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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

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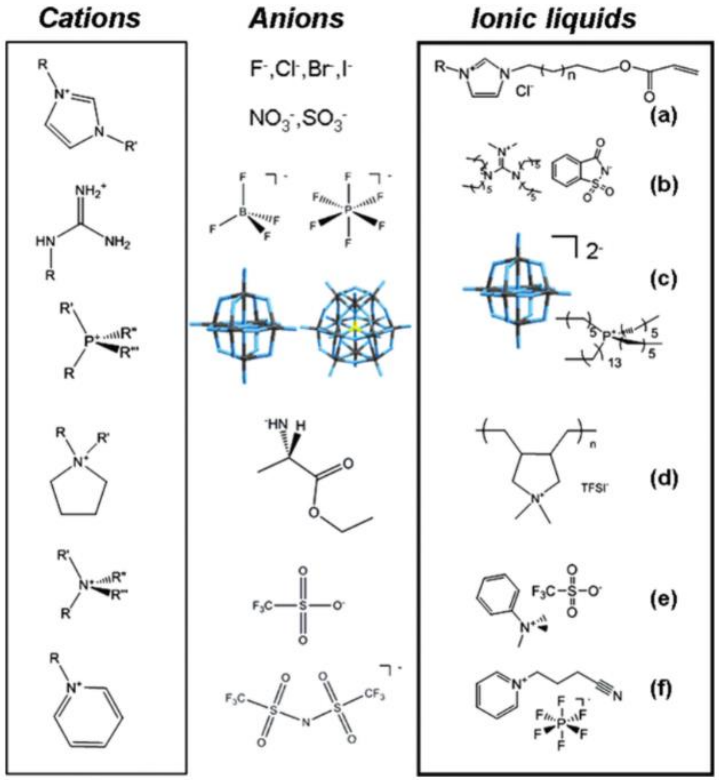
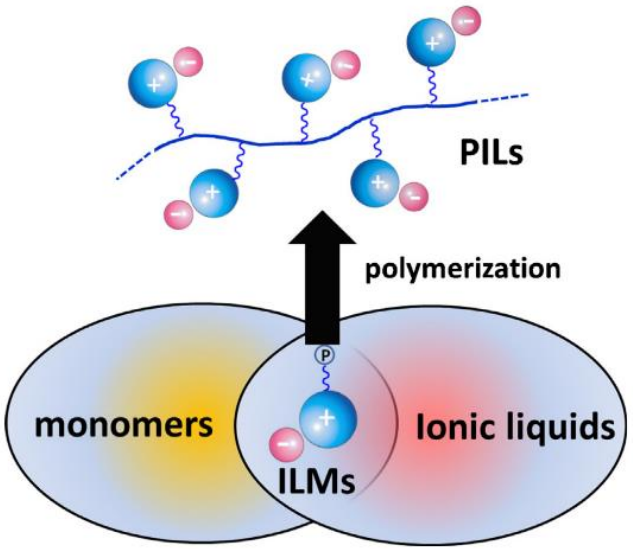
What are PILs?



An **ionic liquid** is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100℃, or even at room temperature.



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.

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Polym. Chem.,**2015**, 6, 6435–6451

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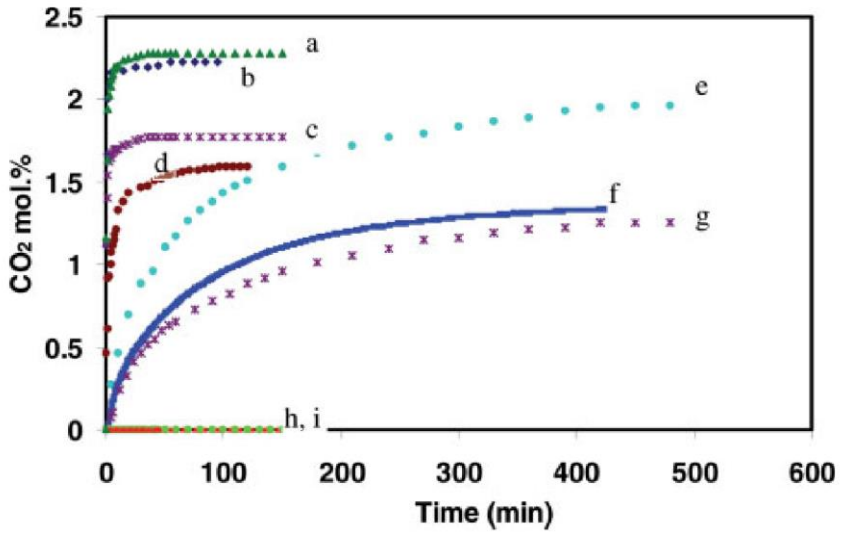
Why PILs?

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

J. Polym. Sci., Part A: Polym. Chem. **2005**, 43, 5477–5489

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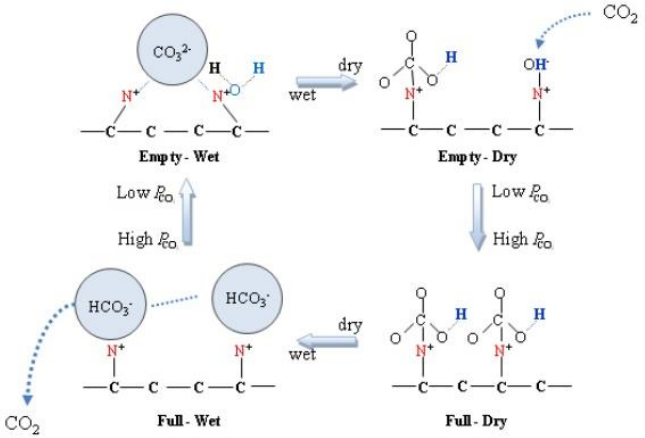
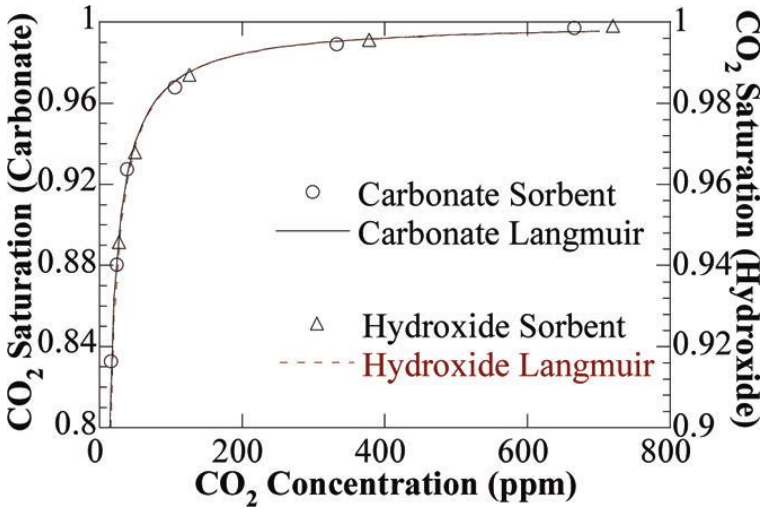
Moisture Swing for Specific PILs

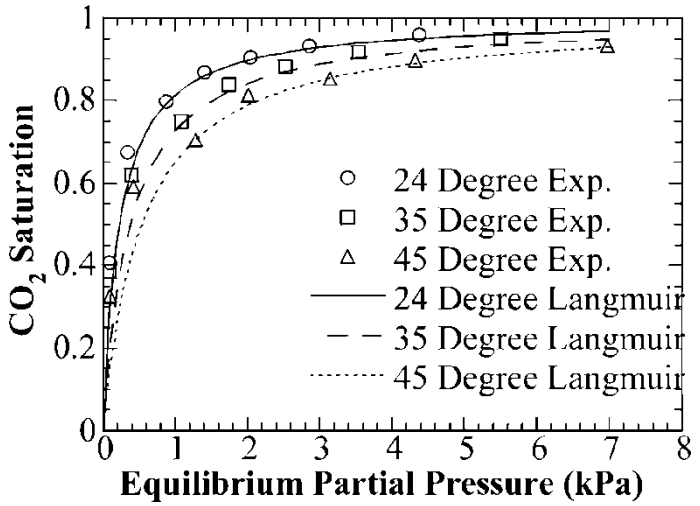


I. The PIL material, called P[VBTEA][CO_3^{2-}], adsorb CO_2 when dry and release CO_2 when wet, which constitutes a humidity swing cycle.

II. Provide an economical approach for air capture.



Under dry condition



Under wet condition

Environ. Sci. Technol. **2011**, 45, 6670–6675

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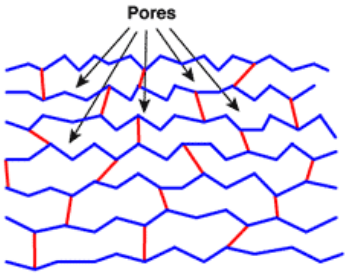
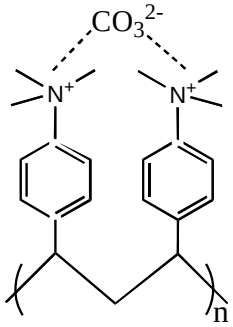
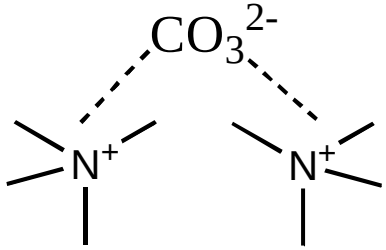
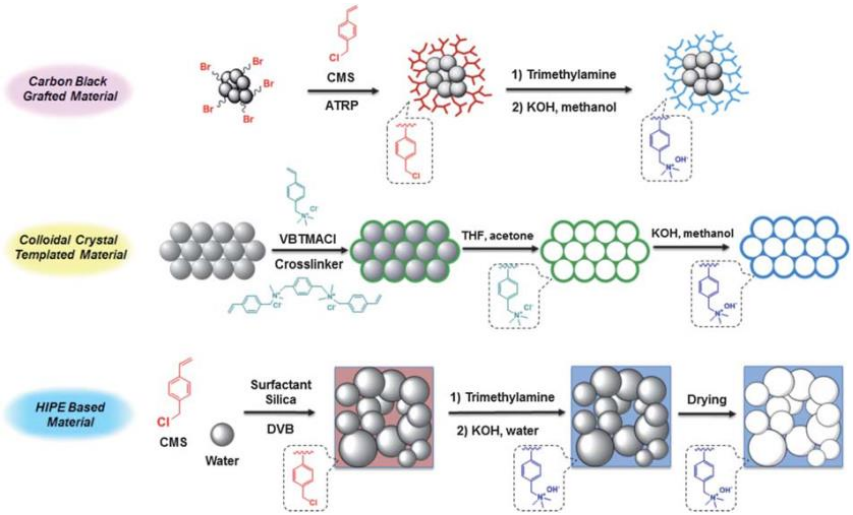
Reveal mechanism of moisture swing through quantum chemistry calculation







Build the computational model：from polymer to simplified model compound



Different materials with the same functional groups

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

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Energy Environ. Sci. **2013**, 6, 488-493

Structures and properties

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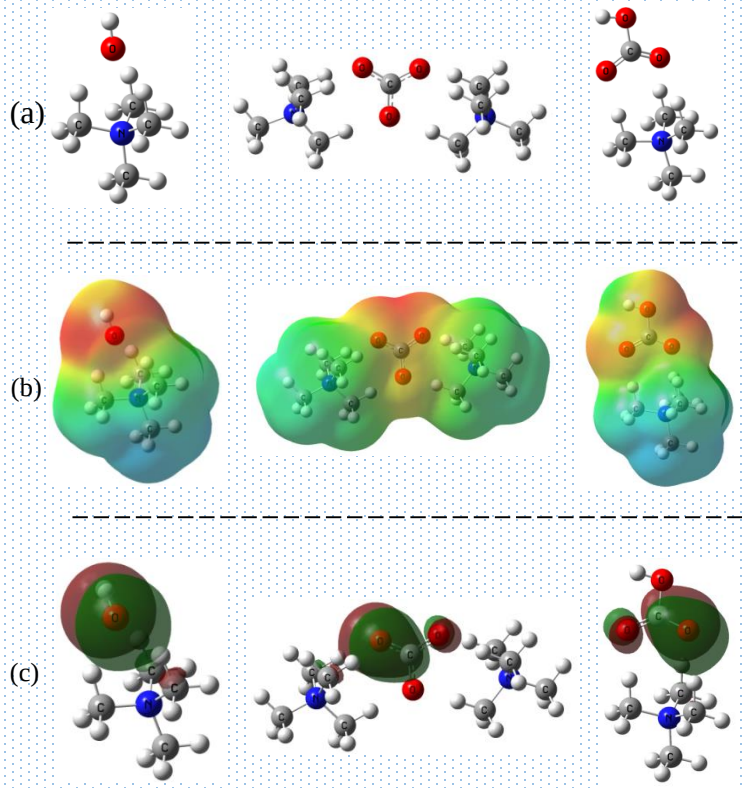

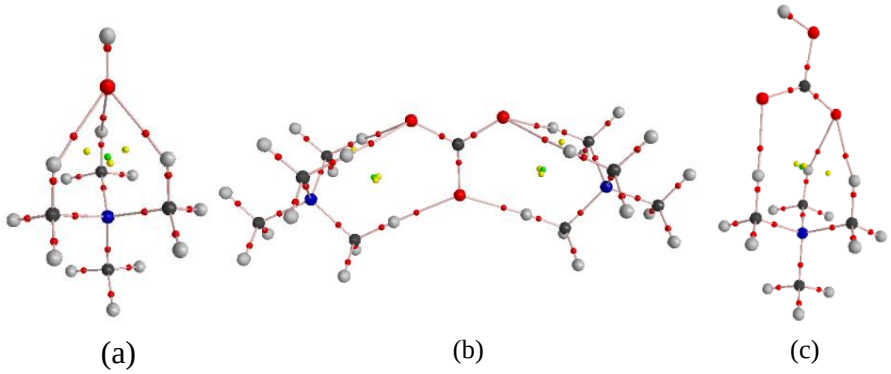

Model compounds	Number of H-bonds	ρ [a]	$\nabla^2\rho$ [b]	ΔE (kJ/mol) [c]	Charge transfer [d]
PILs with hydroxide	3	0.033-0.033	0.112-0.113	496	0.118
PILs with carbonate	6	0.032-0.037	0.104-0.111	1289	0.293
PILs with bicarbonate	3	0.024-0.029	0.080-0.095	395	0.040

The most possible sites for the adsorption of H_2O and CO_2

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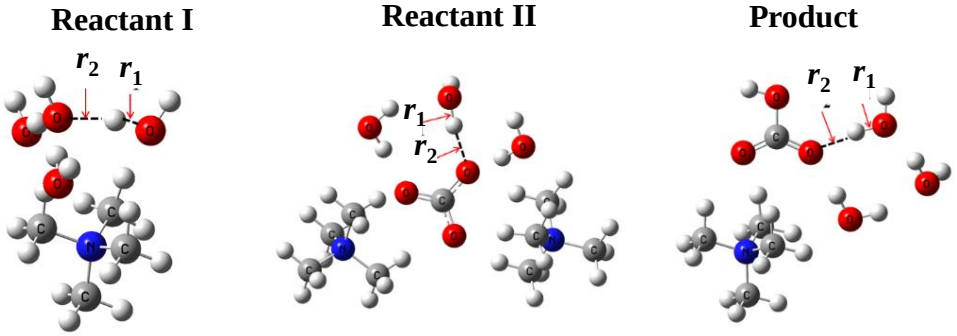
Hydrated water on the interface



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

Model compounds	Number of water molecules	Atomic charge [a]	r_1 (Å) [b]	r_2 (Å) [c]
PILs with hydroxide	1	-1.027	1.021	1.595
	2	-1.024	1.018	1.607
	3	-1.016	1.012	1.623
PILs with carbonate	1	-1.012	1.001	1.647
	2	-1.004	0.999	1.665
	3	-1.001	0.996	1.684
PILs with bicarbonate	1	-1.004	0.992	1.693
	2	-1.001	0.981	1.793
	3	-1.013	0.990	1.717

- As the number of hydrated water molecule increases, HCO_3^- shows the trend of transforming into H_2CO_3, which could resolve and release CO_2.

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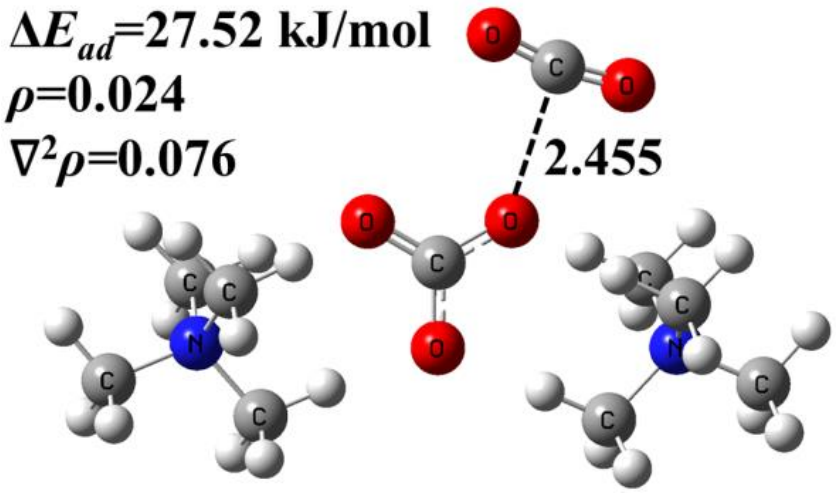
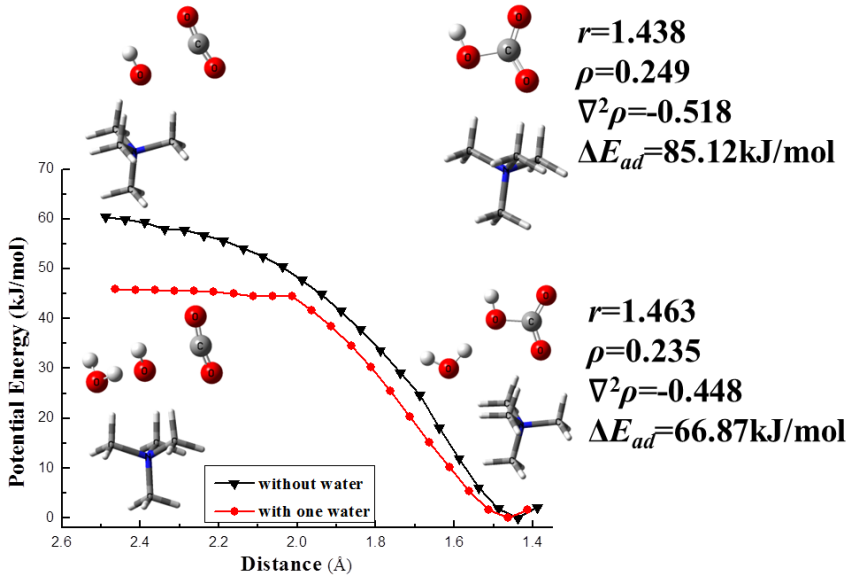
Reaction pathways of CO2 adsorption



Direct interaction between $[N^+CO_3^{2-}N^+]$ and CO2

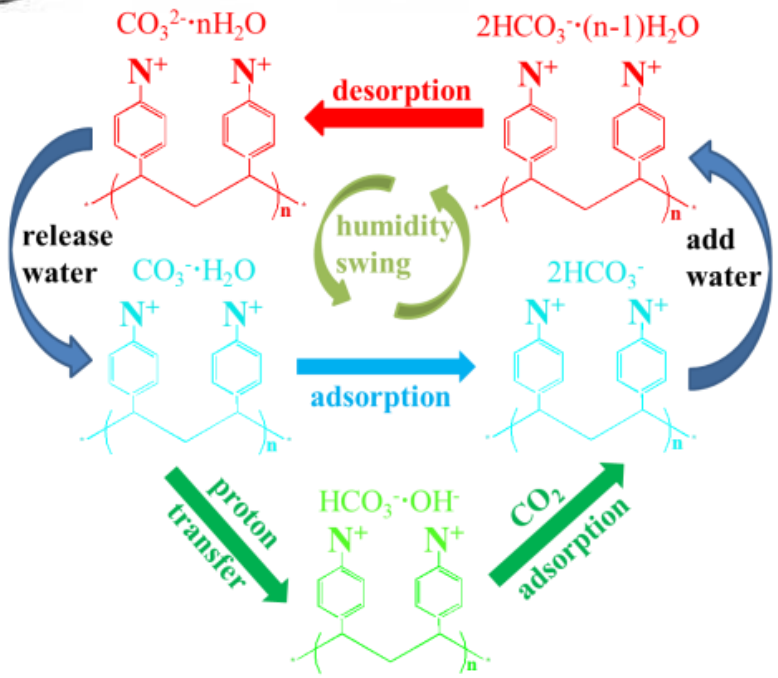


Direct interaction between $[N^+OH^-]$ and CO2

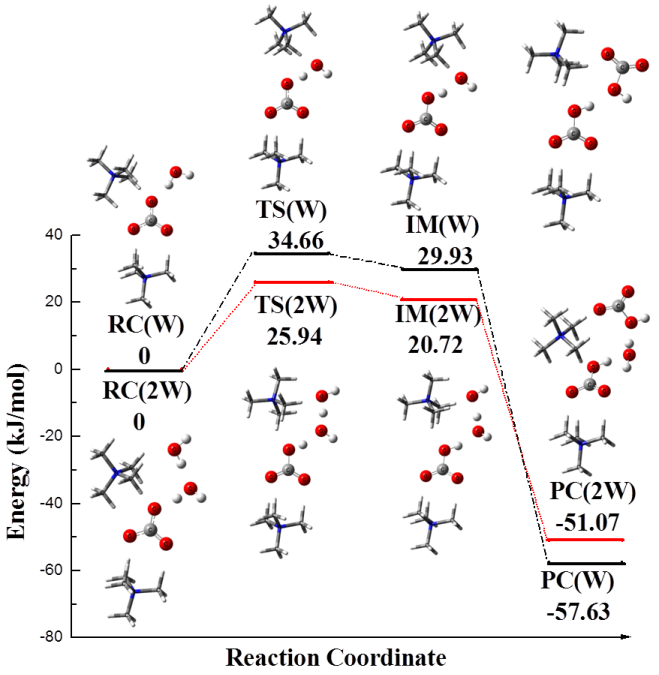
- Hydroxide has strong affinity of CO2. The combination could transform into bicarbonate immediately.

- The proton transfer mechanism: a proton is transferred from hydrated water to carbonate, through which a hydroxide ion is produced.

Reaction pathways of CO2 adsorption



Adsorption/desorption pathways



Energy profile of the reaction pathways

- The activation energy of proton transfer is 34.6kJ/mol, much smaller than that of CO_2 absorption by MEA.
- Water could promote the reaction as catalyst.

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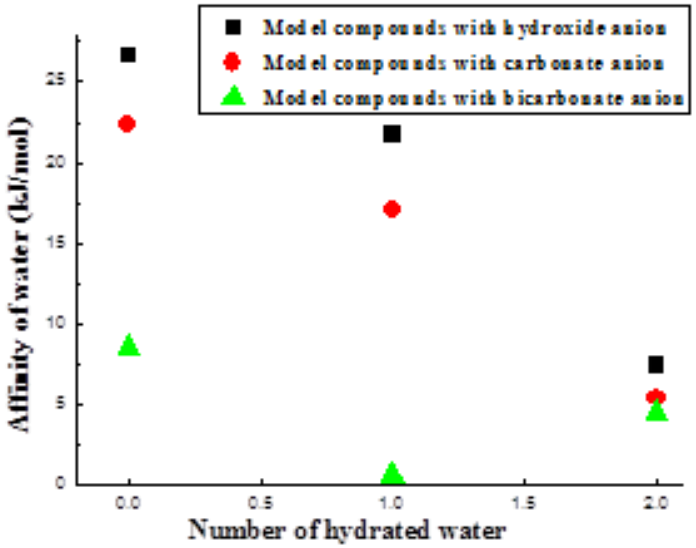
Low enthalpy change of the reaction

$$[N^+CO_3^{2-}N^+]\cdot aH_2O^{(h)}+CO_2\rightarrow[2N^+HCO_3^-]\cdot bH_2O^{(h)}+(a\text{-}b\text{-}1)H_2O^{(g)}$$

Possible coefficient of Equation (5)		Corresponding thermodynamic parameters	
a	*b*	$\Delta G^{\ominus}$ (kJ/mol)	$\Delta H^{\ominus}$ (kJ/mol)
1	0	-16.724	-17.250
	1	-25.284	-66.110
2	1	-6.170	-7.404
	2	-12.471	-56.264
3	2	-8.270	-7.404
	3	-14.624	-48.677



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

- Significant difference of hydrophilicity between states before and after adsorption

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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)

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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.

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