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## Polymeric ionic liquids for CO<sub>2</sub> capture and separation: potential, progress and challenges

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The increasing level of carbon dioxide (CO<sub>2</sub>) in the atmosphere is a big threat to the environment and plays a key role towards global warming and climate change. In this context to combat such issues, polymeric ionic liquids (PILs) serve as potential substitutes that offer an extremely versatile and tunable platform to fabricate a wide variety of sorbents for CO<sub>2</sub> capture, in particular, for flue gas separation (CO<sub>2</sub>/N<sub>2</sub>) and natural gas purification (CO<sub>2</sub>/CH<sub>4</sub>). Formerly, there have been several reports on exploitation of ionic liquids for CO<sub>2</sub> sorption with promising results. However, just a few have focused on polymeric ionic liquids which significantly over-performed the sorption efficiency of the molecular ionic liquids. This review is first ever of its kind which showcases the potential of PILs as a new member of the CO<sub>2</sub> adsorbent family. The most dynamic aspect of PILs research at present is the curiosity to explore their potential as solid sorbents for CO<sub>2</sub> capture and separation. This review not only highlights the recent advances in the area of PILs as sorbents for CO<sub>2</sub> uptake but also portrays the forthcoming challenges in improving their efficiency. The effect of various cations, anions, polymer backbones, alkyl substituents, porosity, cross-linking, molecular weight and moisture on the CO<sub>2</sub> sorption capacity and separating efficiency is scrutinized in detail. Moreover, future strategies to increase the CO<sub>2</sub> capture performance of PILs are also discussed.

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## Introduction

Climate change owing to escalating carbon dioxide (CO<sub>2</sub>) concentration and renewable energy are indeed issues of foremost importance.<sup>1,2</sup> From the environmental perspective, it is vital to mitigate anthropogenic CO<sub>2</sub> emissions emanating from the burning of fossil fuels, which is the world's primary energy source at present.<sup>3</sup> While the chief concern in energy sector is the purification of natural gas which predominantly comprises of methane (CH<sub>4</sub>) along with other non-hydrocarbon contaminants like CO<sub>2</sub>, nitrogen (N<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and helium (He). These impurities ought to be removed prior to use as fuel thus augmenting the calorific value of natural gas and preventing pipeline and equipment corrosion. Utilization of CH<sub>4</sub> is not only limited as clean fuel, rather it is also exploited as a key source of hydrocarbons for petrochemical

feed stocks as well as in the production of syngas and high purity hydrogen.<sup>4</sup> Keeping in view the role of CO<sub>2</sub> in causing greenhouse gas (GHG) emissions and as a principal contaminant found in natural gas, technologies for carbon capture from energy sources and CO<sub>2</sub> removal from natural gas needs special attention. Carbon capture and storage (CCS) is an imperative approach appealing the environmentalists at present. Basically, CCS accounts for reducing CO<sub>2</sub> levels in the atmosphere owing to anthropogenic activities. Nature has its own mode of capturing CO<sub>2</sub> using trees, resulting in its biological fixation. Though experts are more curious in developing novel non-biological processes to capture CO<sub>2</sub> from large point sources, several viable CO<sub>2</sub> capture and separation options entail different processes<sup>3</sup> like pre-combustion capture that involves the removal of CO<sub>2</sub> from fuel prior to combustion. Fuel is reacted with oxygen or air at high pressure and temperature resulting in the production of syn gas consisting of carbon monoxide (CO), hydrogen (H<sub>2</sub>) and carbon dioxide. Reaction of this gas stream containing CO with steam in a catalytic reactor, called a shift converter, produces a mixture of CO<sub>2</sub> and H<sub>2</sub> gases from which H<sub>2</sub> is separated; oxy-fuel or oxy-firing combustion involves the combustion of fuel in the presence of pure oxygen instead of air producing a CO<sub>2</sub>/H<sub>2</sub>O mixture. Flue gas with high concentration of CO<sub>2</sub> is produced as a consequence of this process because of the absence of nitrogen. Subsequently, the water vapors are removed by cooling

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and compression of gas stream; post-combustion capture requires the removal of CO<sub>2</sub> from the flue gas after combustion and before release into the atmosphere. Low CO<sub>2</sub> concentration and high energy for regeneration are among the most significant challenges associated with this process. So far, this strategy has been extensively used for CO<sub>2</sub> capture (Fig. 1) and typically accounts for CO<sub>2</sub>/N<sub>2</sub> separation. Researchers in this domain usually employ various technologies to separate CO<sub>2</sub> from gas streams such as solvent absorption, membrane separation, cryogenic fractionation, chemical looping and physical adsorption (Fig. 2).<sup>5</sup> Solvent absorption entails the use of liquid amine solutions for CO<sub>2</sub> sorption from flue gas and consequently the CO<sub>2</sub> free flue gas is released into the atmosphere. Afterwards, the CO<sub>2</sub> is removed from the liquid and compressed for storage. Membrane technology makes use of preferential separation of the molecules from the mixture and can be used to sieve out CO<sub>2</sub> from the flue gas, however, this process has not yet been employed at the commercial scale. The cryogenic technique utilizes low temperatures to cool, condense and purify CO<sub>2</sub> from flue gas, and can only be applied to reasonably concentrated CO<sub>2</sub> streams. Chemical looping involves the removal of O<sub>2</sub> from air by treating with metal particles yielding metal oxides. The combustion of fuel in the presence of metal oxides produces CO<sub>2</sub> and water. Nevertheless, chemical absorption of CO<sub>2</sub> with alkanolamine solutions is the most extensively used benchmark technology in industry. Owing to volatility and corrosive nature of amines coupled with shortcomings like high energy requirement for regeneration make this process unattractive thus fostering efficient alternative routes.<sup>6</sup> One viable strategy to combat such problems is physical adsorption that exploits solid materials for adsorption of CO<sub>2</sub> from the flue gas. CO<sub>2</sub> free gas stream is then emitted to the atmosphere and subsequently a solid

sorbent is regenerated using pressure swing adsorption (PSA) or temperature swing adsorption (TSA) processes and CO<sub>2</sub> is removed. The key controlling factors in this respect are temperature, partial pressure, surface force and adsorbent pore size.<sup>5</sup> Many efforts are ongoing to design smart and versatile solid sorbents with high surface area, high porosity, low density, high thermal and chemical stability combined with high CO<sub>2</sub> capacity for energy efficient CO<sub>2</sub> separation processes.<sup>5</sup> The pore structure of porous adsorbents is the governing factor for CO<sub>2</sub> capture at a low partial pressure whereas at high pressures, surface area and specific pore volume are more influential. Materials typically known in this field include silica, activated carbons, zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic polymers (POPs), polymers of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), hypercrosslinked polymers (HCPs), porous aromatic frameworks (PAFs) and others.<sup>5,7-16</sup> Besides adsorption efficiency, CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities are also very imperative and are often related to the presence of highly polar functional groups.<sup>17</sup> To curtail CO<sub>2</sub> emissions to the atmosphere, many endeavors have already been carried out with a great degree of success but there are many issues that still need to be addressed. Although several challenges enclosing CO<sub>2</sub> capture, and the different political, regulatory and economic drivers will eventually declare the time-to-deployment for new CCS systems, now is the suitable time for the scientific community to play a crucial role in resolving the challenge of CO<sub>2</sub> capture.

Interestingly, ionic liquids (ILs) broadly known as “green solvents” have recently been noticed for their outstanding physicochemical properties and applications specifically in CO<sub>2</sub> capture and separation.<sup>18-24</sup> It is worth mentioning here that ILs possess significant CO<sub>2</sub> solubility and selectivity over



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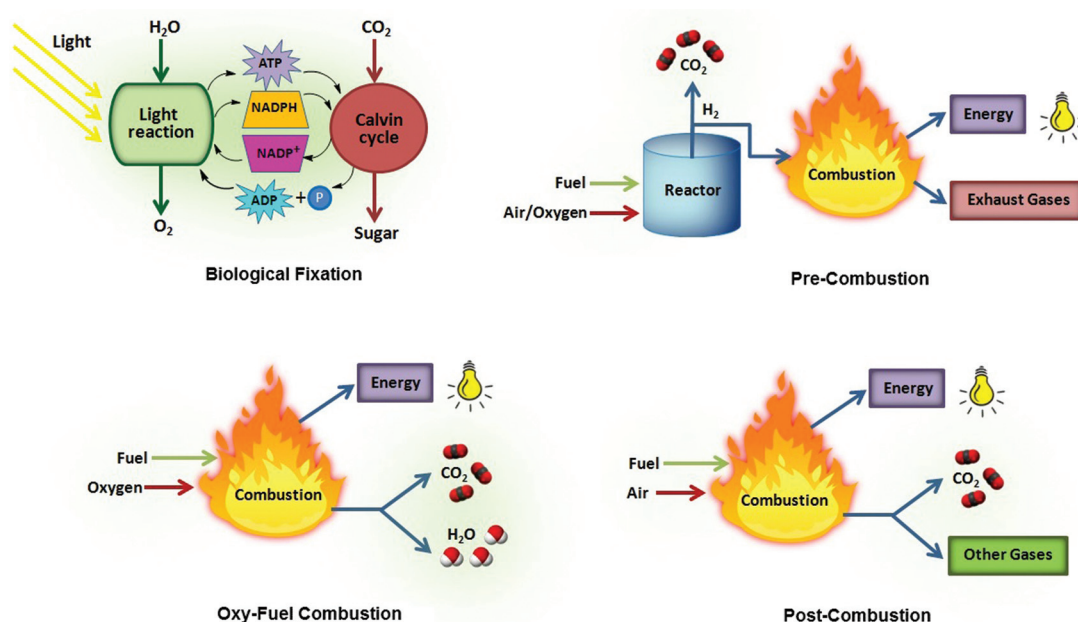


Fig. 1 Illustration of various CO<sub>2</sub> capture processes.

other light gases and also exhibit strong CO<sub>2</sub> affinity that stems from varying cations and anions or by adding functional groups.<sup>20,25–28</sup> Moreover, task-specific ionic liquids having amine moieties have been exclusively designed for improved CO<sub>2</sub> capture.<sup>23</sup> Hence, it has been deduced that anions of the conventional ILs have a substantial impact on CO<sub>2</sub> solubility than the cations.<sup>29–32</sup> Such findings about ILs urge to polymerize IL monomers and constitute a new family of functional polymers generally known as polymeric ionic liquids or poly(ionic liquid)s (PILs) possessing unique characteristics of ILs and a macromolecular framework.<sup>33–35</sup> PILs are a kind of polyelectrolytes bearing IL species in the form of cations or anions,

in monomers attached to the polymeric chain yielding a giant molecular design. The small IL molecules are liquid at room temperature owing to the weak intermolecular forces, while PILs are macromolecules with strong intermolecular forces between the chains and hence are solids demonstrating appreciably higher CO<sub>2</sub> sorption than the corresponding ionic liquids. PILs are usually synthesized from ionic liquid monomers (ILMs) and possess improved processability, enhanced stability, durability, as well as better control over their meso- to nano-structures. Most of the PIL research studies spotlight the incorporation of polymerizable species into IL cations and the extensively studied ones include an acryloyl or a vinyl group. Whereas diversity of anions are available to serve as counterions which are typically introduced by the metathesis reaction of halide ions with a variety of other salts. Polymerization *via* IL anions has been relatively less investigated. The research domain of PILs has progressed incredibly illustrating many synthetic approaches exploited to produce such polymers, their structure–property relationship and relevance as novel promising solutions in the area of electrochemistry, analytical chemistry, biosciences, catalysis, sensors, magnetism, energy, environment, *etc.*<sup>33,34,36–39</sup> Furthermore, the previous investigations envisaged the exploitation of PILs as superior polyelectrolytes, though in a nascent stage, some studies have also been conducted to explore the CO<sub>2</sub> sorption and separation ability of PILs.<sup>33,34</sup> These initial attempts revealed the promise of PILs, nonetheless an extensive research is required to fully understand their potential in this area and more work needs to be done by varying polycation–anion pairs that can control the CO<sub>2</sub> uptake capacity of PILs. These sorbents could be helpful to capture carbon dioxide and facilitate the separation.



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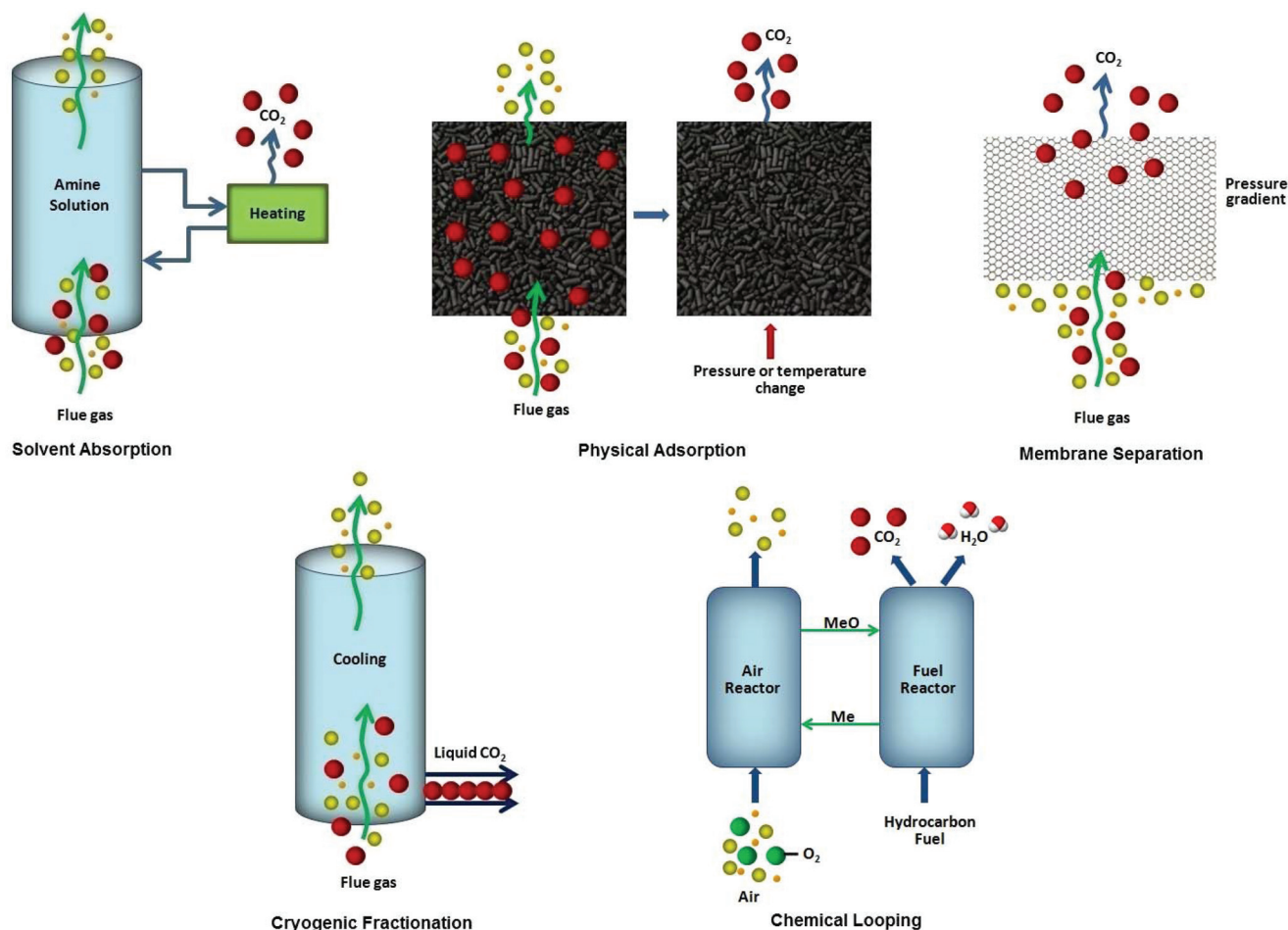


Fig. 2 Overview of various CO<sub>2</sub> capture technologies.

Global climate change mitigation technology based on carbon capture and storage extended from amine-scrubbing to 2<sup>nd</sup> or 3<sup>rd</sup> generation technologies with conceivably superior thermodynamics, such as chemical or carbonate looping. The introduction of porous polymeric sorbents gets optimum benefits of their high surface area and well-developed porosity in many applications. Various functionalities incorporated onto the surface or interior of their polymeric frameworks offer interesting features to the porous polymers, including responding selectively and reversibility. The key parameters for ideal CO<sub>2</sub> uptake are high CO<sub>2</sub> solubility, low energy input for regeneration, low cost, long-term reusability, and being environmentally benign. The current review reveals the potential application of PILs as CO<sub>2</sub> scavengers and describes a green solution to tackle the threatening global environmental issues.

### Factors affecting the PIL performance

Efficient and economical removal of CO<sub>2</sub> from various industrial processes containing light gases (N<sub>2</sub>, CH<sub>4</sub> or H<sub>2</sub>) is very vital and of crucial importance. Ionic liquids offer themselves as better CO<sub>2</sub> sorbents due to their non-volatility, reversibility

and liquid nature. They have extensively been exploited to curb carbon dioxide as green solvent but issues with their long term stability are major hurdles toward successful utilization. To overcome such problems, PILs are being explored as promising alternatives. They are emerging as unique solid members of the adsorbent family that are environmentally friendly and have great potential for CO<sub>2</sub> sorption as compared to ionic liquids.<sup>22,23</sup> Some reports revealed the potential of PILs for CO<sub>2</sub> capture and separation. In the following sections, we analyze the effect of structural variation in PILs on the said phenomena, particularly the choice of cation, anion, backbone, alkyl chain length, porosity and cross-linking are amongst the most noteworthy. The subsequent discussion intends to emphasize on the factors affecting CO<sub>2</sub> capture and separation in this class of sorbents.

### Influence of cations

The choice of cations is of paramount importance in the construction of a PIL skeleton for CO<sub>2</sub> uptake. The type of cation plays a key role in defining the PIL features in contrast to ILs in which anions are more imperative. Curiosity to know the



influence of cations on the CO<sub>2</sub> sorption led to several pioneering studies on imidazolium based **PIL-1** to **PIL-4** synthesized using free radical polymerization of their IL monomers.<sup>40–43</sup> Tang *et al.* have investigated the CO<sub>2</sub> sorption potential of PILs for the first time, namely poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (**PIL-2a**), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (**PIL-2b**) and poly[2-(methacryloyloxy)ethyl-3-butylimidazolium tetrafluoroborate] (**PIL-3**). The CO<sub>2</sub> sorption capacity of room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF<sub>4</sub>] was reported to be 1.30 mol% at 592.3 mmHg CO<sub>2</sub> and 22 °C.<sup>40</sup> While the sorption values for **PIL-2b**, **PIL-2a** and **PIL-3** were found to be 2.8 mol%, 2.27 mol% and 1.78 mol% respectively. In terms of moles, this is around 2.1 (**PIL-2b**), 1.7 (**PIL-2a**), and 1.4 (**PIL-3**) times the capacity of [bmim][BF<sub>4</sub>]. Their IL monomers unexpectedly showed no CO<sub>2</sub> uptake due to the crystalline structures. These PILs reached their 90% sorption capacities in just 3–4 min. Moreover, full CO<sub>2</sub> capacities for these PILs were attained within 30 min relative to RTIL [bmim][BF<sub>4</sub>], that needed above 400 min to reach the equilibrium.<sup>43</sup>

The same group figured out that tetraalkylammonium based PILs exhibited 6.0–7.6 times higher CO<sub>2</sub> sorption capacities<sup>41</sup> and reversible sorption/desorption at faster rates than that of room temperature ILs.<sup>42</sup> Moreover, tetraalkylammonium based PILs with same anions yielded superior CO<sub>2</sub> sorption than the imidazolium-based PILs reported earlier by them.<sup>40,43</sup> The strong interaction of the tetraalkylammonium cation with CO<sub>2</sub> is attributed to its high positive charge density as compared to the imidazolium cation in which the positive charge is delocalized. Various types of PILs, especially, imidazolium and ammonium-based polymers have been extensively synthesized<sup>40–43</sup> and compared for their relative CO<sub>2</sub> uptake. The chemical structures of different imidazolium, ammonium, pyridinium, phosphonium based cationic poly(ionic liquid)s (**PIL-1** to **PIL-16**), anionic poly(ionic liquid)s (**PIL-17**, **PIL-18**), counter cations and anions used for CO<sub>2</sub> sorption are illustrated in Fig. 3. Imidazolium-based polymers exhibited an optimum CO<sub>2</sub> sorption of 3.05 mol% for poly[1-(*p*-vinylbenzyl)-3-methylimidazolium tetrafluoroborate] (**PIL-1**) and 2.8 mol% for poly[1-(*p*-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (**PIL-2b**), whereas ammonium-based PILs displayed a maximum CO<sub>2</sub> uptake of 10.66 mol% for poly[1-(*p*-vinylbenzyl)-trimethylammonium hexafluorophosphate] (**PIL-8b**) and 10.22 mol% for poly[1-(*p*-vinylbenzyl)-trimethylammonium tetrafluoroborate] (**PIL-8a**) respectively.<sup>41–43</sup> These values implied that tetraalkylammonium based PILs rendered higher CO<sub>2</sub> sorption capacities. Additionally, monomers of the above mentioned PILs did not show any CO<sub>2</sub> sorption owing to their crystalline nature.<sup>42</sup> This contrast clearly displays that converting ILs into macromolecules can substantially enhance the CO<sub>2</sub> sorption properties. Moreover, the CO<sub>2</sub> sorption capacities exhibited by these PILs are considerably higher than other polymers such as polystyrenes/polycarbonates, polymethacrylates and polyethylenes.<sup>44–46</sup> The influence of cations can be seen more clearly in the PIL structures having the same

backbone and anion. For instance, poly[2-(methacryloyloxy)ethyltrimethylammonium tetrafluoroborate] (**PIL-11**) and poly[2-(methacryloyloxy)ethyl-3-butylimidazolium tetrafluoroborate] (**PIL-3**) possess the same BF<sub>4</sub> anion and methacrylate backbone but owing to the presence of different cations, *i.e.* ammonium and imidazolium, the former demonstrated higher CO<sub>2</sub> uptake (7.99 mol%) than the latter (1.78 mol%).<sup>42,43</sup> In another study, the same authors established that various types of cations strongly affect the CO<sub>2</sub> sorption and **PIL-1**, poly [1-(*p*-vinylbenzyl)triethylammonium tetrafluoroborate] (**PIL-9a**), poly[1-(*p*-vinylbenzyl)pyridinium tetrafluoroborate] (**PIL-14**), poly[1-(*p*-vinylbenzyl)-triethylphosphonium tetrafluoroborate] (**PIL-15**) with similar structures and the same anions followed the decreasing order: ammonium > pyridinium > phosphonium > imidazolium cations.<sup>47</sup> The CO<sub>2</sub> solubility of ammonium-based PILs is generally higher than that of all the imidazolium- and pyridinium-based PILs, owing to the presence of sp<sup>3</sup> hybridization in the tetraalkylammonium cations that can readily rearrange and become more accessible to CO<sub>2</sub> thus facilitating CO<sub>2</sub> sorption in contrast to other ILs having sp<sup>2</sup> hybridization in the aromatic cation groups. Appropriate changes carried out in the PIL structures and the effects of different functional groups introduced to enhance CO<sub>2</sub> sorption have been scrutinized. In this connection, some studies were focused on ethylene oxide imidazolium, vinylimidazolium, methacrylate imidazolium and ester imidazolium based **PIL-4**, **PIL-5a–f**, **PIL-6a,b** and **PIL-7a–f** to investigate their CO<sub>2</sub> sorption behaviors.<sup>43,48–51</sup> Likewise, other polymers such as vinylbenzyl-tributylammonium, methacrylate dimethylheptylammonium and diallyldimethyl ammonium based **PIL-10**, **PIL-12a–c** and **PIL-13a–j** have also been probed for their CO<sub>2</sub> uptake.<sup>42,52,53</sup>

Instead of using the aforementioned cations, recently Einloft *et al.*<sup>54</sup> adopted two different approaches to fabricate novel polyurethane-based **PIL-16** to **PIL-18**; the first route involved a single step cationic polymer synthesis while the second method produced the anionic polyurethane in two steps (Fig. 3). Imidazolium cations incorporated into the backbone of polyurethane (**PIL-16**) showed lower CO<sub>2</sub> sorption (56.3 mol%) relative to the imidazolium used as a counter-cation in **PIL-17a** (62.3 mol%) at 5 bar. Comparison of **PIL-17a** with **PIL-17b** having counter cations [bmim]<sup>+</sup> and [dmbmim]<sup>+</sup>, respectively, showed that [bmim]<sup>+</sup> exhibited higher CO<sub>2</sub> uptake compared to [dmbmim]<sup>+</sup> due to steric reasons of the branched structure relative to that of the linear one.<sup>54</sup> **PIL-17a** presented a CO<sub>2</sub> sorption of 62.3 mol% and **PIL-18** gave a sorption value of 52.2 mol% implying that introduction of the benzene ring into the polymer chain did not improve appreciably the sorption properties. The aromatic structures are believed to improve the sorption capacity<sup>55,56</sup> but the steric effect is more pronounced making CO<sub>2</sub> interaction difficult with PIL structures at low pressure.

In order to explore the ability of homopolymers/copolymers as CO<sub>2</sub> sensing materials, methacrylate dimethylheptyl ammonium-based **PIL-12a–c** and **coPIL-1a,b** were prepared by a free radical mechanism (Fig. 4).<sup>52</sup> These polymers showed



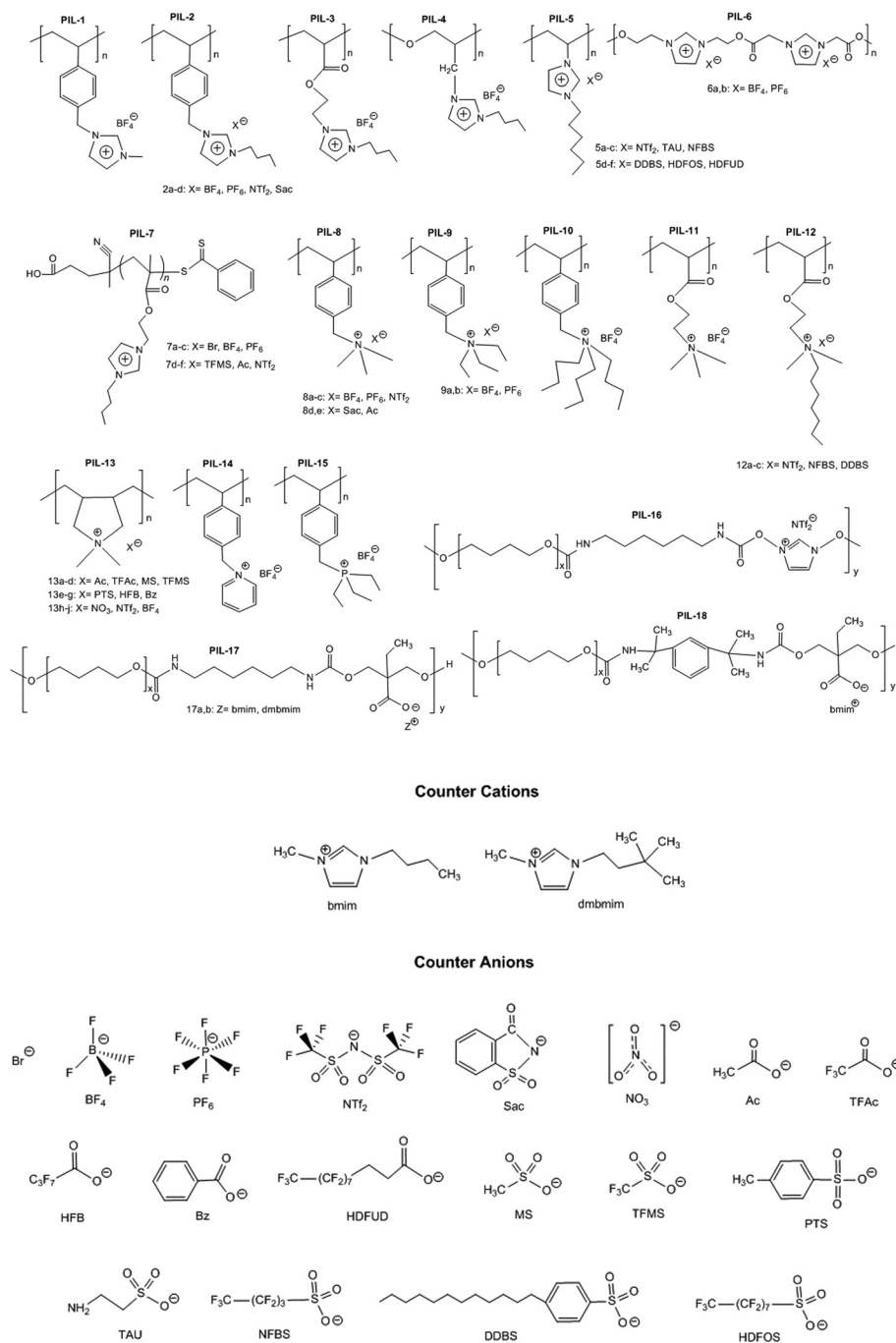


Fig. 3 Chemical structures of various PILs, counter cations and anions used for CO<sub>2</sub> sorption.

significant CO<sub>2</sub>-philicity and potential relevance as sensing materials for CO<sub>2</sub>. Frequency responses were very fast, reversible and no memory-effect provoked. The swiftness of response is a fundamental quality parameter of chemical sensors. Among all the polymers, **PIL-12c** exhibited a response time less than a second that is inadequate for adjusting the N<sub>2</sub> and CO<sub>2</sub> flows. The low cost and easy coating process made these materials as excellent contenders for the development of sensors. To enhance CO<sub>2</sub> uptake, imidazolium and ammonium based co-PILs (**coPIL-2a,b**, **coPIL-3**), crosslinked

PILs (**clPIL-1**, **clPIL-2** and **clPIL-3**) and PIL based nanocomposites (**ncPIL-1a,b**) have also been synthesized.<sup>57-62</sup> Among all the cations, the ammonium cation in simple/porous PILs generally showed better CO<sub>2</sub> sorption than other cations while in cross-linked porous polymers the imidazolium cation gave the highest CO<sub>2</sub> sorption (Table 1).

#### Role of anions

The nature of counter ions influenced the CO<sub>2</sub> sorption of polymers including organic anions such as carboxylates



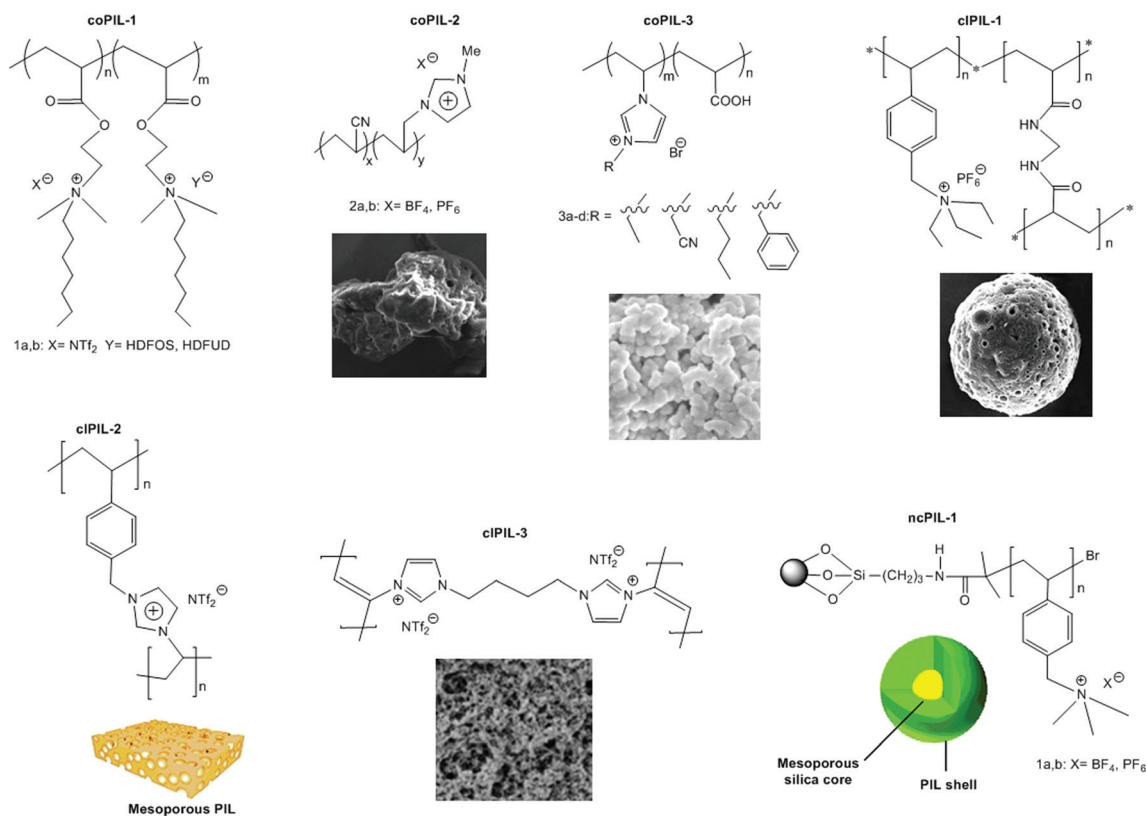


Fig. 4 Chemical structures of co-PILs, crosslinked PILs and PIL based nanocomposites used for CO<sub>2</sub> sorption.

(Ac, TFAc, HFB, Bz, HDFUD), sulfonates (MS, TFMS, PTS, TAU, NFBS, DDBS, HDFOS), imides (NTf<sub>2</sub>, Sac) and inorganic anions (PF<sub>6</sub>, BF<sub>4</sub>, NO<sub>3</sub>, Br). Various anions used in the preparation of PILs for CO<sub>2</sub> uptake are illustrated in Fig. 3. The CO<sub>2</sub> sorption of imidazolium-based PILs with variable anions has been described to be 2.80 mol% for **PIL-2b**, 2.27 mol%, 2.23 mol%, 1.55 mol% for **PIL-2a, c, and d**, 1.78 mol% for **PIL-3** and 1.06 mol% for **PIL-4**, respectively. Higher efficiency was observed in PILs with PF<sub>6</sub> and BF<sub>4</sub> anions than NTf<sub>2</sub> and Sac based polymers. This behaviour is entirely different from smaller IL species and PILs containing inorganic anions gave higher efficiency.<sup>43</sup> To evaluate the effect of changing anion type on CO<sub>2</sub> sorption, five anions with different anionic functional groups (imide, sulfonate, and carboxylate)/fluorination degrees of the alkyl chain were used to make **PIL-5a, c–f** films and were analyzed for their CO<sub>2</sub>-philicity.<sup>49</sup> The results implied outstanding sensitivity towards CO<sub>2</sub> sorption in terms of quickness, reproducibility, and reversibility over the whole concentration range. The performance of **PIL-5e** (sulfonate) was better than **PIL-5f** (carboxylate), although both contain the same polyfluorinated chains but different anion functional groups. On the other hand, nonfluorinated sulfonate **PIL-5d** showed improved CO<sub>2</sub> sensitivity compared to fluorinated sulfonate **PIL-5c**. The effect of anions on uptake of carbon dioxide was further investigated by Xiong *et al.*<sup>50</sup> (**PIL-6a, b**) using two anions (BF<sub>4</sub>, PF<sub>6</sub>) and an imidazolium based polyester pre-

pared through melt condensation polymerization. The CO<sub>2</sub> sorption capacity of **PIL-6a** (4.5 mol%) was higher than **PIL-6b** (4.2 mol%) probably due to the association of CO<sub>2</sub> with the anion.<sup>50</sup>

In previous studies, BF<sub>4</sub> and PF<sub>6</sub> anions were used continuously in the preparation of the PILs while the acetate anion was largely ignored that has proven high efficiency to capture CO<sub>2</sub> in room temperature ILs. Butylimidazolium methacrylate based **PIL-7a–f** have been fabricated including acetate anions along with other counter ions. **PIL-7e** containing acetate as counter ions synthesized for the first time gave CO<sub>2</sub> sorption four-fold higher (12.46 mg g<sub>PIL</sub><sup>-1</sup>) relative to 2.88, 2.99, 3.31, 2.05 and 1.53 mg g<sub>PIL</sub><sup>-1</sup> for **PIL-7a–d, f** respectively (Table 1).<sup>51</sup> Bulky structures of TFMS and NTf<sub>2</sub> anions reduced the free volume hindering CO<sub>2</sub> penetration towards the cation, which is mainly responsible for sorption.<sup>40,42</sup> Exchange of Br in place of NTf<sub>2</sub> can reduce the volume of microvoids in PIL by 37%.<sup>63</sup> The fluorinated organic anions TFMS and NTf<sub>2</sub> lowered the T<sub>g</sub> value of PILs in comparison with inorganic fluorinated phosphates and borates due to the plasticization effect.<sup>40,42</sup> Additionally, a low T<sub>g</sub> was verified for **PIL-7e** with no fluorine atoms. Tang *et al.* reported the CO<sub>2</sub> sorption trend of vinylbenzyl-trimethylammonium based PILs similar to that of imidazolium ones but entirely different from ILs.<sup>42</sup> They studied the effect of four anions (**PIL 8a–d**) with the same cation and CO<sub>2</sub> uptake follows the order PF<sub>6</sub> > BF<sub>4</sub> > NTf<sub>2</sub> > Sac having the





Table 1 CO<sub>2</sub> sorption performance of various types of PILs

PIL	CO <sub>2</sub> loading (mol%)	CO <sub>2</sub> loading (mg g <sup>-1</sup> )	Conditions ( <i>P</i> , <i>T</i> )	Ref.
PIL-1	3.05	4.64	0.78 bar, 295 K	43
PIL-2a	2.27	3.20	0.78 bar, 295 K	43
PIL-2b	2.8	3.16	0.78 bar, 295 K	43
PIL-2c	2.23	1.87	0.78 bar, 295 K	43
PIL-2d	1.55	1.59	0.78 bar, 295 K	43
PIL-3	1.78	2.49	0.78 bar, 295 K	43
PIL-4	1.06	1.72	0.78 bar, 295 K	43
PIL-6a	4.5	4.77	0.86 bar, 298 K	50
PIL-6b	4.2	3.90	0.86 bar, 298 K	50
PIL-7a	—	2.88	1 bar, 298 K	51
PIL-7b	—	2.99	1 bar, 298 K	51
PIL-7c	—	3.31	1 bar, 298 K	51
PIL-7d	—	2.05	1 bar, 298 K	51
PIL-7e	—	12.46	1 bar, 298 K	51
PIL-7f	—	1.53	1 bar, 298 K	51
PIL-8a	10.22	17.09	0.78 bar, 295 K	42
PIL-8b	10.66	14.60	0.78 bar, 295 K	42
PIL-8c	2.85	2.74	0.78 bar, 295 K	42
PIL-8d	2.67	3.27	0.78 bar, 295 K	42
PIL-9a	4.85	6.99	0.78 bar, 295 K	42
PIL-9b	—	10.36	1 bar, 298 K	60
PIL-10	3.1	3.5	0.78 bar, 295 K	42
PIL-11	7.99	14.35	0.78 bar, 295 K	42
PIL-16	56.3	38.86	5 bar, 298 K	54
PIL-17a	62.3	50.52	5 bar, 298 K	54
PIL-17b	66.1	50.96	20 bar, 298 K	54
PIL-18	52.2	37.12	5 bar, 298 K	54
coPIL-2a	—	14.3	1 bar, 273 K	57
coPIL-2b	—	2.2	1 bar, 273 K	57
clPIL-1	—	14.04	1 bar, 298 K	60
PIL	CO <sub>2</sub> loading (mmol g <sup>-1</sup> )	CO <sub>2</sub> loading (mg g <sup>-1</sup> )	Conditions ( <i>P</i> , <i>T</i> )	Ref.
clPIL-2	0.46	20.24	1 bar, 273 K	61
clPIL-3	0.1	4.4	1 bar, 293 K	72
ncPIL-1a	0.4025	17.71	1 bar, 303 K	62
ncPIL-1b	0.3793	16.69	1 bar, 303 K	62

values 10.66, 10.22, 2.85, 2.67 mol% respectively. Unlike ILs, CO<sub>2</sub> uptake by **PIL-8c** with the NTf<sub>2</sub> anion is much lower than **PIL-8a** and **PIL-8b** having BF<sub>4</sub> and PF<sub>6</sub> anions implying the superiority of inorganic anions. Moreover, **PIL-8c** having fluorinated anions possesses CO<sub>2</sub> sorption comparable to **PIL-8d** with Sac as the non-fluorinated anion indicating that the presence of fluorine atoms in the anion doesn't favor CO<sub>2</sub> sorption. Furthermore, the effect of anions on the glass transition temperatures of PILs was established and with the same cation, anions follow the order PF<sub>6</sub> > BF<sub>4</sub> > NTf<sub>2</sub> > Sac (255 °C, 235 °C, 74 °C, 65 °C). **PIL-8c** and **PIL-8d** with NTf<sub>2</sub> and Sac anions significantly reduced the *T<sub>g</sub>* owing to the plasticization of anions. Bhavsar and co-workers used acetate anions with the same vinylbenzyl-trimethylammonium cation (**PIL-8e**) and deduced that the acetate anions would greatly enhance the CO<sub>2</sub> solubility and also possess high selectivity over N<sub>2</sub> as compared with **PIL-8a**<sup>53</sup> owing to the high basicity of acetate anions.<sup>64,65</sup>

Mineo *et al.* studied the dependence of CO<sub>2</sub> uptake by changing various anions. They synthesized **PIL-12a–c** homopolymers based on the 2-(methacryloyloxy)ethyl]dimethylheptylammonium cation and NTf<sub>2</sub>, NFBS, and DDBS anions.<sup>52</sup> **PIL-12b** having the NFBS anion was found to be the best in

terms of sensitivity relative to **PIL-12a** and **PIL-12c**.<sup>52</sup> PILs based on the diallyldimethylammonium cation and different counter ions such as carboxylates (**PIL-13a,b,f,g**), sulfonates (**PIL-13c,d,e**), imide (**PIL-13i**) and inorganic nature (**PIL-13h,j**) were scrutinized.<sup>53</sup> **PIL-13a** with the Ac anion revealed the maximum CO<sub>2</sub> uptake and high selectivity over H<sub>2</sub> and N<sub>2</sub> among all anions studied. Additionally, it was observed that an increase in anion basicity led to enhanced CO<sub>2</sub> uptake similar to ILs.<sup>65</sup> CO<sub>2</sub> uptake of **PIL-13g** and **PIL-13d** with Bz and TFMS anions is superior relative to other polymers<sup>66</sup> such as polysulphone, polyhydroxyether, polyetherimide and polyarylate, signifying the promise of PILs for CO<sub>2</sub> sorption. The selectivity in the case of PILs with sulfonated anions is not significant in contrast to those with carboxylated anions. Some other important factors influencing the CO<sub>2</sub> sorption are fractional free volume (FFV) and molar mass of anion. For instance, **PIL-13h,j** with inorganic anions (NO<sub>3</sub> and BF<sub>4</sub>) displayed increased solubility as well as selectivity with increase in the molar mass of anions.<sup>53</sup> Moreover, the same authors also found that this factor of molar mass is not valid for carboxylated and sulfonated anions and incorporation of the fluorine group into various polymers augments the gas sorption characteristics





because of increase in the free volume. In this context, **PIL-13a,b,c,d** were compared and in the case of carboxylated anions, it was noted that the replacement of just the CH<sub>3</sub> group of Ac with CF<sub>3</sub> in TFAc brought about reduction in CO<sub>2</sub> solubility. It is well recognized that CF<sub>3</sub> is an electron withdrawing group and thus reduces the basicity of anions and ultimately CO<sub>2</sub> solubility. On the contrary, PILs with sulfonated anions showed higher CO<sub>2</sub> solubility in fluorine containing anions. For instance, TFMS possesses 3.8 times higher CO<sub>2</sub> solubility than MS. These results give detailed insight into anion effects and thus are very helpful for further tuning of PIL properties.<sup>53</sup>

High physicochemical stability and surface area, low framework density, tunable porosity and versatile synthetic strategies have developed strong interest in porous polymers as gas sorbents. Porous copolymers derived from methacrylate dimethylheptyl ammonium as the CO<sub>2</sub> sensing material (**coPIL-1a,b**) have been produced as shown in Fig. 4.<sup>52</sup> These PILs were found CO<sub>2</sub>-philic and sensitive to CO<sub>2</sub> sorption. Both the copolymers showed a similar trend as far as the CO<sub>2</sub>-philicity is concerned. **coPIL-1a,b** have anions with same perfluorinated chains and differ for the anionic functional group (carboxylate vs. sulfonate). The gas sensing results displayed that the nature of anionic functionality does not affect CO<sub>2</sub>-philicity. Allylmethylimidazolium and acrylonitrile porous copolymers (**coPIL-2a,b**) were also prepared by the seed swelling method.<sup>57</sup> The CO<sub>2</sub> sorption capacity was dependent on the type of anion used in these polymers. **coPIL-2a** with BF<sub>4</sub> anions gave a higher CO<sub>2</sub> sorption capacity (14.3 mg g<sup>-1</sup>) with a pore-forming agent while **coPIL-2b** with PF<sub>6</sub> anions yielded 2.2 mg g<sup>-1</sup> at 0 °C and 0.101 MPa which is opposite to the trend described in the previous reports.<sup>40,42</sup> The effect of anions was much pronounced in the case of crosslinked PILs and **clPIL-2** with NTf<sub>2</sub> anions resulted in better CO<sub>2</sub> sorption relative to **clPIL-1** with PF<sub>6</sub> anions. Recently, Cheng *et al.* have prepared nanocomposites (**ncPIL-1a,b**) using a mesoporous silica (meso-silica) support by surface-initiated atom-transfer radical polymerization. The sorbents remained porous and possessed reasonably high surface areas after grafting onto the meso-silica. **ncPIL-1a** with BF<sub>4</sub> anions showed higher CO<sub>2</sub> sorption capacity as compared to **ncPIL-1b** with PF<sub>6</sub> anions.<sup>62</sup> The above-mentioned discussion clearly described the superiority of using BF<sub>4</sub> and PF<sub>6</sub> anions in PILs for capturing carbon dioxide whereas, NTf<sub>2</sub> anions in cross-linked PILs performed remarkably well.

### Selection of backbone and alkyl chain substituents

The dependence of CO<sub>2</sub> sorption by changing the backbone of PILs has been investigated by Shen and co-workers.<sup>41–43</sup> **PIL-2a**, **PIL-3** and **PIL-4** serves as a very good example of this effect in which the same butylimidazolium cation and the BF<sub>4</sub> anion was present. The variation of the backbone from polystyrene (PS) to polymethylmethacrylate (PMMA) and then to polyethylene glycol (PEG) was carried out. Interestingly, the results revealed a substantial increase in CO<sub>2</sub> sorption per-

formance in terms of their monomer units for **PIL-2a** with the PS backbone as compared to **PIL-3** with PMMA and **PIL-4** with PEG at 592.3 mmHg of CO<sub>2</sub> and 22 °C. The CO<sub>2</sub> sorption values follow the decreasing order: PS (2.27 mol%) > PMMA (1.78 mol%) > PEG (1.06 mol%) respectively. Incorporation of the PS backbone led to more pronounced sorption owing to its more rigid structure while PMMA appeared moderate and PEG showed the lowest CO<sub>2</sub> uptake.<sup>43</sup> Additionally, the effect of backbone is also evident from the glass transition temperatures (*T<sub>g</sub>*) of PILs. Consequently, **PIL-4** with a more flexible PEG backbone showed lower *T<sub>g</sub>* in contrast to **PIL-3** with PMMA and **PIL-2a** with a rigid PS backbone. The *T<sub>g</sub>* values follow the increasing order as PEG (33 °C) < PMMA (54 °C) < PS (78 °C) correspondingly.<sup>43</sup> Another case study by the same group focused on **PIL-8a** and **PIL-11** having the same ammonium cation and the BF<sub>4</sub> anion. The presence of a PS backbone in **PIL-8a** led to a higher CO<sub>2</sub> sorption capacity<sup>41,67</sup> (10.22 mol%) and higher *T<sub>g</sub>*<sup>42</sup> relative to **PIL-11** (7.99 mol%) owing to the PMMA backbone. Einloft *et al.* also compared the effect of the backbone in **PIL-17a** and **PIL-18** with the same anion and the counter cation.<sup>54</sup> Usually, the presence of aromatic groups in the polymer backbone significantly improves the CO<sub>2</sub> uptake but conversely, at low pressure, **PIL-17a** having an aliphatic backbone demonstrated a higher CO<sub>2</sub> sorption value of 62.3 mol% relative to **PIL-18** (52.2 mol%) with an aromatic backbone. Nonetheless, at higher pressure the CO<sub>2</sub> uptake exhibited by **PIL-18** was comparable to **PIL-17a** suggesting the decrease of the steric effect.<sup>54</sup>

Many attempts have been carried out to study the role of alkyl chain substituents on the CO<sub>2</sub> sorption performance of PILs. Exploitation of oligo(ethylene glycol) or nitrile-containing alkyl groups is believed to enhance CO<sub>2</sub> uptake.<sup>68</sup> Generally, long alkyl substituents attached to cations resulted in reduction of CO<sub>2</sub> uptake in PILs in contrast to ILs in which long alkyl chains promote gas permeability and diffusivity. Low uptake of CO<sub>2</sub> in PILs with increasing alkyl chain lengths may be due to steric hindrance. This effect can be clearly seen in the case of **PIL-1** and **PIL-2a**, both possessing the same imidazolium cation and the same BF<sub>4</sub> anion but different alkyl substituents. The CO<sub>2</sub> sorption capacity of **PIL-1** (3.05 mol%) having smaller methyl substituents is more than **PIL-2a** (2.27 mol%) with longer butyl chains.<sup>43</sup> Furthermore, **PIL-1** with the methyl substituent has a higher *T<sub>g</sub>* (110 °C) as compared to **PIL-2a** with the butyl group (78 °C) due to the loss of plasticization effect of the butyl group on the imidazolium units.<sup>43</sup> In another related work on ammonium based PILs, this effect is much more pronounced. The structures of **PIL-8a**, **PIL-9a** and **PIL-10** serve as very helpful examples in explaining this phenomenon because the three of them possess the same ammonium cation, BF<sub>4</sub> anion and PS backbone and only differ in the alkyl chain length attached to the cation, *i.e.* methyl, ethyl and butyl groups. CO<sub>2</sub> sorption of these PILs follows the decreasing order as **PIL-8a** (10.22 mol%, Me) > **PIL-9a** (4.85 mol%, Et) > **PIL-10** (3.1 mol%, Bu) respectively.<sup>42</sup> Long alkyl substituents attached to cations minimize the CO<sub>2</sub>



uptake owing to the hindrance posed by them in the interaction of cations with CO<sub>2</sub>. A similar trend in  $T_g$ 's of these PILs was also observed following the sequence **PIL-10** (135 °C) < **PIL-9a** (185 °C) < **PIL-8a** (235 °C). Higher  $T_g$  was shown by **PIL-8a** having the methyl substituent while the lowest  $T_g$  was found for **PIL-10** having the butyl chain attached to the cation which resulted in plasticization and a low microvoid volume fraction in the PIL, therefore lowering the CO<sub>2</sub> sorption.<sup>42</sup> In the end, the PS backbone and small alkyl chain substituents were found to be more suitable for optimum CO<sub>2</sub> performance.

### Impact of porosity and crosslinking

Porous sorbents are believed to be versatile materials for CO<sub>2</sub> uptake owing to their unique features such as high surface area, high porosity, low crystal density combined with high thermal and chemical stability. Early kinetic studies indicated that the fast sorption rates of PILs are not dependent on their particle sizes and surface areas.<sup>41</sup> PIL particles with specific areas less than 1 m<sup>2</sup> g<sup>-1</sup> can take up CO<sub>2</sub> as fast as porous **PIL-11** particles with the specific area of 20 m<sup>2</sup> g<sup>-1</sup>. Even **PIL-2c** having larger particles (~500 μm) capture CO<sub>2</sub> quickly. When the BF<sub>4</sub> anion in **PIL-2a** was exchanged with a halide anion, the resulting polymer showed a slower rate of CO<sub>2</sub> sorption even with the same particle sizes. Hence the fast CO<sub>2</sub> sorption is the peculiar feature of PILs. However, these observations contradict the outcome of the latest reports on CO<sub>2</sub> sorption. To enhance CO<sub>2</sub> uptake, porous **coPIL-2a,b** were developed by a two-step swelling method using allylmethylimidazolium and acrylonitrile with a 70:30 monomer ratio (Fig. 4).<sup>57</sup> The results proved that this route was very effective in enhancing CO<sub>2</sub> uptake of **coPIL-2a** to 14.3 mg g<sup>-1</sup> at 0 °C and 0.101 MPa while **coPIL-2b** gave similar CO<sub>2</sub> sorption to the corresponding non-swelling copolymer. Moreover, ammonium-based **PIL-8a** when treated by the same method yielded noticeably smaller CO<sub>2</sub> sorption capacity. The nature of pore-forming agents was also found to affect the porosity of polymers and gave different CO<sub>2</sub> sorption capacities.<sup>58</sup> PILs with a pore size distribution (PSD) in the range of 0.4–0.6 nm and a high cumulative specific surface area revealed ample sorption capacity towards CO<sub>2</sub>. Mesoporous polyampholytes reported by Soll *et al.* through self-complexation of imidazolium cations and the carboxylic acid units of **coPIL-3a–d** led to a network structure upon precipitation in basic organic medium.<sup>59</sup> Interstitial spaces remained open as mesopores of 6–12 nm in diameter and a specific surface area up to 260 m<sup>2</sup> g<sup>-1</sup> was achieved. The CO<sub>2</sub> sorption behaviour of a selected mesoporous polyampholyte was studied through two effective processes: adsorption at the external surface and absorption into the polymer matrix.

Cross-linking also influenced the CO<sub>2</sub> sorption capacity and is generally declined due to the reduced void volume and hindered interaction between CO<sub>2</sub> and the PIL.<sup>42</sup> The CO<sub>2</sub> sorption capacity of **PIL-8a** was decreased by 20%, probably due to the decreased void volume of PIL upon crosslinking. For

improved CO<sub>2</sub> sorption, a cross-linked and porous **clPIL-1** was synthesized using *N,N*-methylenebisacrylamide and vinylbenzyl-triethylammonium by inverse suspension polymerization.<sup>60</sup> **PIL-9b** was also prepared by free radical polymerization to compare the CO<sub>2</sub> uptake of both the polymers. **clPIL-1** rendered a high thermal stability, an average particle size of 16.9 μm, porosity and a specific surface of 64.3% and 39.12 m<sup>2</sup> g<sup>-1</sup>, respectively and a high CO<sub>2</sub> sorption capacity of 14.04 mg g<sup>-1</sup> relative to 10.36 mg g<sup>-1</sup> for **PIL-9b** measured at 0.1 MPa and 25 °C. Under the same conditions, **clPIL-1** gave better sorption efficiency than some other PILs.<sup>40,41,43,58,67,69,70</sup> The recovery and reusability of **clPIL-1** were also evaluated and it can be regenerated with a loss of even <1% CO<sub>2</sub> adsorption capacity after four cycles.<sup>60</sup> Therefore, this study proved that **clPIL-1** is a superior contender for CO<sub>2</sub> sorption. Wilke *et al.* have synthesized a cross-linked imidazolium based **clPIL-2** through a hard-templating of mesoporous silica subsequently yielding mesoporous polymers.<sup>61</sup> The **clPIL-2** captured carbon dioxide at a faster rate than its nonporous counterpart. Several reports indicated that bulk PILs presented rapid and superior CO<sub>2</sub> uptake relative to their ILs. Many porous PILs reported in the literature are macroporous (pore size > 50 nm)<sup>63</sup> but to design mesoporous materials (pore size between 2–50 nm) with a reasonably high surface area is the active area of research at present. Optimum carbon dioxide capture was found with **clPIL-2** (0.46 mmol g<sup>-1</sup>) relative to bulk PILs and monomeric ILs. This sorption occurred with strong interactions giving a high selectivity of ~45 for a 50:50 mixture of CO<sub>2</sub> and N<sub>2</sub> at 273 K and 760 mmHg. The selectivity for a mixture containing 15% CO<sub>2</sub> is even higher (100–200), representing that **clPIL-2** is more appropriate for CO<sub>2</sub> capture.<sup>61</sup> Typically, all samples showed a hysteresis upon desorption; the hysteresis of **clPIL-2** was less pronounced. This hysteresis is either related to kinetic effects, strong binding events, or a mixture of both. The origin of the observed weak hysteresis may be due to CO<sub>2</sub>–PIL interactions. The interaction strength determined from isosteric heat of adsorption ( $q_{st}$ ) was found to be in the range of 40–30 kJ mol<sup>-1</sup>, which is significantly higher than in, for example, activated carbon.<sup>71</sup> The selectivity of **clPIL-2** was even higher, demonstrating that this polymer is a more appropriate material for CO<sub>2</sub> capture. **clPIL-3** gave a maximum CO<sub>2</sub> sorption of 4.4 mg g<sup>-1</sup> which is much lower than **clPIL-1** and **clPIL-2**.<sup>72</sup> Cheng and co-workers prepared vinylbenzyl trimethylammonium based **ncPIL-1a,b** from IL monomers and a mesoporous silica (meso-silica) support by surface-initiated atom-transfer radical polymerization.<sup>62</sup> The sorbents remained porous and possessed reasonably high surface areas after grafting onto the meso-silica. They showed fast and excellent CO<sub>2</sub> sorption capacities, selectivity and reproducibility. **ncPIL-1a** yielded the highest CO<sub>2</sub> sorption of 0.4025 mmol g<sup>-1</sup> at 30 °C, while **ncPIL-1b** gave a maximum CO<sub>2</sub> sorption capacity of 0.3793 mmol g<sup>-1</sup> for a simulated flue gas containing 10 vol% CO<sub>2</sub>. The presence of a meso-silica core enhanced the CO<sub>2</sub> sorption capacity relative to bulk PILs. However, high temperatures reduced the CO<sub>2</sub> sorption capacity, indicating that the nanocomposite polymers should



be used at low temperatures.<sup>62</sup> So, the increase in porosity of PILs augmented the CO<sub>2</sub> uptake to a great extent.

### Effect of molar mass, moisture, temperature & pressure

Privalova and co-workers investigated the effect of the molecular weight of PILs on the CO<sub>2</sub> sorption capacity and deduced that this factor has the least impact on the CO<sub>2</sub> uptake.<sup>51</sup> In this connection, **PIL-7a** with Br anions and **PIL-7b** with BF<sub>4</sub> anions having different molecular weights were compared. CO<sub>2</sub> uptake of Br containing **PIL-7a** was amplified with increase in the molecular weight. For instance the CO<sub>2</sub> loading of **PIL-7a** with molecular weights of 6571 and 19 361 g mol<sup>-1</sup> was found to be 2.88 and 3.34 mg<sub>CO<sub>2</sub></sub> g<sub>PIL</sub><sup>-1</sup> which clearly explains the slight dependence of CO<sub>2</sub> sorption on the molecular weight of PILs. Whereas in **PIL-7b** the effect of molecular weight is not significant and CO<sub>2</sub> loading with molecular weights of 6708, 11 533, 21 937, 22 257 and 77 017 g mol<sup>-1</sup> was observed to be 2.99, 3.10, 3.11, 3.09 and 3.10 mg<sub>CO<sub>2</sub></sub> g<sub>PIL</sub><sup>-1</sup> respectively. These results proved that CO<sub>2</sub> sorption is not much dependent on the particle size.<sup>51</sup> The presence of moisture can also cause problems in processing and practical applications and even trace amounts may considerably alter the functionality of PILs. So, the moisture is considered to decrease CO<sub>2</sub> sorption performance of PILs. For instance, dry **PIL-8a** exhibited 10.22 mol% of CO<sub>2</sub> uptake while, wet **PIL-8a** with 13.8 mol% of water revealed a reduction in CO<sub>2</sub> capacity with only 7.9 mol%. This decrease in the value of CO<sub>2</sub> sorption clearly indicates impairment due to the existence of moisture<sup>41</sup> which forms complexes with anions through hydrogen bonding and occupies the sites for CO<sub>2</sub> sorption. Zhao and Anderson studied two different task-specific PIL-based coatings, **PIL-5a & b** and commercial Carboxen fibers to understand the effect of humidity and temperature on CO<sub>2</sub> extraction.<sup>48</sup> The extraction efficiency of CO<sub>2</sub> for all fibers decreased considerably in the presence of water vapor. However, **PIL-5b** coating displayed the lowest sensitivity drop (28%) in the presence of water vapor, while the sensitivity of **PIL-5a** dropped by 40% and that of Carboxen fibers by about 75%. Moreover, **PIL-5b** demonstrated improved water resistance most likely owing to the exclusive mechanism of CO<sub>2</sub> sorption,<sup>48</sup> thus showing enhanced resistance to reduction of CO<sub>2</sub> extraction sensitivity under humid conditions. **PIL-5a** sorbent coating was found to possess higher CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities relative to **PIL-5b** and Carboxen fibers.

CO<sub>2</sub> sorption performance of PILs is very much dependent on the temperature and to understand this effect, usually the sorption is carried out at various temperatures. Flue gas emanating from power plants mostly contains a mixture of gases like N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O present in various concentrations and its temperature often fluctuates depending on the scrubbing system used. Therefore, it is vital to foster the materials exhibiting high CO<sub>2</sub>/N<sub>2</sub> selectivity in the presence of moisture or water vapor without sacrificing their performance at different temperatures. The effect of temperature on the extraction efficiency of PIL and commercial Carboxen fibers at different temperatures (0 °C, 30 °C, 40 °C and 65 °C) was

monitored.<sup>48</sup> The results inferred that it was lengthy to reach equilibrium for PIL fibers, when extractions were done at 0 °C whereas almost the same extraction time was used for each fiber at all other temperatures. Moreover, the quantity of dry CO<sub>2</sub> extracted by **PIL-5b** coating decreased with increasing temperature and the behavior of coating demonstrated great linearity when the CO<sub>2</sub> pressure was varied between 1.5–125 kPa at all temperatures.<sup>48</sup> In the case of **ncPIL-1a,b**, the increase in temperature resulted in the deterioration of CO<sub>2</sub> sorption performance implying the preferable use of nanocomposites at low temperatures.<sup>62</sup> CO<sub>2</sub> sorption performance of PILs greatly changes with varying pressure. **PIL-8a** was evaluated for its CO<sub>2</sub> uptake as a function of pressure and interestingly, the CO<sub>2</sub> sorption augmented by increasing pressure and adsorbed 44.8 mol% of CO<sub>2</sub> (in terms of its monomer units) at a 12 bar pressure.<sup>41</sup>

### Separation via selective adsorption

For designing new PILs as CO<sub>2</sub> sorbents, it is critical to focus on the adsorption sites and adsorption/binding modes. CCS is conceived as an appropriate strategy for gas separation, predominantly CO<sub>2</sub>/N<sub>2</sub> separation, in post-combustion capture, and CO<sub>2</sub>/CH<sub>4</sub> separation in the purification of natural gas. Selective adsorption of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> is an imperative way in which both adsorption capacity and diffusion selectivity are of particular interest in order to scrutinize the potential of sorbents for separation depending on size exclusion or a favorable gas–pore surface interaction. The main concern in gas separation is the small difference in properties of the gases that have to be separated which is very much evident from the kinetic diameters of CO<sub>2</sub> (3.30 Å), CH<sub>4</sub> (3.76 Å), and N<sub>2</sub> (3.64 Å). On the other hand, the electronic properties of gases, *i.e.* quadrupolar moment and polarization exhibit some differences. Likewise, CO<sub>2</sub> possesses a large quadrupole moment of 13.4 × 10<sup>-40</sup> Cm<sup>2</sup> relative to N<sub>2</sub> (4.7 × 10<sup>-40</sup> Cm<sup>2</sup>) whereas CH<sub>4</sub> is non-polar, but owing to its higher polarizability 26.0 × 10<sup>-25</sup> cm<sup>3</sup>, it adsorbs preferentially over N<sub>2</sub> (17.6 × 10<sup>-25</sup> cm<sup>3</sup> for N<sub>2</sub> and 26.3 × 10<sup>-25</sup> cm<sup>3</sup> for CO<sub>2</sub>).<sup>5</sup> Consequently, the difference in chemical reactivity of gases can facilitate control at the molecular level leading to strong interactions with the pore surface of the sorbents and enhanced selectivity. Therefore, to attain high separation selectivity, the difference in quadrupole of gas molecules and pore size must be taken into account. Accordingly, to calculate sorbent's selectivity factor, single-component isotherms and the Ideal Adsorbed Solution Theory (IAST)<sup>73</sup> are used to give a quantitative estimate of the adsorption selectivity whereas the qualitative information can be acquired from the differences in uptake between the separated gases under the given measurement conditions. From single-component adsorption, at low loadings within Henry's regime, the adsorption selectivity is obtained by the ratio of Henry's constants for each species.<sup>74</sup> On the other hand, at non-dilute loadings, IAST aids in predicting multi-component adsorption isotherms and selectivity based on single-component adsorption isotherms. IAST theory works very well especially in the case of porous materials. The credit goes to pioneering work of





Snurr and Hupp<sup>75</sup> who employed experimental single-component adsorption isotherms to calculate the adsorption selectivity of a multi-component mixture using IAST. They showed that selectivity increases with decreasing CO<sub>2</sub> pressure and also as N<sub>2</sub> content,  $y(N_2)$  approaches unity. Wilke *et al.* used the same approach to calculate the selectivity in the mesoporous PIL network.<sup>61</sup>

Cations and anions play a key role in PILs particularly in CO<sub>2</sub> capture, so modifications in their structures can effectively enhance the sorption performance of PILs. Furthermore, the presence of aromatic rings in sorbents is particularly advantageous for producing more rigid architecture and it is established that the strength of CO<sub>2</sub>-aromatic ring interactions can be tuned by incorporating some polar CO<sub>2</sub>-philic functionalities into the ring structure such as -NH<sub>2</sub>, -SO<sub>3</sub>H, and -COOH, thus enhancing the adsorption capacity and selectivity of CO<sub>2</sub> adsorption. The design, synthetic route, structure and porosity of sorbents, plus the nature of gases involved in CO<sub>2</sub> separation led to the formulation of several approaches for increasing the separation ability of CO<sub>2</sub>. The separation strategies encompass adsorptive separation and membrane-based separation but both are entirely different in terms of the materials used. In the case of adsorptive separation, high CO<sub>2</sub> sorption capacity and selectivity from other gases are equally crucial for a sorbent material; on the contrary, high penetrability and selectivity are of major interest in membrane-based separation. Nonetheless, practical application is the eventual goal of any of these processes and common themes must be taken into account covering all aspects like efficient separation at room temperature or higher and at low pressure; robust materials to withstand harsh real-environmental conditions, and economical preparation and regeneration of materials. In selecting a porous material for separation, the pore size and shape are of primary importance. Zeolites and other porous materials utilized the molecular sieve effect for gas separation. Conversely, in kinetic separation, the performance of a porous material is directly associated with the pore size and shape of adsorbents in both adsorptive and membrane-based separation. A smart balance must be maintained so as to control the separation, being small enough to separate the desired gas mixture and also in trapping the molecules and stop gas flow all together. The pore size of 5.0–10.0 Å is considered to be suitable for CO<sub>2</sub>/N<sub>2</sub> separation.<sup>76</sup> CO<sub>2</sub> is a highly quadrupolar gas in contrast to N<sub>2</sub> and CH<sub>4</sub> being non-polar or weakly polar that led to great differences in the interaction between these gas molecules and the pore surface of porous materials resulting in enhanced adsorption and separation ability. Accordingly, adsorptive separation is getting more popularity owing to the pressing need for green separation procedures thus rendering a significant role in future energy and environmental technologies.

Many studies revealed that PILs can selectively capture CO<sub>2</sub> and possess a sizeable uptake capacity coupled with faster absorption/desorption rates in contrast to ILs rendering them outstanding candidates as CO<sub>2</sub> sorbent materials. **PIL-8b** probed by Supasitmongkol and Styring was also found to

readily desorb CO<sub>2</sub> gas.<sup>77</sup> Flue gas stack from power plants typically contain only 15% concentration of CO<sub>2</sub> as compared to nitrogen, therefore, CO<sub>2</sub>/N<sub>2</sub> selectivity is of foremost importance. Many groups working in the field of PILs extensively studied the selectivity of CO<sub>2</sub> over other gases and found that CO<sub>2</sub> sorption was selective and no weight gain was noticed on exposure of PILs to N<sub>2</sub> or O<sub>2</sub> under similar conditions signifying that PILs can selectively absorb CO<sub>2</sub>.<sup>41–43</sup> Additionally, **PIL-8b** was found to give a remarkable CO<sub>2</sub> selectivity over nitrogen of 70 : 1 which was consistent over repeated cycles.<sup>77</sup> A related study focused on **PIL-5a** demonstrated its superior CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities as compared to Carboxen fibers while the change in morphology evidenced by microscopic examination of **PIL-5b** also showed promise for selectively reacting the amine group of the TAU anion with CO<sub>2</sub> instead of CH<sub>4</sub> or N<sub>2</sub>.<sup>48</sup> Privalova *et al.* also reported that the captured CO<sub>2</sub> was released from **PIL-7a–f** thus validating the reversible nature of CO<sub>2</sub> sorption mechanism without providing extra heat.<sup>51</sup> Another report illustrated the fast desorption of CO<sub>2</sub> by **PIL-8a** and **PIL-11** indicating fast diffusion of CO<sub>2</sub> inside the solid polymers by releasing CO<sub>2</sub> in less than 15 min even under vacuum. Moreover, no changes in sorption/desorption kinetics and sorption capacity were noticed after four cycles of sorption/desorption measurements, implying its reversible nature in contrast to ILs.<sup>41</sup>

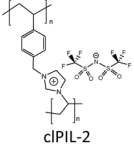
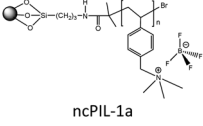
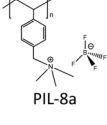
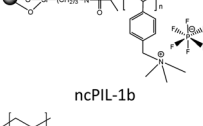
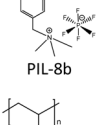
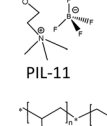
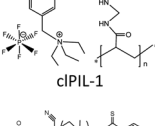
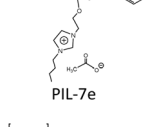
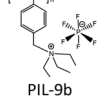
#### Comparison with other sorbents & future outlook

Regardless of the promising characteristics of PILs, their CO<sub>2</sub> sorption performance is, however, lesser than other common sorbents well known for CO<sub>2</sub> capture.<sup>71,78–88</sup> Various sorbents scanned for CO<sub>2</sub> sorption showed better separation and capture ability and the sorption values are typically expressed in mg g<sup>-1</sup> for the evaluation of sorbents (see Table 2). MOFs owing to their large surface area and pore volume adsorbed a significant amount of CO<sub>2</sub> at a high pressure while at low pressure they exhibited small CO<sub>2</sub> uptake. Polar (amine) functionalized MOFs have been ascertained to be useful for improving their affinity to CO<sub>2</sub> at low pressure.<sup>80–82</sup> Zeolites with low Si/Al ratios (ZEO13X) and monoethanolamine modified zeolite (ZEO13X/MEA) took up 206 and 136 mg g<sup>-1</sup> CO<sub>2</sub> at low pressure.<sup>78</sup> Mesoporous silica renders weak CO<sub>2</sub> sorption capacity at low pressure irrespective of their high pore volume. Surface functionalization with alkylamines provided these materials with improved low-pressure CO<sub>2</sub> sorption, *i.e.*, poly(ethyleneimine)/silica gave CO<sub>2</sub> uptake of 105 mg g<sup>-1</sup>.<sup>79</sup> Similarly, pure carbon sorbents possess weak affinity for CO<sub>2</sub> and surface modification/doping significantly augmented their sorption properties, thus, activated carbon rendered CO<sub>2</sub> loading around 83 mg g<sup>-1</sup>.<sup>78</sup> The aforementioned materials have their own advantages and limitations as well. Therefore, porous organic materials such as triazine based microporous polycarbazoles (PCBZ),<sup>83</sup> nanoporous organic frameworks (NPOF-4),<sup>84</sup> porous polymer networks (PPN-80),<sup>85</sup> conjugated microporous polymers (CMP-1-COOH),<sup>71</sup> microporous polyimides (PI-1),<sup>86</sup> porous aromatic frameworks (PAF-1)<sup>87</sup> and hypercrosslinked polymers (HCP-1)<sup>88</sup> have been designed for





Table 2 Comparison of CO<sub>2</sub> sorption capacity of various selected sorbents at low pressure

Sorbent	CO <sub>2</sub> (mg g <sup>-1</sup> )	Conditions ( <i>P</i> , <i>T</i> )	Ref.
ZEO13X	206	1 bar, 298 K	78
ZEO13X/MEA	136	1 bar, 298 K	78
Poly(ethyleneimine)/silica	105	1 bar, 298 K	79
Activated carbon	83	1 bar, 298 K	78
Bio MOF-11	264	1 bar, 273 K	80
Zeolitic tetrazolate framework (ZTF-1)	246	1 bar, 273 K	81
Zeolitic imidazolate framework (ZIF-78)	147	1 bar, 273 K	82
Nanoporous organic framework (NPOF-4)	109.9	1 bar, 273 K	84
Porous aromatic framework (PAF-1)	90.2	1 bar, 273 K	87
Hypercrosslinked polymer (HCP-1)	74.8	1 bar, 298 K	88
Porous polymer network (PPN-80)	71.2	1 bar, 295 K	85
Conjugated microporous polymer (CMP-1-COOH)	70.4	1 bar, 273 K	71
Polycarbazole (PCBZ)	49.7	1 bar, 273 K	83
Polyimide (PI-1)	30.3	1 bar, 273 K	86
 cPIL-2	20.24	1 bar, 273 K	61
 ncPIL-1a	17.71	1 bar, 303 K	62
 PIL-8a	17.09	0.78 bar, 295 K	42
 ncPIL-1b	16.69	1 bar, 303 K	62
 PIL-8b	14.60	0.78 bar, 295 K	42
 PIL-11	14.35	0.78 bar, 295 K	42
 cPIL-1	14.04	1 bar, 298 K	60
 PIL-7e	12.46	1 bar, 298 K	51
 PIL-9b	10.36	1 bar, 298 K	60



better CO<sub>2</sub> sorption. Among the PILs as shown in Table 2, **cPIL-2** adsorbed the highest carbon dioxide (20.24 mg g<sup>-1</sup>) at low pressure (1 bar), which provides opportunities to tailor and design new PILs leading to increase in CO<sub>2</sub> sorption performance especially by immobilizing these PILs on various supports,<sup>89</sup> changing the polycation, and increase of porosity. **PIL-8a,b** bearing BF<sub>4</sub> and PF<sub>6</sub> displayed CO<sub>2</sub> sorption capacities of 17.09 and 14.60 mg g<sup>-1</sup> respectively as reported by Tang *et al.* based on the mole percentages of monomer units.<sup>42</sup> Moreover, the nanocomposites of these two PILs with meso-silica prepared by Cheng *et al.* yielded 17.71 mg g<sup>-1</sup> carbon dioxide uptake for **ncPIL-1a** and 16.69 mg g<sup>-1</sup> CO<sub>2</sub> sorption for **ncPIL-1b** with the same anions. These results showed that introduction of mesoporous silica increased the porosity of these materials, which in turn raised the carbon dioxide uptake of nanocomposites.<sup>62</sup> Hence, high surface area 2D and 3D porous PILs bearing CO<sub>2</sub>-philic groups similar to organic polymers have to be designed and developed.<sup>90–92</sup> Additionally various groups possessing high CO<sub>2</sub> affinity could be inserted into the backbone of PILs like amines, acids, amidoximes and others to coin the versatility and inherent advantages of PILs for CO<sub>2</sub> capture and separation.<sup>93–112</sup> Keeping in mind, all the proposed modifications in PILs, we anticipate that the next generation PILs may surpass the CO<sub>2</sub> sorption values of microporous polymers as given in the Table 2. The potential of PILs as solid sorbents is highly attractive, right now their capture rate is not the same compared to aqueous amine technologies but the fact remains that amines for CO<sub>2</sub> capture have been evolved over the past few years while PILs is relatively a new research area leaving a big challenge for further investigation and improvement. The foremost challenges for the use of PILs as a green solution for CO<sub>2</sub> capture are their availability, cost, purity, and compatibility. These challenges are confronted currently on a laboratory scale and must be addressed before scale up at a commercial level. The benefits and shortcomings of ionic liquids and amines seem to be equally balanced. Amines have the edge over other materials of having high CO<sub>2</sub> solubility and being of low cost nowadays. However, PILs have the potential to be synthesized and developed in such a way so as to reduce the cost through increasing research and commercialization. Therefore, more research on new PIL solid sorbents, and techniques with higher efficiency and cost effectiveness is essential, the challenges to scale-up novel technologies from a laboratory to industrial level have to be addressed to overcome the technical difficulties in the CCS.

## Conclusions

This review uncovers the advancement in the domain of CO<sub>2</sub> capture and adsorptive separation by PILs in the last few years and also highlights all related prospects that might be helpful in designing new high performance polymeric ionic liquid sorbents. As exploitation of PILs for carbon capture is an emerging area of research but still in adolescence and necessitates

much work to be done and many secrets have yet to be revealed since the quest to produce novel PILs for CO<sub>2</sub> sorption and separation is far from being over. Although the CO<sub>2</sub> sorption data of PILs demonstrate their potential for such application relative to ILs, yet their efficiency ought to be improved like well known competitors in this field. The imperative factors which should be kept in mind while tailoring PILs' architecture are the appropriate selection of cations, introduction of new anions, backbones and porosity. The high performance players in this area possess ammonium and imidazolium cations, NTf<sub>2</sub>, BF<sub>4</sub>, PF<sub>6</sub> and acetate anions, rigid polystyrene backbone, high surface area and porosity together with high separation efficiency. Additionally, the variation of CO<sub>2</sub> sorption with temperature and under moist conditions is particularly crucial from real industrial application viewpoint. Innovation in making unique copolymers, nanocomposites and supramolecular networks may help in producing new promising sorbents and improving the performance of the existing ones. Based on our earlier experience, the incorporation of basic groups and enhanced porosity may aid in improving CO<sub>2</sub> capture and separation performance of PILs. From the practical viewpoint, substantial amounts of efforts are required to make use of IL chemistry and explore the broad range of chemical and structural variations to increase both CO<sub>2</sub> uptake and separation performance leading to revitalization of this field.

## List of abbreviations & symbols

Ac	Acetate
BF <sub>4</sub>	Tetrafluoroborate
Bmim	1-Butyl-3-methylimidazolium
Br	Bromide
Bz	Benzoate
CCS	Carbon dioxide capture and storage
CMPs	Conjugated microporous polymers
COFs	Covalent organic frameworks
DDBS	Dodecylbenzenesulfonate
dmbmim	Dimethylbutyl methylimidazolium
FFV	Fractional free volume
GHG	Greenhouse gas
HCP	Hypercrosslinked polymers
HDFOS	Heptadecafluorooctanesulfonate
HDFUD	4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecanoate
HFB	Heptafluorobutyrate
IAST	Ideal adsorbed solution theory
ILs	Ionic liquids
ILMs	Ionic liquid monomers
MOFs	Metal-organic frameworks
MS	Methanesulfonate
NFBS	Nonafluoro-1-butananesulfonate
NO <sub>3</sub>	Nitrate
NPOFs	Nanoporous organic frameworks
NTf <sub>2</sub>	Bis(trifluoromethylsulfonyl)imide



PAFs	Porous aromatic frameworks
PCBZ	Polycarbazole
PEG	Polyethylene glycol
PF <sub>6</sub>	Hexafluorophosphate
PI	Polyimide
PILs	Polymeric ionic liquids
PIMs	Polymers of intrinsic microporosity
PMMA	Polymethylmethacrylate
POPs	Porous organic polymers
PPNs	Porous polymer networks
PS	Polystyrene
PSA	Pressure swing adsorption
PSD	Pore size distribution
PTS	<i>p</i> -Toluenesulfonate
Q <sub>st</sub>	Isosteric heat of adsorption
RTIL	Room temperature ionic liquid
Sac	<i>o</i> -Benzoic sulphimide
TAU	Taurate
TFAc	Trifluoroacetate
TFMS	Trifluoromethanesulfonate
T <sub>g</sub>	Glass transition temperature
TSA	Temperature swing adsorption
ZIF	Zeolitic imidazolate framework
ZTF	Zeolitic tetrazolate framework

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