Green Chemistry and Ionic Liquids, an Alternative to Classical Solvents

Ziya Erdem KOÇ
Selcuk University

To Cite This Chapter:
Koç, Z. E. (2025). Green chemistry and ionic liquids: An alternative to classical solvents. In S. Erten & C. A. Aksoy (Eds.), *Current studies in basic sciences, engineering and technology 2025* (pp. 339-349). ISRES Book Series. ISRES Publishing.

Introduction

Green chemistry applies core chemical principles to address worldwide challenges, including climate change, energy efficiency, sustainable agriculture, and resource depletion by engineering products and processes that avoid generating or utilizing hazardous materials (Poole et al., 1989). Therefore, it is an indispensable tool for sustainable development. Given current global conditions, it has become vital for chemists to integrate considerations related to human health and environmental sustainability into every aspect of their professional work. (Huddleston et al., 1998). When we look at the 150-year history of chemistry, green chemistry is a comparatively recent concept (Chiappe & Pieraccini, 2005). This movement began in the 1990s with the pollution prevention initiative, which called upon industry to reduce or eliminate pollution at its source rather than clean it up afterward (Aki et al., 2004; Jian, 2010). The U.S. Environmental Protection Agency (EPA) defined several environmental pollution prevention approaches, including inventory control, process control, in-process recycling, domestic changes, and green chemistry itself (Reyna-González et al., 2012).

Environmental pollution has become a critical global concern in today's world (Welton, 1999). Hydrometallurgical methods, which play a significant role in metal extraction from primary and secondary sources, are seeking highly efficient and environmentally friendly solvents other than traditional solvents. Ionic liquids, globally recognized as "green solvents," are emerging as a new type of substance that is beginning to replace traditional solvents (Zhang et al., 2009).

Green Solvents

The use of environmentally friendly solvents is an important option when producing new chemicals, and the use of water as a solvent in chemical reactions is an active area of research.

- Ionic Liquids
- Fluorinated Solvents
- Supercritical Fluids

Ionic liquids

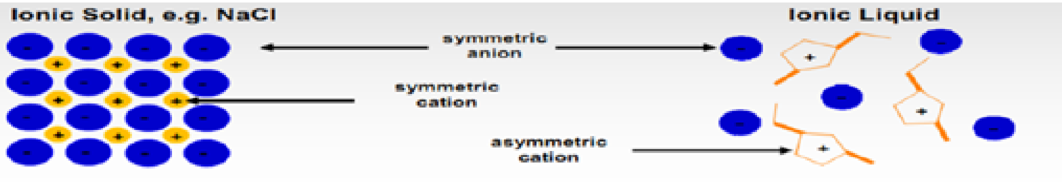
The general properties of ionic liquids are explained, and a literature analysis is provided to understand their usability. Considering the environmental and health concerns of today's world, problems such as the high number of solvents used, high energy and acid consumption, the need to recycle or dispose of waste solvents, and the potential for corrosion have led to the search for alternative solvents. Ionic liquids, with their outstanding properties and synthesizability, constitute a key element of this search (Shukla & Saha, 2013).

Various terms have been used to describe liquid salts such as fused salts, room-temperature ionic liquids, anhydrous ionic liquids, designer solvents, molten salts, liquid organic salts, room-temperature molten salts, and low-temperature molten salts have all been used to describe liquid salts, but ultimately, they all fall under the general concept of ionic liquids.

Ionic liquids, like common table salt (NaCl), consist of an anion–cation pair. However, unlike NaCl, where both ions are simple atomic species, in ionic liquids the ions are molecular and asymmetric in structure (Nockemann et al., 2008; Nockemann et al., 2006). **(Figure 1)**. Because of this asymmetry, the ions cannot easily pack into a crystalline structure, resulting in lower melting points. While conventional solvents such as acetone, dichloromethane, and water have molecular structures, ionic liquids are polar solvents composed of weakly bound positive and negative ions. Therefore, they are good solvents for a wide range of inorganic and organic compounds (halides BF_4^{-}, PF_6^{-}, ClO_4^{-}, CF_3COO^{-} $CF_3SO_3^{-}$ vd.). Ionic liquids (ILs) are defined as salt systems incorporating organic cations, anions, or both, distinguished by melting points below 100°C—significantly lower than those of conventional inorganic salts. Those maintaining a liquid state at ambient conditions are termed Room-Temperature Ionic Liquids (RTILs). Structurally, these salts arise from the weak association between bulky organic cations, such as 1-alkyl-3-alkylimidazolium or 1-alkylpyridinium, and various organic or inorganic anions. The anionic counterparts can be inorganic species, such as hexafluorophosphate (PF_6^{-}), tetrafluoroborate (BF_4^{-}), chloroaluminate ($AlCl_4^{-}$), chloride (Cl^{-}), or organic anions such as acetate (CH_3COO^{-}).

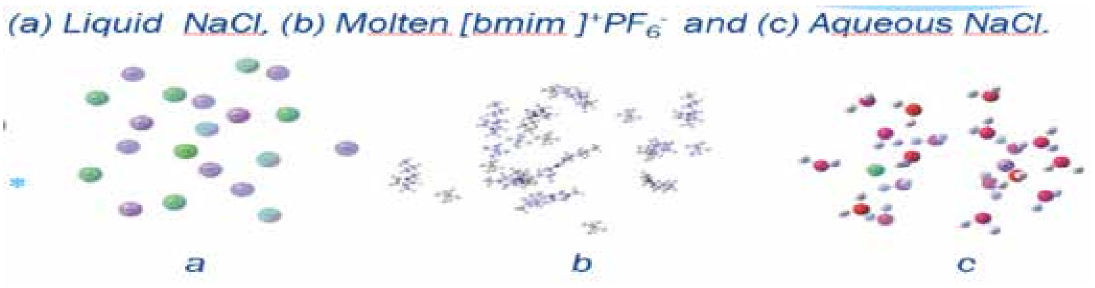
Figure 1

Ionic liquids, like common table salt (NaCl), consist of an anion–cation pair.



When the constituent ions of an ionic liquid are relatively bulky, the resulting charge-to-size ratio is effectively diminished. This leads to low lattice energy, weaker electrostatic interactions, and consequently lower melting points. However, the presence of large ions also results in high viscosity, and therefore the conductivity of the medium tends to be lower **(Figure 2)**.

Figure 2
Liquid, ionic liquids (ILs) and aqueous



Discovery and History

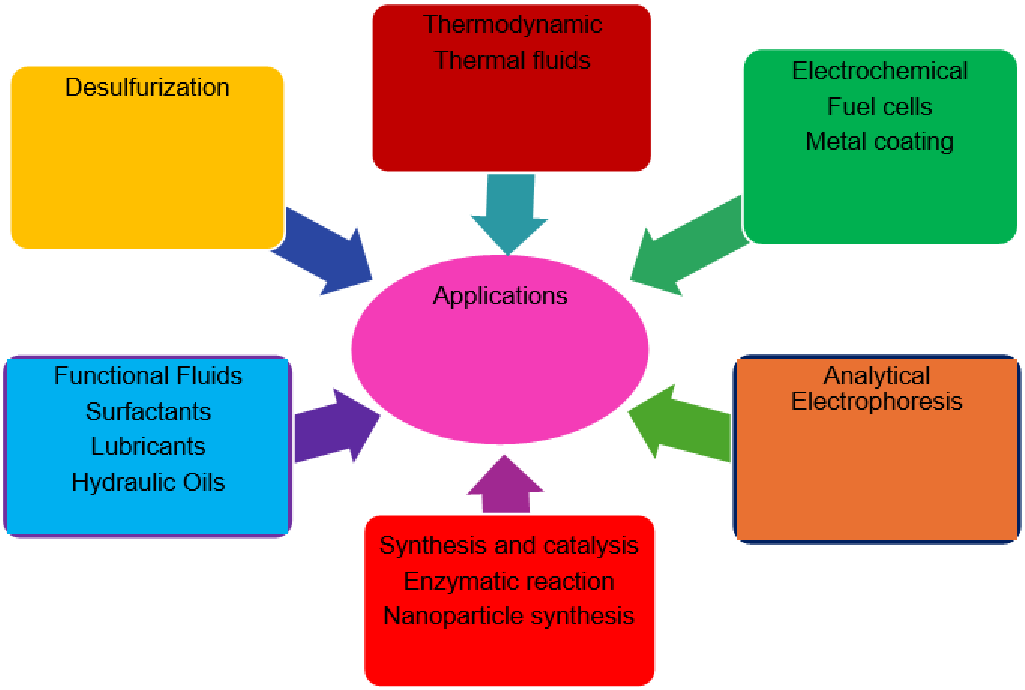
The historical origins of ionic liquids go back to 1914, marked by Paul Walden's identification of ethylammonium nitrate, which represented a pivotal moment in the chemistry of solvents. In 1967, Swain advanced the field by employing tetra-N-hexylammonium benzoate as a solvent in an electrochemical reaction, demonstrating the potential of ionic liquids in electrochemical applications. A breakthrough occurred in 1970 when Oster, Young, and colleagues synthesized the first ionic liquid that was stable at room temperature, greatly expanding practical usage possibilities. In the 1980s, Seddon and his research group pioneered the use of ionic liquids as catalysts in various solvent systems, further showcasing their versatility. By 1992, Wilkes synthesized a new class of ammonium-based salts and introduced them as innovative solvents and ionic liquids, opening the door to modern applications and establishing ionic liquids as important materials in green chemistry and advanced technologies.

Ionic liquids have found extensive application across a wide range of scientific and industrial fields due to their unique physicochemical properties. They serve as highly effective solvents and catalytic assistants in numerous chemical reactions, enhancing reaction efficiency and selectivity (Kumar, 2005). Their broad electrochemical stability has also enabled their use in battery technologies, where they offer improved safety and performance. In biotechnology, ionic liquids act as support materials for enzyme immobilization, providing stable and versatile environments for biocatalytic processes (Hernández-Fernández et al., 2010). Their excellent solvating ability makes them valuable solvents in extraction processes, enabling efficient separation and purification of target compounds (González et al., 2018). Additionally, ionic liquids function as advanced lubricants with high thermal stability and low volatility, improving tribological performance (Bermúdez et al., 2009). They are also used as template materials in the synthesis of nanomaterials, allowing controlled formation of nanostructures (Namboodiri & Varma, 2002). Within the scope of analytical chemistry, ionic liquids act as crucial elements for stationary phases in gas chromatography (Armstrong et al., 1999) and serve as additives in liquid chromatography mobile phases to improve separation performance (Xiaohua et al., 2004). Furthermore, they serve as moving electrolytes in capillary electrophoresis, improving ion transport and analytical resolution. These diverse applications highlight the versatility and growing importance of ionic liquids in modern science and technology.

Properties of Ionic Liquids

These fluids exhibit a variety of beneficial characteristics, such as negligible vapor pressure, significant viscosity, a broad temperature range for the liquid state, and the capacity to solvate both organic and inorganic substances, alongside high thermal and oxidative stability. Their negligible volatility, easy removal from reaction media, resistance to high temperatures, and ability to leave no residue further enhance their usefulness. In addition, their high polarity, low toxicity, non-flammable nature, reusability, catalytic activity, hydrogen-bonding capacity, Lewis's acidity, and immiscibility with many organic solvents expand their application potential. Altogether, these features make ionic liquids superior to conventional solvents and justify their classification as "Green Chemistry Materials" due to their environmentally friendly characteristics **(Figure 3)**.

Figure 3
Application areas of ionic liquid



Binary Ionic Liquids (Equilibrium)

Room-temperature ionic liquids based on halogens- and alkylhalogenoaluminate(III) species represent one of the most extensively investigated classes in literature. However, their sensitivity to moisture and water limits their practical applications. The first member of this class was obtained by mixing 1-alkylpyridinium bromide with $AlCl_3$. Similarly, mixtures of 1-ethyl-3-methylimidazolium chloride ([emim]Cl) and $AlCl_3$ were found to be liquid, which led to extensive studies on imidazolium-based salts. In addition to chloroaluminate systems, [emim]Br–$AlBr_3$ ionic liquids were also prepared. Among these, 1-butyl-3-methylimidazolium ($[bmim]^+$) salts are the most frequently used. Typical equilibrium species found in binary systems include.

Simple Salts (Single Anion and Cation)

The earliest example of an ionic salt is ethylammonium nitrate $[EtNH_3][NO_3]$, which also represents a simple ionic liquid. There exists a vast number of possible anion-cation combinations for synthesizing ionic liquids. The most used cations include 1-alkylpyridinium/1-alkylimidazolium cations.

Tetraalkylphosphonium/Tetraalkylammoniums used liquids and are stable toward both air and moisture, and some are even hydrophobic. Although they are more resistant to hydrolysis than halogenoaluminate(III) ionic liquids, many ammonium and imidazolium salts are hygroscopic, absorbing moisture even when their containers are opened. Modifying the structure of the cation or anion, compounds with diverse physical and chemical properties can be obtained. Because of this tunability, ionic liquids are also referred to as “designer solvents”. It is estimated that millions of anion cation combinations could theoretically be designed using this approach.

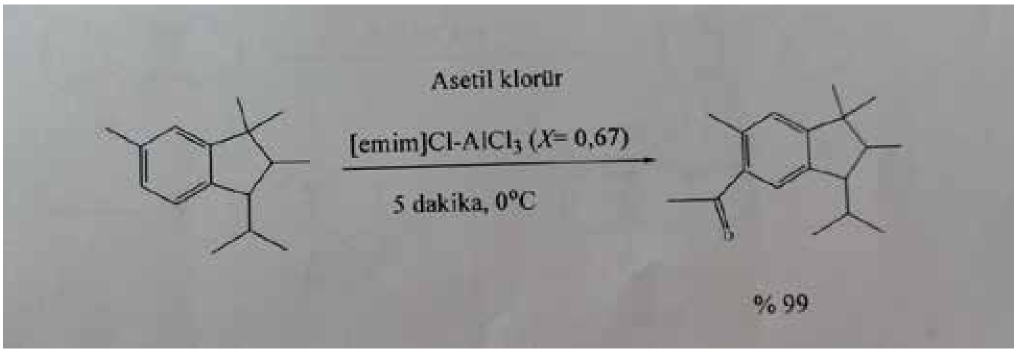
Reactions of Ionic Liquids

Friedel–Crafts Reactions

Friedel-Crafts reactions frequently employ chloroaluminate(III) ionic liquids. Due to their ability to dissolve a diverse array of aromatic compounds, these liquids serve as a superior medium for such reactions. To perform a Friedel–Crafts reaction in ionic liquids, an electrophilic species must first be generated within the medium. Many commercially important fragrance intermediates can be synthesized through Friedel–Crafts acylation reactions conducted in ionic liquids. For instance, Triazolide (5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane) can be synthesized with high yield using [emim] Cl–$AlCl_3$ ($X = 0.67$) ionic liquid as the medium **(Figure 4)**.

Figure 4

Triazolide (5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane) can be synthesized with high yield using [emim]Cl–AlCl₃ (X = 0.67) ionic liquid as the medium

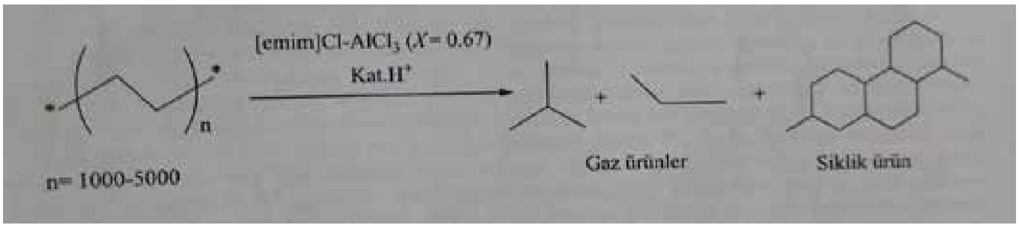


Cracking (Decomposition) Reactions

Decomposition, or cracking reactions, proceed readily within acidic chloroaluminate(III) ionic liquids, with the depolymerization of polyethylene serving as a prime example. When polyethylene is decomposed at elevated temperatures, it converts into volatile alkanes (such as propane, butane, pentane) and cyclic alkanes. While classical catalytic cracking requires very high temperatures (300–1000 °C), the same reactions can proceed in ionic liquids at temperatures as low as 90 °C, making them far more energy-efficient **(Figure 5)**.

Figure 5

Acidic chloroaluminate(III) ionic liquids readily facilitate cracking reactions.

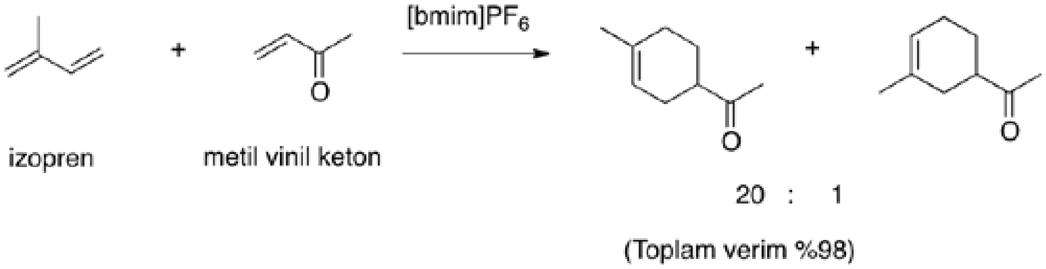


Diels–Alder Reactions

The Diels–Alder reaction, used to synthesize cyclic compounds, can also be carried out in ionic liquids as an alternative to water-based solvent systems. It has been observed that, when mixed with nonpolar organic solvents, the reaction rate increases significantly **(Figure 6)**.

Figure 6

The Diels–Alder reaction

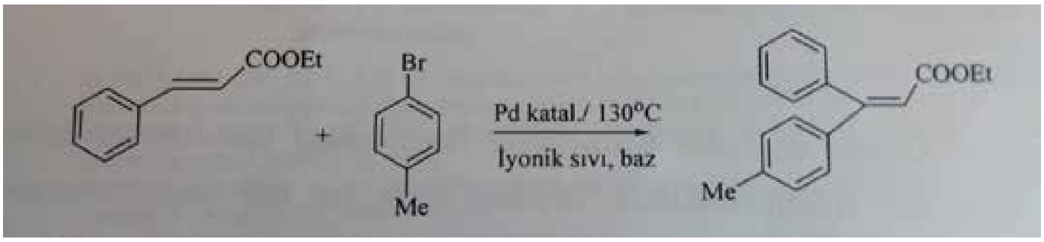


Heck Reactions

The Heck reaction involves palladium(0)-catalyzed coupling between alkenes and aryl halides. In ionic liquids, the catalyst dissolves effectively, and the product can be easily extracted using a nonpolar organic solvent. When water is added, a three-phase system forms, allowing the resulting salts to move into the aqueous phase. The formation of a palladium–carbene complex from the imidazolium cation in [bmim][Br] ionic liquid plays a crucial catalytic role. Studies have shown that iodo or bromobenzene with electron-withdrawing groups undergo Heck coupling reactions with styrene or acrylates more efficiently in [bmim][Br], due to the higher activity of the imidazolium bromide-derived carbene complex **(Figure 7)**.

Figure 7

The Heck reaction involves palladium(0) catalyzed coupling between alkenes and aryl halides. In ionic liquids



Applications for Ionic Liquids

Use of Ionic Liquids in Fuel Cells

With the increasing global demand for energy, research on clean and renewable energy sources has gained great importance. At the same time, studies focusing on the methods of energy utilization have rapidly expanded. Fuel cells are distinguished among alternative energy technologies by their exceptional efficiency, cost-effectiveness, quiet operation, and environmental compatibility. They are therefore expected to be widely adopted in the future. In Polymer Electrolyte Membrane (PEM) fuel cells, energy production performance largely depends on ion (proton) transport through the polymer electrolyte membrane. Ensuring the long-term stability of PEM fuel cells under high-temperature conditions is a critical requirement. Studies have shown that polyimide–ionic liquid composite membranes, both acid-doped and undoped, exhibit superior mechanical and thermal properties compared to conventional membranes used in the literature.

Chemical behavior of polynuclear transition-metal complexes in ionic liquid environments

Ionic liquids incorporating transition metals are viewed as promising hybrid materials that merge the intrinsic characteristics of ionic liquids with specific magnetic, optical, or catalytic functionalities. Various traditional methodologies exist for the synthesis of polynuclear transition-metal complexes. Historically, these compounds were primarily produced through high-temperature techniques, such as melt crystallization or chemical vapor transport [22–31]. Alternatively, synthesis involved processing precursors within various solvent environments, including inorganic media (like aqueous HCl or water) and organic solvents ranging from non-polar types (e.g., benzene, ether) to polar ones (e.g., acetonitrile, dichloromethane) **(Figures 8, 9, 10, 11).**

Figure 8

Binuclear complexes in ionic liquids

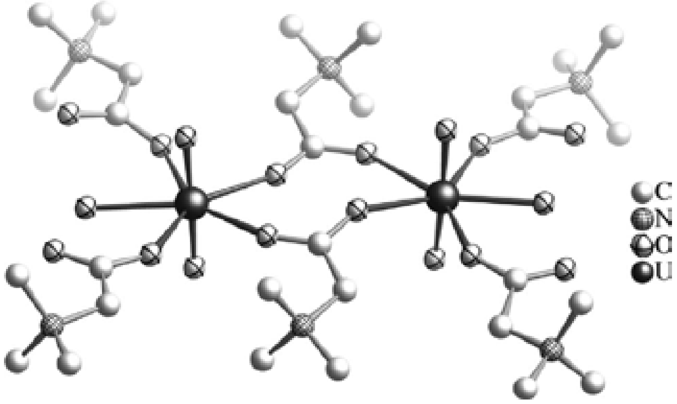


Figure 9

Trinuclear complexes in ionic liquids

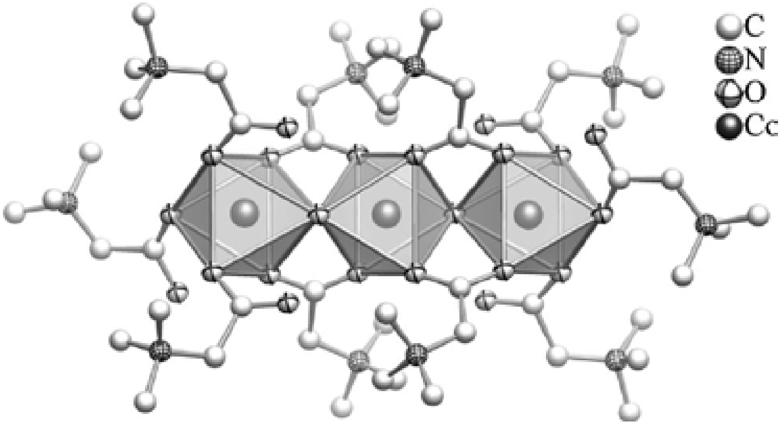


Figure 10

Tetranuclear complexes in ionic liquids

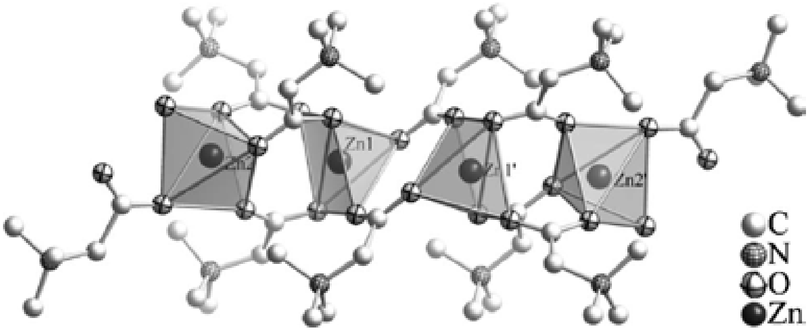
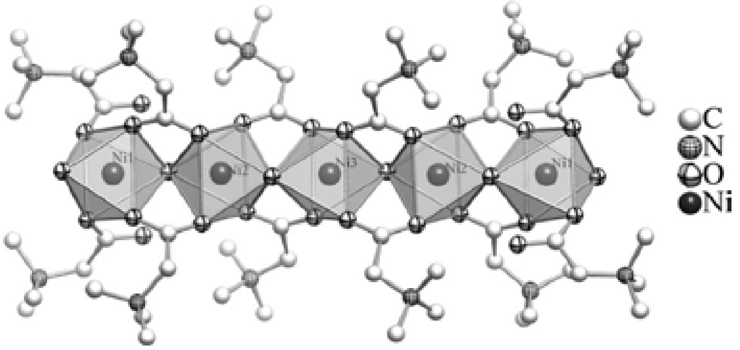


Figure 11

Pentanuclear complexes in ionic liquids

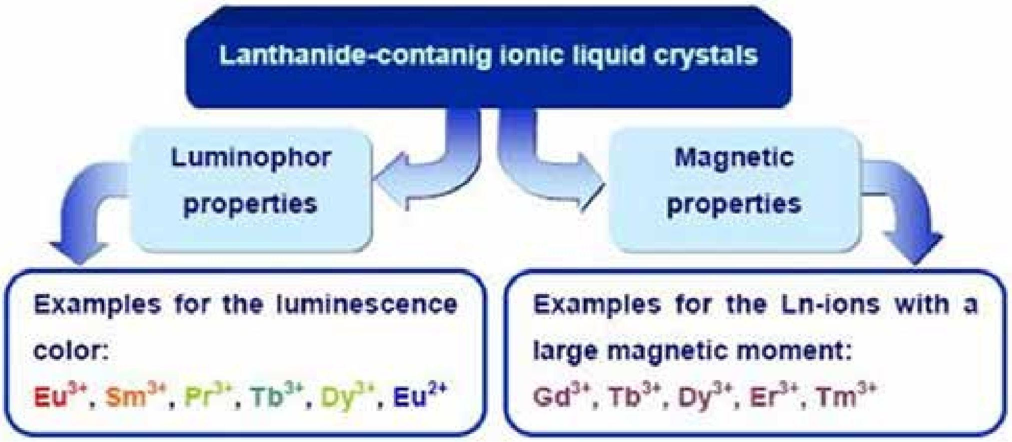


Magnetic Ionic Liquids

Magnetic Ionic Liquids (MILs) represent a specialized category of ionic fluids designed to possess magnetic characteristics by integrating paramagnetic or ferromagnetic ions or complexes into their structure **(Figure 12)**. While maintaining the inherent benefits of ionic liquids, such as negligible volatility, thermal endurance, and adjustable physicochemical properties, these advanced materials also possess the unique ability to respond to external magnetic fields. This added functionality allows MILs to be applied in advanced separation processes, targeted extraction, magnetic switching, catalysis, sensing technologies, and smart material design, making them highly promising for next-generation green and multifunctional chemical systems.

Figure 12

The Effect of Magnetism on Ionic Liquids



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About The Authors

Prof. Dr. Ziya Erdem KOÇ is an academic working in the field of inorganic chemistry at Selcuk University, Faculty of Science, Department of Chemistry in Konya. His research portfolio covers coordination chemistry, ionic liquids, metal chemistry, heterocyclic compounds, magnetic materials, and environmentally sustainable chemical compounds. Throughout his career, he has supervised numerous research projects, and many of his studies have been published in high-impact scientific journals. Prof. Koç has trained undergraduate, graduate, and doctoral students and participated in national/international scientific conferences.

E-mail : zkoc@selcuk.edu.tr, **ORCID :** 0000-0002-5875-9779

Note: This work, Supported under the 2224-B-Grant Program for Participation in Scientific Meetings within the Country, 2025/3rd Term, application number 1919B022508115.