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Supporting information

CO_2 capture by imidazolium-based deep eutectic solvents: the effect of steric hindrance of N-heterocyclic carbenes

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Experimental sections

Materials and Characterizations

1,3-Bis(isopropyl)imidazolium chloride ([IiPim][Cl], 97%) and 1,2,4-triazole (98 %) was obtained from Innochem (Beijing). Ethylene glycol (EG, 99.5 %) was supplied by J&K Scientific (Beijing). Ambersep 900(OH) ion exchange resin was purchased from Alfa Aesar. CO_2 (99.995 %) and N_2 (99.999 %) were supplied from Beijing ZG Special Gases Sci. and Tech. Co. Ltd (Beijing, China).

A Nicolet 6700 spectrometer with an attenuated total reflection (ATR) accessory is used to record FTIR spectra. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were obtained on a Bruker spectrometer, using DMSO-d_6 as the solvent.

Synthesis of [IiPim][Triz]

At first, the aqueous solution of [IiPim][Cl] was transformed to aqueous solution of [IiPim][OH] by flowing through a glass column containing Ambersep 900(OH) ion exchange resin. The concentration of [IiPim][OH] was titrated using potassium hydrogen phthalate. Then, 1, 2, 4-triazole (TrizH) was added to the solution of [IiPim][OH] at an equimolar ratio (TrizH: [IiPim][OH]=1:1) and the mixture was stirred about 2 hours at room temperature. The water was removed using a rotary evaporator to obtain the solid salt [IiPim][Triz], which then was dried under vacuum at 70 °C prior to use.

Synthesis of DESs

[IiPim][Triz]-EG DESs were prepared by mixing [IiPim][Triz] with EG at desired molar ratios. [IiPim][Triz]-EG mixtures were stirred at 60 °C until homogenous solutions were formed, which were cooled to room temperature to obtain DESs.

Absorption and Desorption of CO_2

The procedure for absorption and desorption of CO_2 by DESs can be found in our previous work.[1,2] Generally, CO_2 (~50 ml/min) was bubbled into DESs present in a glass tube, and the amount of CO_2 absorbed by DESs can be calculated through the weight change before and after absorption. During desorption process, N_2 (~50 ml/min) was bubbled into the mixture of DESs+CO_2 at 60 °C to release CO_2.

NMR and FTIR data of absorbents

[IiPim][Triz]:

^{1}H NMR (400 MHz, DMSO-d_6): δ =10.16 (s, 1H), 8.16 (s, 2H), 7.81 (s, 2H), 4.68 (sept, J = 6.7 Hz, 2H), 1.44 ppm (d, J = 6.7 Hz, 12H).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 149.4, 134.7, 120.9, 52.3, 22.3 ppm.

FTIR (solution in DMSO-d_6): ν = 3070, 2979, 2874, 2815, 2247, 2122, 1554, 1470, 1428, 1376, 1335, 1281, 1238, 1186, 1142, 1053, 1026, 1006, 960, 846, 820, 757, 683, 660, 623 cm^{-1}.

[IiPim][Triz]+CO_2:

^{13}C NMR (100.6 MHz, DMSO-d_6): δ =155.3, 147.5, 144.2, 142.2, 134.2, 120.8, 117.9, 52.4, 50.6, 22.2 ppm.

FTIR (solution in DMSO-d_6): ν =3082, 2981, 2336, 2249, 2123, 1738, 1665, 1554, 1476, 1375, 1318, 1273, 1185, 1151, 1053, 1025, 1006, 881, 820, 794, 756, 682, 655, 622 cm^{-1}.

[IiPim][Triz]:EG (1:3)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.31 (s, 1H), 7.83 (s, 2H), 7.80 (s, 2H), 4.58 (sept, J = 6.7 Hz, 2H), 3.49 (s, 12H), 1.44 ppm (d, J = 6.7 Hz, 12H).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ =149.0, 133.9, 120.9, 63.2, 52.7, 22.5 ppm.

FTIR: ν = 3317, 3131, 2983, 2931, 2866, 1552, 1483, 1462, 1428, 1376, 1329, 1255, 1183, 1146, 1089, 1037, 976, 883, 857, 750, 677, 654, 515 cm^{-1}.

[IiPim][Triz]:EG (1:3) + CO_2

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 157.7, 147.2, 134.0, 120.8, 66.2, 63.2, 61.0, 52.5, 22.4 ppm.

FTIR: ν = 3303, 3130, 2934, 2867, 2337,1638, 1553, 1462, 1428, 1377, 1332, 1285, 1274, 1184, 1150, 1088, 1040, 969, 950, 882, 858, 824, 748, 681, 649, 591, 500 cm^{-1}.

[IiPim][Triz]:EG (1:4)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.26 (s, 1H), 7.82 (s, 2H), 7.77 (s, 2H), 4.58 (sept, J = 6.7 Hz, 2H), 3.45 (s, 16H), 1.45 ppm (d, J = 6.7 Hz, 12H).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ =148.9, 133.8, 120.9, 63.2, 52.7, 22.5 ppm.

FTIR: ν = 3302, 3136, 2984, 2932, 2867, 1552, 1485, 1461, 1428, 1377, 1332, 1257, 1183, 1147, 1087, 1035, 976, 883, 857, 743, 677, 654, 515 cm^{-1}.

[IiPim][Triz]:EG (1:4) + CO_2

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 158.1, 147.3, 134.0, 120.9, 66.4, 63.3, 61.1, 52.7, 22.5 ppm.

FTIR: ν = 3307, 3131, 2936, 2869, 2337, 1638, 1553, 1461,1428, 1377,1287, 1275,

1183, 1151, 1087, 1038, 970, 882, 860, 825, 681, 648, 589, 512 cm^{-1}.

[IiPim][Triz]:EG (1:5)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.26 (s, 1H), 7.82 (s, 2H), 7.78 (s, 2H), 4.58 (sept, J = 6.7 Hz, 2H), 3.46 (s, 20H), 1.45 ppm (d, J = 6.7 Hz, 12H).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 148.9, 133.8, 120.9, 63.2, 52.7, 22.5 ppm.

FTIR: ν = 3315, 3133, 2982, 2931, 2866, 1554, 1484, 1460, 1428, 1376, 1337, 1257, 1183, 1147, 1088, 1035, 977, 883, 857,747, 677, 655, 514 cm^{-1}.

[IiPim][Triz]:EG (1:5) + CO_2

^{13}C NMR (100.6 MHz, DMSO-d_6): δ =157.8, 147.3, 133.9, 120.9, 66.2, 63.2, 61.1, 52.6, 22.5 ppm.

FTIR: ν = 3300, 3132, 2934, 2868, 1637, 1554, 1460, 1428, 1377, 1332, 1288, 1275, 1183, 1150, 1087, 1038, 970, 882, 858, 825, 745, 680, 649, 591, 505 cm^{-1}.

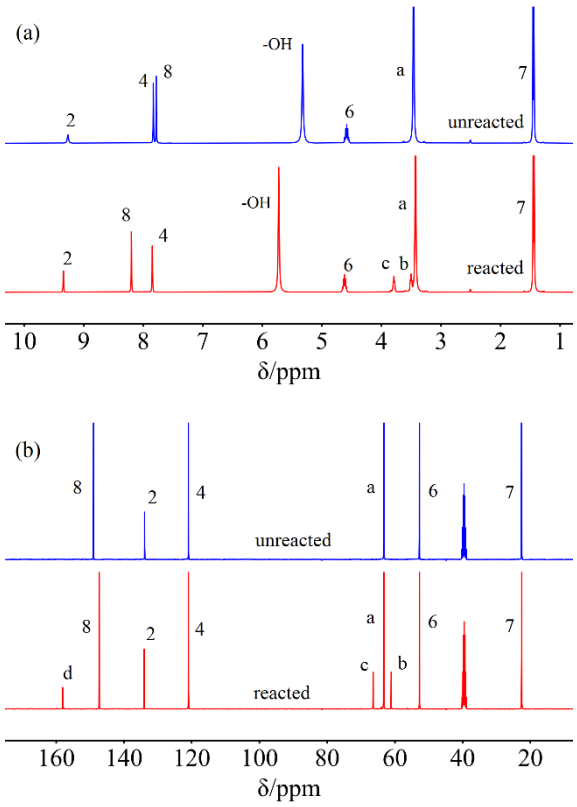

Fig. S1 The ^{1}H (a) and ^{13}C (b) NMR spectra of [IiPim][Triz]:EG (1:4) before and after capture.

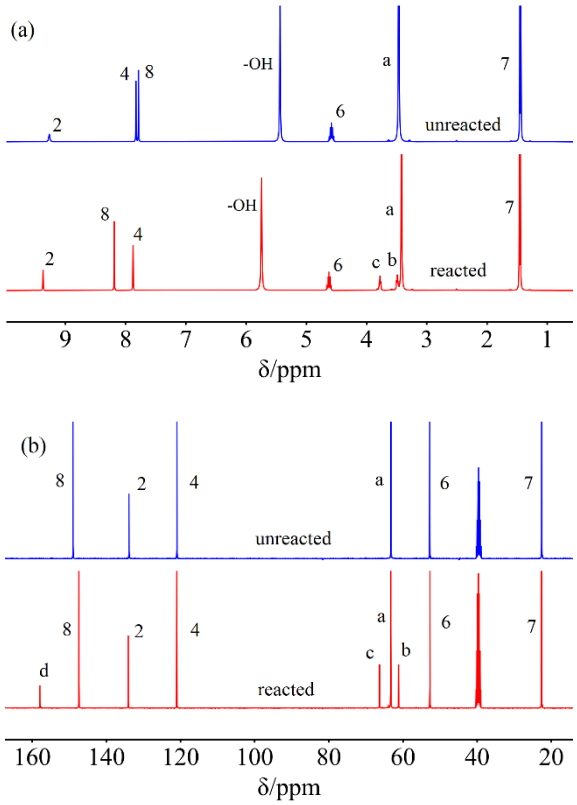

Fig. S2 The ^{1}H (a) and ^{13}C (b) NMR spectra of [IiPim][Triz]:EG (1:5) before and after capture.

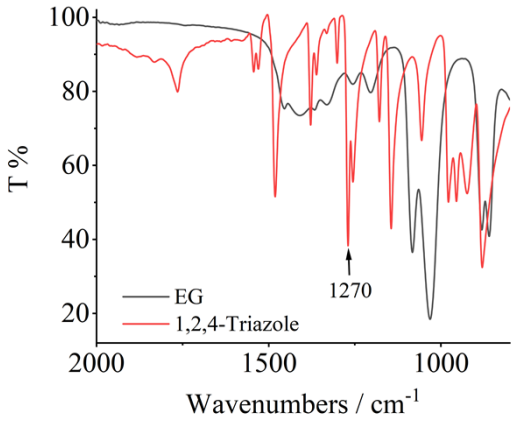

Fig. S3 Partial FTIR spectra of EG and 1,2,4-Triazole.

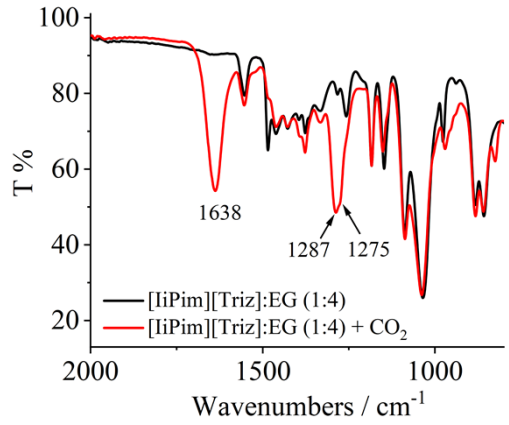

Fig. S4 The FTIR spectra of [IiPim][Triz]:EG (1:4) before and after capture.

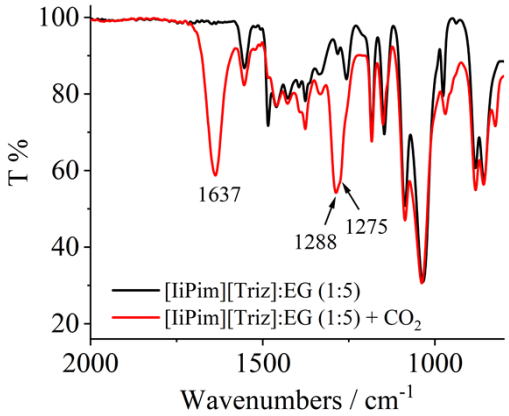

Fig. S5 The FTIR spectra of [IiPim][Triz]:EG (1:5) before and after capture.

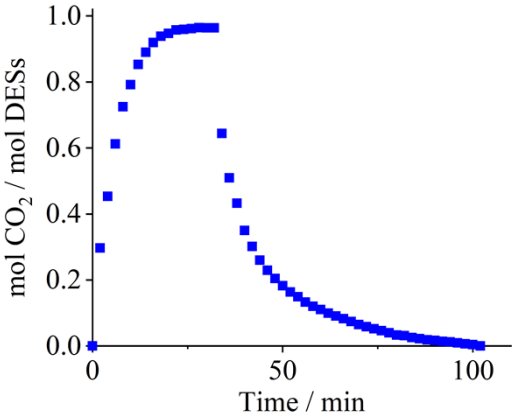

Fig. S6 Absorption (25 ℃) and desorption (60 ℃) of CO_2 by [IiPim][Triz]:EG (1:3).

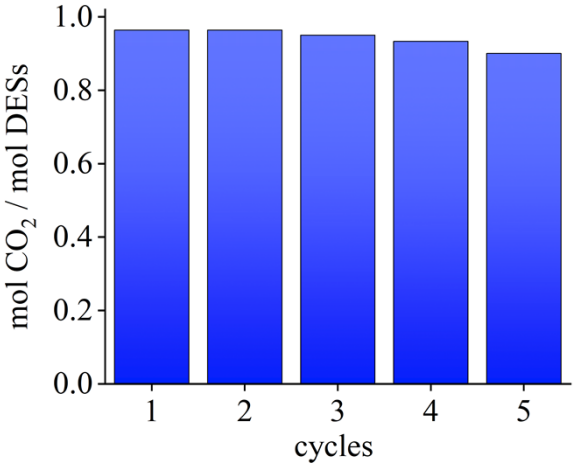

Fig. S7 Five absorption-desorption cycles by [IiPim][Triz]:EG (1:3). Absorption: 25 ℃; desorption: 60 ℃.

Table S1. The comparison of CO_2 capture performances by [IiPim][Triz]-based DESs with other DESs reported.

Solvents	Absorption		Capacity (mol/mol)	Desorption T/℃	References
	T/ ℃	P/atm			
[IiPim][Triz]:EG (1:3)	25	1.0	0.96	60	This work
[IiPim][Triz]:EG (1:4)	25	1.0	0.98	60	This work
[IiPim][Triz]:EG (1:5)	25	1.0	0.99	60	This work
[Et_4N][Tz]:EG (1:2)	25	1.0	0.80	60	3
[DBUH][Car]:EG (1:2)	25	1.0	0.97	70	4
[DBUH][Thy]:EG (1:2)	25	1.0	0.97	70	4
[DBUH][Im]:EG (7:3)	40	1.0	1.01[a]	70	5
DBN:BmimCl:Im (1:1:2)	25	1.0	0.97	—[b]	6
[P_{2222}][Triz]:EG (1:2)	25	1.0	0.92	70	1
[DBUH][4-F-PhO]:EG (1:3)	25	1.0	0.99	75	2
[N_{2222}][Car]:EG (1:2)	25	1.0	0.87	80	7
K[Maba]:EG (1:2)	40	1.0	0.76	80	8
[DBUH][MLU]:EG (1:1)	40	1.0	0.90	80	9
[EMIM][2-Npyr]:EG (1:2)	25	1.0	0.85	40	10
[MEAH][Im]:EG (1:1)	25	1.0	0.62	—[b]	11
MEA:BmimCl (1:1)	25	1.0	0.45	—[b]	12
DBN-Triz (1:1)	25	1.0	0.67	80	13
[Ch][1,2,4-Triz]: EG (1:2)	25	1.0	0.75	—[b]	14
[Ch][Pro]: EG (1:5)	25	1.0	0.71	—[b]	15
DBN-EU (2:1)	45	1.0	0.875[c]	80	16
Bet:1,2-Pro:DBU (1:6:1)	30	1.1	1.02	90	17
[TETA]Cl:Thymol (1:3)	50	1.0	1.339	100	18
L-Arg:EG (1:5)	65	1.0	0.819	100	19
[N_{2222}][$CH(CN)_2$]:Eim (1:1)	30	1.0	0.89	120	20

[a] mol CO_2/mol [DBUH][Im]; [b] unavailable; [c] mol CO_2/mol DBN

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