Optimal molecular design of poly (ionic liquids) for CO2 capture from the atmosphere

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OPTIMAL MOLECULAR DESIGN OF POLY(IONIC LIQUID)S FOR CO$_2$ CAPTURE FROM ATMOSPHERE

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Outline

- Introduction
- Quantum Chemistry Calculation
- Case for molecular design
- Conclusions
Poly(ionic liquid)s (PILs), also called polymerized ionic liquids, refer to a subclass of polyelectrolytes that feature an ionic liquid (IL) species in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular architecture.

An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature.
Why PILs?

PILs combine the unique properties of ionic liquids with the flexibility and properties of macromolecular architectures:

- Fine tunability
- Enhanced mechanical stability
- Improved processability, durability and spatial controllability

More advantages have been found in the application of CO2 adsorption.

- Compared to the corresponding ionic liquid monomers, the CO$_2$ adsorption capacities of PILs can be several times higher and the sorption-desorption rates can be 10 times faster.
Moisture Swing for Specific PILs

I. The PIL material, called P[VBTEA][CO$_3^{2-}$], adsorb CO$_2$ when dry and release CO$_2$ when wet, which constitutes a humidity swing cycle.

II. Provide an economical approach for air capture.

Under dry condition

Under wet condition

Environ. Sci. Technol. 2011, 45, 6670–6675
Reveal mechanism of moisture swing through quantum chemistry calculation

Build the computational model: from polymer to simplified model compound

Computational method: Gaussian 03 package B3LYP, 6-311++G**

Different materials with the same functional groups
Structures and properties

<table>
<thead>
<tr>
<th>Model compounds</th>
<th>Number of H-bonds</th>
<th>$\rho^a$</th>
<th>$\nabla^2\rho^b$</th>
<th>$\Delta E$ (kJ/mol)</th>
<th>Charge transfer $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PILs with hydroxide</td>
<td>3</td>
<td>0.033-0.033</td>
<td>0.112-0.113</td>
<td>496</td>
<td>0.118</td>
</tr>
<tr>
<td>PILs with carbonate</td>
<td>6</td>
<td>0.032-0.037</td>
<td>0.104-0.111</td>
<td>1289</td>
<td>0.293</td>
</tr>
<tr>
<td>PILs with bicarbonate</td>
<td>3</td>
<td>0.024-0.029</td>
<td>0.080-0.095</td>
<td>395</td>
<td>0.040</td>
</tr>
</tbody>
</table>

The most possible sites for the adsorption of H$_2$O and CO$_2$
Hydrated water on the interface

- Uniform distribution for carbonate and hydroxide;
- Self-association for bicarbonate.

As the number of hydrated water molecule increases, $\text{HCO}_3^-$ shows the trend of transforming into $\text{H}_2\text{CO}_3$, which could resolve and release $\text{CO}_2$.

<table>
<thead>
<tr>
<th>Model compounds</th>
<th>Number of water molecules</th>
<th>Atomic charge $^a$</th>
<th>$r_1$ (Å) $^b$</th>
<th>$r_2$ (Å) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PILs with hydroxide</td>
<td>1</td>
<td>-1.027</td>
<td>1.021</td>
<td>1.595</td>
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<tr>
<td>PILs with hydroxide</td>
<td>2</td>
<td>-1.024</td>
<td>1.018</td>
<td>1.607</td>
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<tr>
<td>PILs with hydroxide</td>
<td>3</td>
<td>-1.016</td>
<td>1.012</td>
<td>1.623</td>
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<tr>
<td>PILs with carbonate</td>
<td>1</td>
<td>-1.012</td>
<td>1.001</td>
<td>1.647</td>
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<tr>
<td>PILs with carbonate</td>
<td>2</td>
<td>-1.004</td>
<td>0.999</td>
<td>1.665</td>
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<tr>
<td>PILs with carbonate</td>
<td>3</td>
<td>-1.001</td>
<td>0.996</td>
<td>1.684</td>
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<tr>
<td>PILs with bicarbonate</td>
<td>1</td>
<td>-1.004</td>
<td>0.992</td>
<td>1.693</td>
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<tr>
<td>PILs with bicarbonate</td>
<td>2</td>
<td>-1.001</td>
<td>0.981</td>
<td>1.793</td>
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<tr>
<td>PILs with bicarbonate</td>
<td>3</td>
<td>-1.013</td>
<td>0.990</td>
<td>1.717</td>
</tr>
</tbody>
</table>
Reaction pathways of CO2 adsorption

$\Delta E_{ad}=27.52 \text{ kJ/mol}$
$\rho=0.024$
$\nabla^2 \rho=0.076$

Direct interaction between $[\text{N}^+\text{CO}_3^{2-}\text{N}^+]$ and CO2

Hydroxide has strong affinity of CO2. The combination could transform into bicarbonate immediately.

The proton transfer mechanism: a proton is transferred from hydrated water to carbonate, through which a hydroxide ion is produced.
The activation energy of proton transfer is 34.6 kJ/mol, much smaller than that of CO$_2$ absorption by MEA.

Water could promote the reaction as catalyst.
Low enthalpy change of the reaction

\[ [\text{N}^+\text{CO}_3^{2-}\text{N}^+] \cdot a\text{H}_2\text{O}^{(h)} + \text{CO}_2 \rightarrow [2\text{N}^+\text{HCO}_3^-] \cdot b\text{H}_2\text{O}^{(h)} + (a-b-1)\text{H}_2\text{O}^{(g)} \]

<table>
<thead>
<tr>
<th>Possible coefficient of Equation (5)</th>
<th>Corresponding parameters</th>
<th>thermodynamic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(\Delta G^\ominus) (kJ/mol)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>-16.724</td>
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<tr>
<td>1</td>
<td>1</td>
<td>-25.284</td>
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<tr>
<td>1</td>
<td>2</td>
<td>-6.170</td>
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<td>2</td>
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<td>-12.471</td>
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<td>2</td>
<td>3</td>
<td>-8.270</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-14.624</td>
</tr>
</tbody>
</table>

- An interesting “self-cooling” effect was obtained during adsorption process.

- Significant difference of hydrophilicity between states before and after adsorption
Multi-roles of hydrated water

• The hydrated water could form strong H-bonds with anions. But the distribution of hydrated water is different between reactant (carbonate or hydroxide) and product (bicarbonate), which is the basis of moisture swing and low reaction enthalpy.

• The hydrated water could promote the proton transfer reaction. But at the same time, it also inhibit the reaction between hydroxide and CO2. (e.g. CO2 absorption by carbonate solution as an extreme example)
Conclusions

- PILs are promising CO2 sorbent, especially in the field of air capture.

- The unique properties of P[VBTEA][CO$_3^{2-}$], such as moisture swing and low reaction enthalpy, are related to the hydrated water on the interface.

- The quantum chemistry model we developed here is a useful tool for molecular design.