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## Anion size-dependent carbon dioxide adsorption capacity in high-purity diallyldimethylammonium-based poly(ionic liquid)s

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Poly(ionic liquid)s (PILs) are solid materials composed of cationic or anionic polymers combined with counter ions. PILs are investigated and applied as CO<sub>2</sub> adsorbents because they possess both the high CO<sub>2</sub> affinity of ionic liquids and the excellent stability and processability of polymeric materials. This work explored the correlation between the type of anion in PILs and their CO<sub>2</sub> adsorption capacity *via* anion-exchange. As the skeleton of PILs, we focused on poly(diallyldimethylammonium chloride) (P[DADMA][Cl]). Among the quaternary ammonium cations known to exhibit high CO<sub>2</sub> adsorption capacity, P[DADMA][Cl] contains the highest density of cationic sites, indicating the potential for further enhanced CO<sub>2</sub> adsorption capacity. However, conventional anion-exchange reactions often yield residual by-products in the resulting PILs, making it difficult to reveal the inherent correlation between counter anions and CO<sub>2</sub> adsorption capacity. In this work, high-purity PILs (P[DADMA][AcO], P[DADMA][TFMS], and P[DADMA][SCN]) without by-products were successfully prepared for the first time through careful dialysis. The CO<sub>2</sub> adsorption capacity of these PILs increased in proportion to the size of the counter anion, and P[DADMA][TFMS] exhibited a seven-fold increase in the adsorption capacity compared to that of P[DADMA][Cl]. This work truly demonstrates that CO<sub>2</sub> adsorption capacity can be enhanced by designing the counter anions in PILs.

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### Introduction

Ionic liquids are salts that exist as liquids at ambient temperatures, and are characterized by low volatility, high thermal and chemical stability, and the ability to design physical properties based on the combination of anion and cation species.<sup>1–5</sup> Meanwhile, poly(ionic liquid)s<sup>6–9</sup> (PILs) are polymer materials composed of ionic liquids<sup>10,11</sup> as their building blocks. In particular, owing to their high solubility for carbon dioxide<sup>12</sup> (CO<sub>2</sub>), they have good potential as CO<sub>2</sub> adsorbents. While PILs retain these excellent properties, they also possess mechanical stability and processability resulting

from their polymerization.<sup>13</sup> Consequently, they have been extensively investigated for practical applications such as gas separation membranes<sup>14</sup> and solid adsorbents.<sup>15</sup>

Among PILs, those with a quaternary ammonium cation skeleton are known to exhibit higher CO<sub>2</sub> adsorption capacities than PILs with other imidazolium or pyridinium cation skeletons.<sup>16</sup> The CO<sub>2</sub> adsorption capacities of PILs are expected to depend significantly on their anion species as well as the cation skeletons.<sup>17</sup> Therefore, the CO<sub>2</sub> adsorption capacity of PILs containing various anion species introduced *via* anion-exchange reactions,<sup>18</sup> where the halides of PILs react with the inorganic salts of each anion, has been revealed.<sup>19,20</sup> However, conventional anion-exchange reactions involve difficulty in completely separating the resulting PILs from the by-product inorganic salts, and residual metal ions derived from the inorganic salts have been overlooked.<sup>21</sup> The residual metal ions in the PILs prevent the evaluation of the influence of the counter anion on the CO<sub>2</sub> adsorption capacity.<sup>22</sup>

In this work, we aim to resolve these issues by performing precise purification by dialysis<sup>23</sup> and clarify the correlation between the type of anion in PILs and their inherent CO<sub>2</sub> adsorption capacity. In details, among quaternary ammonium cations, we focused on poly(diallyldimethylammonium chloride)<sup>24</sup> (P[DADMA][Cl]), which was expected to exhibit

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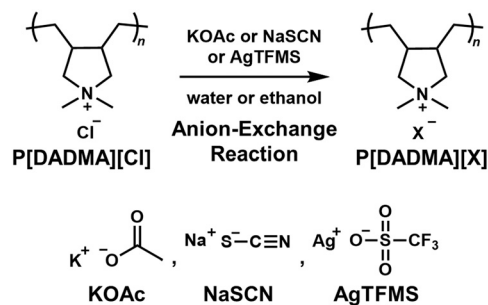


Fig. 1 Synthesis of PILs based on P[DADMA][Cl].

particularly high  $\text{CO}_2$  adsorption capacity owing to its exceptionally high ammonium cation density. To quantitatively elucidate the effect of counter anion size on  $\text{CO}_2$  adsorption capacity, we also focused on three different-sized anions ( $\text{AcO}^-$ : 0.252 nm <  $\text{SCN}^-$ : 0.289 nm < trifluoromethane sulfonate ( $\text{TFMS}^-$ ): 0.304 nm) that are larger than  $\text{Cl}^-$  (0.214 nm) and performed anion-exchange reactions. Consequently, the purification of the obtained PILs *via* dialysis allowed for the first time the preparation of high-purity PILs (P[DADMA][AcO], P[DADMA][TFMS], P[DADMA][SCN]) that are free from residual impurities (Fig. 1). The  $\text{CO}_2$  adsorption capacity of the obtained PILs increased in proportion to the size of the anion. This work provides new design principles for PILs towards efficient  $\text{CO}_2$  absorbents.

## Experimental section

### Synthesis of P[DADMA][AcO]

P[DADMA][Cl] (1000 mg, 6.19 mmol) was added to ethanol (10 mL) and potassium acetate (607 mg, 6.19 mmol) was added at room temperature and stirred overnight. The reaction mixture was filtered and concentrated under reduced pressure using an evaporator. The resulting residue was dissolved in 10 mL of water, dialyzed in 1 L water for 24 h, and dried in a freeze dryer. After one day of drying, a yellow solid (117 mg, 0.63 mmol, 10%) was obtained. The synthesis methods for other PILs (P[DADMA][SCN] and P[DADMA][TFMS]) are described in the SI.

## Results and discussion

### 1. PILs preparation

Each PIL (P[DADMA][AcO], P[DADMA][TFMS], P[DADMA][SCN]) was prepared by an anion-exchange reaction in solution using P[DADMA][Cl] as the starting material, following the procedure given in the experimental section and SI. Inorganic salts of several anions (KOAc, NaSCN, and AgTFMS) were selected for anion-exchange because of their high solubility in the reaction solvent and efficient reaction progress. In the anion-exchange reactions, the amount of inorganic salt was determined based on the solubility of the resulting byproduct in the reaction solvent. Specifically, an equimolar amount of inorganic salt was sufficient to drive the reaction to completion when the

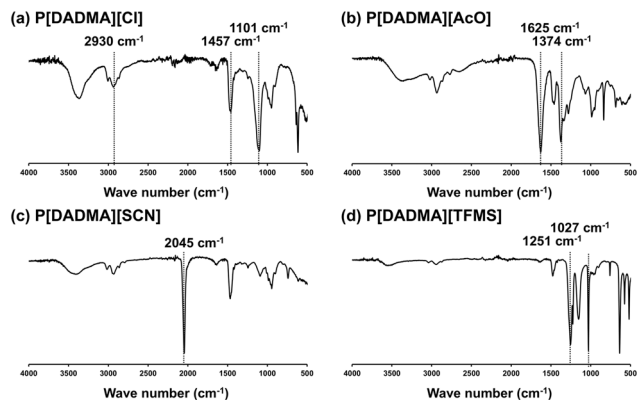


Fig. 2 FT-IR spectra of (a) P[DADMA][Cl], (b) P[DADMA][AcO], (c) P[DADMA][SCN], and (d) P[DADMA][TFMS].

byproduct was insoluble in the reaction solvent, as its precipitation effectively shifted the equilibrium. Conversely, an excess amount was used when the byproduct was soluble. After the reaction, the removal of impurities *via* dialysis allowed us to yield high-purity PILs.

### 2. Characterization

As shown in Fig. 2 and 3, the progress of the anion-exchange was confirmed by the FT-IR and energy-dispersive X-ray spectroscopy (EDX) spectra. First, as shown in Fig. 2a as a representative example, the FT-IR spectra of all PILs exhibited peaks derived from the C–H stretching vibration ( $1457 \text{ cm}^{-1}$ ), C–H bending vibration ( $2930 \text{ cm}^{-1}$ ), and C–N stretching vibration ( $1101 \text{ cm}^{-1}$ ) of the polymer moiety<sup>21</sup> (Table S1). Subsequently, as shown in Fig. 2b, the FT-IR spectrum of P[DADMA][AcO] exhibited peaks derived from the  $\text{COO}^-$  antisymmetric stretching vibration ( $1625 \text{ cm}^{-1}$ ) and  $\text{COO}^-$  symmetric stretching vibration ( $1374 \text{ cm}^{-1}$ ) of  $\text{AcO}^-$ <sup>21</sup> (Table S2). As shown in Fig. 2c, the FT-IR spectrum

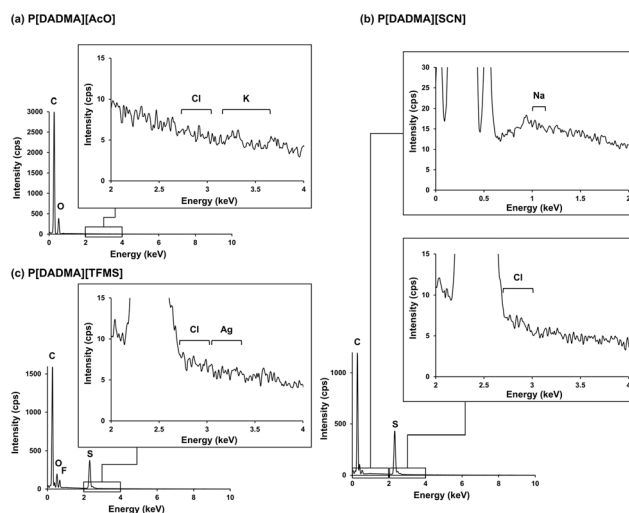


Fig. 3 EDX spectra of (a) P[DADMA][AcO], (b) P[DADMA][SCN], and (c) P[DADMA][TFMS].



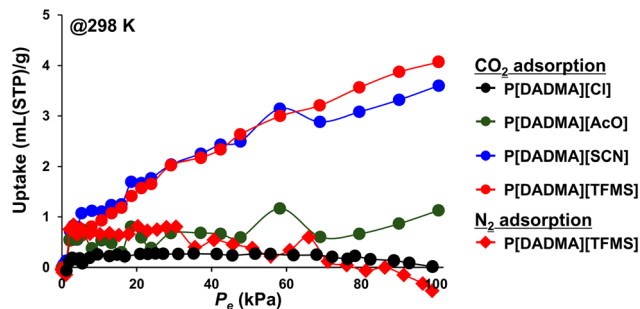


Fig. 4 CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms of P[DADMA][Cl] (black), P[DADMA][AcO] (green), P[DADMA][SCN] (blue), and P[DADMA][TFMS] (red), measured at 298 K.

of P[DADMA][SCN] exhibited a peak corresponding to the CN stretching vibration (2045 cm<sup>-1</sup>) of SCN<sup>-21</sup> (Table S3). As shown in Fig. 2d, the FT-IR spectrum of P[DADMA][TFMS] exhibited peaks derived from the C-F stretching vibration (1251 cm<sup>-1</sup>) and O=S=O stretching vibration (1027 cm<sup>-1</sup>) of TFMS<sup>-25</sup> (Table S4).

As shown in Fig. 3, the EDX spectra of each PIL demonstrate the complete disappearance of Cl atoms derived from the starting material, P[DADMA][Cl]. These peak changes indicated the completion of the anion-exchange reaction. In addition, the same SEM-EDX spectra exhibited only peaks corresponding to the respective PILs as products, indicating that impurities in the PILs were below the detection limit of SEM-EDX (0.1 wt%<sup>26</sup>). This result demonstrates that purification *via* dialysis after the anion-exchange reaction is effective for the synthesis of high-purity PILs without impurities. To the best of our knowledge, this is the first time that such high-purity PILs have been synthesized in DADMA-based PILs. As shown in Fig. S1 and Table S5, the differential scanning calorimetry (DSC) curves of the PILs revealed glass transition temperatures ( $T_g$ ) that varied depending on the counter anion. The  $T_g$  of P[DADMA][Cl] is consistent with previously reported values,<sup>20</sup> whereas the other PILs exhibit lower  $T_g$  values. This trend is generally attributed to the increased size of the counter anions, which enhances free volume (space between polymer chains<sup>27</sup>) and facilitates segment motion.<sup>28</sup> As mentioned later, this increase in free volume also leads to increased CO<sub>2</sub> adsorption. Notably, P[DADMA][AcO] exhibited the lowest  $T_g$  despite its relatively small anion size. This is attributed to the strong interaction between AcO<sup>-</sup> and electron-deficient sites<sup>29</sup> such as the methyl group of the DADMA backbone owing to the high hydrogen-bonding capability of AcO<sup>-</sup>,<sup>30</sup> which inhibited the close packing between polymer chains.

### 3. Gas sorption properties

As shown in Fig. 4, the CO<sub>2</sub> adsorption capacity of each PIL was evaluated using the CO<sub>2</sub> adsorption isotherm at 298 K. As shown in Table 1, the CO<sub>2</sub> adsorption amounts followed the order: P[DADMA][TFMS] > P[DADMA][SCN] > P[DADMA][AcO] > P[DADMA][Cl]. This order corresponds to the size of the anions (TFMS<sup>-</sup> > SCN<sup>-</sup> > AcO<sup>-</sup> > Cl<sup>-</sup>). As shown in Fig.

Table 1 CO<sub>2</sub> and N<sub>2</sub> adsorption amount of PILs

Sample	Anion radius <sup>a</sup> /nm	$V_{\text{CO}_2}$ <sup>b</sup> /mL g <sup>-1</sup>	$V_{\text{N}_2}$ <sup>c</sup> /mL g <sup>-1</sup>
P[DADMA][Cl]	0.214	0.155	—
P[DADMA][AcO]	0.252	1.13	0.449
P[DADMA][SCN]	0.289	3.60	0.502
P[DADMA][TFMS]	0.304	4.07	—

<sup>a</sup> Estimated based on density functional theory (DFT) calculations (B3LYP/6-31+G(d,p)). <sup>b</sup> CO<sub>2</sub> adsorption amount at 100 kPa. <sup>c</sup> N<sub>2</sub> adsorption amount at 100 kPa.

S2, the CO<sub>2</sub> adsorption capacity was found to increase in general proportion to the anion size. This result supports that larger counter anions increase the CO<sub>2</sub> adsorption capacity by contributing to the expansion of the free volume and promoting CO<sub>2</sub> diffusion within the PILs.<sup>31</sup> In a previous work, PILs (P[DADMA][AcO]) bearing the more basic AcO<sup>-</sup> as the counter anion exhibited higher adsorption capacity than that of TFMS<sup>-</sup>, indicating some contribution of chemical affinity based on the counter anion's basicity.<sup>21</sup> However, this result likely includes the influence of residual inorganic salts that can fill the free volume. In contrast, the high-purity PILs obtained in this work revealed the opposite trend, with P[DADMA][TFMS] exhibiting a higher CO<sub>2</sub> adsorption than that of P[DADMA][AcO]. This result supports the conclusion that CO<sub>2</sub> adsorption on high-purity PILs is governed by the free volume derived from the size of the counter anion, which becomes more dominant than the chemical affinity derived from the basicity of the counter anion. As shown in Fig. S3, the CO<sub>2</sub> adsorption capacities of P[DADMA][TFMS] before (P[DADMA][TFMS] with 0.12 atomic% of Ag atoms) and after purification by dialysis were compared. The CO<sub>2</sub> adsorption capacity of the unpurified P[DADMA][TFMS] (3.56 mL g<sup>-1</sup> at 100 kPa) was lower than that of the purified, high-purity P[DADMA][TFMS] (4.04 mL g<sup>-1</sup> at 100 kPa), supporting the inhibition of CO<sub>2</sub> adsorption caused by impurities remaining in the PILs. In addition, as shown in Fig. 4 and S4, the N<sub>2</sub> adsorption isotherms at 298 K indicated negligible N<sub>2</sub> adsorption for all PILs, demonstrating that the type of anion in the PILs did not significantly affect the N<sub>2</sub> adsorption capacity. Therefore, this work confirms that improving the CO<sub>2</sub> adsorption capacity by the designing of anions in PILs also contributes to enhancing the adsorption selectivity of CO<sub>2</sub>/N<sub>2</sub>.

## Conclusions

In this work, we successfully synthesized three high-purity PILs (P[DADMA][AcO], P[DADMA][TFMS], P[DADMA][SCN]) from P[DADMA][Cl] as the starting material by anion-exchange and dialysis. These PILs exhibited enhanced CO<sub>2</sub> adsorption capacity proportional to the size of their counter anions, and P[DADMA][TFMS] exhibited seven-times higher adsorption capacity than that of the starting material P[DADMA][Cl]. This is attributed to the large anions expanding the free volume of the PILs, facilitating CO<sub>2</sub> diffusion. This work truly demonstrates



that CO<sub>2</sub> adsorption capacity can be enhanced by designing the counter anions in PILs.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The supporting data has been provided as part of the supplementary information (SI).

Supplementary information: Fig. S1–S4 and Tables S1–S5, and further experimental details. See DOI: <https://doi.org/10.1039/d5re00535c>.

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