RSC Advances

REVIEW

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2025, **15**, 31706

A comprehensive review on PTSA-based deep eutectic solvents

Anna Canela-Xandri, * Oriol Tomàs-Badell and Mercè Balcells

A key challenge in industrial processes is replacing fossil-based solvents with sustainable, renewable alternatives while minimizing industrial waste and enhancing sustainability. Deep eutectic solvents (DESs), with their exceptional properties, offer a promising solution. These solvents can be tailored from a wide variety of hydrogen bond donors (HBDs) and acceptors (HBAs), making them highly customizable, cost-effective, and versatile. Moreover, their excellent biocompatibility and biodegradability position them as ideal candidates for green chemistry applications. DESs are easy to prepare and offer numerous advantages, often serving a dual role as both solvents and active catalysts, depending on their composition and molar ratios. One particularly interesting HBD component for DESs is *p*-toluenesulfonic acid (PTSA)—a solid, stable, and affordable strong organic acid. PTSA interacts effectively with various HBAs, making it highly valuable for applications requiring strong acidity and proton availability. This review explores PTSA's diverse applications and highlights its untapped potential in DES formulations. Additionally, it provides insights into HBA selection tendencies based on specific applications and starting materials. By showcasing PTSA's advantageous properties and versatility, this review underscores its role in advancing green chemistry and fostering innovation in sustainable solvent development.

Received 27th March 2025
Accepted 25th August 2025

DOI: 10.1039/d5ra02149a

rsc.li/rsc-advances

Introduction

A key challenge in industrial processes is replacing fossil-based solvents with sustainable, renewable alternatives while minimizing industrial waste and enhancing sustainability.[1–3] Chemical industrial processes predominantly occur in liquid solutions, where the choice of solvent plays a crucial role in facilitating interactions between components. Factors such as solubility, stability, reusability, and sustainability of the solvent must be carefully considered to optimize process efficiency and reduce environmental impact.[4–6] Deep eutectic solvents (DESs), which have evolved from eutectic mixture studies, have emerged as solvents with unique properties, including good biocompatibility, very low vapor pressure, high viscosity, and excellent chemical, thermal, and electrochemical stability.[7] They can be synthesized from low-cost raw materials and are known for being easy to prepare and purify.[8–12] Due to their versatility, DESs have been extensively studied for a wide range of applications, including: reaction solvents,[13–16] electrochemistry,[17,18] pharmaceuticals,[19] separation processes[20–24] biomass fractionation[25–28] and carbohydrate conversion[29–31] among a broad spectrum of applications.

DESs are composed of two or more components, classified as hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), which typically include Brønsted or Lewis acids and bases.[24,32] A key characteristic of DESs is that at least one of the components must be solid at working temperature.[33] As the name suggests, hydrogen bonding interactions between the components create a eutectic mixture that remains liquid at a lower temperature than its individual components.

Generally, DESs are easy to synthesize,[34] produce no byproducts, and require no purification before use.[35] They exhibit low or negligible toxicity and are known for their high biodegradability.[35–37] A key advantage of DESs is their high tunability, as they can be customized by selecting from a wide range of hydrogen bond donors (HBDs) and acceptors (HBAs), as well as adjusting their molar ratios.[38] This adaptability has led to their classification as "designer solvents".[39–42] To date, most DESs have been categorized into five main classes based on the nature of the complexing agent.[43]

Among the various hydrogen bond donors (HBDs) investigated for DESs, notable examples include ethylene glycol,[44] urea,[45] and carboxylic[46] and sulfonic acids.[47] Among the different DES types, acid deep eutectic solvents (ADES) have been studied for many applications. The acidity of ADES can be designed and controlled according to the acidity of HBD. Particularly, sulfonic acids, such as *p*-toluenesulfonic acid (PTSA), have attracted significant attention. PTSA is a solid-, air- and water-stable compound, making it easy to handle, while also being a strong organic acid.[48] Its high proton-donating capacity[47] makes it an effective component in the formation of acidic DESs, particularly in applications requiring strong acidity and proton availability.[49] PTSA-based DESs have demonstrated

---

ETSEAFiV, UdL, Av. de l'Alcalde Rovira Roure, 191, 25198 Lleida, Spain. E-mail: anna.canela@udl.cat

considerable potential in various applications.[50] This review provides a comprehensive analysis of PTSA's role in DESs, highlighting its advantages and applications. Additionally, it explores the relationship between the hydrogen bond acceptors (HBAs) used and their specific applications, offering insights into how different HBAs influence the properties and performance of PTSA-based DESs.[50]

PTAS based DES in organic synthesis

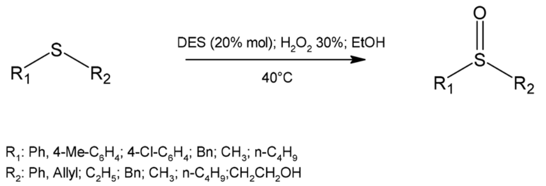
Reactive deep eutectic solvents (RDES)

In organic synthesis, a typical batch chemical operation used to produce building blocks, fine chemicals, or pharmaceutical products often requires the use of organic solvents and catalysts. Organic solvents, typically derived from crude oil, not only account for 80–90% of the mass utilized in such processes, but they also contribute significantly to the toxicity of the final products,[51] being usually volatiles, inflammables and harmful. On the other hand, catalysts for synthesis include a wide range of compounds from solid catalysts containing metal nanoparticles to homogeneous organometallic complexes, which despite the excellent activity and selectivity has several drawbacks.[52] Therefore, any development that enables to carried out a synthetic process in a more sustainable, easy to handle and environmentally friendly manner represents a valuable advancement aligned with the principles of green chemistry.[53]

DES can be used in a synthetic greener approach as Reactive Deep Eutectic Solvents (RDESs). They acting as both the reaction medium and catalyser thus minimizing waste, improving atom economy, facilitating product separation through precipitation, and enhancing overall process efficiency.[11,12,54–56] Here are various types of DES described in organic synthesis, between them acid DES. Acid DES, with an activity typically related with acid strength[57] are mainly Lewis-acid-based DESs (LADES) and Brønsted acid-based DES (BADES). Generally, RDES have been described as catalysts and solvents in various organic reactions including aldol condensation, Michael additions, Knoevenagel condensations, and transesterification reaction. Their use in organic synthesis simplifies the process (less steps, easier purification processes…), avoid excessive use of strong acidic catalyst,[58] eliminates the need for volatile and often toxic organic solvents, and sometimes the generation of for example acid sewage.[59] RDES enables reactions under mild conditions while offering recyclability and scalability.[60,61] Although sometimes a slow mass transfer can be caused by the viscosity of the reaction medium that DES promotes.[59,62] This can be solved adding smalls amounts of water or alcohol.[58] These approaches result in greener and more streamlined procedures.

Some of these DES-enabled methods allow the synthesis of compounds that are difficult or inefficient to produce using conventional strategies.[57] Their low toxicity, simple preparation, and low cost, coupled with the elimination of harmful solvents, intermediate isolation steps, and harsh conditions,[58] position DESs as sustainable alternatives to traditional multi-step procedures. In particular, PTSA-based DESs stand out for their high selectivity and reusability.

Table 1 summaries the use of PTSA based DEs as RDES to synthesize organic compounds. Whereas PTSA is used as HBD, mainly choline chloride (ChCl) as HBA is used. In these reactions the effective of these is based on the formation of hydrogen bonds with some reagent and/or the acid catalysis provided by PTSA. One example is the PTSA DES described Dai *et al.* (2014) to improve the oxidation of different sulfides (Scheme 1, entry 1.1) using H_2O_2 as the oxidant.[59] The yields achieved range from 81 to 97% after 4 h reaction. It is justified

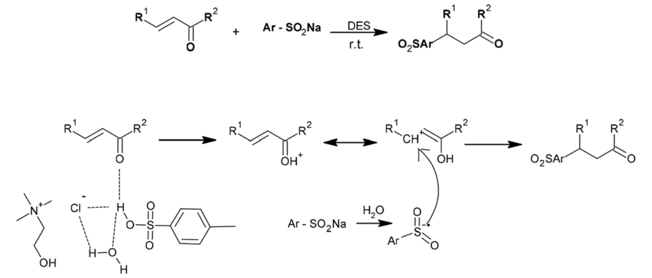


Scheme 1 Sulfide oxidation to sulfoxide.

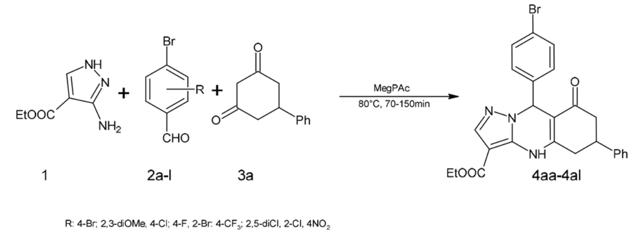
Table 1 PSTA based DES used as reaction medium and reaction promoters

Entry	HBA	Molar ratio	Application	Yield model substrate (%)	DES cycles[a] (yields, %)	Solvent	Ref.
1.1	ChCl	1 : 1	Sulfide oxidation to sulfoxide	95	4 (83)[b]	EtOH	59
1.2	ChCl	1 : 1	One-pot synthesis on phthalazine derivatives	86	5 (80)	MeOH	68
1.3	ChCl	1 : 1	Aza-Michael addition	93	5 (90)	H_2O	69
1.4	ChCl	1 : 1	Sulfonylation of activated alkenes	88	4 (74)[b]	H_2O	58
1.5	ChCl	1 : 1	Deprotection of *N*-Boc amino acid derivatives and *N*-Boc dipeptide	98	n.p.	—	12
1.6	ChCl	1 : 1	α-Chlorination of ketones	93	5	ACN	66
1.7	ChCl	1 : 2	One-pot strategy for γ-keto sulfones and γ-keto phosphine oxides synthesis	98[c]	5 (91)[c]	—	57
1.8	Imidazole (Im)	1 : 2	Prins condensation	n.p.	n.p.	—	70
1.9	Meglumine	1 : 2	One-pot synthesis of pyrazolo-quinazoline derivatives	64–94	n.p.	—	71

[a] Yields without a 10% decrease. [b] Yield slightly higher than 10% decrease. [c] 5 cycles can be done with 48 h reaction time, only 3 with 24 h. n.p. = not provided.



Scheme 2 Sulfonylation of activated alkenes.



Scheme 3 MegPAc catalyzed pyrazolo-quinazoline synthesis.

by the formation of hydrogen bond between the DES and H_2O_2 resulting in the polarization of the H_2O_2 bonds enhancing its reactivity.[63]

A facile sulfonylation of activated alkenes employing sodium arylsulfinates in ChCl : PSTA DES at room temperature was described, Scheme 2 entry 1.4.[58] Although similar yields were obtained using other acidic catalysts such as $FeCl_3$ (20 mol%)/TMSCl (1.2 equiv.) in DMC[64] (85%) or HCl in water (98%)[65] at the same temperature, longer times were needed for those ones. Also, ChCl/$FeCl_3$ (1 : 1) compared with PTSA : ChCl gave much lower yields with longer, reaction times (36% *vs.* 88%). The ChCl : PSTA DES used enhance the acid strength of the media needed for this reaction.

An acid media is also used in the *N*-Boc deprotection of a wide variety of *N*-Boc derivatives (entry 1.5). The use of ChCl : PTSA DES has been improved the recovery step of the Boc cleaved product when comparing with the Boc deprotection using dichloromethane (DCM).[12] The α,α-dichlorination of ketones (entry 1.6) in acetonitrile;[66] and the one-pot concurrent synthesis of alpha-keto sulfones and alpha-keto phosphine oxides with yields (entry 1.7) are also acid catalysed. The last reaction goes through 3 steps: (1) the regioselective hydration of terminal alkynes; (2) the reaction of the *in situ* generated enol with aromatic aldehydes through a Claisen–Schmidt condensation; and (3) chemo selective formation of C–S or C–P bonds *via* hetero-Michael reactions using $NaSO_2R$ or $O{=}P(H)R_2$. It was observed that decreasing the proportion of PTSA in the eutectic mixture led to a concomitant reduction in the yield, which confirms the necessity of the presence of protons in the reaction medium.[67]

Other PTSA DES without ChCl has also been described. 4-Phenyl-1,3-dioxane (PDO) was synthesized through the Prins condensation, an acid catalysed process, of styrene with formaldehyde, entry 1.8, using a deep eutectic solvent with imidazole (Im) in a 1 : 2 ratio [Im : 2PTSA].[70] The 1 : 2 ratio assure the acidity of the media. A meglumine-based (MegPAc), three-component deep eutectic solvent (3c-DES) was prepared using meglumine, PTSA, and acetic acid (AA). This BADES (Scheme 3, entry 1.9) enabled the efficient synthesis of functionalized pyrazolo[5,1-*b*]quinazoline-3-carboxylates with yields ranging 69 to 94%.[71]

However, does DESs are not effective for all reactions. For example, a Lewis-acid eutectic mixture such as $FeCl_3 \cdot 6H_2O$/Gly (3 : 1) failed to promote the formation of C–C and C–S bonds.[57] Other described similar results.

On the other hand, BADES, such as those based on PTSA, have been identified as highly selective media for cascade bond-forming reactions, including C–C and C–heteroatom bond formation.[57,58] Although other BADES have been tested on reactions where high acidity is needed PTSA tends to be more efficient on most of the reactions described in this review. The use of eutectic mixtures containing moderately strong and sustainable hydrogen bond donors, for example, oxalic acid (OA), uses to give lower, or even no react[57] on the same reaction conditions than PTSA.[12,58] On other hand, citric acid-based DES tend to present higher viscosity of the reaction media, which difficulties the reaction.[12]

Finally, while systems such as choline chloride/PTSA DESs do still generate waste, this is generally considered less hazardous compared to conventional volatile organic solvents and corrosive acids.[66]

Esterification

Esters are important synthetic products widely used, for example as additive and intermediate in the food,[72–75] cosmetic,[76,77] flavor[72] and fragrance,[73,74,78] pharmaceutical, and chemical industries,[79] as a fuel additives, solvents and plasticizers[79,80] industries as well as in the biodiesel industry[81–83] and in polymer synthesis.[84]

Esterification is conventionally carried out *via* Fischer esterification using a mineral acid, such as sulfuric acid, as a homogeneous catalyst.[85] However, this approach has several drawbacks, including equipment corrosion, difficulties in catalyst recycling, the occurrence of undesirable side reactions,[86] and conversion limitations caused by reaction equilibrium.[75] In esterification synthesis, replacing mineral catalysts with Deep Eutectic Solvents (DESs) not only allows for milder reaction conditions but also enhances the overall efficiency of the process. Considering the acid-catalysed mechanism of esterification, an ideal catalyst should possess strong acidity.

PTSA based DES, have been widely investigated as alternative catalysts for esterification reactions. These DESs have demonstrated effective catalytic performance in the synthesis of various esters. Notably, PTSA-based DESs offer the dual functionality of acting both as catalysts and as extractants, enabling reactive extraction of the ester product during the reaction.

This *in situ* separation helps shift the chemical equilibrium toward ester formation, thereby enhancing yields and reducing the need for energy-intensive downstream purification—

Table 2 PSTA based DES used in esterification reactions

Entry	HBA	Alcohol	Acid	Ref.
2.1	BTMAC	MeOH, BuOH, HexOH, 2-EH	Acetic (AA)	87
2.2	TCyAMsO TBnAMsO TOAMsO TCyATos	MeOH	Lauric	89
2.3	TCyAMsO	Primary alcohols	Lauric, octanoic, palmitic, estearic, acetic, isobutiric, trimethylacetic	
2.4	ChCl	Isobutanol	Cinnamic	73
2.5	ChCl	MeOH	Cinnamic	78
2.6	BTMAC	Isoamyl alcohol	Hexanoic	72
2.7	BAC	EtOH	Lauric	90
2.8	ChCl	MeOH	*p*-*tert*-Butylbenzoic	76
2.9	Im	Isobutanol	Isobutiric	91
2.10	1,2,3-Triazole Im	Isobutanol	Acetic (AA), propanoic (PAC), isobutanoic (IBAC), isopentanoic (IPAC), hexanoic (HexAC), heptanoic (HepAC)	92
2.11	2-MIm	BuOH	Hexanoic	75
2.12	Im	2-EH	Acrylic	84
2.13	ChCl	Cetyl alcohol	Oleic	77
2.14	ChCl	Ethanol	Levulinic	79
2.15	Im	2-EH	Phthalic anhydride	80
2.16	DTAC	Ethanol	Palmitic	93

especially critical for long-chain esters that are otherwise difficult to isolate.

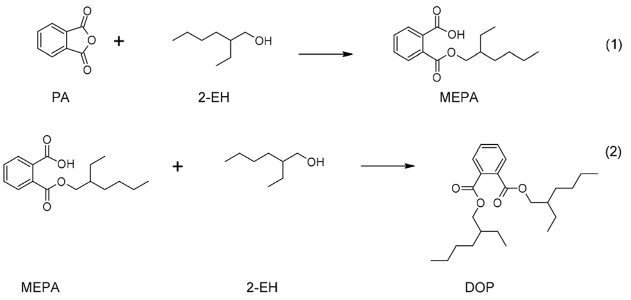
As will be further discussed in this review, and can be seen in Table 2, in PTSA-based DES esterification, ammonium-based hydrogen bond acceptors (HBAs) are typically used as primary components. However, other components such as ChCl, Im, and various alternatives have also been explored for different applications.

Taysun *et al.* studied esterification reactions using a DES composed of benzyl-triethylammonium chloride (BTMAC) and PTSA (entry 2.1).[87] Their research first focused on evaluating the optimal alcohol-to-acid ratio, followed by an assessment of the best reaction conditions with different alcohols. Their studies continued, specifically investigating the esterification of acetic acid with 2-ethylhexanol.[88]

Four different DESs based on quaternary ammonium salts were designed, entry 2.2. Using *N*-cyclohexyl-*N*-*N*-*N*-trimethylammonium methanesulfonate (TCyAMsO) as HBA, at 60 °C for 2 h methyl laurate was synthesised with a 97% yield. The method was extended to various acids, entry 2.3, and alcohols. Primary alcohols gave good yields over 75% for 2 h at 60 °C. However, for secondary alcohols, cyclohexanol or isopropanol, yields did not exceed 50%.[90] The reaction of EtOH with lauric acid, entry 2.7, was studied using different molar ratios of BTMAC : zPTSA ($z = 1/2/3$) DES. Being BTMAC : 3PTSA the DES that offered the better conversion yield, 84.6% at 3 h and 95 °C.[90] The same DES with a ratio 1 : 1.2 was also used to prepare isoamyl hexanoate, a flavoring agent, entry 2.6. The conversion of hexanoic acid reached 92.15% after 120 min at temperatures ranging from 65.15 to 95.15 °C.[72]

The direct esterification of palmitic acid with ethanol using a *N*-dodecyl-*N*,*N*,*N*-trimethyl ammonium chloride (DTAC) DESs. DTAC–zPTSA, at three molar ratios ($z = 1/2/3$) was investigated (entry 2.16). The DES 1 : 3 use at 75.15 °C, achieved a conversion rate of palmitic acid around 89%.[93]

Qin *et al.* (2019) Im based DES were studied for the esterification of long-chain carboxylic acids, at two molar ratios.[91] [3-Im : PTSA] was considered a weakly basic DES meanwhile [Im : 2PTSA] a strongly acidic DES, entry 2.9. A 92.5% of conversion of isobutanol was achieved using the acidic DES at 80 °C for 2 h. The same Im as HBA in PTSA based DES was used to prepare dioctyl phthalate (DOP), a widely used plasticizer,[94] in a high yield of 98.61% (entry 2.15, Scheme 4);[80] 2-ethylhexyl acrylate (2-EHA), entry 2.12, a widely used acrylate in the polymer industry;[84] and a set of aliphatic esters, entry 2.10, with chains lengths from C6 to C11, also a triazole : PTSA DES was obtained and evaluated.[84]



Scheme 4 2-Step reaction for PA and 2-EH to obtain DOP.

An effect of the length on the enthalpy of the reaction was described[92,95] set the reaction temperature at 70 °C for isobutyl ethanoate (IBEE) and isobutyl propanoate (IBPE) synthesis, and a little higher 80 °C for the synthesis of longer esters, such as isobutyl isobutanoate (IBIBE), isobutyl isopentanoate (IBIPE), isobutyl hexanoate (IBHexE), and isobutyl heptanoate (IBHepE).

Reactive extraction was also used by Zhou *et al.* (2021) to prepare the butyl hexanoate (BuHE) ester, widely used in the food, beverage and cosmetic industries. They prepared a DES using 2-methylimidazole (2-MIm) and PTSA (2-MIm : 2PTSA), entry 2.11. At 80.15 °C and 20% (mass) DES dosage a HeA conversion of 91.27% was achieved.[75]

Other authors proposed ChCl as HBA for PTSA based DES, many of them work on formulation of aromatic esters, such as isobutyl cinnamate, entry 2.4, commonly used as fragrances. With a 1 : 1 molar ratio, 2 h at 110 °C a 93% yield was obtained.[96] Similarly, entry 2.5, the esterification of cinnamic acid with methanol at various molar ratios of ChCl : zPTSA DES ($z = 1/2/3$) was studied. ChCl : 3PTSA provided the highest conversion rate.[78] Additionally, a process for esterifying cinnamic acid with various alcohols at 50 °C in a ChCl : PTSA eutectic solvent was patented, producing different cinnamates with yields of 90–91%.[74] ChCl : PTSA with different molar ratios ($z = 1/1.5/2/3$) was used to prepare methyl *p-tert*-butyl benzoate, entry 2.8, a valuable intermediate with extensive applications in cosmetic, flavour, fragrance, pharmaceutical, and chemical industries. Among these, ChCl : 1.5PTSA exhibited the best performance after 3.5 h at 76.15 °C.[76] ChCl : PTSA DES was also used to synthesize liquid wax esters from oleic acid, entry 2.13. At 70 °C for 3 h they achieved a conversion rate of 99.1%.[77] Ethyl levulinate (a fuel additive, solvent and plasticizers) was also synthesised, entry 2.14, with a 99.8% levulinic acid conversion at 80 °C after 1 h.[79]

In summary, PTSA based these have been described to synthesis aliphatic and aromatic esters using primary and secondary aliphatic alcohols. Yields ranged from 50% to quantitative depending on the alcohol used (secondary alcohols tend to give lower yields as expected) and the DES used. Usual temperatures are between 70 °C and 90 °C and reaction times 2–3 h. Nevertheless, many of the reported DESs contain halogenated components that raise environmental and safety concerns, potentially compromising product quality. Therefore, ongoing efforts aim to develop halogen-free DES systems with comparable acidity and catalytic efficiency, while also being environmentally benign.[75,89]

Biodiesel synthesis

Traditional biodiesel production involves converting vegetable fats and animal oils into fatty acid methyl esters (FAMEs) or ethyl esters (FAETs) through a basic catalyst transesterification process using methanol (MeOH) or ethanol. Biodiesel offers several advantages over petroleum-based fuels,[97] but it is still necessary to produce it from renewable feedstocks that do not compete with food crops.[98] So, there is growing interest in reusing materials and utilizing non-edible feedstocks to enhance sustainability. Because of that, nowadays research is focused on utilizing alternative feedstocks, such as low-quality/value oils. However, vegetable oils like acidic crude palm oil (ACPO), low-grade palm oil (LGPO), low-grade crude palm oil (LGCPO) and waste cooking oil (WCO) cannot be directly used for basic catalysis transesterification to produce fatty acid methyl esters (FAMEs) due to their high free fatty acid (FFA) content, which leads to soap formation and reduce biodiesel yields.[99] Typically, FFA content has been reduced through acid-catalysed esterification, obtaining fatty mixtures that can then be transesterified.[99,100] BADES can be perfect as catalysers for these reactions.[101]

Table 3 shows various PTSA-based DES used as pretreatment agents for high-FFA oils, facilitating the conversion of FFAs into FAMEs prior to the basic transesterification traditional process. As observed, halogen ammonium HBAs are predominantly used. For example, Haga clic o pulse aquí para escribir texto., entry 3.4, BTMAC as HBA was used into a PTSA based DES to esterify the FFA to FAMEs in LGPO, after 30 min reaction at 60 °C a content of FFA below 2% was achieved.[103] Similarly, *N*,*N*-diethylenethanol ammonium chloride (DEAC) was used as HBA, entry 3.1, on the reduction of FFAs in LGCPO, achieving an FFA content below 1% under the same reaction conditions.[81] In 2014 in a follow-up study, entry 3.2, a ChCl-based HBA : PTSA-based DES allowed reducing the FFA content to 0.07% under identical conditions (30 min reaction at 60 °C).[107] A ChCl : PTSA DES supported on silica gel or unsupported using methanol or MBTE as solvents was also used to study the biodiesel production of a high free fatty acids non-edible oil such as *P. pinnata* oil. Supported DES was capable to be recycled up to 7 cycles meanwhile unsupported one at the 4th cycle lose about 30% of its activity. Although that, biodiesel conversion with the silica supported DES was 89.3%, *versus* a 97.53% of conversion with the unsupported DES. Supported DES also required higher reaction temperature and longer reaction times.[102] In 2022,

Table 3 Preparation of biodiesel using PTSA based DES

Entry	HBA	FAME/FFA source	Ref.
3.1	DEAC	LGCPO	81
3.2	ChCl	ACPO	82
3.3	ChCl	*Pongamia pinnata* (Karanja) seed oil	102
3.4	BTMAC	LGPO	103
3.5	ChCl, TEAB, TBAB, THAB, TOAB	Cooked and waste vegetable oil	104
3.6	TBAB, TBAC, ChCl, BTAB, BTAC	Yellow horn seed	105
3.7	MTPB	ACPO	106
3.8	Paracetamol	LGPO-microalgae oil	107

entry 3.7, the high hygroscopic DES using methyltriphenylphosphonium bromide (MTPB) and PTSA[108] was encapsulated in medical capsules. Encapsulation was described as beneficial for ease of handling and storage, preventing moisture absorption and exposure to air.[106] Using the already proposed reaction conditions – 30 min reaction at 60 °C – and the encapsulated DES, a FFA content below 1% was achieved.[106] Building on this work, entry 3.8, paracetamol was introduced as the HBA. This DES, also encapsulated in medical capsules, was used to esterify FFAs in LGPO and 15% microalgae oil. Under a reaction temperature of 60 °C and an extended reaction time of 60 min, the FFA content was reduced to below 2%.[107]

Five different PTSA-based DES has also been studied as a transesterification agent, entry 3.5, for cooked and waste vegetable oil. Among these DESs, the tetraoctylammonium bromide (TOAB)–PTSA-based DES, which contained the longest carbon chain, demonstrated the highest FAME transesterification yield. This enhanced performance was attributed to the increased lipophilicity of the longer-chain DESs. Under reaction conditions of 5–6 h at 69.5 °C, a yield of approximately 90% was reported.[104] The tetrabutylammonium bromide (TBAB) based DES, yielded from yellow horn seeds a FAME conversion rate of 96.53% at 72 °C for 40 min using a microwave at 500 W.[105]

Experimental results have shown a significant reduction in FFA content in low-grade oils such as LGCPO and ACPO when treated with PTSA-based DESs formulated with different hydrogen bond acceptors (HBAs). DES acidity has been demonstrated as a crucial parameter in esterification and transesterification process where ADES are described as solvent and catalyst. All of those PTSA DES have been shown to improve esterification reactions, particularly in pretreatment steps.

Although LADES such as ChCl : $ZnCl_2$ or ChCl : $FeCl_3$ have been described for the process.[109,110] PTSA-based BADESs have been deeply studied and demonstrated as effective pretreatment agents for fats and vegetable oils with high free fatty acid (FFA) content. These DESs facilitate the conversion of FFAs into FAMEs prior to transesterification, offering a sustainable alternative to mineral acid catalysts and the need for high reaction temperatures, which are both environmentally and economically unfavourable.

Achievements in biopolymer treatments

The advancement of biorefinery processes using biomass as a raw material to produce value-added products is an area of significant research interest. From these biomass components, numerous high-value products can be obtained. From platform compounds like levoglucosenone,[31] chitin,[111] and furfural,[112] which are valuable in materials and fuel industries[113,114] to carbon microspheres,[115] textiles,[116] and nanocrystals[117–122] or nanocellulose (CNC) or lignin containing nanocellulose (LNC).[121,123] One of the main challenges in these processes is the effective separation of lignin, cellulose and hemicellulose, known as fractionation, obtaining the different fractions in conditions to be revalorized.

DES as lignocellulosic biomass fractionation improver

Despite considerable advancements in recent years, efficiently overcoming the recalcitrance of lignocellulosic biomass remains a significant challenge. Traditional strategies for breaking these structures—such as physical, chemical, physicochemical, and biological pretreatments—often involve high energy consumption, or high treatment periods or pose environmental concerns. Organosolv results more consistent with the principles of green chemistry and integrated biorefinery systems but still have some drawbacks and lead to basic lignin. DESs, have been studied as alternatives or complements to those methods. DESs as pretreatment has been demonstrated as effective to fractionate lignocellulose breaking covalent bonds between hemicellulose and lignin.

Recognizing the excellent solvent strength and ability to break the strong interactions between lignin and holocellulose, many binary and ternary DES compositions have been applied for lignocellulose fractionation with promising results. Between them, PTSA-based DES can act as depolymerization agent, selectively breaking β-O-4 linkages, producing for example low molecular weight lignin's,[124] due to its capacity to make hydrogen bond interactions in between its C=O double bonds with the π–π monosaccharide system.[125] This is described to prevent one of the biggest lignin classic fractionation processes problems: lignin condensation.[126–128]

While many of the processes described focus on lignin removal, it is important to note that lignin is a valuable biomass resource with numerous potential applications.[115,129–132] It is known that the molecular weight of lignin directly influences its properties. Low molecular weight (MW) lignins, characterized by a high hydroxyl content, due to the high β-O-4 linkages breaking, are suitable for the preparation of bioactive compounds.[133] In contrast, high molecular weight lignins, due to their high carbon content and viscosity, serve as ideal raw materials to produce carbon fibers and other advanced materials.[134]

As can be seen in Table 4, most of the described processes uses ChCl as HBA. ChCl is described to have the capacity to form H-bonds with lignin, also to be able to decrease the solute surface energy in solid phase, which plays a catalytic conversion role to decrease the surface energy of solute in solid phase both promoting lignin dissolution.[135] It must be noted that three-constituent deep eutectic solvent (3c-DES or 3DES) were also studied for effective fractionation.[49,136,137] These DES mostly content ethylene glycol (EG) as third constituent.

From entries 4.1 to 4.5 of the Table 4, all the authors used ChCl : PTSA DES. In the first entry 4.1, alkaline lignin was used to study the aryl ether bond cleavage capacity of deep eutectic solvents (DES). Their findings showed that the resultant lignin had a lower molecular weight and higher reactivity, attributed to the increased presence of phenolic hydroxyl groups and a more homogeneous dispersion.[133] DES pretreatment to delignify two different lignin biomass sources: woody biomass and herbaceous biomass was also applied, entry 4.2. Following the pretreatment, a NaOH post-treatment and enzymatic hydrolysis were conducted.[138] Entry 4.4 describes the application of DES fractionation on *Eucalyptus globulus* Labill. wood

Table 4 PTSA based DES in lignocellulose fractionation

Entry	HBA : HBD	Biomass source	Lignin fractionation yield/removal rate/delignification	Ref.
4.1	ChCl : PTSA	Alkaline lignin: Nanjing pulp and paper mill	—	133
4.2	ChCl : PTSA	Woody poplar sawdust (PL) herbaceous *Miscanthus* (MC)	90.0%	138
4.3	ChCl : 2PTSA	*Phragmites australis*	65.0%	140
4.4	ChCl : PTSA	*Eucalyptus globulus* Labill. wood	80.6%	139
4.5	ChCl : PTSA	Wheat straw, Moso bamboo, poplar and pine woods	75.5%	141
4.6	ChCl : EG : PTSA	Balsa wood samples	87.3%	137
4.7	ChCl : EG : PTSA	Bagasse	97.9%	136
4.8	ChCl : EG : PTSA	Bamboo	90.3%	49
4.9	ChCl : EG : PTSA	Water chestnut shells	84.2%	142
4.10	ChCl : Gly : PTSA	Cocoa bean	95.5%	143
4.11	GH–EG–PTSA	Switchgrass	82.0%	145

using an aqueous DES solution (containing 50 wt% water) as a green solvent for delignification.[139] Based on their results, the authors concluded that the high acidity of the aqueous DES solution degraded part of the cellulose content in the sample. Both approaches showed a delignification rate between 80% and 90% using various biomass source.[138,139]

Using the same DES but microwave irradiation (MW), which can maximize the ionic character of ChCl : PTSA DES and increase its molecular polarity, entry 4.3, a *Phragmites australis* fractionation was described.[140] The same DES was proposed for a mechanochemical delignification process using ball milling (BM) for various lignocellulosic biomass materials.[141] The results demonstrated high delignification efficiency for wheat straw and bamboo biomass.[140,141]

Other authors reported the use of ternary DES systems, consistently employing ChCl and PTSA, but with a third component, typically polyol-based hydrogen bond donor (HBD). In entries 4.6–4.9, ethylene glycol (EG) served as the third component, whereas in entry 4.10, glycerol (Gly) was used. Removal lignin percentages ranged from 87% to 90% depending on the starting material and the molar rations used.[49,128,136,137] Using a PTSA : ChCl : Gly (2 : 1 : 1) DES and microwaves 95.5% of lignin from cocoa bean shells (CBS) was recovered (entry 4.10).[143]

Six ternaries DESs containing ChCl or guanidine hydrochloride (GH) as HBA; EG, PG or GLY as a polyol-based hydrogen bond donor (HBD), and PTSA as an acidic HBD, were studied, entry 4.11. The authors showed GH–EG–PTSA DES as the most effective for lignin removal.[144]

Among the various PTSA-based DES systems studied for lignin removal, the ChCl : EG : PTSA combination applied to bagasse achieved the best performance, with an impressive 97.94% delignification under relatively mild conditions. This highlights the significant advantage of using ternary DESs—particularly those incorporating ethylene glycol (EG) or glycerol (Gly)—over traditional binary systems like ChCl : PTSA.

These ternary mixtures not only deliver higher efficiency but also offer greater ease of operation, often requiring lower temperatures and shorter reaction times. Moreover, microwave- and mechano-assisted methods, such as microwave irradiation or planetary ball milling, have proven highly effective in enhancing delignification, even when applied at reduced thermal or time inputs. These techniques increase solvent penetration and biomass accessibility, accelerating the fractionation process. Importantly, the type of biomass plays a critical role in determining delignification outcomes. Softwoods, hardwoods, and herbaceous plants exhibit varying resistance to lignin removal, with some responding more readily to specific DES formulations and process conditions. This underscores the necessity of tailoring the DES composition and treatment strategy to the unique structure and composition of each biomass source. Notably, acidic DESs have demonstrated greater effectiveness than neutral ones.[146–148] In general, Strong acid ADESs are effective for biomass fractionation.[124] The extent and efficiency of hemicellulose and lignin removal are closely linked to catalytic activity, which can be explained by the cleavage capacity of acidic protons (H^+) dissociated from the DES. Additionally, the intermolecular hydrogen bonding between the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) influences the proton dissociation capacity.[124] DES for lignin recovery is described to be ChCl : acid or polyol DES based on. Among them, few are described with PTSA. Overall, carboxylic acid-based DES pretreatments are effective for lignin removal but require long pretreatment needs of long-time reactions and high temperatures, also lead to low molecular weight and high purity lignin, with structures that can be more suitable for chemical functionalization due to more phenolic hydroxyl groups as a consequence of major demethylation degrees. Anyway, from the practical and economical perspective, pretreatment performance needs much improvement. But, among the various systems explored, PTSA-based DESs are particularly attractive due to the solid organic acid nature of PTSA, which enables effective lignin removal under milder conditions—atmospheric pressure and moderate temperatures—while also offering the potential for recyclability. Interestingly, the reactivity of lignin during depolymerization in DESs can be modulated by adjusting the relative ratios of HBDs and hydrogen bond acceptors (HBAs). By varying the amount of diols used as HBDs, it is possible to tailor the DES environment to favour either selective cleavage or the protection of lignin fragments, offering a tuneable strategy for targeted biomass processing. However, one drawback is their corrosive nature, which can compromise equipment durability. To address this limitation, polyol-containing DESs have been introduced. The incorporation of polyols as hydrogen bond donors (HBDs) improves the DES physical properties (fluidity, recyclability, and thermal stability).[149] It is important to emphasize that lignocellulosic biomass fractionation should focus not only on cellulose recovery but also on preserving lignin and hemicellulose. As many of these components as possible should be retained, as highlighted in the majority of studies reviewed, which adopt a holistic biorefinery approach. Regarding other HBDs, mostly are also based on cellulose recovery where carboxylic acid type DESs are particularly effective in biomass fractionation, being able to solubilize lignin meanwhile cellulose is preserved.[150] Although those processes still present drawbacks, such as long reaction times and high temperatures,[151] following with the esterification that can occur between the cellulose hydroxyl groups and carboxylic acid from DES.[152,153] This side-esterification process is described to difficult the enzymatic hydrolysis, potentially affecting their binding interaction with cellulase.[154] Generally, hemicellulose results overlooked being generally degraded during the process and lost. Few studies with PTSA based DES are addressed to this recovery. Zhou *et al.* described a 27.6% of furfural detected as degradation product from the DES pretreatments poplar while only 0.2% in *Miscanthus*.[138] It must be pointed that some authors have improved the fractionation yields by preprocessing the DES system with microwave, or ball milling. DES recovering, and reusing can be challenging, also antisolvent is typically used, and it uses to depends on the solubility of DES on it to precipitate lignin, different solvents and conditions can be further studied to improve the efficiency of the process. Despite various categories of DES constituents have been investigated, the most suitable DES type for biomass processing application is non-conclusive. Researchers need to define the pretreatment goal, for instance enzymatic hydrolysis enhancement or lignin extraction, to select the best performing solvent. Establishment on the fundamental knowledge on how DES interacts with different biopolymer solutes would greatly help in the selection process.

DES to obtain platform chemicals from biomass

Table 5, entries 5.1–5.7, summarize different platform chemicals obtained from biomass through DES or 3DES.

Polyester–cotton blended fabric (WPBFs) is one of the most important blended products on the market. However, it is difficult to recycle because of its heterogeneity.[155]

A process where PET, MCC (microcrystalline cellulose), and a small amount of glucose were extracted from waste polyester–cotton blended fabrics (WPBFs) using ChCl : PTSA DES was described, entry 5.6. WPBFs were treated with 75 vol% DES for 10 min at 110 °C.

During this treatment, the cotton component was rapidly degraded into cotton fiber powder, while the PET component was easily separated. This method not only quickly recovered PET from the waste textile with high yield and nearly its original properties, but also efficiently extracted MCC and glucose. The yields of R-PET and MCC were 99.20 and 69.46%, respectively, while 38.91% glucose was recovered.[116]

Another example is provided in entry 5.3. Using ChCl : 2PTSA on *Lycium barbarum* L. fruits myricetin, morin, and rutin could be extracted through ultrasound-assisted extraction (UAE) method.[156] FeCl$_3$ was introduced as a hydrogen bond donor (HBD) into the previously described ternary system, entry 5.4, creating a quaternary DES: ChCl : EG : PTSA : FeCl$_3$ (1 : 2 : 0.3 : 0.3). This system achieved an anthocyanin extraction yield of 173.71 mg g^{-1} and the highest lignin removal rate of 40.80%.[96] A biphasic system combining ChCl : PTSA DES and ethyl acetate to yield 50% of furfural from xylose was described, entry 5.5.[112] Indole—an important organic chemical used in the production of spices, dyes, amino acids, and pesticides was extracted with a 97.2 ± 2% of efficiency from wash oil using a TEAC : PTSA (1 : 2) (entry 5.7).[157]

DES for nanocrystal preparation

The use of cellulose in the preparation of cellulose nanocrystals (CNC), a renewable nanomaterial derived from biomass, has

Table 5 PTSA based DES to obtain materials or platform chemicals

Entry	HBA : HBD	Material	Product	Ref.
5.1	ChCl : PTSA TEAPTS : PTSA TPAB : PTSA	Microcrystalline cellulose	Levoglucosenone	31
5.2	TEAPTS : PTSA	Cedar wood		
5.3	ChCl : 2PTSA	*Lycium barbarum* L. fruits	Flavonoids	156
5.4	ChCl : EG : PTSA	Rose petals	Anthocyanin	96
5.5	ChCl : PTSA	Xylose	Furfural	112
5.6	ChCl : PTSA	Waste polyester–cotton blended fabrics	Polyester and microcrystalline cellulose	116
5.7	TEAC : PTSA	Wash oil		
5.8	ChCl : PTSA	Wood cellulose fibers	CNC	122
5.9	ChCl : PTSA	CFII commercial cellulose	CNC	120
5.10	ChCl : PhoA : PTSA			
5.11	ChCl : OA : PTSA	TMP	LCNC	118
5.12		TMP	LCNC	158
5.13	ChCl : EG : PTSA	Walnut shell	LNPs	128
5.14	ChCl : LA : PTSA	Poplar (*Populus* L.)	LCNC	121
5.15			LCNC	123

attracted attention due to its desirable structural characteristics, such as excellent mechanical strength, large aspect ratio, extensive surface area, low density, and modifiable surface properties, high stiffness, and potential chemical functionality.[119] Also, the production of lignin-containing nanocellulose (LNC),[121] has been described as a sustainable material of significant interest.[118,158]

Table 5 summarizes the production of different nanocrystals. At the entry 5.8 is described the preparation of wood microsized fibers by the pretreatment of wood cellulose fibers with ChCl and PTSA monohydrate.[122] The production of CNCs from commercial cellulose with the same DES at stoichiometries ChCl : PTSA (1 : 1) and (1 : 2) was studied. Also was studied a ternary eutectic mixture, adding phosphoric acid (PhoA) with the aim to improve the thermal stability of the CNC obtained, entry 5.10. The resulting 3c-DES at a molar ratio of 1ChCl : 1PTSA : 1.35PhoA yielded 81% of CNC.[120]

Lignin-containing nanocellulose (LNC) was prepared *via* a two-step process using a ChCl : LA : PTSA DES at a 2 : 10 : 1 molar ratio, followed by sequential microfluidizer mechanical disintegration, entry 5.14. The yield and lignin content of the LNC reached 64.65% and 27.65%, respectively.[121] Subsequently, $FeCl_3$ was introduced into the ChCl : LA : PTSA system, entry 5.15. The $FeCl_3$-catalyzed ternary DES (TDES) produced LNC with a yield of 60.68% and a reduced particle size.[123] Jiang *et al.* (2020), nanocrystals of lignin-containing cellulose (LCNCs) were prepared using a 3-component DES (3c-DES) composed of ChCl : OA : PTSA at a 2 : 1 : 1 molar ratio, entry 5.11. After DES pretreatment, a mild mechanical disintegration process was applied, resulting in a lignin content of 47.8% and a yield of 66%.[118] The same DES and molar ratio yielded 68% of LCNCs from thermomechanical pulp (TMP).[158] Finally, entry 5.13, lignin nanoparticles (LNPs) were prepared using both ChCl : PTSA DES and ChCl : PTSA : EG 3c-DES at different molar ratios (1 : 1 : 1 and 1 : 1 : 2). The use of the 1 : 1 : 2 molar ratio 3c-DES on walnut shell biomass as a pretreatment led to the production of LNPs with a yield of 42.72%.[128]

PTSA based DES can be used in recycling fibers, extracting bioactive compounds and obtain several derivate materials. Production of fermentable sugar from cellulose-rich SF is achieved by depolymerisation of polysaccharides into monomers. Apart from that, cellulose can also be utilized in its polymeric form for advanced material production. Several successful attempts have been made in producing nanocrystals and nanofibrils cellulose from pure cellulose source such as cotton fibres, microcrystalline cellulose or cellulose pulp using DES as pretreatment agent.[120] Although using cellulose obtained from lignocellulose samples to cellulose nanocrystal (CNC) production, results in moderate yields. Consequently, PTSA-based DESs have not been identified as the most efficient system.[122] However, they can interact with cellulose through hydrogen bonding. Specifically, the formation of competing hydrogen bonds between the DES and cellulose can modify the cellulose network, thereby promoting its dissolution. This behaviour is advantageous for the separation of cellulose nanofibers (CNFs).

Carboxylic acid-based DESs have also been studied to liberate CNFs. They have been described as cellulose structure disruptors through cellulose esterification, which reduce its polarity improving then its dispersibility in nonpolar solvents.[152] In another hand, when lignin is used as a precursor for the synthesis of LCNC 3DES have shown better results.[118,121,158]

Other material prepared from biomass

Mainly ChCl as HBA is described in other PTSA based DES applications to prepare other materials from lignocellulosic biomass. The synthesis of materials with a 3D porous texture and hierarchical structure are one of the most described. This kind of material offers outstanding properties as separation and catalytic processes materials[159] and also as electrodes in fuel cells and capacitors.[160] For example, hierarchical carbon–carbon nanotubes, were synthesized using ChCl : PTSA DES, obtaining materials capable to act as electrodes. Supercapacitors were prepared from a lignin based phenolic resin[115] and from chitin using shrimp shells, ChCl : 4PTSA on water and EtOH as antisolvent step.[111] Another chitin application as biomass through the reaction with ChCl : PTSA DES was described to prepare chitin nanocrystal (ChiNC) to immobilize porcine pancreas lipase (PPL), which was used to create carbon microspheres used as electrodes.[117] Biochar was obtained from lignocellulosic biomass using ChCl : PTSA DES in a simple one-pot method.[162]

DES for cleaning crude oil

Considering that most NO_x and SO_x emissions increased due to anthropogenic actions[163,164] the reduction of nitrogen- and sulphur-containing compounds has gained significant attention. One of the main focuses is being to develop a feasible solution to remove the S-/N-containing compounds from fuels to avoid the NO_x and SO_x release under its combustion.[165] The primary method for nitrogen removal in oil refining is hydrodenitrogenation (HDN) using Co–Mo or Ni–Mo as catalysts.[166] Also, non-hydrogenation treatments such as extraction, adsorption, bioprocessing and oxidation.[167,168] These methods involve high operational costs, substantial hydrogen consumption, and harsh conditions, limiting its efficiency. Similarly, hydrodesulfurization (HDS) is widely used for sulphur removal but is less effective against certain cyclic sulphur compounds like thiophene and dibenzothiophene. Both processes are costly due to high temperature, pressure, and hydrogen requirements, highlighting the need for more economical and efficient alternatives for denitrogenation and desulfurization. The use of acidic DESs has been proposed as a new route for N and S compound desulfurization of fuels.[169–171] For example, the acidity of BADES shows a positive correlation with the desulfurization performance.[172,173]

Table 6 shows several of these processes based on using PTSA based DES for crude oil purification. Typically, H_2O_2 is used as oxidant improving substantially the desulfurization processes. Entry 6.1 describes a process where both S and N are removed through a process using ChCl : 2PTSA DES.[174] However, desulphuration and denitrification processes are not

Table 6 PTSA based DES for crude oil cleaning best results

Entry	HBA	Molar ratio	Removed compounds	Ref.
6.1	ChCl	1 : 2	N/S	145
6.2	ChCl	1 : 1	Sulfur	146
6.3	ChCl : OA	1 : 2 : 0.2	Sulfur	147
6.4	TBAC	1 : 1	Sulfur	144
6.5	L-Pro	1 : 2	Sulfur	149
6.6	PEG4000	1 : 2	Sulfur	148
6.7	PEG200 : L-Pyro	1 : 2 : 2	Aromatic sulfur compounds	152
6.8	Acetamide	1 : 3	Sulfur	151
6.9	TBPBr	1 : 1	Nitrogen	136

always feasible to carry out simultaneously. Although ChCl is the main HBA used[179,180] other HBA such as tetrabutylammonium chloride (TBAC);[171] amino acids, compounds with low cost and nontoxicity,[175] acetamide[176] used to desulfurize commercial biodiesel, and PEG-based DESs[177,178] have been proposed.

Sun *et al.* (2019) introduced a system using Anderson-type polyoxometallate (POM) $(NH_4)_3Co(OH)_6Mo_6O_{18}$ a dissolved in the DES, PTSA : PEG*n* (PEG*n*: PEG1000, PEG2000, PEG4000, and PEG6000) as cocatalyst. PTAS : 2PEG4000 combined with POM achieved 99% DBT removal at the optimal conditions (entry 6.6).[178]

Until this paper was written, only one article has described the use of tetrabutylphosphonium bromide (TBPBr) PTSA DES at a 1 : 1 molar ratio for only N removal, entry 6.9, describing a. Due to the high effectivity demonstrated by this to remove compounds from fuels with low-nitrogen-concentration they propose it as a previous step before the desulfurization process.[163]

DES with better performances is a matter of concern. So, efforts go in the direction to avoid that kind of DES compounds. On the other hand, although PTSA based DES shows good performance for ODS the reaction mechanism of the above systems is not clear. Therefore, there are a plenty of space to explore other similar potential DESs for deep ODS. Regarding N compounds extraction, PTSA based DES has been little studied, but since the HBD plays a vital role in extracting nitrogen compounds, a high-acidity HBD is required to create enough affinity toward basic nitrogen compounds the acidity should also be appropriate to avoid unnecessary chemical reactions.

DES on metal recovery

World demand for metals is continuously increasing, with a high increment on electronic devices and electric vehicles applications for example in Li-ion batteries (LIBs), meanwhile society faces metal-finite resources. Due that, the develop environmentally friendly recycling technologies[181] strategies to recover metals from "postconsumer" scrap.[182]

PTSA based DES that solubilize metals include ChCl but also PEGs as HBA components. The efficiency of the solubilization process is typically measured on its leaching efficiency, which represents the mass or mole fraction of metals dissolved from battery materials. Table 7 summarizes the PTSA based DES used for this application. Four main applications are summarized: purification of metals, recovery of spent catalysis, improving the nuclear industry processes, and recovery of cathode materials.

The purification of lithium and cobalt was investigated using a DES mixture of PTSA : ChCl : H_2O, entry 7.6, in various molar ratios (1 : 1 : 1, 1 : 1 : 2, and 1 : 1 : 3), achieving lithium leaching efficiencies of 85–100% and cobalt leaching efficiencies of 88–100%. The 1 : 1 : 2 mixture yielded the highest recovery for both metals under mild leaching conditions (90 °C, 15 min, and concentrations of 63, 60, and 56 g L^{-1}). PEG200 system have also been studied, entry 7.5, in two ratios (4 : 1 and 1 : 1), which achieved lithium leaching efficiencies of 49.8–61.6% and cobalt

Table 7 PTSA based DES for metal solubilization

Entry	HBA	HBD	H_2O	Application	Ref.
7.1	ChCl	—	2	Leaching valuable metals in ternary LIBs cathode	155
7.2	ChCl	—	1,2,3	$LiCoO_2$ dissolution	156
7.3	ChCl	—	1	Metal oxide solubilization	45
7.4	TBAC			Metal oxide solubilization	
7.5	TBPCl			Metal oxide solubilization	
7.6	ChCl	H_2O		$LiCoO_2$ dissolution	157
7.7	PEG2000	—	1		
7.8	PEG400	—	—	Leaching spent Co–Mo catalyst	159
7.9	ChCl	—	—		
7.10	PEG400	—	—	Nickel leaching from hydroprocessing catalysts	158
7.11	ChCl	EG	—		
7.12	ChCl	—	1	Uranium oxides solution	152
7.13	ChCl	—	1	Leaching of oxidized stainless steel 304 specimens	157
7.14	PEG200	—	1	$LiCoO_2$ dissolution	160
7.15	ChCl	EG	—	Spent $LiNi_xCo_yMn_zO_2$ (NCM)	163
7.16	ChCl	—	1	Decontamination of radioactive solid surfaces	161
7.17	ChCl	—	0/1	Deoxidation of stainless steel 304	162

leaching efficiencies of 37.7–50.5% at 60 °C for 24 h.[183] Various conditions (hydrated, heated, and stirred) on simulant oxidized stainless steel 304 specimens to optimize leaching rates were tested. While all conditions showed satisfactory leaching, hydrated and stirred ChCl : PTSA at 60 °C yielded the highest leaching rate of 0.1647 mg min^{-1}, entry 7.17. Oxidized specimens with an average mass gain of 1.2 ± 1 mg experienced a mass reduction of 558 ± 22 mg after 26 h, attributed to enhanced physical properties of ChCl : PTSA with hydration. Hydration improved the solubility of metal oxides such as CoO and NiO, although solubility for Cr_2O_3 and Fe_3O_4 declined. Complete removal of the oxide film produced by high-temperature oxidation was achieved with 10 wt% hydrated ChCl : PTSA at 60 °C, stirred at 400 rpm for 26 h, with significant oxide dissolution noted within the first 300 min. While hydration reduced the solubilities of Fe_3O_4 and Cr_2O_3, the leaching performance remained effective as minor dissolution of the base stainless-steel alloy also occurred.[184]

Several approaches to recover metals from spent catalysis by an eco-friendly process using PTSA-based DESs was described. PEG-400 : PTSA, entry 7.10, and ChCl : EG : PTSA DESs, entry 7.11, allow extracting nickel from spent hydroprocessing catalysts, achieving over 90% nickel extraction at 100 °C with a 48 h leaching time. PEG-400 : PTSA, entry 7.8, and ChCl : PTSA, entry 7.9, describes the recovery of cobalt and molybdenum from spent catalysts. Those DES systems achieved high extraction rates, dissolving 93% of cobalt and 87% of molybdenum at 100 °C and 20 g L^{-1} pulp density over 48 h.[185–187]

Uranium is highly significant in the nuclear industry, as its oxides are essential for nuclear reactor fuel fabrication. Uranium oxide dissolution—a critical process for nuclear fuel reprocessing—was studied by examining the solubility of various uranium oxides (UO_3, UO_2, and U_3O_8) in different DES formulations.

These included DESs PTSA : ChCl (1 : 1/1 : 2), entry 7.12. The solubility was measured by mixing an excess of uranium oxide (approximately 0.1 g) with 2 mL of each DES for 24 h at 80 °C, stirring at 700 rpm with a temperature-controlled magnetic stirrer. A sustainable and innovative method based on a DESs-in-CO_2 system to decontaminate radioactive solid waste, entry 7.16, was also described.

DES microemulsions in supercritical carbon dioxide (SC-CO_2) where used. DES at different molar ratios (2 : 1/1 : 1/1 : 2) with nonylphenol polyoxyethylene ether (NP-10), a surfactant with affinity to CO_2, were prepared achieving high solvation properties. Optimal conditions for de decontamination on UO_3-contaminated samples, included a temperature of 60 °C, pressure of 15 MPa, and a cleaning time of 75 min. The DES-in-CO_2 system effectively decontaminated various materials, simulated radionuclides, and even actual radioactive metal wastes, achieving decontamination efficiencies exceeding 95% for radioactive contaminants on solid surfaces.[188,189]

Recovery of 97.96% of Li, 99.46% of Ni, 100% of Co, and 100% of Mn from ternary LIBs cathode materials was studied using a DES consisting of ChCl and PTSA·$2H_2O$, entry 7.7.[190] Similarly, entry 7.4, describes the recovery of Co and Li yielded Co recovery efficiencies up to 94%. When the PTSA : ChCl : H_2O molar ratio was adjusted to 1 : 1 : 2, Co and Li leaching efficiencies approached 100%.

These findings indicate that modifying DES component ratios is a simple yet effective approach to enhance the metal leaching capabilities of DESs.[191] The effect of the DES composition and HBD : HBA molar ratio (2 : 1, 1 : 1, and 1 : 2) was also studied. The solubilities of metal oxides in PTSA : ChCl (1 : 2) were found to be higher than in any of the previously reported DESs, showing that the adaptation of HBA and HBD molar ratios can optimize leaching from different materials.[47] A DES composed of PEG200 and PTSA allow achieving nearly 100% leaching efficiency of lithium cobalt oxide (LCO) at 100 °C within 24 h, entry 7.14.[192] The ChCl–EG–PTSA DES, entry 7.15, showed a strong leaching capabilities and low viscosity, which facilitates the recovery of Li, Ni, Co, and Mn from NMC cathode material.[187]

Anyway, the current DESs systems for recycling waste LIBs is considered to be in the initial stage, and researchers still need to explore better application strategies to establish the DESs system for recycling waste LIBs that is both efficient, green, economic and sustainable.[183]

Abbott *et al.* already demonstrated in 2005 that DESs can dissolve metal oxides through proton attack and exhibit selective leaching by forming specific metal complexes. However, their solubility in each BADES is remarkably different.[45] In 2006, the solubility of different metal oxides using different HBDs (urea, polyols and acids) and ChCl as HBA was studied.[44] Results showed that generally acidic DES provides the higher solubility although metal oxides with a high ionic nature were highly soluble while more covalent oxides exhibit negligible solubility. Among various DESs, ChCl : PTSA showed superior metal oxide solubility due to its optimal acidity, low viscosity, and broad thermal stability. The HBD : HBA molar ratio also significantly influences solubility, with different metal oxides favouring different acidity levels. A higher HBA concentration could lead to higher solubilities for most metal oxides (including the metal oxides of Mn, Cu, Co, In and Pb), while the metal oxides of Fe and Zn showed higher solubilities in the more acidic DES with higher HBD concentration. Although research efforts are still required to further understand the mechanism behind, which should be related to both chemical and physical effects, it could be expected that selective metal recovery from complex matrices by DESs could be achievable *via* the HBA and HBD molar ratios.[182]

As it is described that the reducibility/oxidizability of the DES is also known to control the dissolving capacity of DESs for metals,[193] all together with the presence of other reducing agents such as Al or Cu could accelerate the leaching process,[194] one interesting future study may be directed to the leaching processes of 3DES using PTSA and reducing/oxidizing agents.

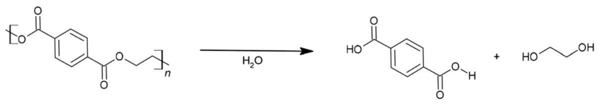
Other applications with PTSA based DES

PTSA based DES have been also used in applications such as different as CO_2 capture, chemical degradation of plastics or material synthesis. Efficient CO_2 capture is crucial for addressing global warming, a topic of significant global interest. Qin *et al.* (2021) investigated the use of DESs prepared from Im and PTSA for CO_2 absorption. They measured CO_2 solubility in [3-Im : PTSA], [3.5-Im : PTSA], and [4-Im : PTSA] across temperatures from 30.15 to 60.15 °C and pressures from 110 to 1500 kPa. The CO_2 absorption capacity showed a slight increase as the Im molar ratio shifted from 3 : 1 to 4 : 1. Additionally, higher temperatures and lower pressures enhanced CO_2 absorption efficiency was described.[195]

Other application of DES on the waste accumulation reduction is on the PET degradation. A $FeCl_3\cdot6H_2O$: PTSA was described. $FeCl_3\cdot6H_2O$ has been chosen as Lewis's acid, because of the low price and scarce toxicity of iron. Although in 1 : 1 molar ratio this DES is kinetically unstable and turns into a heterogeneous system within some hours (>12 h). It was described to promote a 100% conversion and 56.1% yield of terephthalic acid (TA) in half an hour, Scheme 5. The system $FeCl_3\cdot6H_2O$/MSA (methanesulfonic acid) 1 : 1 M ratio, had superior performance than system with PTSA, in terms of both PET conversion and yield of isolated TA. The suggested mechanism for PET depolymerization is the double activation of the ester group, with the metal that coordinates to the carbonyl moiety and the acid that protonates the alkyl oxygen, sensibly increasing the carbon electrophilicity. The method resulted robust in the treatment of different PET sources (textile, thicker bottles for carbonated drinks or milk, colourless and coloured…) under the same experimental conditions and with the same final TA purity.[196]

Zirconium-based metal–organic frameworks (MOFs) have attracted extensive attention owing to their robust stability and facile functionalization. MOFs with organic inorganic hybrid compositions, high surface areas, and versatile porous structures have gained extensive attention in gas adsorption and storage,[83,197] separation,[198] drug delivery,[199] and catalysis.[200] Particularly, they possess steric characters of active metal sites and adjustable pore sizes, facilitating accessibility and transport of catalytic substrates and products.[201,202]

Two (DESs) using 2-MIm and PTSA to produce MOF (UiO-66) nanoparticles have been described. Depending on the ratio of both reagents, the resulting DES has basic properties [3-MIm : PTSA] or acidic properties [MIm : 2PTSA]. These solvents were used to dissolve the ligand (terephthalic acid) and the metal precursor ($ZrOCl_2$), respectively. The two solutions were mixed and stirred at 50 °C for 2 h. The resulting precipitate was collected by centrifugation, washed by de-ionized water and dried under vacuum. The tuned acid-based DESs accelerated the formation of zirconium-based MOF and high yield of MOF was obtained in a short reaction time in comparison with conventional solvothermal method. Moreover, non-aggressive additives were used. Thus, UiO-66 was quickly assembled with small particle sizes and used as an excellent catalyst for the acetalization of benzaldehyde and methanol.[203]



Scheme 5 Hydrolysis of PET to terephthalic acid.

Conclusions

PTSA-based deep eutectic solvents (DESs), a subclass of acidic DESs known as ADES, are emerging as highly versatile and tuneable solvents with promising potential across numerous fields. These solvents are prepared through simple and feasible methods by combining PTSA as HBD with a variety of HBAs in different molar ratios. This compositional flexibility allows for precise tailoring of DES properties to suit specific applications, making them attractive in chemical synthesis, biomass processing, metal recovery, and environmental remediation.

ChCl is one of the most used HBAs, particularly effective in the treatment of biomass. However, other HBAs such as polyethylene glycols (PEGs), Im, and various ammonium salts are also employed depending on the desired function. For instance, PEG-based DESs are often used for oil cleaning and metal extraction, while DESs with imidazole are mainly applied in organic synthesis, particularly for processes like esterification. These combinations enhance DES performance by reducing toxicity, increasing biocompatibility, or improving solubility and catalytic behaviour.

PTSA-based DESs have demonstrated the ability to catalyse and promote a wide range of organic reactions, often eliminating the need for traditional catalysts. Their high polarity and strong hydrogen-bond donating capability enable efficient proton transfer, activating substrates that are typically inert in conventional solvents. Moreover, PTSA-based DESs have shown superior solubilization and selectivity compared to other Brønsted acid DESs, making them particularly effective for challenging processes such as biomass fractionation, natural product extraction, crude oil and biogas desulfurization, and metal leaching.

Despite the promising applications of PTSA-based DESs across biomass processing, metal recovery, catalysis, and desulfurization, several research gaps still need to be addressed to enable their broader and more sustainable industrial use.

One key gap is the limited understanding of the molecular mechanisms governing their performance. While acidity and hydrogen bonding are known to influence solubility and reactivity, the precise interactions between PTSA and various hydrogen bond acceptors (HBAs) remain poorly characterized. Additionally, the corrosive nature of strongly acidic PTSA-based DESs can damage metal equipment, which poses challenges for long-term and large-scale applications.

Another important concern is the potential toxicity and lack of biodegradability of some DES components, which undermines their reputation as green solvents. Furthermore, most studies focus on idealized lab-scale systems, with little validation in real-world waste streams or under industrial conditions, limiting the practical relevance of current findings. There is also a lack of standardized methods for evaluating and comparing DES properties, making it difficult to assess performance consistently across studies.

Looking ahead, future research should focus on gaining a deeper molecular-level understanding of PTSA-based DES behaviour using computational tools like COSMO-RS and experimental techniques such as spectroscopy. Designing greener and less toxic formulations, will be essential for improving environmental compatibility. Additionally, mitigating corrosiveness, improving recyclability, and enabling process integration are important for industrial scaling.

High-throughput experimentation and AI-driven predictive models could accelerate the discovery of tailored DES systems for specific applications. Moreover, expanding the application scope to include biogas purification, digestate valorisation, CO_2 capture, and reactive separations offers exciting new opportunities. Finally, the development of shared property databases and standardized testing protocols will be crucial to support the rational design and benchmarking of PTSA-based DESs.

In summary, PTSA-based DESs show great potential, but realizing their full capabilities will require a combination of fundamental research, green design principles, and technological integration.

Author contributions

Writing – original draft: Anna Canela-Xandri. Conceptualization and visualization: Oriol Tomàs-Badell. Writing – review & editing: Mercè Balcells and Anna Canela-Xandri.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

We are grateful to Prof. Ramon Canela-Garayoa for his valuable suggestions on this work.

References

1 R. A. Sheldon, *Green Chem.*, 2017, **19**, 18–43.
2 Y. Aryanfar, H. G. Castellanos, K. A. Hammoodi, M. Farifteh, A. Keçebaş, S. M. Ghasemlou, A. Mammadova, E. A. Yengejeh and Z. H. Neghabi, *Environ. Prog. Sustainable Energy*, 2024, **43**, e14483.
3 Z. Ali, J. Ma and R. Sun, *Green Chem.*, 2024, **26**, 11061–11082.
4 C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl and J. P. Hallett, *Chem. Rev.*, 2018, **118**, 747–800.
5 C.-J. Li and B. M. Trost, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 13197–13202.
6 C. Árvai and L. T. Mika, *Chin. J. Chem.*, 2024, **42**, 406–429.
7 P. Mainkar, A. Ray and S. Chandrasekhar, *ACS Omega*, 2024, **9**, 7271–7276.
8 A. P. Abbott, J. C. Barron, G. Frisch, S. Gurman, K. S. Ryder and A. Fernando Silva, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10224–10231.
9 M. Francisco, A. van den Bruinhorst and M. C. Kroon, *Green Chem.*, 2012, **14**, 2153–2157.
10 X. Li and K. Binnemans, *Chem. Rev.*, 2021, **121**, 4506–4530.
11 D. Procopio, C. Siciliano, S. Trombino, D. E. Dumitrescu, F. Suciu and M. L. Di Gioia, *Org. Biomol. Chem.*, 2022, **20**, 1137–1149.
12 D. Procopio, C. Siciliano, R. De Rose, S. Trombino, R. Cassano and M. L. Di Gioia, *Catalysts*, 2022, **12**, 1480.
13 P. Liu, J.-W. Hao, L.-P. Mo and Z.-H. Zhang, *RSC Adv.*, 2015, **5**, 48675–48704.
14 M. C. Serrano, M. C. Gutiérrez, R. Jiménez, M. L. Ferrer and F. Del Monte, *Chem. Commun.*, 2012, **48**, 579–581.
15 P. Torres, M. Balcells and R. Canela-Garayoa, *ACS Omega*, 2021, **6**, 19392–19399.
16 Z.-H. Zhang, X.-N. Zhang, L.-P. Mo, Y.-X. Li and F.-P. Ma, *Green Chem.*, 2012, **14**, 1502–1506.
17 A. P. Abbott, K. El Ttaib, G. Frisch, K. S. Ryder and D. Weston, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2443–2449.
18 H.-R. Jhong, D. S.-H. Wong, C.-C. Wan, Y.-Y. Wang and T.-C. Wei, *Electrochem. Commun.*, 2009, **11**, 209–211.
19 H. G. Morrison, C. C. Sun and S. Neervannan, *Int. J. Pharm.*, 2009, **378**, 136–139.
20 D. Carriazo, M. C. Serrano, M. C. Gutiérrez, M. L. Ferrer and F. del Monte, *Chem. Soc. Rev.*, 2012, **41**, 4996–5014.
21 A. García, E. Rodríguez-Juan, G. Rodríguez-Gutiérrez, J. J. Rios and J. Fernández-Bolaños, *Food Chem.*, 2016, **197**, 554–561.
22 M. A. Kareem, F. S. Mjalli, M. A. Hashim and I. M. AlNashef, *Fluid Phase Equilib.*, 2012, **314**, 52–59.
23 Y. Wang, Y. Hou, W. Wu, D. Liu, Y. Ji and S. Ren, *Green Chem.*, 2016, **18**, 3089–3097.
24 Q. Zhang, K. De Oliveira Vigier, S. Royer and F. Jérôme, *Chem. Soc. Rev.*, 2012, **41**, 7108–7146.
25 P. Torres, M. Balcells, E. Cequier and R. Canela-Garayoa, *Molecules*, 2020, **25**, 2157.
26 J. L. K. Mamilla, U. Novak, M. Grilc and B. Likozar, *Biomass Bioenergy*, 2019, **120**, 417–425.
27 V. Jančíková and M. Jablonský, *Sustainability*, 2024, **16**(2), 504.
28 Y. T. Tan, A. S. M. Chua and G. C. Ngoh, *Bioresour. Technol.*, 2020, **297**, 122522.
29 X. Guo, H. Zhu, Y. Si, X. Lyu, Y. Cheng, L. Zheng, L. Wang and X. Li, *Ind. Eng. Chem. Res.*, 2022, **61**, 7216–7224.
30 Y. Liu, N. Deak, Z. Wang, H. Yu, L. Hameleers, E. Jurak, P. J. Deuss and K. Barta, *Nat. Commun.*, 2021, **12**, 5424.
31 S. Saragai, S. Kudo, J. Sperry, U. P. M. Ashik, S. Asano and J. Hayashi, *Bioresour. Technol.*, 2022, **344**, 126323.
32 M. Francisco, A. Van Den Bruinhorst and M. C. Kroon, *Angew. Chem., Int. Ed.*, 2013, **52**, 3074–3085.
33 D. O. Abranches and J. A. P. Coutinho, *Annu. Rev. Chem. Biomol. Eng.*, 2023, **14**, 141–163.

34 C. Florindo, F. S. Oliveira, L. P. N. Rebelo, A. M. Fernandes and I. M. Marrucho, *ACS Sustain. Chem. Eng.*, 2014, **2**, 2416–2425.

35 A. Hayyan, M. H. Zainal-Abidin, S. S. S. Putra, Y. M. Alanazi, J. Saleh, M. R. M. Nor, M. A. Hashim and B. Sen Gupta, *Sci. Total Environ.*, 2024, **948**, 174758.

36 M. Hayyan, M. A. Hashim, A. Hayyan, M. A. Al-Saadi, I. M. AlNashef, M. E. S. Mirghani and O. K. Saheed, *Chemosphere*, 2013, **90**, 2193–2195.

37 K. Radošević, M. Cvjetko Bubalo, V. Gaurina Srček, D. Grgas, T. Landeka Dragičević and I. Radojčić Redovniković, *Ecotoxicol. Environ. Saf.*, 2015, **112**, 46–53.

38 B. Tang and K. H. Row, *Monatsh. Chem.*, 2013, **144**, 1427–1454.

39 E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.*, 2014, **114**, 11060–11082.

40 A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2001, 2010–2011.

41 A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142–9147.

42 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71.

43 A. Prabhune and R. Dey, *J. Mol. Liq.*, 2023, **379**, 121676.

44 A. P. Abbott, G. Capper, D. L. Davies, K. J. McKenzie and S. U. Obi, *J. Chem. Eng. Data*, 2006, **51**, 1280–1282.

45 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and P. Shikotra, *Inorg. Chem.*, 2005, **44**, 6497–6499.

46 A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142–9147.

47 N. Rodriguez Rodriguez, L. Machiels and K. Binnemans, *ACS Sustain. Chem. Eng.*, 2019, **7**, 3940–3948.

48 R. M. Coates, *Handbook of Reagents for Organic Synthesis*, 1999, vol. 4.

49 Q. Zhai, F. Long, X. Jiang, C. Hse, J. Jiang and J. Xu, *Ind. Crops Prod.*, 2020, **158**, 113018.

50 I. Juneidi, M. Hayyan and M. A. Hashim, *RSC Adv.*, 2015, **5**, 83636–83647.

51 D. J. C. Constable, C. Jimenez-Gonzalez and R. K. Henderson, *Org. Process Res. Dev.*, 2007, **11**, 133–137.

52 V. B. Saptal, V. Ruta, M. A. Bajada and G. Vilé, *Angew. Chem., Int. Ed.*, 2023, **62**, e202219306.

53 P. T. Anastas and J. C. Warner, *Green chemistry: Theory and Practice*, 2000.

54 L. Maiuolo, B. Russo, V. Algieri, M. Nardi, M. L. Di Gioia, M. A. Tallarida and A. De Nino, *Tetrahedron Lett.*, 2019, **60**, 672–674.

55 F. M. Perna, P. Vitale and V. Capriati, *Curr. Opin. Green Sustainable Chem.*, 2020, **21**, 27–33.

56 A. E. Ünlü, A. Arıkaya and S. Takaç, *Green Process. Synth.*, 2019, **8**, 355–372.

57 M. Ramos-Martín, J. García-Álvarez and A. Presa Soto, *ChemSusChem*, 2025, 2500679.

58 Y.-J. Fan, D. Wang and L. Wang, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2023, **198**, 981–985.

59 D. Dai, L. Wang, Q. Chen and M.-Y. He, *J. Chem. Res.*, 2014, **38**, 183–185.

60 D. Arnodo, E. De Nardo, S. Ghinato, S. Baldino, M. Blangetti and C. Prandi, *ChemSusChem*, 2023, **16**, e202202066.

61 S. Nejrotti, M. Iannicelli, S. S. Jamil, D. Arnodo, M. Blangetti and C. Prandi, *Green Chem.*, 2020, **22**, 110–117.

62 E. Durand, J. Lecomte, B. Baréa, E. Dubreucq, R. Lortie and P. Villeneuve, *Green Chem.*, 2013, **15**, 2275–2282.

63 L. Hao, G. Ding, D. A. Deming and Q. Zhang, *Eur. J. Org. Chem.*, 2019, 7307–7321.

64 B. K. Peters, T. Zhou, J. Rujirawanich, A. Cadu, T. Singh, W. Rabten, S. Kerdphon and P. G. Andersson, *J. Am. Chem. Soc.*, 2014, **136**, 16557–16562.

65 R. Ten Eyck and I. Danishefsky, *J. Org. Chem.*, 1951, **16**, 1683–1689.

66 Z. Chen, B. Zhou, H. Cai, W. Zhu and X. Zou, *Green Chem.*, 2009, **11**, 275–278.

67 L. Ye, Z. Zhao, E. Lei and L. Wang, *Mendeleev Commun.*, 2024, **34**, 709–710.

68 L. Wang, M. Zhou, Q. Chen and M.-Y. He, *J. Chem. Res.*, 2013, **37**, 598–600.

69 A. Gutiérrez-Hernández, A. Richaud, L. Chacón-García, C. J. Cortés-García, F. Méndez and C. A. Contreras-Celedón, *J. Org. Chem.*, 2021, **86**, 223–234.

70 L. Chen, F. Mo, H. Cheng and Z. Qi, *Chem. Lett.*, 2021, **50**, 1194–1197.

71 J. N. Parekh, M. S. Patel, D. D. Chudasama, H. C. Patel, P. G. Sutariya, H. N. Soni, C. V Rajput and K. R. Ram, *Chem.–Asian J.*, 2024, **19**, e202301116.

72 J. Sun, J. Xu, Z. Zeng and W. Xue, *J. Chem. Technol. Biotechnol.*, 2023, **98**, 2812–2822.

73 J. Xu, N. Zhao, Z. Zeng and W. Xue, *Int. J. Chem. Kinet.*, 2024, **56**, 296–309.

74 D. Yin, J. Sun, Y. Liu and J. Li, *CN111269115A*, Shaanxi University of Science & Technology, China, 2020, **https://patents.google.com/patent/CN111269115A/en**.

75 Y. Zhou, H. Qin, H. Cheng, L. Chen, B. Zhang and Z. Qi, *Chin. J. Chem. Eng.*, 2021, **36**, 120–127.

76 Y. Guo, L. Tang, W. Xue and Z. Zeng, *Int. J. Chem. Kinet.*, 2021, **53**, 1241–1252.

77 Z. Li, W. Liu and G. Yang, *Grasas Aceites*, 2022, **73**, e444.

78 L. Tang, Y. Guo, J. Xu, Z. Zeng and W. Xue, *Braz. J. Chem. Eng.*, 2022, **39**, 715–726.

79 M. Sert, *Renewable Energy*, 2020, **153**, 1155–1162.

80 H. Qin, R. Wang, Q. Zeng, H. Cheng, L. Chen and Z. Qi, *Chem. Eng. Process.*, 2020, **157**, 108060.

81 A. Hayyan, M. A. Hashim, M. Hayyan, F. S. Mjalli and I. M. AlNashef, *Ind. Crops Prod.*, 2013, **46**, 392–398.

82 A. Hayyan, M. A. Hashim, M. Hayyan, F. S. Mjalli and I. M. AlNashef, *J. Cleaner Prod.*, 2014, **65**, 246–251.

83 B. Wang, L.-H. Xie, X. Wang, X.-M. Liu, J. Li and J.-R. Li, *Green Energy Environ.*, 2018, **3**, 191–228.

84 R. Wang, H. Qin, J. Wang, H. Cheng, L. Chen and Z. Qi, *Green Energy Environ.*, 2021, **6**, 405–412.

85 D. C. Forbes and K. J. Weaver, *J. Mol. Catal. A: Chem.*, 2004, **214**, 129–132.

86 G. Jyoti, A. Keshav, J. Anandkumar and S. Bhoi, *Int. J. Chem. Kinet.*, 2018, **50**, 370–380.

87 M. B. Taysun, E. Sert and F. S. Atalay, *J. Mol. Liq.*, 2016, **223**, 845–852.

88 M. B. Taysun, E. Sert and F. S. Atalay, *J. Chem. Eng. Data*, 2017, **62**, 1173–1181.

89 V. De Santi, F. Cardellini, L. Brinchi and R. Germani, *Tetrahedron Lett.*, 2012, **53**, 5151–5155.

90 K. Li, W. Xue, Z. Zeng and X. Shi, *Can. J. Chem. Eng.*, 2019, **97**, 1144–1151.

91 H. Qin, Z. Song, Q. Zeng, H. Cheng, L. Chen and Z. Qi, *AIChE J.*, 2019, **65**, 675–683.

92 R. Wang, H. Qin, Z. Song, H. Cheng, L. Chen and Z. Qi, *Chem. Eng. J.*, 2022, **445**, 136664.

93 S. Jiang, Z. Zeng, W. Xue, W. Zhang and Z. Zhou, *Korean J. Chem. Eng.*, 2020, **37**, 1482–1489.

94 H. Li, S. Yu, F. Liu, C. Xie and L. Li, *Catal. Commun.*, 2007, **8**, 1759–1762.

95 N. Calvar, B. González and A. Dominguez, *Chem. Eng. Process.*, 2007, **46**, 1317–1323.

96 Y. Xu, B. Zhu, H. Ge, S. Wang, B. Li and H. Xu, *Int. J. Biol. Macromol.*, 2024, **258**, 129058.

97 A. Gholami, F. Pourfayaz and A. Maleki, *Front. Energy Res.*, 2020, **8**, 144.

98 D. Z. Troter, Z. B. Todorović, D. R. Đokić-Stojanović, O. S. Stamenković and V. B. Veljković, *Renewable Sustainable Energy Rev.*, 2016, **61**, 473–500.

99 V. C. Eze, A. N. Phan and A. P. Harvey, *Fuel*, 2018, **220**, 567–574.

100 M. Balajii and S. Niju, *Renewable Energy*, 2020, **146**, 2255–2269.

101 D. A. Alonso, A. Baeza, R. Chinchilla, G. Guillena, I. M. Pastor and D. J. Ramón, *Eur. J. Org. Chem.*, 2016, 612–632.

102 Y. Alhassan and N. Kumar, *Waste Biomass Valorization*, 2016, **7**, 1055–1065.

103 S. N. Rashid, A. Hayyan and M. A. Hashim, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2017, **210**, 012012.

104 Y. Liu, H. Yan, J. Liu, W. Dong, Z. Cao, X. Hu and Z. Zhou, *Renewable Energy*, 2020, **162**, 1842–1853.

105 C. Shen, X. Wang, Y. Zhu, J. Jiao, S. Bao, P. Kou, H. Pan, Y. Li and Y. Fu, *Ind. Crops Prod.*, 2020, **152**, 112517.

106 A. Hayyan, H. F. Hizaddin, K. M. Abed, F. S. Mjalli, M. A. Hashim, A. Abo-Hamad, J. Saleh, A. S. M. Aljohani, Y. M. Alharbi, F. A. Alhumaydhi, A. A. Ahmad, A. T. H. Yeow, A. K. Aldeehani, F. D. H. Alajmi and I. Al Nashef, *Biomass Convers. Biorefin.*, 2022, **12**, 3725–3735.

107 A. Hayyan, F. L. W. Qing, M. Z. M. Salleh, W. J. Basirun, M. D. Hamid, J. Saleh, A. S. M. Aljohani, F. A. Alhumaydhi, M. Y. Zulkifli, W. Al Abdulmonem, A. T. H. Yeow, M. R. M. Nor, M. A. Hashim and J. N. Al-Sabahi, *Ind. Crops Prod.*, 2023, **195**, 116322.

108 Y. Chen, D. Yu, W. Chen, L. Fu and T. Mu, *Phys. Chem. Chem. Phys.*, 2019, **21**, 2601–2610.

109 T. Long, Y. Deng, S. Gan and J. Chen, *Chin. J. Chem. Eng.*, 2010, **18**, 322–327.

110 M. K. Najaf-Abadi, B. Ghobadian and M. Dehghani-Soufi, *Biomass Convers. Biorefin.*, 2024, **14**, 3117–3134.

111 M. Feng, J. Yan, B. He, X. Chen and J. Sun, *Int. J. Biol. Macromol.*, 2021, **193**, 347–357.

112 D. M. E. Delgadillo, G. A. D. Castro and S. A. Fernandes, *React. Chem. Eng.*, 2024, **9**, 1560–1568.

113 H. Chang, I. Bajaj, G. W. Huber, C. T. Maravelias and J. A. Dumesic, *Green Chem.*, 2020, **22**, 5285–5295.

114 X. Li, P. Jia and T. Wang, *ACS Catal.*, 2016, **6**, 7621–7640.

115 P. Li, C. Yang, D. Yi, S. Li, M. Wang, H. Wang, Y. Jin and W. Wu, *Int. J. Biol. Macromol.*, 2023, **252**, 126271.

116 M. Wang, S. Shi, F. Li, W. Hou, H. Guo, S. Wang, H. Jia and J. Dai, *Chem. Pap.*, 2022, **76**, 5601–5612.

117 S.-L. Cao, W.-M. Gu, W.-D. Ou-Yang, D.-C. Chen, B.-Y. Yang, L.-H. Lai, Y.-D. Wu, Y.-J. Liu, J. Zhu, W.-J. Chen, Z.-Q. Gai, X.-D. Hou, Y.-Z. Ma and Y.-X. An, *Carbohydr. Polym.*, 2019, **213**, 304–310.

118 J. Jiang, N. C. Carrillo-Enríquez, H. Oguzlu, X. Han, R. Bi, M. Song, J. N. Saddler, R.-C. Sun and F. Jiang, *ACS Sustain. Chem. Eng.*, 2020, **8**, 7182–7191.

119 Q.-L. Lu, J. Wu, Y. Li, L. Li and B. Huang, *J. Mater. Sci.*, 2021, **56**, 12212–12223.

120 M. A. Mariño, M. G. Paredes, N. Martinez, D. Millan, R. A. Tapia, D. Ruiz, M. Isaacs and P. Pavez, *Front. Chem.*, 2023, **11**, 1233889.

121 F. Shu, Y. Guo, L. Huang, M. Zhou, G. Zhang, H. Yu, J. Zhang and F. Yang, *Ind. Crops Prod.*, 2022, **177**, 114404.

122 J. A. Sirviö, M. Visanko and H. Liimatainen, *Biomacromolecules*, 2016, **17**, 3025–3032.

123 S. He, F. Shu, X. Liu, K. Yan, S. Lei, Y. Liu, M. Zhou, H. Yu, J. Zhang and F. Yang, *Ind. Crops Prod.*, 2023, **203**, 117200.

124 C. Alvarez-Vasco, R. Ma, M. Quintero, M. Guo, S. Geleynse, K. K. Ramasamy, M. Wolcott and X. Zhang, *Green Chem.*, 2016, **18**, 5133–5141.

125 J. AlYammahi, A. S. Darwish, T. Lemaoui, A. Boublia, Y. Benguerba, I. M. AlNashef and F. Banat, *ACS Omega*, 2023, **8**, 26533–26547.

126 L. Chen, J. Dou, Q. Ma, N. Li, R. Wu, H. Bian, D. J. Yelle, T. Vuorinen, S. Fu, X. Pan and J. Zhu, *Sci. Adv.*, 2024, **3**, e1701735.

127 A. M. da Costa Lopes, J. R. B. Gomes, J. A. P. Coutinho and A. J. D. Silvestre, *Green Chem.*, 2020, **22**, 2474–2487.

128 H. Li, J. Liang, L. Chen, M. Ren and C. Zhou, *Ind. Crops Prod.*, 2023, **192**, 116034.

129 M. M. Abu-Omar, K. Barta, G. T. Beckham, J. S. Luterbacher, J. Ralph, R. Rinaldi, Y. Román-Leshkov, J. S. M. Samec, B. F. Sels and F. Wang, *Energy Environ. Sci.*, 2021, **14**, 262–292.

130 E. Lizundia, M. H. Sipponen, L. G. Greca, M. Balakshin, B. L. Tardy, O. J. Rojas and D. Puglia, *Green Chem.*, 2021, **23**, 6698–6760.

131 J. T. Sutton, K. Rajan, D. P. Harper and S. C. Chmely, *ACS Appl. Mater. Interfaces*, 2018, **10**, 36456–36463.

132 S. Chandna, C. A. Olivares M., E. Baranovskii, G. Engelmann, A. Böker, C. C. Tzschucke and R. Haag, *Angew. Chem., Int. Ed.*, 2024, **63**, e202313945.

133 P. Li, Y. Lu, X. Li, J. Ren, Z. Jiang, B. Jiang and W. Wu, *Polymers*, 2022, **14**, 5100.

134 H. Jin, H. Shi, W. Jia, Y. Sun, X. Sheng, Y. Guo, H. Li and H. Sun, *Int. J. Biol. Macromol.*, 2022, **207**, 531–540.

135 X.-J. Shen, J.-L. Wen, Q.-Q. Mei, X. Chen, D. Sun, T.-Q. Yuan and R.-C. Sun, *Green Chem.*, 2019, **21**, 275–283.

136 Y. Zhu, L. Li, Y. Hou, C. Xu, G. Hu, Y. Man, V. S. Vladimirovich, J. Li and Q. Xiong, *J. Cleaner Prod.*, 2024, **447**, 141652.

137 H. Yu, X. Han, T. Zhang, Y. Peng, H. Chen and J. Pu, *Ind. Crops Prod.*, 2024, **217**, 118839.

138 X. Zhou, T. Huang, J. Liu, H. Gao, H. Bian, R. Wang, C. Huang, J. Sha and H. Dai, *Bioresour. Technol.*, 2021, **320**, 124327.

139 B. Soares, A. M. da Costa Lopes, A. J. D. Silvestre, P. C. Rodrigues Pinto, C. S. R. Freire and J. A. P. Coutinho, *Ind. Crops Prod.*, 2021, **160**, 113128.

140 Q. Xia, L. Zhang, P. Zhan, Z. Tong, Y. Qing, J. He, Z. Wu, H. Wang, L. Shao and N. Liu, *Renewable Energy*, 2024, **225**, 120286.

141 X. Sun, Z. Zhou, D. Tian, J. Zhao, J. Zhang, P. Deng, H. Zou and C. Lu, *Int. J. Biol. Macromol.*, 2023, **234**, 123593.

142 F. Li, W. Lv, D. Huang, C. Zeng and R. Wang, *Molecules*, 2023, **28**, 4088.

143 Y. Mao, A. Gerrow, E. Ray, N. D. Perez, K. Edler, B. Wolf and E. Binner, *Bioresour. Technol.*, 2023, **372**, 128680.

144 J. Cheng, K. Hirth, Q. Ma, J. Zhu, Z. Wang and J. Y. Zhu, *Ind. Eng. Chem. Res.*, 2019, **58**, 7063–7073.

145 Z. Chen, W. A. Jacoby and C. Wan, *Bioresour. Technol.*, 2019, **279**, 281–286.

146 Y. Bai, X.-F. Zhang, Z. Wang, T. Zheng and J. Yao, *Bioresour. Technol.*, 2022, **347**, 126723.

147 W.-X. Li, W.-Z. Xiao, Y.-Q. Yang, Q. Wang, X. Chen, L.-P. Xiao and R.-C. Sun, *Ind. Crops Prod.*, 2021, **170**, 113692.

148 Q. Xia, Y. Liu, J. Meng, W. Cheng, W. Chen, S. Liu, Y. Liu, J. Li and H. Yu, *Green Chem.*, 2018, **20**, 2711–2721.

149 W. M. A. Wan Mahmood, A. Lorwirachsutee, C. Theodoropoulos and M. Gonzalez-Miquel, *ACS Sustain. Chem. Eng.*, 2019, **7**, 5018–5026.

150 Y. Wang, K. H. Kim, K. Jeong, N.-K. Kim and C. G. Yoo, *Curr. Opin. Green Sustainable Chem.*, 2021, **27**, 100396.

151 W. Wang and D.-J. Lee, *Bioresour. Technol.*, 2021, **339**, 125587.

152 S. Liu, Q. Zhang, S. Gou, L. Zhang and Z. Wang, *Carbohydr. Polym.*, 2021, **251**, 117018.

153 E. S. Morais, A. M. Da Costa Lopes, M. G. Freire, C. S. R. Freire and A. J. D. Silvestre, *ChemSusChem*, 2021, **14**, 686–698.

154 G. Zeng, L. Zhang, B. Qi, J. Luo and Y. Wan, *Bioresour. Technol.*, 2023, **380**, 129085.

155 S. Haslinger, M. Hummel, A. Anghelescu-Hakala, M. Määttänen and H. Sixta, *Waste Manage.*, 2019, **97**, 88–96.

156 M. C. Ali, J. Chen, H. Zhang, Z. Li, L. Zhao and H. Qiu, *Talanta*, 2019, **203**, 16–22.

157 L. Yi, X. Wu, S. Ouyang, L. Guo, J. Chen, M. Gauthier and W.-Y. Li, *Arabian J. Chem.*, 2023, **16**, 105341.

158 S. Zargar, J. Jiang, F. Jiang and Q. Tu, *Biotechnol. Biofuels Bioprod.*, 2022, **16**, 68–80.

159 Z.-Y. Yuan and B.-L. Su, *J. Mater. Chem.*, 2006, **16**, 663–677.

160 E. Raymundo-Piñero, M. Cadek and F. Béguin, *Adv. Funct. Mater.*, 2009, **19**, 1032–1039.

161 M. C. Gutiérrez, D. Carriazo, A. Tamayo, R. Jiménez, F. Picó, J. M. Rojo, M. L. Ferrer and F. del Monte, *Chem.–Eur. J.*, 2011, **17**, 10533–10537.

162 Y. Zhang, Y. Meng, L. Ma, H. Ji, X. Lu, Z. Pang and C. Dong, *J. Cleaner Prod.*, 2021, **324**, 129270.

163 A. F. Kamarudin, H. F. Hizaddin, L. El-blidi, E. Ali, M. A. Hashim and M. K. Hadj-Kali, *Molecules*, 2020, **20**(21), 5093.

164 W. Aas, A. Mortier, V. Bowersox, R. Cherian, G. Faluvegi, H. Fagerli, J. Hand, Z. Klimont, C. Galy-Lacaux, C. M. B. Lehmann, C. L. Myhre, G. Myhre, D. Olivié, K. Sato, J. Quaas, P. S. P. Rao, M. Schulz, D. Shindell, R. B. Skeie, A. Stein, T. Takemura, S. Tsyro, R. Vet and X. Xu, *Sci. Rep.*, 2019, **9**, 953.

165 R. Martínez-Palou and R. Luque, *Energy Environ. Sci.*, 2014, **7**, 2414–2447.

166 Z. Yao, H. N. Miras and Y.-F. Song, *Inorg. Chem. Front.*, 2016, **3**, 1007–1013.

167 P. Misra, J. M. Chitanda, A. K. Dalai and J. Adjaye, *Chem. Eng. J.*, 2016, **295**, 109–118.

168 D. Todescato, D. Maass, D. A. Mayer, J. Vladimir Oliveira, D. de Oliveira, S. M. A. G. Ulson de Souza and A. A. Ulson de Souza, *Appl. Biochem. Biotechnol.*, 2017, **183**, 1375–1389.

169 C. Li, D. Li, S. Zou, Z. Li, J. Yin, A. Wang, Y. Cui, Z. Yao and Q. Zhao, *Green Chem.*, 2013, **15**, 2793–2799.

170 G. Li, C. Yan, B. Cao, J. Jiang, W. Zhao, J. Wang and T. Mu, *Green Chem.*, 2016, **18**, 2522–2527.

171 J. Yin, J. Wang, Z. Li, D. Li, G. Yang, Y. Cui, A. Wang and C. Li, *Green Chem.*, 2015, **17**, 4552–4559.

172 W. Jiang, K. Zhu, H. Li, L. Zhu, M. Hua, J. Xiao, C. Wang, Z. Yang, G. Chen, W. Zhu, H. Li and S. Dai, *Chem. Eng. J.*, 2020, **394**, 124831.

173 W. Jiang, H. Jia, H. Li, L. Zhu, R. Tao, W. Zhu, H. Li and S. Dai, *Green Chem.*, 2019, **21**, 3074–3080.

174 Z. Li, D. Liu, Z. Men, L. Song, Y. Lv, P. Wu, B. Lou, Y. Zhang, N. Shi and Q. Chen, *Green Chem.*, 2018, **20**, 3112–3120.

175 L. Hao, M. Wang, W. Shan, C. Deng, W. Ren, Z. Shi and H. Lü, *J. Hazard. Mater.*, 2017, **339**, 216–222.

176 D. Hao, L. Hao, C. Deng, W. Ren, C. Guo and H. Lü, *Chem. Eng. Technol.*, 2019, **42**, 1276–1282.

177 D. Jin, G. Yu, X. Li, T. Li, F. Zhang, S. Tian, Z. Zhou and Z. Ren, *Fuel*, 2022, **329**, 125513.

178 L. Sun, T. Su, J. Xu, D. Hao, W. Liao, Y. Zhao, W. Ren, C. Deng and H. Lü, *Green Chem.*, 2019, **21**, 2629–2634.

179 G. Yu, D. Jin, F. Zhang, Q. Li, Z. Zhou and Z. Ren, *Fuel*, 2022, **329**, 125495.

180 M. Mofidi and S. Shahhosseini, *Chem. Eng. Process.*, 2022, **171**, 108724.

181 R. Nithya, C. Sivasankari and A. Thirunavukkarasu, *Environ. Chem. Lett.*, 2021, **19**, 1347–1368.

182 Z. Yuan, H. Liu, W. F. Yong, Q. She and J. Esteban, *Green Chem.*, 2022, **24**, 1895–1929.

183 Y. Li, M. Sun, Y. Cao, K. Yu, Z. Fan and Y. Cao, *ChemSusChem*, 2024, **17**, e202301953.

184 N. Kim, W. Yang, J. Amphlett, D. Kang, Y. Lee, J. J. Kim, H. J. Ryu and S. Choi, *J. Hazard. Mater.*, 2022, **425**, 128000.

185 E. Ebrahimi, H. Safari, M. Rezaee, A. Rezaei and H. Abdollahi, *Environ. Sci. Pollut. Res.*, 2023, **30**, 90243–90255.

186 E. Ebrahimi, H. Abdollahi, S. Ziaedin Shafaei, M. Ghanbarzad and E. Talebi, *Sep. Purif. Technol.*, 2023, **313**, 123461.

187 E. Ebrahimi, M. Kordloo, G. Khodadadmahmoudi, A. Rezaei, M. Ganjali and G. Azimi, *Hydrometallurgy*, 2023, **222**, 106184.

188 R. Gupta, J. Gamare, S. K. Gupta and S. S. Kumar, *J. Mol. Struct.*, 2020, **1215**, 128266.

189 H. Lv, J. Gao, J. Chen, T. Li, Y. Liang, B. Hu, F. Ma, Y. Xue, Y. Yan and E. Osei Tutu, *Chem. Eng. J.*, 2024, **490**, 151793.

190 T. He, J. Dai, Y. Dong, F. Zhu, C. Wang, A. Zhen and Y. Cai, *Ionics*, 2023, **29**, 1721–1729.

191 M. J. Roldán-Ruiz, M. L. Ferrer, M. C. Gutiérrez and F. del Monte, *ACS Sustain. Chem. Eng.*, 2020, **8**, 5437–5445.

192 Y. Chen, Y. Wang, Y. Bai, Y. Duan, B. Zhang, C. Liu, X. Sun, M. Feng and T. Mu, *ACS Sustain. Chem. Eng.*, 2021, **9**, 12940–12948.

193 S. Wang, Z. Zhang, Z. Lu and Z. Xu, *Green Chem.*, 2020, **22**, 4473–4482.

194 N. Peeters, K. Binnemans and S. Riaño, *Green Chem.*, 2020, **22**, 4210–4221.

195 H. Qin, Z. Song, H. Cheng, L. Deng and Z. Qi, *J. Mol. Liq.*, 2021, **326**, 115292.

196 M. Rollo, F. Raffi, E. Rossi, M. Tiecco, E. Martinelli and G. Ciancaleoni, *Chem. Eng. J.*, 2023, **456**, 141092.

197 J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670–4679.

198 G. González-Rodríguez, I. Taima-Mancera, A. B. Lago, J. H. Ayala, J. Pasán and V. Pino, *Molecules*, 2019, **24**, 3656.

199 J. Zhuang, C.-H. Kuo, L.-Y. Chou, D.-Y. Liu, E. Weerapana and C.-K. Tsung, *ACS Nano*, 2014, **8**, 2812–2819.

200 A. H. Vahabi, F. Norouzi, E. Sheibani and M. Rahimi-Nasrabadi, *Coord. Chem. Rev.*, 2021, **445**, 214050.

201 Z. Liang, C. Qu, D. Xia, R. Zou and Q. Xu, *Angew. Chem., Int. Ed.*, 2018, **57**, 9604–9633.

202 S. Yuan, L. Feng, K. Wang, J. Pang, M. Bosch, C. Lollar, Y. Sun, J. Qin, X. Yang, P. Zhang, Q. Wang, L. Zou, Y. Zhang, L. Zhang, Y. Fang, J. Li and H.-C. Zhou, *Adv. Mater.*, 2018, **30**, 1704303.

203 L. Chen, X. Ye, T. Zhang, H. Qin, H. Cheng and Z. Qi, *Molecules*, 2022, **27**, 7246.