

Supporting information

CO₂ capture by 1,2,3-triazole-based deep eutectic solvents: the unexpected role of hydrogen bonds

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Experimental sections

Materials and Characterizations

Tetraethylammonium hydroxide (35 %, w / w) aqueous solution was purchased from Alfa Aesar. 1,2,3-triazole (98 %) was purchased from Innochem and Aladdin. Ethylene glycol (99.5 %) and sulfolane (99 %) were purchased from J&K Scientific Ltd. 1,2,3-triazole and ethylene glycol were dried by 4Å molecular sieve prior to use. CO₂ (99.995 %) and N₂ (99.999 %) were obtained from Beijing ZG Special Gases Sci. and Tech. Co. Ltd (Beijing, China).

FTIR spectra were recorded on a Perkin-Elmer frontier spectrometer with an attenuated total reflection (ATR) accessory. ¹H NMR (600 MHz) and ¹³C NMR (151 MHz) spectra were obtained on a Bruker spectrometer, and DMSO-d₆ or CDCl₃ was used as the internal reference.

Synthesis of the [Et₄N][Tz] and DESs

Tetraethylammonium hydroxide ([Et₄N][OH]) (35% w / w) aqueous solution was mixed with 1, 2, 3-triazole (Tz) at the equimolar ratio in a glass vial, and then the solution was stirred for about 2 hours at room temperature. After that, the water in the solution was removed by using a rotary evaporator at 80 °C. The obtained solid salt [Et₄N][Tz] was dried under vacuum at 80 °C before use.

Binary DESs were synthesized by mixing [Et₄N][Tz] with Tz or EG at desired molar ratios, and the mixtures were stirred at room temperature for about 2 hours to obtain DESs. Ternary DESs were prepared by mixing [Et₄N][Tz], Tz, and EG at desired molar ratios, and then the mixtures were stirred at room temperature for about 2 hours.

Absorption and Desorption of CO₂

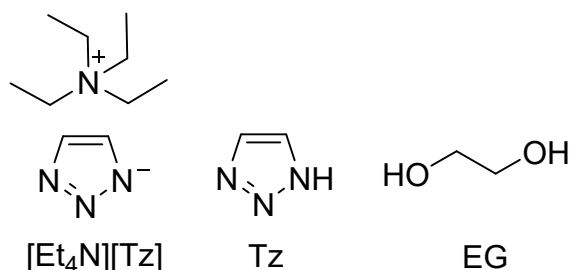
DES (about 2.0 g) was charged into a glass tube with an inner diameter of 10 mm, and a rubber lid with two needles was used to seal the tube. One needle was for the CO₂ inlet, and the other one was for the CO₂ outlet. Then the glass tube was partially immersed in a water bath of the desired temperature (±0.2 °C). CO₂ was bubbled into the solvents in the tube through the needles at a flow rate of ~50 mL / min under 1 atm. The CO₂ absorbed by the DES was calculated through the weight change of the tube at regular intervals during the absorption process by an electronic balance with an

accuracy of ± 0.1 mg.

In the desorption of CO_2 , N_2 (~ 50 mL / min) at atmospheric pressure was bubbled into the solution in the tube, which was partially immersed in a water bath at required temperature. The weight of the solution was also determined by the electronic balance (± 0.1 mg) at regular intervals during the desorption process.

Computational methodology

All of these calculations were carried out with the Gaussian 09 suite of programs.¹ The geometries of all the complexes under study were fully optimized by means of the M06-2x/aug-cc-pVDZ theoretical level.²⁻³ Frequency calculations were performed at the same theoretical levels to ensure that all the structures are genuine minima on the potential energy surface. The atoms-in-molecules (AIM) analysis⁴ and atomic dipole moment corrected Hirshfeld (ADCH) charge⁵ are calculated using the Multiwfn program⁶ and visualized with the VMD package⁷.



Scheme S1. The structures of $[\text{Et}_4\text{N}][\text{Tz}]$, Tz and EG.

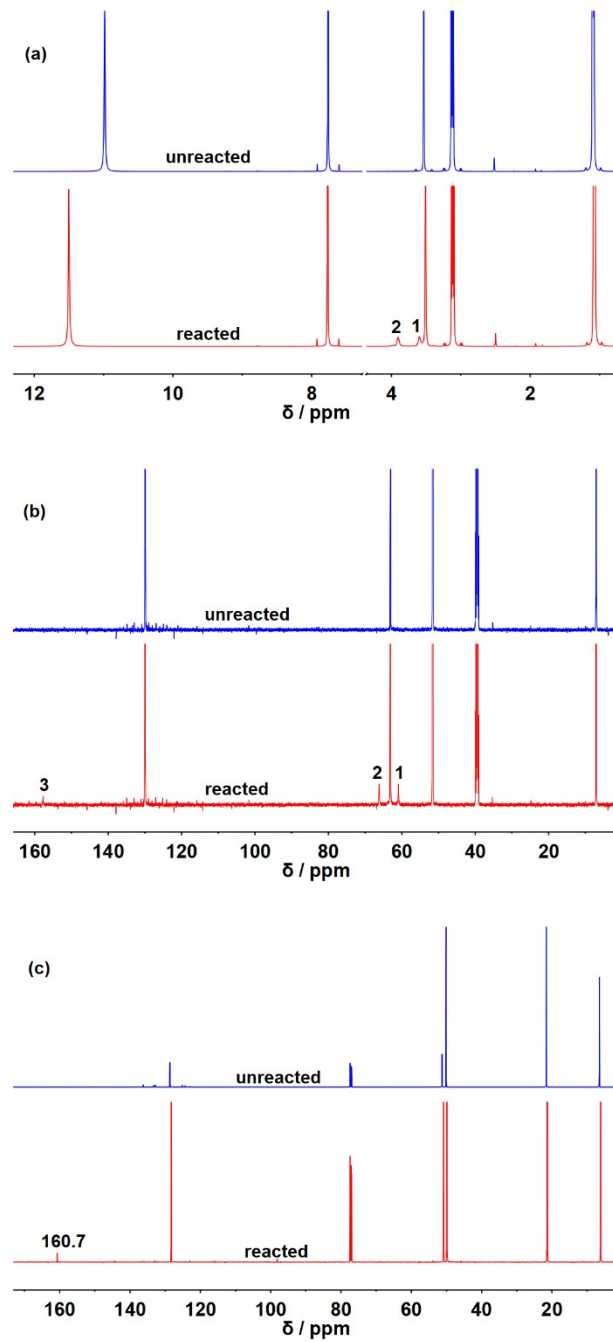


Fig. S1 ¹H (a) and ¹³C (b) NMR spectra of [Et₄N][Tz]:Tz:EG (1:2:2) DESs before and after CO₂ capture; ¹³C NMR spectra (c) of [Et₄N][Tz] solution (30 wt%) in sulfolane (Sulf) before and after CO₂ capture.

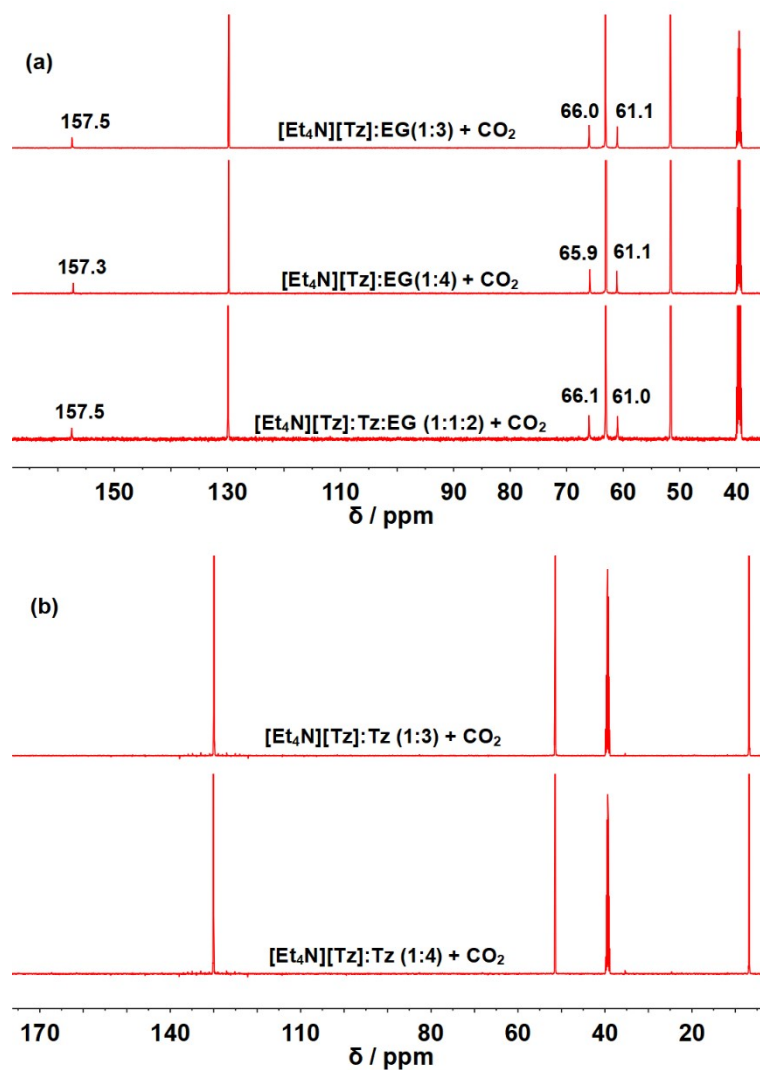


Fig. S2 a): ^{13}C NMR spectra of $[\text{Et}_4\text{N}][\text{Tz}]:\text{EG}(1:3)$, $[\text{Et}_4\text{N}][\text{Tz}]:\text{EG}(1:4)$, and $[\text{Et}_4\text{N}][\text{Tz}]:\text{Tz}:\text{EG}(1:1:2)$ DESs after capture; b): ^{13}C NMR spectra of $[\text{Et}_4\text{N}][\text{Tz}]:\text{Tz}(1:3)$ and $[\text{Et}_4\text{N}][\text{Tz}]:\text{Tz}(1:4)$ after capture.

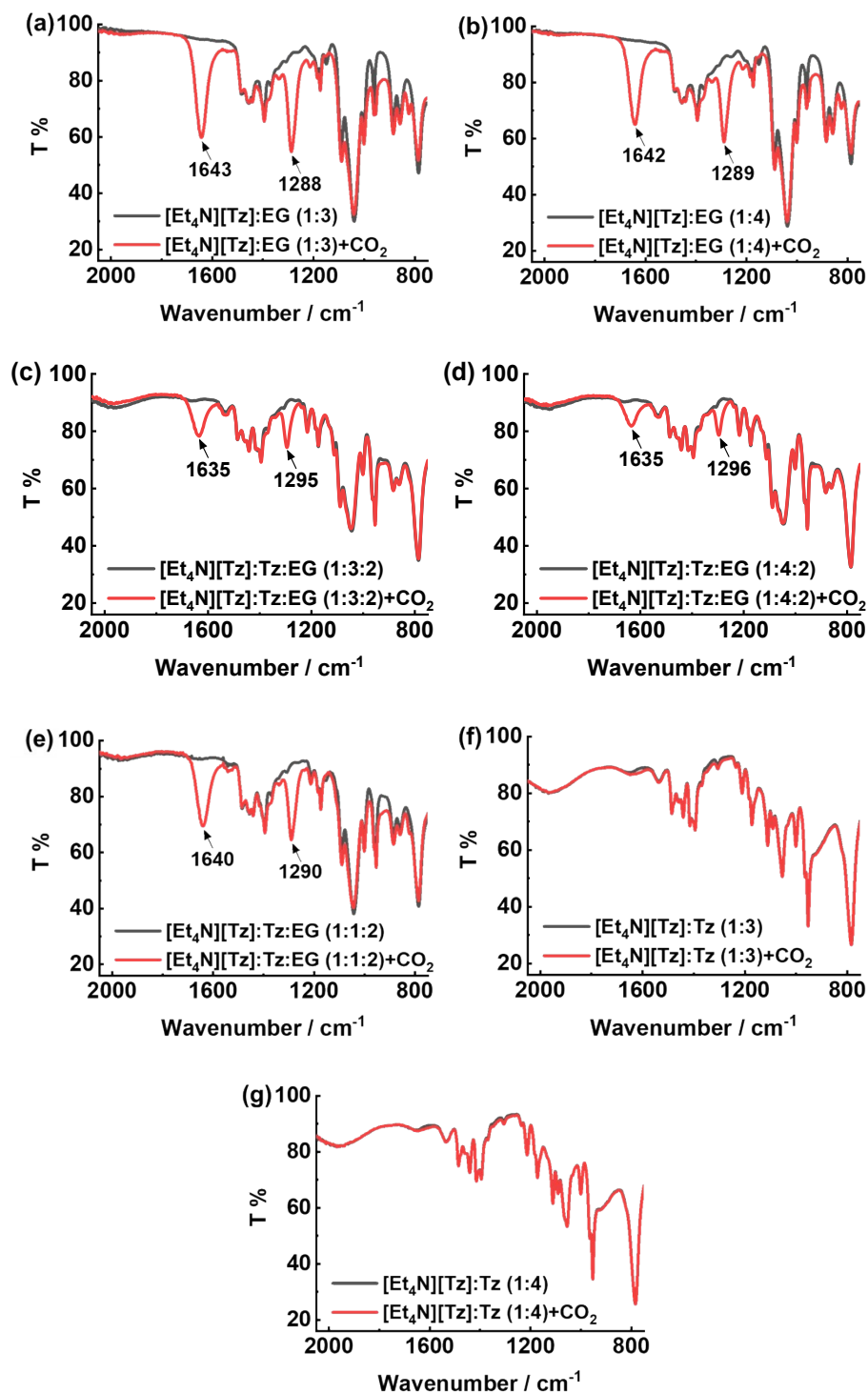


Fig. S3 a) FTIR spectra of [Et₄N][Tz]:EG (1:3) before and after CO₂ capture; b) FTIR spectra of [Et₄N][Tz]:EG (1:4) before and after CO₂ capture; c) FTIR spectra of [Et₄N][Tz]:Tz:EG (1:3:2) before and after CO₂ capture; d) FTIR spectra of [Et₄N][Tz]:Tz:EG (1:4:2) before and after CO₂ capture; e) FTIR spectra of [Et₄N][Tz]:Tz:EG (1:1:2) before and after CO₂ capture; f) FTIR spectra of [Et₄N][Tz]:Tz (1:3) before and after CO₂ capture; g) FTIR spectra of [Et₄N][Tz]:Tz (1:4) before and after CO₂ capture.

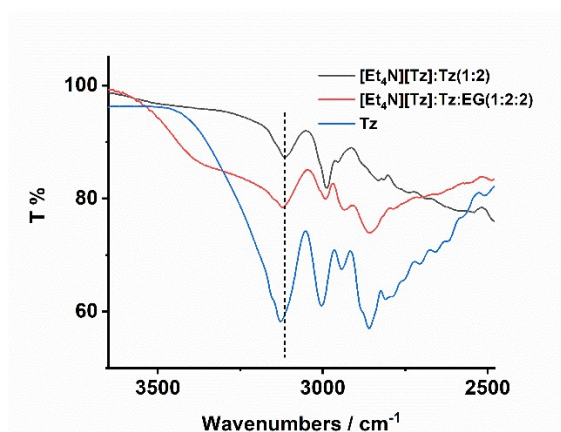


Fig. S4 The FTIR spectra of $[\text{Et}_4\text{N}][\text{Tz}]:\text{Tz}$ (1:2), $[\text{Et}_4\text{N}][\text{Tz}]:\text{Tz}:\text{EG}$ (1:2:2) and Tz.

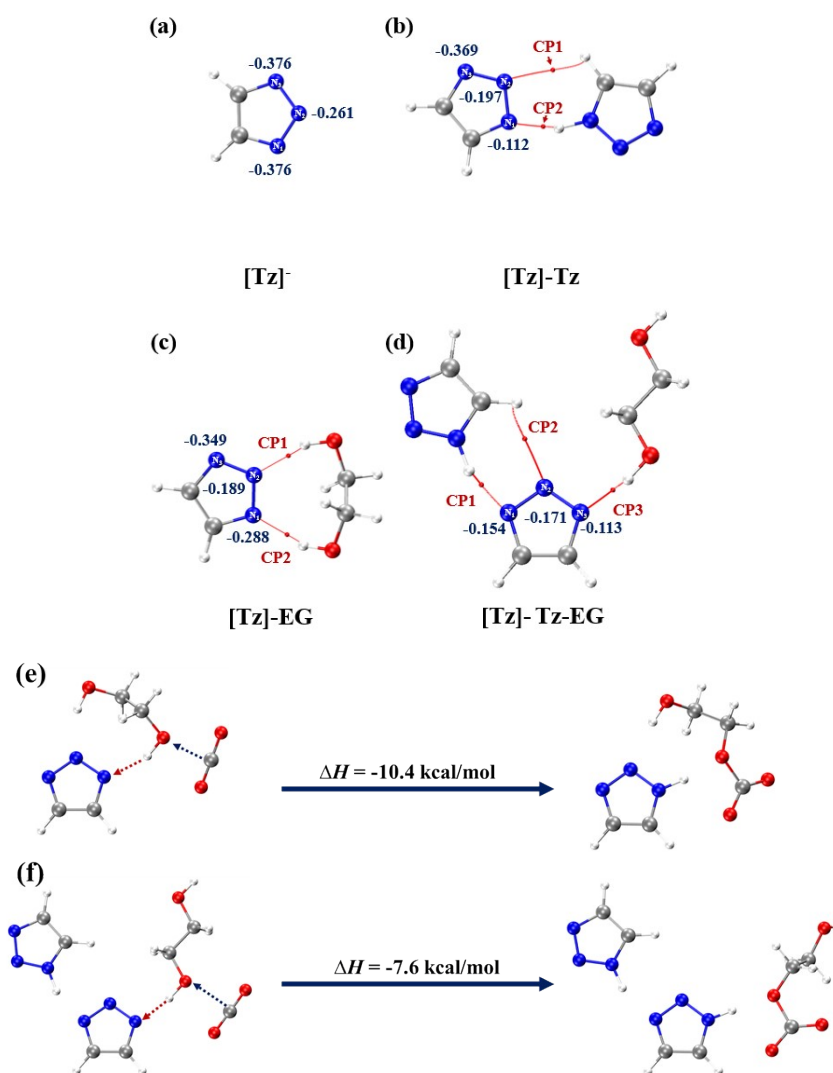


Fig. S5 The atoms in molecules (AIM) molecular graph for the calculated systems. The ADCH charge for the N atoms (N1, N2, N3) on $[\text{Tz}]^-$ anion are shown in blue. The critical points (CPs) for intermolecular hydrogen bonds are labeled in red dots, and the bond paths for hydrogen bonding are linked through red lines. (a) $[\text{Tz}]^-$; (b) $[\text{Tz}]-\text{Tz}$; (c) $[\text{Tz}]-\text{EG}$; (d) $[\text{Tz}]-\text{Tz}-\text{EG}$; (e) the reaction of CO_2 with $[\text{Tz}]-\text{EG}$; (f) the reaction of CO_2 with $[\text{Tz}]-\text{Tz}-\text{EG}$.

Table S1. The ADCH charge and charge transfer for N atoms of [Tz]⁻ anion, and the geometric and energetic data for the hydrogen bonds in studied systems.

System	ADCH Charge and (charge transfer) ^a			structures and energies			
	N ₁	N ₂	N ₃	CP ^b	HB	<i>d</i> _{HB} ^c	<i>E</i> _{HB} ^d
[Tz] ⁻	-0.376 (0.000)	-0.261 (0.000)	-0.376 (0.000)				
[Tz]+ Tz	-0.112 (0.264)	-0.197 (0.064)	-0.369 (0.007)	CP1	C-H···N ₂	2.781	-5.4
				CP2	N-H···N ₁	1.658	-69.4
[Tz] + EG	-0.288 (0.088)	-0.189 (0.072)	-0.349 (0.027)	CP1	O-H···N ₂	1.941	-27.0
				CP2	O-H···N ₁	1.916	-28.6
[Tz]+ Tz + EG	-0.154 (0.222)	-0.171 (0.090)	-0.113 (0.263)	CP1	N-H···N ₁	1.755	-47.5
				CP2	C-H···N ₂	2.715	-6.3
				CP3	O-H···N ₃	1.765	-45.2

^a The N atoms are labeled in white in Fig. S5. ^b The CPs are labeled in red in Fig. S5.

^c The bond length (*d*_{HB}) for hydrogen bonds are given in Å. ^d The bond energies (*E*_{HB}) are in kcal/mol.

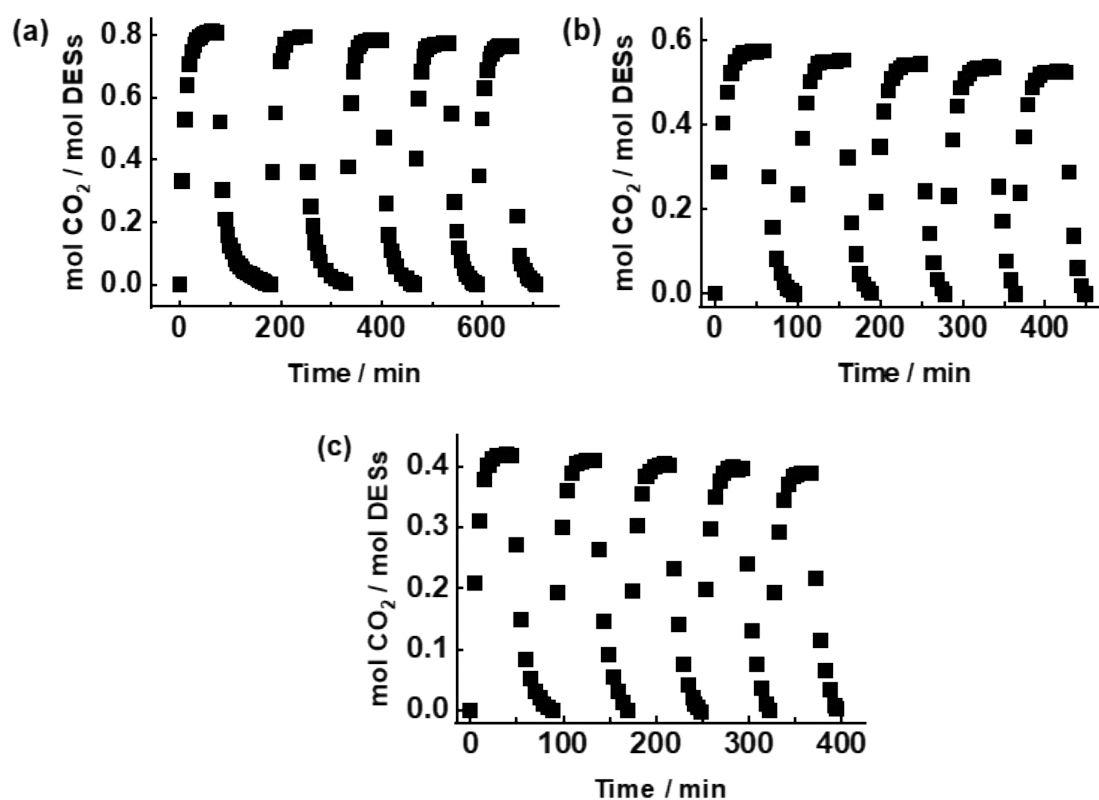


Fig. S6 Five consecutive CO₂ absorption-desorption cycles of (a) [Et₄N][Tz]:EG (1:2) (absorption: 25 °C, desorption: 60 °C), (b) [Et₄N][Tz]:Tz:EG (1:1:2) (absorption: 25 °C, desorption: 40 °C), and (c) [Et₄N][Tz]:Tz:EG (1:2:2) (absorption: 25 °C, desorption: 30 °C).

References

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