Electronic Supplementary Information

Highly Efficient I₂ Capture by simple and low-cost Deep Eutectic Solvents

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1 Measurement of solvatochromic parameters

The measurement of the solvatochromic parameters was carried out according to the literature\textsuperscript{1-4}. Solvatochromic parameters (Table S1) were determined by the absorption peaks of three dyes, N,N-diethyl-4-nitro-aniline (DENA), 4-nitroaniline (NA) and Reichardt’s dye 30. Three kinds of stock solution was prepared by adding the dyes in methanol and mixed homogeneously. The methanol was then removed by placing the solutions under vacuum at 40 °C. UV/Vis spectra have been carried out with a sample pool with an optical length of 1 mm, within the wavelength range 200–800 nm, using the same DES in the analyzed solution as a blank. The determined wavelengths of three dyes at the maximum absorption were used to calculate the solvatochromic parameters and the $\lambda_{\text{max}}$ stated is the average of three separate scans.

The $\pi^*$ parameters were determined by DENA, using eqn. (1) and (2):

$$\pi^* = 0.314(27.52 - \nu_{\text{DENA}}) \quad (1)$$

$$\nu_{\text{Dye}} = 1 / (\lambda_{\text{Dye}} \times 10^{-4}) \quad (2)$$

The $\beta$ values were determined by DENA and NA, using eqn. (3)

$$\beta = (1.035\nu_{\text{DENA}} + 2.64 - \nu_{\text{NA}}) / 2.80 \quad (3)$$

The $\alpha$ values were determined by the $E_T(30)$ and $\pi^*$, using eqn. (4) and (5)

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (4)$$

$$E_T(30) = 28592/\lambda_{\text{RD30}}^{\text{max}} \quad (5)$$

<table>
<thead>
<tr>
<th>DESs</th>
<th>ET(30)</th>
<th>$\pi^*$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\alpha-\beta$</th>
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<tbody>
<tr>
<td>ChCl-Urea</td>
<td>58.00</td>
<td>1.20</td>
<td>0.87</td>
<td>0.49</td>
<td>0.38</td>
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<tr>
<td>ChCl-Methylurea</td>
<td>55.30</td>
<td>1.14</td>
<td>0.74</td>
<td>0.59</td>
<td>0.15</td>
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<tr>
<td>ChCl-Ethylene glycol</td>
<td>57.44</td>
<td>1.13</td>
<td>0.88</td>
<td>0.47</td>
<td>0.41</td>
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<tr>
<td>ChCl-Glycerol</td>
<td>57.81</td>
<td>1.18</td>
<td>0.87</td>
<td>0.50</td>
<td>0.37</td>
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<tr>
<td>ChCl-Oxalic acid</td>
<td>58.18</td>
<td>1.17</td>
<td>0.90</td>
<td>0.42</td>
<td>0.48</td>
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<td>ChCl-Malonic acid</td>
<td>58.16</td>
<td>1.16</td>
<td>0.91</td>
<td>0.52</td>
<td>0.39</td>
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<td>ChCl-1,4-Butanediol</td>
<td>55.43</td>
<td>1.04</td>
<td>0.82</td>
<td>0.63</td>
<td>0.19</td>
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<tr>
<td>ChBr-Oxalic acid</td>
<td>56.77</td>
<td>1.22</td>
<td>0.78</td>
<td>0.38</td>
<td>0.40</td>
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</table>
2 Iodine recyclability and capture capacity experiments

The procedure of DESs reusability/recyclability experiment is similar to the I$_2$ storage experiment. After the capture of I$_2$ from cyclohexane, most of the cyclohexane could be separated from the DESs by just dumping. Then the DESs with captured I$_2$ and small amount of cyclohexane were putting in the platinum pan of thermal gravimetric analysis (TGA) instrument. After that the TGA experiments were carried out at different temperatures for checking the reusability/recyclability of DESs.

The procedure of I$_2$ capture capacity by DESs was investigated by the following methods. A desired amount of selected DESs (~0.2 g) was putting in a solution of I$_2$ in cyclohexane. For a goal of rapid equilibrium, a larger amount of solution (20 ml) was used for 5 hours. Then, the cyclohexane solution was separated from the I$_2$ saturated DES by damping. This procedure was repeated for several times till the concentration of I$_2$ in cyclohexane was not changed which could be verified by UV-Vis experiment. After that, most of the cyclohexane solution was separated from DES. Then about 100 mg of I$_2$ saturated DES was put in the platinum pan of TGA at 30 °C and with a N$_2$ flow of 40 ml/min for removal of cyclohexane from the DES/I$_2$ until the weight almost keeps constant, which is deemed as the weight of DES/I$_2$ ($m_1$). Then the temperature was raised to 80 °C until the weight almost keeps constant again, which is deemed as the weight of DES ($m_2$). Thus, the I$_2$ capture capacity could be calculated as ($m_1$-$m_2$)/$m_2$. 
3 Calibration plot of iodine in cyclohexane by UV/vis spectrum.

Fig. S1  Calibration plot of iodine in cyclohexane by UV/vis spectrum.
4 DFT calculations

In order to uncover the capture mechanism of radioiodine by DES, computational studies applying DFT have been performed. The structure formed by interaction between iodine molecule and isolated DESs were optimized and shown in Fig. S2. From the optimized structures of N(Bu)$_4$Cl/urea and N(Bu)$_4$Cl/urea-I$_2$ complex, it can be easily seen that the intermolecular interactions between ionic pairs and two urea molecules were weakened when iodine molecule approached to the N(Bu)$_4$Cl/urea DES, which can be demonstrated by the following bond distances analysis. For the details, the bond distances of O17-Cl$_2$, H15-Cl$_2$, H7-Cl$_2$ and H9-Cl$_2$ were somewhat elongated from 2.41462, 2.39575, 2.44446 and 2.47341 Å in N(Bu)$_4$Cl/urea to 2.47605, 2.64045, 2.47700, 2.53325 Å in N(Bu)$_4$Cl/urea-I$_2$, respectively. Besides, the newly formed Cl-I bond was observed when iodine molecule approached to the N(Bu)$_4$Cl/urea DES, which can be considered as halogen bond for its bond distance of 2.84945 Å.
The most stable geometries of DES and DES-I₂ complexes include:

- ChCl/urea
- ChCl/urea-I₂
- ChCl/methylurea
- ChCl/methylurea-I₂
- ChCl/glycerol
- ChCl/glycerol-I₂
- ChI/methylurea
- ChI/methylurea-I₂
Fig. S2  The most stable geometries of the isolated DES and DES-\textsubscript{I\textsubscript{2}} complexes optimized at B3LYP/6-311++G(d,p) level.
6 The visual colour change after adsorption of I$_2$ with DESs
**Fig. S3**  Picture showing the visual colour change after adsorption of iodine with various DESs ($C_i = 0.01\text{M}$, $t = 24\text{h}$ and at room temperature), (a) Methylurea-based DESs; (b) ChCl-based DESs; (c) Urea-based DESs; (d) DESs which removed all of the iodine from the starting solution.
### Table S2  Materials and their removal efficiency of I$_2$ in 5 hours.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Removal efficiency (5h)</th>
<th>Materials</th>
<th>Removal efficiency (5h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101-NH$_2$</td>
<td>76%$^5$</td>
<td>Chl-Methylurea</td>
<td>96%</td>
</tr>
<tr>
<td>MIL-120</td>
<td>68%$^5$</td>
<td>[Bmim][Br]</td>
<td>96%$^6$</td>
</tr>
<tr>
<td>CAU-1</td>
<td>58%$^5$</td>
<td>[Bmim][Cl]</td>
<td>87%$^6$</td>
</tr>
<tr>
<td>MIL-53(Al)-NH$_2$</td>
<td>42%$^5$</td>
<td>[Bmim][Ac]</td>
<td>84%$^6$</td>
</tr>
<tr>
<td>MIL-53(Al)-Br</td>
<td>31%$^5$</td>
<td>[Bmim][NO$_3$]</td>
<td>39%$^6$</td>
</tr>
<tr>
<td>MIL-53(Al)-(OH)$_2$</td>
<td>22%$^5$</td>
<td>[Bmim][BF$_4$]</td>
<td>7%$^6$</td>
</tr>
</tbody>
</table>

Although there is no I$_2$ removal efficiency about activated carbon$^7$ and zeolite-like aluminosilicates$^8$-$^{11}$, their low porosity limits their absorption capacities and efficiency. It was also validated by Falaise et al.$^4$. Besides, the best MOF MIL-101-NH$_2$$^4$ shows a relative low absorption efficiency of 75% in 5 hours. All of them are of high cost and difficult to prepare. [Bmim][Br]$^6$ exhibits high I$_2$ absorption efficiency, but ILs are relatively expensive, difficult in preparation and purification, and the toxicity of imidazolium cations of these ILs is also a discussable issue.
Fig. S4  TGA curve of weight loss of DES and DES/I₂ under nitrogen (N₂) gas sweeping (N₂ flow = 40 ml min⁻¹, temperature = 30 °C): the percentage of the remaining mass of I₂ in ILs was calculated to be 100% minus the lost mass of the TGA curve divided by the original mass of I₂.
Fig. S5 The remained mass of I\textsubscript{2} after 10 hours of N\textsubscript{2} gas sweeping

Fig. S5  The remained mass of I\textsubscript{2} after 10 hours of N\textsubscript{2} gas sweeping (N\textsubscript{2} flow = 40 ml min\textsuperscript{-1}, temperature = 30 °C): the percentage of the remained mass of I\textsubscript{2} in DESs was calculated to be 100% minus the lost mass divided by the original mass of I\textsubscript{2}. In this graph, 1, 2, 3, 4 stands for Chl-methylurea-I\textsubscript{2}, N(Bu)\textsubscript{4}Cl-urea-I\textsubscript{2}, Chl-malonic acid-I\textsubscript{2} and ChBr-methylurea-I\textsubscript{2}, respectively.
10 References


