

Ionic Liquids: Synthetic Methodology and Applications A Chronological and Sustainability-Focused Review (2019-2026)

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ABSTRACT

Ionic liquids (ILs) - salts that melt below 100 degC - have been recognised as highly versatile and customisable materials, exhibiting negligible vapour pressure, broad electrochemical windows, and outstanding solvation characteristics. This review consolidates advancements in synthetic methodology and diverse applications reported between 2019 and 2026, organising the synthetic literature chronologically to make the pace and direction of the field explicit, and emphasising the transition toward fourth-generation bio-based, biodegradable, and multifunctional ionic liquids sourced from renewable precursors.

Traditional synthesis methods - quaternization, neutralisation, and metathesis - continue to serve as essential techniques, while green methodologies including microwave- and ultrasound-assisted processes, mechanochemical (ball-milling) techniques, one-pot reactions, and bio-derived approaches offer efficient, high-yield, halide-free alternatives. Task-specific functionalisation enables precise applications across catalysis (heterocycle synthesis, biomass valorisation), energy storage (high-voltage battery and supercapacitor electrolytes, CO₂ electroreduction), environmental separations (CO₂ capture exceeding 1 mol/mol, metal and rare-earth-element extraction), biomedicine (drug solubilisation, transdermal delivery, antimicrobial agents), and industrial processes (alkylation, lubricants, cellulose fibres).

Persistent challenges - high production cost, viscosity-limited mass transfer, variable toxicity, and regulatory hurdles - are weighed against a projected market growth to USD 110-136 million by 2032-2034 (CAGR 8-13.5%). Future progress is expected to depend on AI-driven molecular design, hybrid solvent systems, and circular-economy principles to realise the potential of ILs in sustainable, low-carbon technologies.

Introduction

Ionic liquids (ILs) are a distinctive class of materials in modern chemistry, generally defined as salts composed entirely of ions that remain liquid below 100 degC, with many existing as liquids at room temperature (Welton, 2018; Zhang et al., 2006). Unlike conventional molten salts, which require temperatures above 200 degC to remain liquid, ILs possess exceptionally low vapour pressure, high thermal and chemical stability, non-flammability, and broad electrochemical stability windows.

Their physicochemical properties can be finely tuned through variation of the cation-anion pair, enabling materials tailored to specific functions (Plechko & Seddon, 2008; Hallett & Welton, 2011). Because of this tunability, ILs are often called "designer solvents", offering an attractive alternative to volatile organic compounds (VOCs) and aligning with the principles of green chemistry (Earle & Seddon, 2000; Rogers & Seddon, 2003; Seddon, 1997).

The field's history stretches back to 1914, when Paul Walden first reported ethylammonium nitrate ([EtNH₃][NO₃]), a salt with a melting point of approximately 12-14 degC and the first documented room-temperature ionic liquid (Welton, 2018). Sustained research interest did not emerge until the 1990s, when air- and moisture-stable imidazolium ILs paired with weakly coordinating anions such as tetrafluoroborate ([BF₄]⁻) and hexafluorophosphate ([PF₆]⁻) accelerated the field (Wilkes & Zaworotko, 1992; Bonhote et al., 1996; Huddleston et al., 2001). Foundational reviews and monographs through the 2000s (Dupont et al., 2002; Sheldon, 2001; Marsh et al., 2004; Hapiot & Lagrost, 2008; Freemantle, 2010) established ILs as solvents for organic synthesis, catalysis, and separation.

This review traces the field's evolution across four conceptual generations, with particular emphasis on developments reported since 2019, when the transition toward sustainable, bio-derived, and multifunctional ILs accelerated markedly. The synthesis literature (Sections 4-5) is organised chronologically, year by year, so that the pace of green-chemistry innovation is visible directly rather than buried inside method-type subsections. Applications are then surveyed across catalysis, energy storage, environmental separation, biomedicine, and industry, before the review closes with a critical look at outstanding challenges and future directions.

Classification and Generations of Ionic Liquids

Ionic liquids exhibit remarkable structural diversity, allowing classification by cation-anion composition, proton-transfer capability (protic vs. aprotic), functionalisation (task-specific, chiral, etc.), and historical generation (Amde et al., 2025; Alreshidi et al., 2025). This tunability enables tailoring of melting point, viscosity, conductivity, and biodegradability for specific applications.

Classification by Cation-Anion Composition

Common cation families and their characteristic properties are summarised in Table 1.

Cation family	Representative examples	Key characteristics
Imidazolium	[Bmim] ⁺ , [Emim] ⁺	Low viscosity, high conductivity, thermal stability to ~400 degC; most widely studied family (Pradhan, 2025)
Pyridinium	[CnPy] ⁺	Good stability; used in catalysis and electrochemistry (Amde et al., 2025)
Ammonium Cholinium	/ [NR ₄] ⁺ , [Ch] ⁺	Biocompatible, low-cost, biodegradable; [Ch] ⁺ common in bio-based ILs (Alreshidi et al., 2025)

Cation family	Representative examples	Key characteristics
Phosphonium	[PR ₄] ⁺	High thermal/chemical stability (>400 degC), low volatility (Vekaria et al., 2023)
Sulfonium	[SR ₃] ⁺	Lower viscosity, higher conductivity than phosphonium; emerging for energy storage (Amde et al., 2025)
Other	Pyrrolidinium, piperidinium, triazolium, guanidinium	Diverse tunable families (Pradhan, 2025)

Common anions span inorganic species ([BF₄]⁻, [PF₆]⁻, [NTf₂]⁻, [FSI]⁻, halides, [NO₃]⁻) and organic species (carboxylates, sulfonates, amino-acid-derived, phosphates). Anion choice governs hydrophobicity, stability, and toxicity; [NTf₂]⁻ provides electrochemical windows exceeding 5 V (Amde et al., 2025).

Protic vs. Aprotic Ionic Liquids

Protic ILs (PILs) form by proton transfer from a Bronsted acid to a Bronsted base and are simple to synthesise, hydrogen-bond capable, low-cost, and often biodegradable; they are used in biomass pretreatment and pharmaceuticals (Alreshidi et al., 2025). Aprotic ILs (AILs) are quaternised cations with no exchangeable proton (e.g., [Bmim][NTf₂]); they offer higher stability and broader electrochemical use but higher cost and variable toxicity (Pradhan, 2025). PILs typically show better biodegradability (>60% in OECD tests) and lower ecotoxicity than AILs (Alreshidi et al., 2025).

Task-Specific and Specialised Ionic Liquids

Task-Specific ILs (TSILs): functional groups for targeted roles such as metal extraction or catalysis (Singh & Savoy, 2020)

Chiral ILs (CILs): enantiopure cations/anions for asymmetric synthesis and separations (Pradhan, 2025)

Bio-based / Bio-ILs: derived from choline, amino acids, fatty acids; biodegradable, low-toxicity (Alreshidi et al., 2025)

Polyionic liquids (PILs): polymerisable units for membranes and materials (Amde et al., 2025)

Energetic ILs (E-ILs): for propellants, e.g. triazolium-based systems (Pradhan, 2025)

Magnetic ILs (MILs): paramagnetic anions enabling magnetic separation

Zwitterionic ILs (ZILs): dual-charged species for protein stabilisation (Pradhan, 2025)

Deep eutectic solvents (DES) / NADES: hydrogen-bonded mixtures (e.g., choline chloride:urea), often grouped with ILs for their comparable tunability, though generally lower-cost and more readily biodegradable (Bajpai, 2021; Malolan et al., 2021)

Historical Generations of Ionic Liquids

Generation	Period	Key features	Representative examples	Main limitation
First	Pre-1990s	Water/air-sensitive chloroaluminates	[EtAlCl ₄]- systems	Moisture-sensitive, toxic
Second	1990s-2000s	Air/water-stable, non-coordinating anions	[Bmim][PF ₆], [Bmim][BF ₄], [Emim][NTf ₂]	Fluorinated anions: toxicity, persistence
Third	2000s-2010s	Task-specific, biocompatible	Functionalised imidazolium, amino-acid-based	Cost, variable biodegradability
Fourth	Post-2019	Sustainable, biodegradable, multifunctional	Bio-based choline-amino-acid ILs, NADES hybrids	Scalability

Fourth-generation ILs prioritise renewable feedstocks, achieving greater than 80% biodegradability alongside multifunctionality (e.g., API-ILs, CO₂ capture) (Alreshidi et al., 2025). Current trends layer hybrid IL-DES systems, supported ILs, and AI-aided property prediction on top of this generational shift - bio-based ILs such as [Ch][Lys] now reduce toxicity while retaining performance in drug-delivery contexts (Alreshidi et al., 2025).

Physicochemical Properties Relevant to Synthesis and Applications

The physicochemical behaviour of ionic liquids arises from their ionic nature and the structural diversity of their constituent cations and anions. Unlike conventional molecular solvents, ILs exhibit highly tunable properties, enabling rational design of solvents for catalysis, electrochemistry, separations, and biomass processing (Plechkova & Seddon, 2008; Hallett & Welton, 2011). Rather than scatter the relevant figures through prose, Table 2 collects the key property ranges reported across the recent literature.

Property	Typical range / value	Governing factors	Key reference
Vapour pressure	< 10 ⁻¹⁰ Pa (negligible)	Strong Coulombic ion-ion interactions	Rogers & Seddon, 2003
Viscosity	20 to several hundred cP at 25 degC	Ion size, symmetry, H-bonding, van der Waals forces	Tokuda et al., 2004
Density	1.0-1.6 g/cm ³	Ion molecular weight, packing efficiency	Tokuda et al., 2004
Thermal decomposition	> 300 degC (up to ~450 degC for [NTf ₂]- salts)	Anion coordinating strength	MacFarlane et al., 2014

Property	Typical range / value	Governing factors	Key reference
onset			
Ionic conductivity	10^{-3} to 10^{-2} S/cm at RT	Ion mobility, viscosity, temperature	Armand et al., 2009
Electrochemical window	4-6 V (up to >5.5 V for [NTf ₂]- systems)	Anion oxidative/reductive stability	MacFarlane et al., 2014
Glass transition (T _g)	-80 to -50 degC (typical RTILs)	Cation flexibility, alkyl chain length	Alreshidi et al., 2025

The negligible vapour pressure of ILs allows their use in high-temperature processes without significant solvent loss (Welton, 2018), while their capacity for hydrogen bonding and strong electrostatic interaction underlies the dissolution of cellulose and lignocellulosic biomass that underpins many green-chemistry applications discussed in Sections 8 and 10 (Swatloski et al., 2002; Pinkert et al., 2009). High viscosity remains the principal practical drawback, limiting mass transfer in flow processes and motivating much of the ion-design work summarised in Section 6.

Synthetic Methodologies: A Chronological View (2019-2026)

Conventional synthetic methodologies remain the foundation of IL preparation, but the last seven years have seen a steady, traceable shift toward faster, halide-free, and bio-based routes. Rather than presenting conventional and advanced methods as two separate, disconnected sections, this revision lays the synthesis literature out chronologically - year by year - so the direction of the field is visible at a glance. Table 3 gives the year-wise overview; the subsections that follow (4.1-4.7) walk through each period with the underlying chemistry and schemes.

Year-wise overview

Year period /	Dominant method(s)	Representative advance	Typical yield / time	Reference
Pre-2019 (baseline)	Quaternization, neutralisation, metathesis	[Bmim]Br, [Bmim][NTf ₂] via conventional heating, 24-72 h	80-99%, hours-days	Wilkes & Zaworotko, 1992; Huddleston et al., 2001
2019-2020	Solvent-free / mechanochemical exploration	Ball-milling routes for ammonium and imidazolium salts begin to appear alongside early bio-derived PILs	30-120 min, >90%	Al-Humaidi et al., 2021 (mechanochemical precedent)
2020-2021	Toxicity-aware redesign	Systematic (eco)toxicity and biodegradability screening reshapes	N/A (screening)	Flieger & Flieger, 2020; Beil et al., 2021

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Year period /	Dominant method(s)	Representative advance	Typical yield / time	Reference
		cation/anion choice for new syntheses		
2021-2022	Ultrasound-assisted synthesis matures	Sonochemical quaternization and neutralisation routes shorten reaction times to 30-120 min under ambient conditions	1-2 h, >90%	Messali et al., 2015 (methodology); Alreshidi et al., 2025 (post-2019 extension)
2022-2023	Halide-free / dialkyl-sulfate routes; CO ₂ -targeted TSILs	Direct quaternization with dialkyl carbonates/sulfates; amine-functionalised ILs reaching ~0.55-2.1 mol CO ₂ /mol IL	Minutes-hours, >90%	Zhang et al., 2022; Pradhan, 2025
2023-2024	Microwave-assisted one-pot quaternization-metathesis	[Emim][NTf ₂] in 10 min at 120 degC/300 W, >98% yield, <50 ppm halide	5-30 min, >95%	Kumar et al., 2024; Alreshidi et al., 2025
2024-2025	Mechanochemical scale-up; bio-based one-pot routes	Ball milling of choline bicarbonate with citric/lactic acid; solvent-free extruder-compatible processes	<1 h, >95%	Alreshidi et al., 2025; Amde et al., 2025
2025-2026	Solid-to-liquid mechanochemistry at multigram scale; AI-guided design	Planetary-mixer mechanosynthesis scaled from 4 g to 99 g (97% conversion, 30 min); COSMO-RS/ML-guided ion selection	30 min, >95%, scalable	Solid-to-liquid mechanochemistry, 2026; Pradhan, 2025

Baseline (pre-2019): Quaternization and Acid-Base Neutralization

Conventional IL preparation is typically divided into two steps: formation of the cation (quaternization or protonation) and anion exchange to install the target anion (Pradhan, 2025; Alreshidi et al., 2025). Quaternization of tertiary amines or nitrogen heterocycles with alkyl halides - the Menshutkin reaction - remains the most common route to aprotic ILs. For imidazolium ILs, 1-methylimidazole reacts with an alkyl halide (e.g., 1-bromobutane) under heating (60-90 degC, 24-72 h) to give 1-butyl-3-methylimidazolium bromide, [Bmim]Br (Scheme 1).

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Scheme 1. Quaternization (Menschutkin reaction) forming [Bmim]Br



Scheme 1. Quaternization (Menschutkin reaction) forming [Bmim]Br. All structures use clean line-angle notation with charges shown explicitly.

The reaction is exothermic and usually run neat to suppress side products; yields exceed 90% with excess alkyl halide or prolonged heating, though longer alkyl chains slow the reaction through steric hindrance (Alreshidi et al., 2025). Phosphonium ILs form analogously from trialkylphosphines (PBu₃ + RBr $\rightarrow$ [PBu₃R]⁺Br⁻), with higher thermal stability but slower kinetics (Vekaria et al., 2023). The main drawback is halide contamination: residual Br⁻ or Cl⁻ reduces the electrochemical window, so post-2019 protocols increasingly add inert-atmosphere stirring and recrystallisation to reach >99% purity (Amde et al., 2025).

Protic ILs (PILs) are made instead by direct acid-base neutralisation - halide-free, low-cost, and the greener baseline route. Ethanolamine and acetic acid, for example, combine at room temperature or under mild heating (40-80 degC, often under vacuum) to give ethanolammonium acetate (Scheme 2).

Scheme 2. Acid-base neutralization forming an ethanolammonium acetate protic ionic liquid



Scheme 2. Acid-base neutralization forming [HOCH₂CH₂NH₃][CH₃COO].

Yields approach 100% with stoichiometric control, and choline-based PILs such as [Ch][amino acid] are made the same way from natural amino acids, giving biodegradable ILs with low toxicity (Pradhan, 2025) - a direct precursor to the fourth-generation, bio-based routes discussed below. Anion metathesis (silver-salt, acid, or ammonium/phosphonium-salt exchange) then converts a halide precursor into a target anion such as [NTf₂]⁻ or [PF₆]⁻ (Scheme 3), most effectively via silver-salt metathesis, where insoluble AgX precipitates out; expense limits this route's scalability (Pradhan, 2025).

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Scheme 3. Anion metathesis forming hydrophobic [Bmim][NTf2]



Scheme 3. Anion metathesis forming hydrophobic [Bmim][NTf2].

Post-2019 refinement of this baseline chemistry has focused on halide-free variants: direct quaternization with dialkyl sulfates or carbonates (tertiary amine + (MeO)₂SO₂ → [amine-Me]⁺MeSO₄⁻) produces methylsulfate ILs that avoid halide intermediates entirely (Scheme 9 in Section 4.5), while residual halides in conventional routes are now routinely targeted to below 100 ppm via ion-exchange resins (Alreshidi et al., 2025).

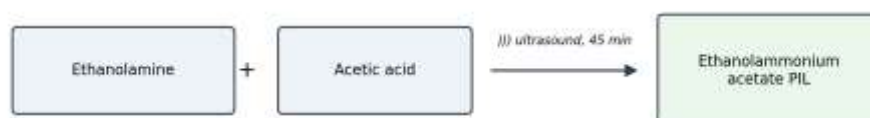
2019-2021: Early Green-Chemistry Exploration and Toxicity-Aware Redesign

The years immediately following 2019 were marked less by a single new synthetic method than by a shift in design philosophy: growing (eco)toxicity and biodegradability data (Flieger & Flieger, 2020; Beil et al., 2021) began to actively steer which cations and anions researchers chose to synthesise in the first place. Imidazolium and pyridinium cations with long alkyl chains or fluorinated anions were increasingly flagged for aquatic toxicity and poor biodegradation (<20-30% in OECD 301 tests), while protic, cholinium, and amino-acid-derived ILs were confirmed as substantially safer (Egorova & Ananikov, 2014; Flieger & Flieger, 2020). This period also saw early solvent-free mechanochemical precedents in adjacent heterocyclic and materials chemistry (Al-Humaidi et al., 2021), which would be adapted specifically to IL synthesis over the following several years.

2021-2023: Ultrasound-Assisted Synthesis Matures

Ultrasound (US) irradiation facilitates acoustic cavitation, generating localised temperatures above 5000 K and pressures above 1000 atm. This enhances mass transfer and disrupts aggregates without bulk heating, cutting quaternization times to 30-120 minutes under ambient conditions, frequently solvent-free. Sonication (20-40 kHz, 100-500 W) of 1-methylimidazole with alkyl halides gives imidazolium ILs within 1-2 hours at yields exceeding 90%. For protic ILs, ultrasound accelerates acid-base neutralisation directly (Scheme 5).

Scheme 5. Ultrasound-assisted acid-base neutralization



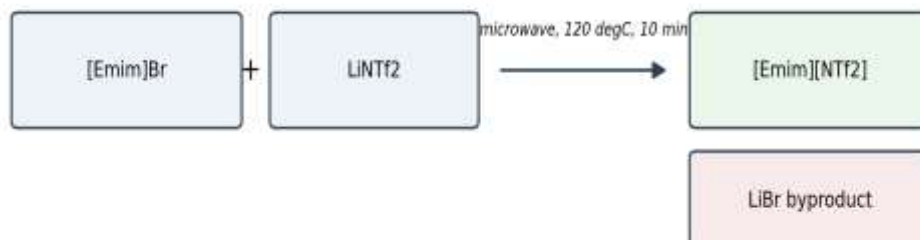
Scheme 5. Ultrasound-assisted acid-base neutralization (45 min).

Work through 2023-2025 extended ultrasound to bio-feedstocks, producing amino-acid-derived ILs such as [Ch][glycinate] within 45 minutes, with strong biodegradability and minimal ecotoxicity (Alreshidi et al., 2025). E-factors below 1 are now reported routinely for US-assisted, extraction-integrated task-specific IL synthesis.

4.4 2023-2024: Microwave-Assisted One-Pot Synthesis

Microwave-assisted synthesis (MAS) uses volumetric dielectric heating - IL precursors absorb microwaves through ionic conduction and dipolar polarisation, giving rapid, uniform heating and cutting reaction times from hours to minutes, usually solvent-free. Microwave irradiation of 1-methylimidazole with alkyl halides (50-150 degC, 100-800 W) gives [Bmim]Br or [Bmim][NTf₂] within 5-30 minutes at greater than 95% conversion - versus 24-72 hours conventionally (Alreshidi et al., 2025). The clearest marker of this period is the one-pot quaternization-metathesis: [Emim][NTf₂] was reported in just 10 minutes at 120 degC and 300 W, with yields exceeding 98% and halide content below 50 ppm after a simple wash (Scheme 4; Pradhan, 2025).

Scheme 4. One-pot quaternization-metathesis under microwave irradiation



Scheme 4. One-pot quaternization-metathesis under microwave irradiation (10 min, 120 degC).

Choline-based ILs derived from natural acids (e.g., [Ch][lactate]) were produced by microwave neutralisation in 5-15 minutes, with biodegradability exceeding 80% over 28 days under OECD 301 guidelines (Alreshidi et al., 2025). Hybrid systems - microwaves combined with an IL susceptor such as [Bmim][Cl] - improved heating efficiency further, and reviews of "MAIL" (microwave-assisted ionic liquid) technology from this period report energy savings up to 80% with enhanced selectivity for task-specific applications (Amde et al., 2025).

2022-2024: Halide-Free Routes and Task-Specific CO₂-Capture ILs

In parallel with the microwave work, this period produced systematic halide-free conventional routes. Direct quaternization with dialkyl sulfates or carbonates (Scheme 9) avoids halide intermediates from the outset, producing methylsulfate ILs directly convertible by metathesis (Pradhan, 2025).

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Scheme 9. Halide-free quaternization using dimethyl sulfate



Scheme 9. Halide-free quaternization using dimethyl sulfate.

The same window saw a wave of task-specific amine-, alcohol-, and carboxylate-functionalised ILs purpose-built for CO₂ chemisorption (Scheme 10), with capacities climbing from roughly 0.1-0.3 mol CO₂/mol IL for simple physical absorption to 0.55-2.2 mol CO₂/mol IL for dual-amino-functionalised systems (Zhang et al., 2022; Schaeffer et al., 2023).

Scheme 10. CO₂ chemisorption by an amine-functionalized task-specific ionic liquid

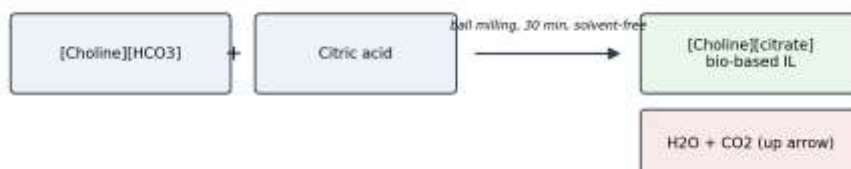


Scheme 10. CO₂ chemisorption by an amine-functionalized task-specific ionic liquid.

2024-2025: Mechanochemical (Ball-Milling) Scale-Up and Bio-Based One-Pot Routes

Mechanochemical methods use mechanical energy - ball milling or grinding - to drive reactions without solvent, supporting zero-waste synthesis. High shear and impact activate precursors for halide-free or direct anion metathesis. Recent protocols mill tertiary amines with alkyl halides or acids for 30-120 minutes at 20-50 Hz, giving near-quantitative yields of ammonium/phosphonium ILs (Amde et al., 2025). Bio-based variants mill choline bicarbonate with renewable acids such as citric or lactic acid to give biodegradable ILs in under an hour (Scheme 6).

Scheme 6. Solvent-free mechanochemical synthesis of a choline-citrate bio-based ionic liquid



Scheme 6. Solvent-free mechanochemical synthesis of a choline-citrate bio-based ionic liquid.

One-pot strategies from the same period combine quaternization with metathesis or functionalisation in a single vessel, most often under MW or US assistance - the one-pot synthesis of [Bmim][NTf₂] via microwave quaternization followed by in-situ

metathesis with LiNTf₂ completes in 20 minutes at over 96% yield (Pradhan, 2025). Bio-based one-pot routes using betaine and amino acids under MW/US conditions now give sustainable polymeric ILs directly (Alreshidi et al., 2025).

2025-2026: Multigram Mechanochemistry and AI-Guided Design

The most recent literature demonstrates that solvent-free mechanochemistry can be scaled well beyond laboratory ball mills. A 2026 solid-to-liquid mechanochemical route to five electrochemically relevant ILs (including Pyr14TFSI and Pyr14TfO) was scaled from 4 g to 99 g of reagents by moving from ball milling to a multi-shaft planetary mechanical mixer, reaching 97% conversion in 30 minutes with yields above 80% and low impurity levels (Solid-to-liquid mechanochemistry, 2026) - a concrete step toward the kind of continuous, scalable, halide-minimised production the field has been working toward since 2019.

Running alongside this scale-up is a growing reliance on computational and AI-assisted screening - COSMO-RS activity-coefficient modelling and machine-learning property prediction (trained on datasets of 40,000+ points) now guide cation/anion selection before synthesis is attempted at all, reducing trial-and-error and aligning new IL design directly with the fourth-generation sustainability goals introduced in Section 2.4 (Pradhan, 2025; Amde et al., 2025).

One-Pot and Multicomponent Reactions: A Cross-Cutting Summary

Because one-pot and multicomponent strategies recur across almost every year discussed above, Table 4 collects them for direct comparison rather than repeating the chemistry a third time.

System	Conditions	Time	Yield	Notable feature
[Bmim][NTf ₂] one-pot	MW quaternization + in-situ LiNTf ₂ metathesis	20 min	>96%	Single-vessel, halide by-product only
[Emim][NTf ₂] one-pot	MW, 120 degC, 300 W	10 min	>98%	<50 ppm residual halide
Betaine/amino-acid PILs	MW/US, bio-precursors	15-45 min	>90%	Sustainable polymeric ILs directly
Choline-citrate bio-IL	Ball milling, solvent-free	<60 min	>95%	Zero solvent, extruder-compatible
Pyr14TFSI / Pyr14TfO	Planetary-mixer mechanosynthesis	30 min	>80% (97% conversion)	Scaled 4 g -> 99 g

Across this seven-year window, the trajectory is consistent: reaction times fall from hours-to-days toward minutes, halide by-products are progressively designed out, and an increasing share of new syntheses start from renewable, bio-derived precursors - the empirical basis for describing post-2019 work as "fourth-generation" IL chemistry (Section 2.4).

Task-Specific and Functionalized Ionic Liquids: Design and Synthesis

Task-specific ionic liquids (TSILs) - also called functionalised ionic liquids - mark a significant step in IL chemistry: the cation, anion, or side chains are deliberately modified with functional groups to confer properties tailored to a particular use. Where conventional ILs mainly serve as solvents, TSILs act as catalysts, extractants, stabilisers, or multifunctional agents, embodying the "designer solvent" concept through deliberate molecular engineering (Alreshidi et al., 2025; Amde et al., 2025). Post-2019 work has advanced TSIL design markedly, with emphasis on sustainability, performance, and green processing across biomass conversion, CO₂ capture, metal extraction, asymmetric catalysis, and supported/polymeric heterogeneous systems (Pradhan, 2025; Mao & Zhu, 2026).

Design Principles

Cation functionalization: -OH, -COOH, -NH₂, -SO₃H, cyano, epoxy, or chiral groups introduce acidity/basicity, hydrogen bonding, or chirality (Alreshidi et al., 2025)

Anion engineering: carboxylates, sulfonates, amino acids, phosphates, or metal complexes supply catalytic sites or coordination ability (Amde et al., 2025)

Structure-property relationships: sulfonic-acid groups enhance Bronsted acidity for catalysis; amine groups enable CO₂ chemisorption (Pradhan, 2025)

Sustainability focus: post-2019 designs prioritise bio-derived precursors for biodegradability (70-90% in OECD tests) and low toxicity (Alreshidi et al., 2025)

Computational tools such as COSMO-RS and AI-assisted screening increasingly predict optimal structures ahead of synthesis, reducing experimental trial-and-error (Amde et al., 2025) - a theme that, as Section 4.7 shows, has become central to the most recent (2025-2026) synthesis literature.

Synthesis Strategies and Representative Case Studies

Direct functionalisation during cation formation, e.g. hydroxyl-functionalised 1-(2-hydroxyethyl)-3-methylimidazolium bromide from 1-methylimidazole and 2-bromoethanol (Pradhan, 2025)

Anion metathesis with functional anions, e.g. [Bmim][lactate] via silver-lactate metathesis for ZnO dispersion in elastomers (Alreshidi et al., 2025)

One-pot multicomponent synthesis of acidic -SO₃H TSILs under MW/US/mechanicochemical conditions (Amde et al., 2025)

Post-polymerisation/grafting for supported TSILs and porous poly(ionic liquid)s (PILs) with surface areas exceeding 500 m²/g (Mao & Zhu, 2026)

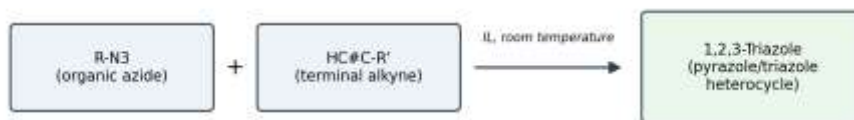
Chiral TSILs from enantiopure precursors (natural amino acids, terpenes) for asymmetric induction (Pradhan, 2025)

Magnetic TSILs incorporating paramagnetic anions (FeCl₄⁻, MnCl₄(2-)) for field-assisted separation

Zwitterionic ILs via ring-opening or betaine quaternization for protein stabilisation without net charge (Amde et al., 2025)

A recurring TSIL application is click chemistry for heterocycle synthesis, in which an IL serves simultaneously as solvent and catalyst (Scheme 7).

Scheme 7. Click chemistry in an ionic-liquid reaction medium



Scheme 7. Click chemistry in an ionic-liquid reaction medium, giving 1,2,3-triazoles at room temperature.

Sulfonic-acid-functionalised imidazolium ILs catalyse fructose dehydration to 5-hydroxymethylfurfural (5-HMF) with over 90% selectivity, and supported variants on silica retain activity over more than five cycles (Amde et al., 2025). Hydroxyl- or amine-functionalised basic ILs such as [Bmim]OH enable heterocycle synthesis (e.g. pyranopyrazoles) at 85-95% yield with good reusability (Pradhan, 2025). Amino-functionalised ILs chemisorb CO₂ via carbamate formation at capacities above 0.5 mol/mol under mild conditions, and recent hybrids with porous supports improve kinetics further (Alreshidi et al., 2025).

The main constraints on TSIL design remain maintaining low viscosity alongside functionalisation, ensuring thermal/chemical stability, and controlling synthesis cost at scale. Hybrid TSIL-DES designs, supported immobilisation for recyclability, and renewable precursors are the principal strategies used to address these constraints while staying aligned with fourth-generation goals (Alreshidi et al., 2025).

Characterization Techniques for Ionic Liquids

Characterisation of ILs confirms purity, elucidates structure, and validates structure-property relationships. Because ILs are ionic, non-volatile, and highly tunable, a multi-technique approach combining spectroscopic, thermal, electrochemical, diffraction, and computational methods is standard practice. Purity assessment typically targets <200 ppm water, <100 ppm halides, and >99% ionic content, since impurities significantly alter viscosity, conductivity, and stability (Pradhan, 2025; Alreshidi et al., 2025).

Technique	Primary use	Typical detection / range
¹ H / ¹³ C NMR	Structural confirmation, stoichiometry	Integration ratios confirm purity
¹⁹ F / ³¹ P / ¹¹ B NMR	Fluorinated anions, phosphonium/borate species	Multinuclear, 2D (COSY/HSQC/NOESY) for ion pairing
DOSY-NMR	Ion mobility, aggregation	Self-diffusion 10 ⁻¹⁰ -10 ⁻⁹ m ² /s
FTIR / Raman	Vibrational fingerprinting, ion pairing	C-H 2800-3200 cm ⁻¹ ; [NTf ₂]-bands ~740, ~1350 cm ⁻¹
TGA	Thermal decomposition onset	350-450 degC for [NTf ₂]- ILs;

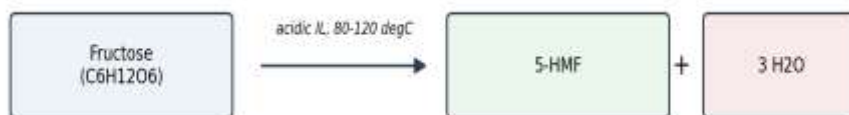
Technique	Primary use	Typical detection / range
	(Td)	200-300 degC for protic ILs
DSC	Melting point, glass transition, heat capacity	Tg typically -80 to -50 degC
XRD / WAXS / SAXS	Crystallinity, nanoscale structuring	Peaks at 2-5 Å (ion pair), 8-15 Å (alkyl segregation)
EIS (impedance)	Bulk ionic conductivity	10^{-3} - 10^{-2} S/cm at RT
CV / LSV	Electrochemical stability window	4-6 V typical
ESI-MS / XPS / IGC	Mass confirmation, surface analysis	Cluster detection, surface energy
DFT / MD (computational)	Ion-pair energetics, dynamics, property prediction	Increasingly coupled with machine learning (post-2019)

Ionic Liquids in Catalysis and Organic Synthesis

ILs function in catalysis in several distinct roles: as polar, non-coordinating solvents that accelerate reactions through ion-pair effects; as Bronsted-acidic or -basic catalysts/cocatalysts in their own right; as stabilisers preventing nanoparticle agglomeration or enzyme denaturation; and as promoters that enable clean phase separation for product isolation and IL recycling over 5-10 cycles with minimal activity loss (Alreshidi et al., 2025). Bio-based acidic ILs now show over 90% recyclability in multicomponent reactions (Amde et al., 2025).

Acidic ILs such as imidazolium sulfonates catalyse esterification, acetalisation, and dehydration with turnover numbers above 1000 and selectivity exceeding 95%; silica-supported variants valorise fructose to 5-HMF at over 90% yield under mild conditions (80-120 degC), as shown in Scheme 8.

Scheme 8. Acid-ionic-liquid-catalyzed dehydration of fructose to 5-hydroxymethylfurfural (5-HMF)



Scheme 8. Acid-ionic-liquid-catalyzed dehydration of fructose to 5-hydroxymethylfurfural (5-HMF).

Basic ILs such as [Bmim]OH promote Knoevenagel condensation, Michael addition, and heterocycle formation; in Biginelli reactions for dihydropyrimidines, [Bmim]OH gives 85-98% yield in 10-30 minutes solvent-free, with recyclability up to six cycles.

Heterocycle Synthesis

ILs are effective dual solvent-catalyst systems for nitrogen-containing heterocycles (pyrroles, pyrazoles, imidazoles, triazoles, tetrazoles). For pyrazoles and triazoles, ILs cut reaction times to 15-60 minutes and improve yields to 80-99% via activation of carbonyls or alkynes - [Bmim][BF₄] or task-specific ILs enable click chemistry for 1,2,3-triazoles under mild conditions (Kumar et al., 2024). Bridged nitrogen-based ILs facilitate oxazolidinones, benzimidazoles, and pyranopyrazoles at low catalyst loading (1-5 mol%) with E-factors below 1, while porous poly(ionic liquid)s serve as heterogeneous catalysts with surface areas above 500 m²/g in continuous-flow settings (Mao & Zhu, 2026).

Asymmetric and Metal-Catalyzed Reactions

Chiral ILs derived from amino acids or terpenes enable enantioselective transformations - as solvents or ligands in organocatalysis (e.g., proline-mediated aldol reactions), they achieve ee >90% through the ionic microenvironment (Amde et al., 2025). Metal catalysis benefits from ILs as ligands or supports: Pd, Ru, or Cu coordinated in TSILs catalyse Heck, Suzuki, and hydrogenation reactions with good recyclability, and magnetic ILs enable catalyst recovery via external magnetic fields.

Biomass Conversion

ILs dissolve lignocellulose and catalyse its valorisation: acidic ILs pretreat biomass for biofuel production, and [Ch][Lys] or supported ILs convert cellulose to glucose or HMF at over 80% efficiency with good recyclability. Continuous supported-IL-phase (SILP) processes integrate synthesis and catalysis for biodiesel and platform chemicals (Recent advances in lignocellulosic biorefineries, 2025).

Overall, the catalytic literature shows a consistent pattern - reduced waste, high selectivity, and strong recyclability - tempered by high viscosity limiting mass transfer and the cost of specialty TSILs. Continuous-flow catalysis, AI-optimised TSILs, and integration with enzymes or photocatalysis for tandem processes are the clearest near-term directions (Alreshidi et al., 2025; Mao & Zhu, 2026).

Applications in Energy Storage and Conversion

ILs are among the most promising materials for advanced energy storage and conversion because of their wide electrochemical stability windows, high ionic conductivity, negligible volatility, non-flammability, and thermal/chemical stability - properties that make them safer alternatives to conventional aqueous or organic electrolytes wherever operating voltage, temperature range, and cycle life are critical. Post-2019 research has concentrated on fourth-generation (bio-based, low-toxicity) ILs, hybrid electrolytes, and task-specific ILs for lithium-ion, post-lithium, and supercapacitor chemistries (Amde et al., 2025; Alreshidi et al., 2025).

Lithium-Ion and Lithium-Metal Batteries

IL-based electrolytes routinely provide electrochemical stability windows (ESW) of 5-6 V, well above the ~4.3 V of conventional carbonate electrolytes, enabling higher energy density and safer operation. Imidazolium and pyrrolidinium ILs such as [Pyr14][NTf₂] and [Pyr13][FSI] combine low viscosity with high conductivity (>1

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mS/cm at RT when mixed with Li salts) and support stable cycling of high-voltage cathodes up to 4.5-4.8 V (Amde et al., 2025; Ma et al., 2023). Adding Li[NTf2], Li[FSI], or LiBOB to ILs forms solvent-in-salt systems that suppress lithium-dendrite growth and improve Coulombic efficiency beyond 99.5% over hundreds of cycles (Zhang et al., 2023). Bio-based ILs with [FSI]- or [TFSI]- anions now match conventional IL performance with markedly lower toxicity (Alreshidi et al., 2025).

Post-Lithium Batteries

For sodium-ion batteries (SIBs), [Pyr14][NTf2] or [Emim][FSI] paired with Na[FSI] give ESW >5 V and capacity retention above 90% after 1000 cycles in hard-carbon/layered-oxide systems (Domingues et al., 2023; Sirengo et al., 2023). Magnesium and zinc batteries benefit from weakly coordinating anions that improve cation transport and suppress passivating layers or hydrogen evolution (Darjazi et al., 2024). Chloroaluminate ILs remain the aluminium-ion benchmark, though air-stable alternatives are under active development.

Supercapacitors, Fuel Cells, and CO₂ Electroreduction

Application	Representative IL system	Key metric	Reference
EDLC supercapacitors	[Pyr14][NTf2], [P6,6,6,14][NTf2] + activated carbon/graphene/MXene	3.5-4.5 V operating voltage; 30-70 Wh/kg; >10,000 cycles	Amde et al., 2025; Venancio et al., 2025
Intermediate-T fuel cells	[Im][NTf2], [Ch][NTf2], diethylmethylammonium triflate	>10 ⁻² S/cm proton conductivity at 100-150 degC	Alreshidi et al., 2025
Redox flow batteries	IL-modified vanadium electrolytes	Reduced crossover, improved cycle life	MacFarlane et al., 2014
CO ₂ electroreduction	Imidazolium [NTf2]-/[BF4]- on Cu, Ag, Sn electrodes	>90% Faradaic efficiency for CO/formate	Amde et al., 2025
DSSC solar cells	[Bmim][I3/I] electrolyte	8-10% efficiency, improved thermal stability	MacFarlane et al., 2014

Across these applications the recurring advantages are non-flammability, a wide operating temperature range (-40 to >150 degC), and long cycle life; the recurring constraints are high viscosity (limiting power density), high cost of pure ILs, and lower ionic conductivity at low temperature relative to organic electrolytes. Low-viscosity bio-based ILs, hybrid IL-organic systems, and solid-state/quasi-solid-state IL electrolytes are the clearest paths forward (Alreshidi et al., 2025; Pradhan, 2025).

Environmental and Separation Applications

ILs' negligible vapour pressure, tunable hydrophobicity, high thermal stability, and broad solvation capacity make them powerful tools for environmental remediation and advanced separation, with recyclability in the 95-99% range for many systems. Post-2019 work emphasises bio-based, biodegradable, task-specific ILs that meet increasingly strict environmental regulation while improving performance in metal recovery, gas separation, and pollutant removal (Alreshidi et al., 2025; Amde et al., 2025).

Application	Representative system	Performance	Reference
CO ₂ physical absorption	[P666,14][NTf ₂], [Bmim][NTf ₂]	0.1-0.3 mol CO ₂ /mol IL, 1 bar, 25 degC	Zhang et al., 2022
CO ₂ chemical absorption	Amine/carboxylate/azolate-functionalized TSILs	>1.0-2.2 mol CO ₂ /mol IL via carbamate formation	Zhang et al., 2022; Sosa et al., 2020
Supported IL phases / PIL membranes	PIL on silica, polymers, or MOFs	CO ₂ /N ₂ selectivity >100; permeability >1000 Barrer	Alreshidi et al., 2025
Heavy-metal extraction	Cyphos 101, Aliquat 336, [Hbet][NTf ₂]	>99% removal of Hg(II), Cd(II), Pb(II); distribution ratios >10 ⁴	Selective recovery of REEs from e-waste, 2022
Rare-earth-element separation	Bifunctional ILs, e.g. [P666,14][NO ₃]	Separation factors La/Lu >1000, Nd/Dy >200	Extraction processes with ILs and DES, 2026
Lithium recovery from brine	Phosphonium/ammonium ILs with crown ethers	Li/Na selectivity >500; >99.5% Li recovery (pilot scale)	Task-specific ILs for REE separation, 2023
Dye / pollutant removal	[Omim][PF ₆], [P666,14][Cl], magnetic ILs	>99% removal of methylene blue, Congo red, methyl orange	Amde et al., 2025
H ₂ S / SO ₂ gas removal	Amine-functionalized ILs, [P666,14][Tetz]	>99.9% H ₂ S removal; SO ₂ uptake >5 mol/mol IL	Alreshidi et al., 2025

Fourth-generation ILs derived from choline, amino acids, and natural organic acids (e.g., [Ch][Lys], [Ch][Gly], betainium ILs) show 70-95% biodegradability (OECD 301D) and low aquatic toxicity (EC₅₀ > 100 mg/L), and have replaced conventional ILs in metal extraction and dye removal without sacrificing efficiency (Alreshidi et al., 2025). Industrially, PetroChina and Chevron use Cyphos-family ILs for mercury removal from natural gas, and Proionic/Solvionic produce bio-based ILs at tonne

scale for extraction processes; cost analyses show IL-based separation processes become competitive once solvent loss, waste treatment, and energy regeneration are properly accounted for (total cost reduction of 20-60% versus conventional methods).

Biomedical and Pharmaceutical Applications

ILs have moved from niche solvents to multifunctional biomedical platforms, leveraging structural tunability, low volatility, high solvation capacity, and the ability to interact with biological membranes and macromolecules. Post-2019 research emphasises third- and fourth-generation, often bio-based (choline, amino-acid, fatty-acid-derived) ILs with improved biocompatibility, reduced toxicity, and biodegradability (Hu et al., 2023; Zhuo et al., 2024; Curreri et al., 2021).

Drug Solubilization and Delivery

ILs increase solubility of poorly water-soluble drugs (BCS Class II/IV) by 10^3 - 10^6 -fold through ion pairing, hydrogen bonding, and disruption of crystal lattices. Imidazolium- and choline-based ILs dissolve hydrophobic APIs such as ibuprofen, curcumin, paclitaxel, and itraconazole at concentrations above 100 mg/mL. API-ILs - where the drug itself is converted to an ionic form (e.g., lidocaine docusate) - eliminate polymorphism issues and enhance dissolution rate more than tenfold (Zhuo et al., 2024).

For transdermal delivery, third-generation ILs such as choline geranate disrupt stratum-corneum lipid packing without significant irritation, increasing flux of drugs such as lidocaine, ibuprofen, and doxorubicin by 5-30-fold with minimal cytotoxicity (Zhuo et al., 2024; Ribeiro et al., 2020). IL microemulsions and micelles also protect encapsulated biologics such as insulin from enzymatic degradation during oral delivery, and thermoresponsive IL-based ionogels provide sustained release over weeks to months for injectable/depot systems (Curreri et al., 2021).

Antimicrobial, Antitumor, and Stabilisation Roles

Long-alkyl-chain imidazolium or ammonium ILs disrupt bacterial membranes with MIC values below 10 microg/mL against MRSA and E. coli (Fang et al., 2022). Certain fluorinated-anion ILs induce apoptosis in cancer cells via mitochondrial disruption, and API-ILs of chemotherapeutics improve tumour accumulation while reducing systemic toxicity (Hu et al., 2023). Choline-based ILs also maintain enzyme activity at elevated temperature (e.g., lipase stability above 80 degC) and prevent aggregation of monoclonal antibodies during storage.

Third-generation ILs generally show low acute toxicity ($LD_{50} > 2000$ mg/kg oral in rats) and high biodegradability (60-90% in 28 days), though long-term chronic-exposure data remain limited; regulatory pathways such as FDA GRAS status for choline-based systems are beginning to emerge alongside preclinical support for IND filings of IL-enhanced drugs (Zhuo et al., 2024).

Industrial and Emerging Applications

ILs have progressed from laboratory-scale curiosities to genuine, if still niche, industrial processes. Specialty ILs remain costly (often USD 100-500/kg), and synthesis is energy-intensive, but several commercial processes demonstrate real

viability. Post-2019 emphasis has shifted toward scalable halide-free production (e.g., Proionic's CBILS(R) process), bio-based ILs, and integration into higher-value sectors.

Sector	Process / product	Scale / status	Reference
Petrochemical refining	Chevron Isoalkyl(TM) chloroaluminate-IL alkylation	~5,000 barrels/day (commissioned ~2021-2023)	Amde et al., 2025
Acid scavenging	BASF BASIL(TM) process	Multi-tonne scale since 2003, expanded post-2019	Alreshidi et al., 2025
Lubricants / heat-transfer fluids	Kluber, Proionic IL greases and compression lubricants	Tonne-scale commercial supply	Alreshidi et al., 2025
Cellulose fibre processing	Ioncell-F process, [Emim][OAc]	10 kg/day pilot (2025-2026), targeting commercial scale	Anceschi, 2025
Biodiesel production	Acidic supported-IL transesterification catalysts	>95% yield from waste oils	Alreshidi et al., 2025
Gas purification	Hycapure(R) (PETRONAS) mercury removal	Commercial deployment	Amde et al., 2025
Selective hydrogenation	Clariant SCILL supported catalysts	Commercial petrochemical use	Amde et al., 2025

Market data place the IL sector at roughly USD 50-66 million in 2023-2025, projected to reach USD 110-136 million by 2032-2034 (CAGR 8-13.5%), driven by energy storage, green solvents, and Asia-Pacific manufacturing (Precedence Research, 2025; Mordor Intelligence, 2025). Suppliers including BASF (Basionics(TM)), Proionic, Solvionic, Evonik, Merck, and Solvay currently dominate supply, with continuous-flow, halide-free production (e.g., CBILS(R)) reducing prices roughly five- to tenfold relative to early batch routes.

Challenges, Limitations, and Future Perspectives

Economic Challenges

Production cost remains the primary barrier: specialty ILs often exceed USD 100-500/kg against less than USD 1/kg for conventional solvents. Even optimised continuous-flow routes such as Proionic's CBILS(R) reach only around USD 290-340/kg at pilot scale (Precedence Research, 2025). Capital expenditure for a 100-tonne/year plant can exceed USD 18 million, and high viscosity, hygroscopicity, and energy-intensive purification (vacuum distillation, ion-exchange resins) all add to scale-up cost.

Toxicity, Ecotoxicity, and Biodegradability

Early-generation ILs - particularly imidazolium and pyridinium cations with long

alkyl chains or fluorinated anions - show moderate to high aquatic toxicity ($EC_{50} < 1$ -10 mg/L for algae, daphnia, fish) and resist biodegradation (<20 -30% in OECD 301 tests) (Flieger & Flieger, 2020; Beil et al., 2021). Some fluorinated anions hydrolyse to HF, and imidazolium cores' environmental persistence has drawn comparison to PFAS-type behaviour. Fourth-generation choline-, betaine-, and amino-acid-based ILs mitigate this substantially, reaching 60-95% biodegradability and $EC_{50} > 100$ mg/L, though comprehensive chronic-exposure and bioaccumulation data remain limited (Alreshidi et al., 2025).

Recyclability, Regulation, and Scale-Up

Although ILs offer theoretical recyclability above 95-99% in lab settings, practical recovery faces thermal decomposition during distillation, contamination with reactants/products, and regeneration energy cost. REACH (EU) and TSCA (US) classify many ILs as substances requiring registration, and toxicity-data gaps continue to delay regulatory approval, particularly for fluorinated systems (Beil et al., 2021).

Future Directions

Sustainable, bio-based design: choline-amino-acid, fatty-acid, and NADES hybrids for low cost/toxicity and biorefinery compatibility

AI and computational acceleration: machine-learning property prediction (viscosity, toxicity, CO₂ solubility) guiding rational design ahead of synthesis

Circular-economy integration: recyclable solvate ILs, closed-loop battery-electrolyte recovery, waste-derived precursors

Hybrid and smart systems: IL-MOFs, PIL membranes, magnetic/thermo-responsive ILs for efficient separation and catalysis

Industrial scaling: continuous synthesis, strategic partnerships, and policy incentives (EU Green Deal, US IRA) driving growth toward USD 110-136 million by 2032-2034

Conclusions

Ionic liquids have evolved from low-melting curiosities into a versatile, tunable class of materials underpinning progress across chemistry, materials science, energy, environment, biomedicine, and industry. This review has traced that evolution across four generations - air/moisture-sensitive chloroaluminates, stable aprotic systems such as [Bmim][PF₆], task-specific and biocompatible variants, and, since 2019, fully sustainable, bio-derived, biodegradable, multifunctional ILs built on renewable feedstocks and circular-economy principles.

Laid out chronologically, the synthetic literature from 2019 to 2026 shows a clear and consistent trajectory: reaction times have fallen from hours-to-days toward minutes, halide by-products have been progressively designed out through dialkyl-sulfate and mechanochemical routes, and an increasing share of new ILs now start from renewable, bio-derived precursors. Task-specific functionalisation - acidic and basic groups, chiral centres, magnetic moieties, zwitterionic designs - has enabled precise applications, and characterisation by NMR, FTIR/Raman, TGA/DSC, XRD/SAXS, impedance spectroscopy, and DFT/MD now validates structure-property relationships at a level of rigour the field lacked a decade ago.

Applications span catalysis and heterocycle synthesis; energy storage and conversion, where electrochemical stability windows exceeding 5-6 V now support lithium-ion, post-lithium, and supercapacitor chemistries; environmental separations, where functionalised ILs capture more than 1 mol CO₂ per mol IL and extract heavy metals and rare-earth elements with selectivity above 1000; biomedicine, where ILs raise poorly soluble drugs' solubility by up to a millionfold and enhance transdermal and oral delivery; and industry, where Chevron's Isoalky(TM) process, BASF's BASIL(TM) technology, and the Ioncell-F cellulose-fibre process demonstrate genuine commercial traction. The market is projected to grow to USD 110-136 million by 2032-2034 at a CAGR of 8-13.5%, driven substantially by Asia-Pacific manufacturing and sustainability policy.

Real challenges remain - elevated cost, viscosity-limited mass transfer, variable toxicity (particularly in early fluorinated and imidazolium systems), incomplete long-term biodegradability data, and regulatory hurdles under REACH and TSCA. Fourth-generation bio-ILs, AI-guided computational design, and hybrid systems such as IL-MOFs, PILs, and SILPs, combined with the continuous, scalable synthesis methods documented through 2025-2026, are the clearest routes forward. Ionic liquids remain a genuinely promising - not yet fully realised - enabler of a sustainable, low-carbon chemical future.

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