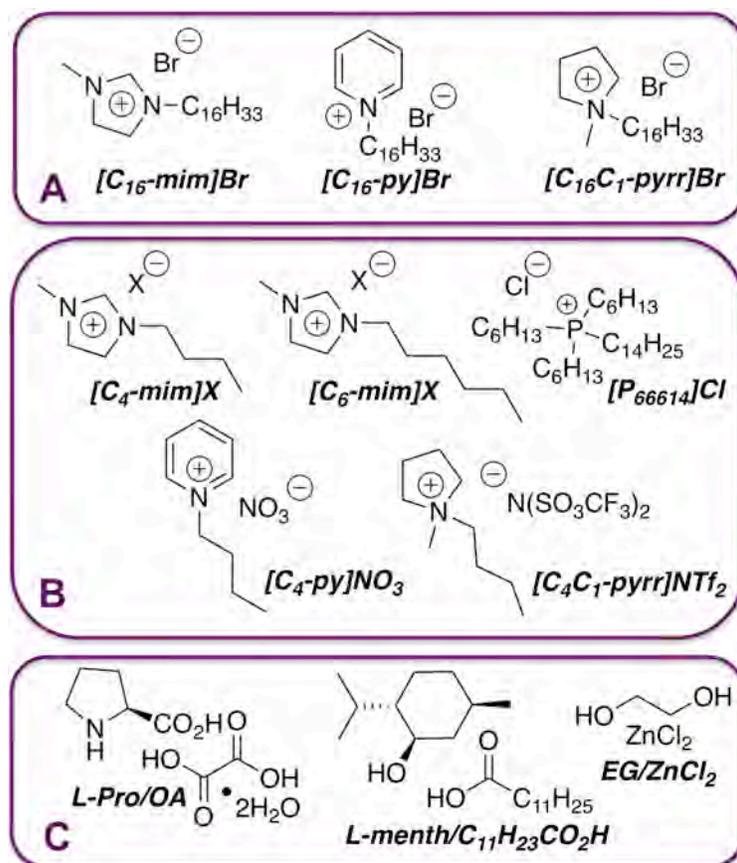


Figure 8. Structures of ionic gelators and fluids: (A) N-hexadecyl-containing imidazolium, pyridinium, and pyrrolidinium bromides used as LMWGs; (B) imidazolium, phosphonium, pyridinium, and pyrrolidinium ILs, where X is an anion, e.g., NO_3 , PF_6 , BF_4 , NTf_2 , etc.; and (C) DESs. Adopted from ref. 22.

(Figure 8B), deep eutectic solvents (DESS; Figure 8C), and a few organic molecular solvents, such as dioxane and toluene.

Initially, we evaluated the gelating ability of [C₁₆-mim]Br towards several [C₄-mim]-based ILs, where the anion of ILs was varied (Table 1). In this aspect, changing the anion of the IL exhibits the diverse way in which manipulating the flexible structure of an IL changes the properties of the resulting gel. In the concentration range of 5–15% w/v, [C₁₆-mim]Br was able

Table 1. Gelation ability of [C₁₆-mim]Br towards [C_n-mim]X ILs.

entry	ILs	MGC, ^a % w/v (m.p., °C) ^b
1	[C ₄ -mim]PF ₆	6.0 (41)
2	[C ₆ -mim]PF ₆	5.0 (30)
3	[C ₄ -mim]NO ₃	10.6 (27)
4	[C ₆ -mim]NO ₃	11.0 (28)
5	[C ₄ -mim]BF ₄	5.5 (47)
6	[C ₄ -mim]TFA	NG ^c
7	[C ₄ -mim]NTf ₂	NG ^c
8	[C ₆ -mim]NTf ₂	NG ^c

a – MGC: minimum gelator concentration; b – average melting points, determined using the inverted vial method after 12-24 hours; c – NG = no gelation; no gelation upon addition of 15 % w/v of [C₁₆-mim]Br. TFA = CF₃CO₂, NTf₂ = N(SO₂CF₃)₂.

to gel PF₆⁻, BF₄⁻, and NO₃⁻ containing ILs (Table 1, entries 1-5). On the other hand, [C₄-mim]TFA, [C₄-mim]NTF₂, and [C₆-mim]NTF₂ did not undergo gelation even when the concentration of [C₁₆-mim]Br was increased to 15% w/v of (Table 1, entries 6–8). These results demonstrated that there seemed to be a balance between the length of the alkyl substituent of the

[C_n-mim], i.e., *n*, of the ILs and the specific anion, i.e., X of ILs, which appeared to contribute to the gelation process.

In order to further explore the gelation ability of [C₁₆-mim]Br of other types of ILs, we examined the gelation of phosphonium, pyridinium, and pyrrolidinium ILs (Table 2). Though both phosphonium and pyridinium IL underwent gelation in the presence of [C₁₆-mim]Br (Table 2, entries 1 and 2) was observed, no gel formation was recorded in the case of [C₄C₁-pyrr]NTf₂ (Table 2, entry 3). It should be noted that the results gelation results with [C₄C₁-pyrr]NTf₂ should be taken with caution, since NTf₂-containing imidazolium ILs (Table 1, entries 8 and 9) also did not undergo gelation in the presence of [C₁₆-mim]Br. Thus, conclusions as to whether the observed lack of gelation relates to NTf₂ or pyrrolidinium-scaffold would require more elaborate investigations with a wider range of ILs.

Table 2. Gelation ability of [C₁₆-mim]Br towards several types of ILs.

entry	ILs	MGC, ^a % w/v (m.p., °C) ^b
1	[P ₆₆₁₄]Cl	10.0 (37)
2	[C ₄ -py]NO ₃	4.4 (29)
3	[C ₄ C ₁ -pyrr]NTf ₂	NG ^c

a – MGC: minimum gelator concentration; b – average melting points, determined using the inverted vial method after 12-24 hours; c – NG = no gelation; no gelation upon addition of 15 % w/v of [C₁₆-mim]Br.

NTf₂ = N(SO₂CF₃)₂. See Figure 8B for structures of the ILs.

Gelation ability of [C₁₆-mim]Br was further extended to DESs (Table 3). As noted in the Introduction, DESs have become as a relatively affordable alternatives to ILs, although the range of their applications is still inferior to the one of the ILs.^{12,13} It appeared that commonly used DESs, such as L-Pro/OA, L-menth/C₁₁H₂₃CO₂H, and ethylene glycol/ZnCl₂ (see Figure 8C for

structures), could be gelled by [C₁₆-mim]Br (Table 3). It is of interest to note that the MGC-values for gelation of DESs were significantly lower than those for ILs (Tables 1 and 2). Tentatively, this observation might indicate that the molecules of the components that compose DESs are more “pre-organized”/“pre-assembled” than the components of the ILs. Without a doubt further studies are required prior to formulating any definitive rationales.

Table 3. Gelation ability of [C₁₆-mim]Br towards several types of DESs.

entry	ILs	MGC, ^a % w/v (m.p., °C) ^b
1	L-Pro/OA	1.0 (37)
2	L-menth/C ₁₁ H ₂₃ CO ₂ H	0.9 (41)
3	EG/ZnCl ₂	1.1 (38)

a – MGC: minimum gelator concentration; b – average melting points, determined using the inverted vial method after 12-24 hours.

See Figure 8C for structures of DESs.

Finally, the ability of [C₁₆-mim]Br to gel molecular organic solvents was evaluated. Of the organic solvents tested, only toluene and dioxane formed gels with ca. 10% w/v of the gelator, where [C₁₆-mim]Br failed to gel methanol, acetone, dimethylsulfoxide (DMSO), chloroform and pyridine to name a few. It is of interest to mention that although ethylene glycol did not undergo gelation even when 15% w/v of [C₁₆-mim]Br was used, yet when ethylene glycol was used in combination with ZnCl₂, *i.e.*, DES = EG/ZnCl₂, was gelled in the presence only 1.1 % of [C₁₆-mim]Br (Table 3, entry 3). [C₁₆-mim]Br was insoluble in water, hexane, and cyclohexane even at elevated temperatures; hence no gelation of these solvents was possible.

Subsequently, in order to determine the nature of the gelation process as well as the structure of $[C_{16}\text{-mim}]\text{Br}$ in the gel phase, the gels of various fluids were examined using polarized optical microscopy (POM), and the morphology of the gels was found to be strongly dependent on the nature of the fluid (Figure 9).

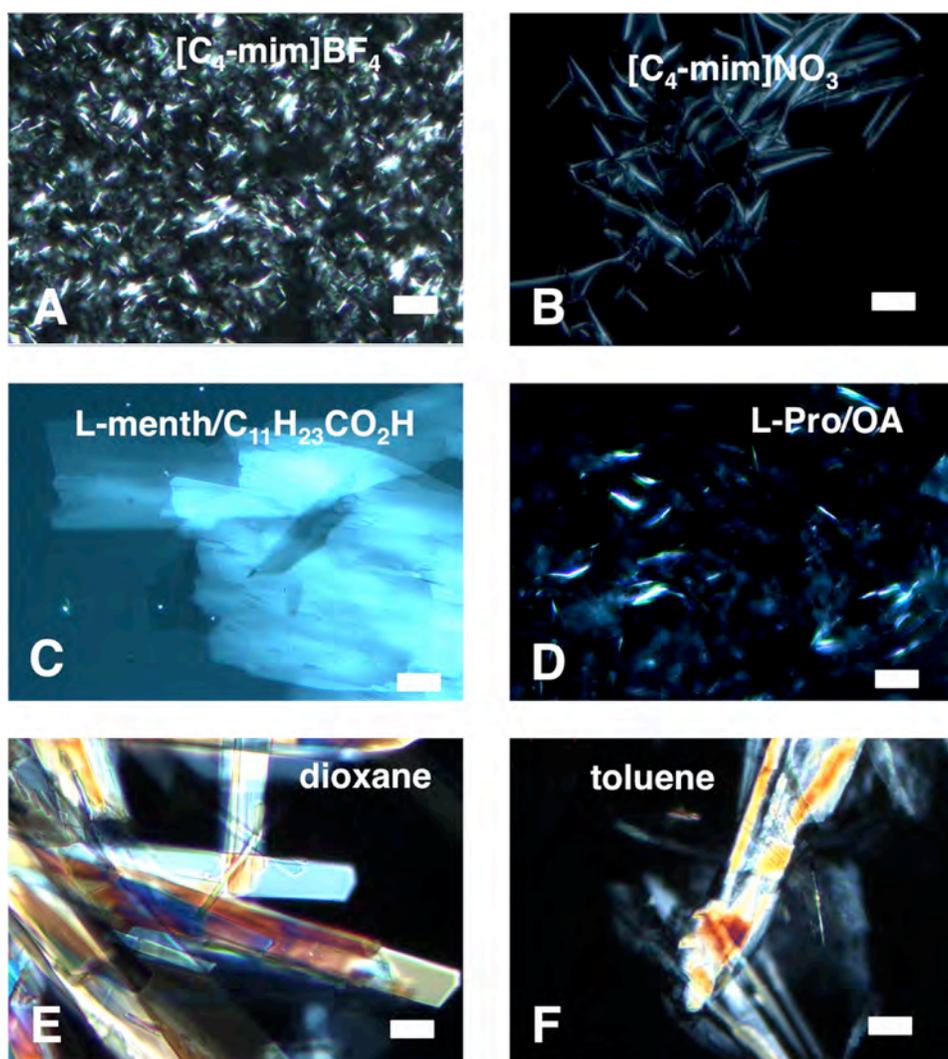


Figure 9. Representative POM images of gels of ILs (A, B), DESs (C, D), and molecular solvents (E, F) with minimum $[C_{16}\text{-mim}]\text{Br}$ concentration. White scale bar in the right bottom corner is 20 μm .

This microscopy investigation, which was conducted in collaboration with Professor Onofrio Annunziata (Department of Chemistry and Biochemistry), allowed for the assessment of the morphology of the gels without perturbing the overall structure of the gels. In the case of ILs, POM images showed optical anisotropy, which could be attributed to the formation of ordered crystalline structures. Importantly, a qualitative change in the morphology was observed in the crystalline structure of the [C₁₆-mim]Br.

Specifically, for [C₄-mim]BF₄ gel (Figure 9A), needlelike small crystals with thicknesses on the order of 1 μm were observed. On the other hand, for [C₄-mim]NO₃ gel (Figure 9B), clusters of rod-like crystalline fragments. Distinct morphologies were also noted for DES gels, with L-menth/ C₁₁H₂₃CO₂H exhibiting relatively large crystalline structures (Figure 9C), while needlelike microcrystals were observed in the L-Pro/OA solvent (Figure 9D).

Interestingly, well-defined and relatively large crystals with fairly similar morphologies were observed for dioxane (Figure 9E) and toluene (Figure 9F) gels. It is important to note that in all examples [C₁₆-mim]Br exhibited crystalline structure. It is important to note that the presence of crystalline-like structure in the gels of several fluids was further confirmed by powder X-ray diffraction measurements.²²

The obtained data, including POM and XRD, suggested that gelator was present in a crystalline form in the gel, and the specific shape, size, and the morphology of its crystals strongly depended on the specific nature and identity of the environment.

Next, to better understand the phase transitions between gel and sol states, differential scanning calorimetry (DSC) studies were conducted. In general, the nature of phase transitions of the liquids (ILs and DES) appeared to be largely unaffected by [C₁₆-mim]Br, while additional transitions related to the melting and crystallization of the gels were noted. Please see ACS OMEGA for detailed description of DSC traces.²² Arguably, the DSC results indicated that [C₁₆-mim]Br might be used to modulate the phase transitions of various ILs over a wide range of temperatures.

In order to determine whether the anion of the cetyl containing imidazolium salts had an effect on gelation, we prepared a set of [C₁₆-mim]X, where X = PF₆, NTf₂, TFA, and BF₄ and evaluated their ability to gel [C₄-mim]PF₆ (Table 4). No significant variations in the MGCs or in melting points of the gels were noted upon changing the anion of the [C₁₆-mim]-based salts (Table 4).

Table 4. Effect of the gelator's anion on the gelation of [C₄-mim]PF₆.

entry	LMWGs	MGC, ^a % w/v (m.p., °C) ^b
1	[C ₁₆ -mim] Br	6.0 (41)
2	[C ₁₆ -mim] BF₄	5.0 (34)
3	[C ₁₆ -mim] PF₆	3.4 (36)
4	[C ₁₆ -mim] TFA	5.9 (39)
5	[C ₁₆ -mim] NTf₂	5.8 (39)

a – MGC: minimum gelator concentration; b – average melting points, determined using the inverted vial method after 12-24 hours. TFA = CF₃CO₂, NTf₂ = N(SO₂CF₃)₂.

Although the phase transition temperatures and MGCs were largely unaffected by the nature of the anion of the LMWGs (Table 4), the morphology of gelators appeared to be dependent on the anion of the gelator. POM images of the gels (Figure 10) revealed fairly large platelet-like structures for $[\text{C}_{16}\text{-mim}]\text{Br}$ and $[\text{C}_{16}\text{-mim}]\text{PF}_6$ (Figure 10, A and B). Whereas in the case when $[\text{C}_{16}\text{-mim}]\text{NTf}_2$ was used as a gelator, amorphous morphology were observed (Figure 10C). On the other hand, crystalline, rod-like structures were observed in the case of $[\text{C}_{16}\text{-mim}]\text{BF}_4$ (Figure 10D).

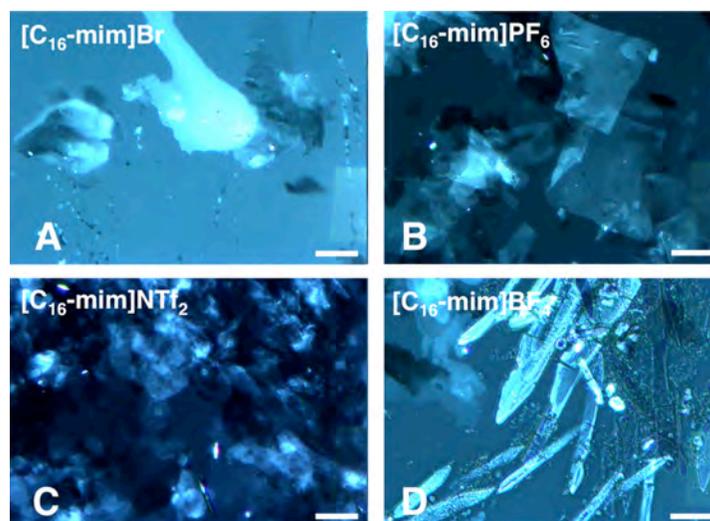


Figure 10: POM images of $[\text{C}_4\text{-mim}]\text{PF}_6$ gels in the presence of $[\text{C}_{16}\text{-mim}]$ -gelators with different anions. White scale bar is 20 μm . $\text{NTf}_2 = \text{N}(\text{SO}_2\text{CF}_3)_2$. See Table 4 for MGC values and m.p. of the gels.

Albeit preliminary, the results are promising as they indicate that simply by using various anions with one cation allowed to generate a set of LMWGs from a common precursor, which is in line with the objectives and hypothesis that were set at the beginning of the project. Furthermore, the morphologies of LMWGs could be tuned by simply changing the anion-component of the ionic LMWGs.

In order to further evaluate the designer approach towards other LMWGs, we evaluated the ability of N-hexadecylpyridinium bromide, [C₁₆-py]Br, and N-hexadecyl-N-methylpyrrolidinium bromide, [C₁₆C₁-pyrr]Br (Figure 8A) to induce gelation of various liquids (Table 5). It appeared that these new LMWGs can gel various types of liquids, albeit their ability was somewhat distinct from that exhibited by [C₁₆-mim]Br.

Table 4. Effect of the gelator's cation on the gelation of various fluids.

gelator	MGC, ^a % w/v (m.p. / °C) ^b			
	[C ₄ -mim]PF ₆	[P ₆₆₆₁₄]Cl	EG/ZnCl ₂	dioxane
[C ₁₆ -mim]Br	6.0 (41)	10.0 (37)	11 (38)	9.9 (41)
[C ₁₆ -py]Br	2.9 (43)	8.7 (48)	4.0 (35)	8.0 (29)
[C ₁₆ C ₁ -pyrr]Br	5.9 (33)	9.9 (38)	10.0 (28)	15.0 (35)

a – MGC: minimum gelator concentration; b – average melting points, determined using the inverted vial method after 12-24 hours. See Figure 8 for structures.

These preliminary results indicated that both [C₁₆-py]Br and [C₁₆C₁-pyrr]Br could gel ILs, DESs, and molecular solvents (Table 4). Importantly these results established a notion that gelation of various types of fluids, including ionic, eutectic and molecular, could be achieved with structurally simple and easily accessible gelators.

CONCLUSIONS

In this work, the ability of n-hexadecyl imidazolium-, pyridinium-, and pyrrolidinium based organic salts to gel various types of ILs, DESs, and a few molecular solvents had been investigated. The obtained results suggested that these salts induce the gelation of the aforementioned fluids via a crystallization mechanism. It is proposed that the crystals that are forming upon cooling hot solutions “trap” the solvent molecules in their network. Minimum gelator concentrations for these salts were determined to be in the range of 0.9–11.0% (w/v), which is on par with other types of LMWGs. Collectively, the obtained results indicated that structurally minimalistic and easily accessible organic salts could act as LMWGs for various types of fluids, and which opens an opportunity to produce designer gels.

EXPERIMENTAL SECTION²³

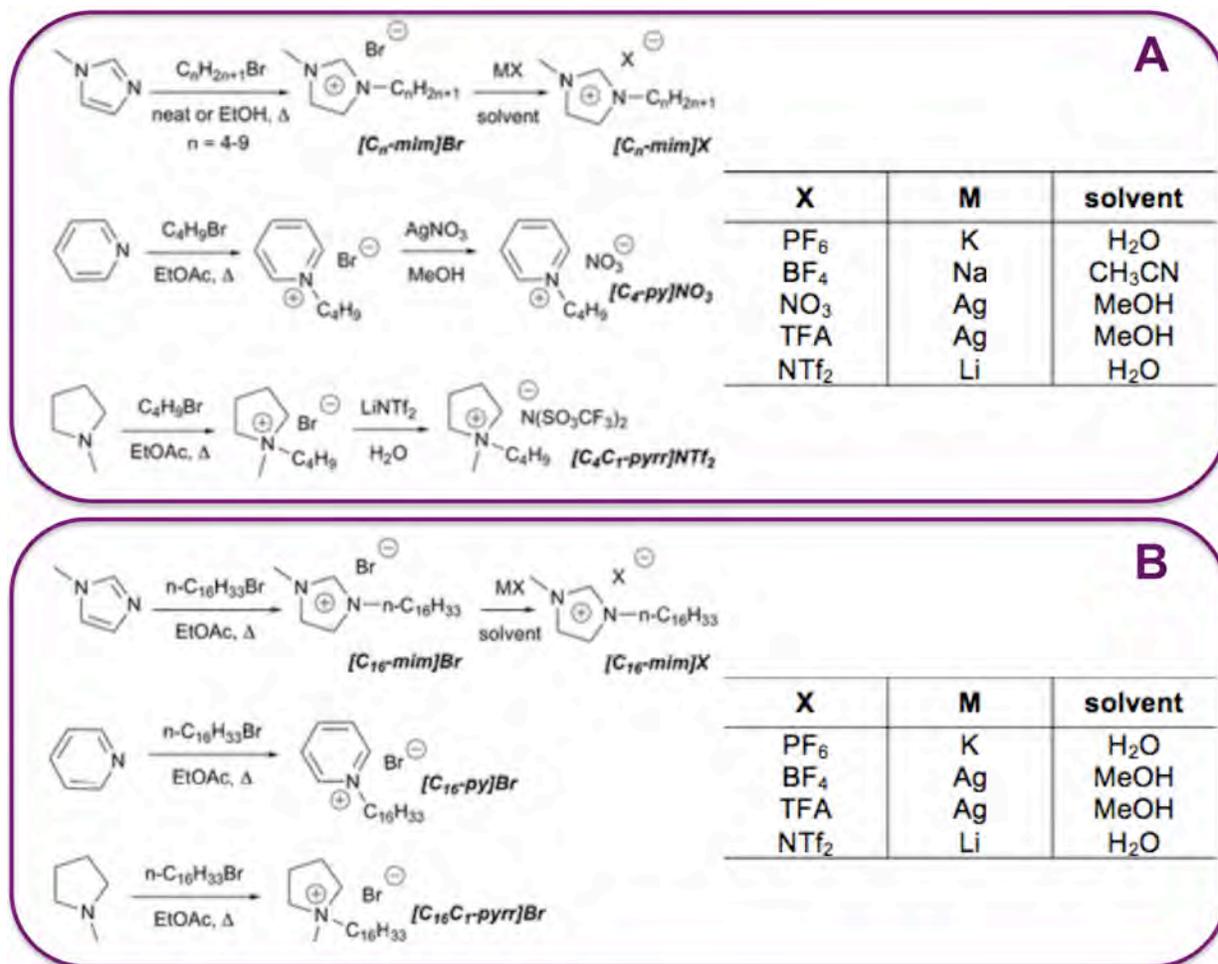
All chemicals and solvents were purchased from major commercial manufacturers (i.e. Sigma-Aldrich, Tokyo Chemical Industry-TCI, and Acros), and they were used as received.

Preparation of Gels and Gel Melting Temperature Measurements: Gelation tests were performed by the inverted vial method. This method was used to classify the product of an organogelator and a solvent as a gel. In summary, a screw-cap vial was charged with the appropriate amount of organogelator and the appropriate liquid (typically 0.5 mL). The vial was sealed and heated using a heat gun until a homogeneous solution was obtained. The vial was allowed to cool to room temperature, and after 12–24 hours, it was inverted and observed closely for any fluids that may be sliding down the wall. The absence of fluid sliding down was considered as a positive test for gelation. Melting points were determined by using test-tube-tilting method.²⁴ In summary, a similar screw-cap vial containing the gel was tested in two positions—inverted vertically and placed horizontally. In both positions, the vial was immersed into a water bath and the temperature was raised at 1°/min. The T_{gel} was recorded as the temperature when the gelled mass started to flow downward (*i.e.*, melted). Averages of at least two independent measurements are reported; the standard deviation (\pm SD) was less than 2° in all cases.

Morphological Study of the Gels: POM images were obtained using a light microscope (Axioskop 40, Zeiss), and images were taken by a digital camera (AxioCam MRc, Zeiss) and processed using a manufacturer-provided software (AxioVision AC 4.5, Zeiss). Samples were

pipetted from the vials using plastic disposable pipettes and placed in between glass slides for visualization.

Synthesis of Gelators, ILs, and DESs: DESs were prepared according to modified literature procedures.²⁵⁻³² In summary, appropriate molar amounts of each compound were mixed in a screw-cap glass vial, capped, and repeatedly heated using a heat gun followed by short periods (20–30 seconds) of vortexing until transparent, homogeneous fluids were obtained. These liquids were used as prepared. L-Pro/OA:²⁶⁻²⁸ L-proline and oxalic acid dehydrate were mixed in 1:1 molar ratio. L meth/ C₁₁H₂₃CO₂H:³⁰ L-menthol and dodecanoic acid were mixed in 1:1 molar ratio. ZnCl₂/EG:^{31,32} ZnCl₂ and ethylene glycol were mixed in 1:4 molar ratio. Imidazolium, pyridinium, and pyrrolidinium ILs as well as the corresponding gelators were made according to literature procedures (Scheme 1).³³⁻⁴⁰ [P₆₆₆₁₄]Cl was a commercial sample from TCI. All IL samples were dried for several hours under a vacuum prior to the addition of the gelator. All ILs were purified as follows: ILs were dissolved in CH₂Cl₂, followed by filtration to facilitate the removal of inorganic impurities. Next, ILs were repeatedly treated with charcoal in EtOH at elevated temperatures followed by filtration and removal of EtOH in vacuo (for an azeotropic removal of residual water). Finally, the ILs were dried under vacuum for 2–4 hours. The identity of ILs and LMWGs was established using ¹H, ¹⁹F, ³¹P NMR spectroscopy. For full characterization details, see ref. 22.



Scheme 1. Synthesis of ILs (A) and ionic LMWGs (B). Adopted from ref. 22.

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