Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Deep eutectic solvents composed of bio-phenol-derived superbase ionic liquids and ethylene glycol for CO_2 capture

Ze Wang, Zonghua Wang, Xin Huang, Dezhong Yang*, Congyi Wu*, Jie Chen*

School of Science, China University of Geosciences, Beijing 100083, China

Email: yangdz@cugb.edu.cn; wucongyi@ cugb.edu.cn; chenjie@cugb.edu.cn

Experimental section

Materials and characterizations

CO_2 (99.995%) and N_2 (≥99.99%) were obtained from Beijing ZG Special Gases Sci. and Tech. Co. Ltd. Ethylene glycol (99.5%) was purchased J&K Scientific Ltd. 1,8-Diazabicyclo[5.4.0]undec-7-ene(DBU,99%) , Thymol (98%) and Carvacrol (99%) were supplied by Innochem. FTIR spectra were recorded on a Perkin-Elmer Frontier spectrometer with an attenuated total reflection (ATR) accessory. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were obtained on a Bruker spectrometer using DMSO-d_6 as the internal solvent. The viscosity was measured in an Anton Paar series MCR92 rheometer. A TA Instruments Q200 differential scanning calorimeter (DSC) was used to determine the melting point of solvents from -80 to 25°C at a heating rate of 10 °C/min under N_2 atmosphere. The decomposition temperature of DESs was determined by a Mettler Toledo TG 3+ instrument from 25~400°C at a heating rate of 10 °C/min under N_2 atmosphere.

Syntheses of DESs

At first, DBU and phenols (thymol or carvacrol) were added to a flask with the molar ratio of 1:1 and the mixtures were stirred at 40 °C for about 6 hours. After that, DBU-based ILs were mixed with EG at desired molar ratios (from 1:2 to 1:4) in a glass vial, and then the mixtures were stirred at room temperature for 2 hours to obtain DESs.

NMR and FTIR data of DESs:

[DBUH][Car]:EG (1:2)

^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.87 (d, J = 7.56 Hz, 1H), 6.62 (s, 1H), 6.42 (d, J = 7.56 Hz, 1H), 3.44 (s, 8H), 3.19-3.22 (m, 4H), 3.13 (t, J = 5.58 Hz, 2H), 2.66-2.71 (m, 1H), 2.37 (t, 2H), 2.07 (s, 3H), 1.69-1.73 (m, 2H), 1.50-1.58 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.3, 157.9, 146.9, 130.0, 121.7, 114.9, 113.3, 63.0, 52.3, 47.7, 41.9, 34.7, 33.4, 29.0, 27.7, 25.3, 24.1, 21.6, 16.1 ppm

FTIR: ν = 3348, 2928, 2861, 2252, 2127, 1645, 1611, 1489, 1457, 1445, 1422, 1370, 1316, 1263, 1183, 1115, 1094, 1050, 1024, 1005, 960, 864, 821, 758, 698 cm^{-1}.

[DBUH][Car]:EG (1:3)

^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.87 (d, J = 7.56 Hz, 1H), 6.61 (s, 1H), 6.42 (d, J = 7.56 Hz, 1H), 3.43 (s, 12H), 3.20-3.23 (m, 4H), 3.12 (t, J = 5.58 Hz, 2H), 2.67-2.71 (m, 1H), 2.37 (t, 2H), 2.06 (s, 3H), 1.70-1.73 (m, 2H), 1.50-1.59 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.2, 157.6, 146.9, 130.0, 121.6, 115.2, 113.3, 63.0, 52.2, 47.7, 42.1, 34.8, 33.3, 29.0, 27.7, 25.4, 24.1, 21.6, 16.0 ppm

FTIR: ν = 3255, 2928, 2864, 2222, 1964, 1848, 1645, 1599, 1560, 1489, 1446, 1406, 1361, 1323, 1269, 1204, 1182, 1089, 1042, 990, 943, 916, 816, 795, 755, 690 cm^{-1}.

[DBUH][Car]:EG (1:4)

^1H NMR (600 MHz, DMSO-d_6): δ = 6.87 (d, *J* = 7.56 Hz,1H), 6.60 (s, 1H), 6.43 (d, *J* = 7.56 Hz, 1H), 3.43 (s, 16H), 3.20-3.24 (m, 4H), 3.12 (t, *J* = 5.58 Hz, 2H), 2.67-2.70 (m, 1H), 2.36 (t, 2H), 2.06 (s, 3H), 1.70-1.74 (m, 2H), 1.49-1.60 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.1, 157.5, 146.9, 130.1, 121.6, 115.3, 113.2, 63.0, 52.2, 47.7, 42.1, 34.9, 33.3, 29.0, 27.7, 25.4, 24.1, 21.6, 16.0 ppm

FTIR: ν = 3268, 2928, 2864, 2199, 1977, 1932, 1846, 1645, 1598, 1561, 1489, 1456, 1406, 1361, 1323, 1270, 1204, 1182, 1088, 1040, 990, 943, 916, 882, 861, 796, 755, 689 cm^{-1}.

[DBUH][Thy]:EG (1:2)

^1H NMR (600 MHz, DMSO-d_6): δ = 6.90 (d, *J* = 7.62 Hz, 1H), 6.56 (s, 1H), 6.43 (d, *J* = 7.62 Hz, 1H), 3.43 (s, 8H), 3.18-3.22 (m, 5H), 3.12 (t, *J* = 5.52 Hz, 2H), 2.36 (t, 2H), 2.14 (s, 3H), 1.69-1.73 (m, 2H), 1.50-1.58 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.0, 156.3, 135.0, 131.8, 125.3, 118.2, 116.2, 63.0, 52.2, 47.7, 42.2, 34.9, 29.0, 27.7, 26.1, 25.4, 22.8, 21.7, 20.8 ppm

FTIR: ν = 3251, 2928, 2861, 2040, 1985, 1845, 1644, 1603, 1560, 1491, 1445, 1398, 1370, 1339, 1317, 1288, 1264, 1203, 1164, 1151, 1089, 1043, 982, 949, 916, 884, 860, 795, 740, 689 cm^{-1}.

[DBUH][Thy]:EG (1:3)

^1H NMR (600 MHz, DMSO-d_6): δ = 6.90 (d, *J* = 7.62 Hz, 1H), 6.55 (s, 1H), 6.44 (d, *J* = 7.62 Hz, 1H), 3.43 (s, 12H), 3.19-3.22 (m, 5H), 3.12 (t, *J* = 5.52 Hz, 2H), 2.35 (t, 2H), 2.14 (s, 3H), 1.69-1.73 (m, 2H), 1.50-1.59 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.0, 156.2, 135.1, 131.8, 125.4, 118.4, 116.2, 63.0, 52.2, 47.7, 42.2, 34.9, 29.0, 27.8, 26.1, 25.4, 22.8, 21.7, 20.8 ppm

FTIR: ν = 3257, 2936, 2862, 1855, 1645, 1600, 1560, 1491, 1445, 1398, 1339, 1322, 1288, 1263, 1204, 1164, 1151, 1088, 1041, 983, 950, 884, 860, 794, 740, 688 cm^{-1}.

[DBUH][Thy]:EG (1:4)

^1H NMR (600 MHz, DMSO-d_6): δ = 6.90 (d, *J* = 7.62 Hz, 1H), 6.55 (s, 1H), 6.43 (d, *J* = 7.62 Hz, 1H), 3.43 (s, 16H), 3.19-3.23 (m, 5H), 3.12 (t, *J* = 5.52 Hz, 2H), 2.36 (t, 2H), 2.14 (s, 3H), 1.69-1.73 (m, 2H), 1.50-1.58 (m, 6H), 1.12 (d, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-d_6): δ = 162.2, 156.4, 135.1, 131.9, 125.4, 118.3, 116.4, 63.0, 52.3, 47.7, 42.2, 34.9, 29.0, 27.8, 26.1, 25.4, 22.8, 21.6, 20.8 ppm

FTIR: ν = 3268, 2928, 2863, 1963, 1645, 1599, 1561, 1491, 1446, 1398, 1339, 1323, 1287, 1262, 1205, 1164, 1152, 1087, 1040, 983, 950, 883, 860, 795, 740, 690 cm^{-1}.

CO_2 absorption and desorption experiments

The procedures of CO_2 absorption and desorption were similar to the methods reported in our previous work.[1] DESs (~2.0 g) was placed into a glass tube, which was sealed with a rubber lid equipped with two needles, and then the tube was partially immersed in a water bath at 25 ºC. Subsequently, CO_2 was bubbled into the DESs in the tube at a flow rate of ~50 mL/min. The weight of the tube was determined by an electronic balance with an accuracy of ±0.1 mg. The mass change of the tube before and after CO_2 uptake was considered as the mass of CO_2 captured by DESs.

In the desorption process, the tube was placed in an oil bath at 70 ºC, and N_2 was flushed through DESs saturated with CO_2 at a flow rate of ~40 mL/min.

Table S1. The viscosity (η), melting point (T_m), decomposition temperature (T_d) of ILs and DESs.

Absorbents	η / mPa·s (25℃)	T_m / ℃	T_d / ℃
[DBUH][Car]	590	-49	134
[DBUH][Car]:EG (1:2)	389	Not observed	125
[DBUH][Car]:EG (1:3)	228	Not observed	122
[DBUH][Car]:EG (1:4)	166	Not observed	114
[DBUH][Thy]	1228	-44	143
[DBUH][Thy]:EG (1:2)	477	Not observed	125
[DBUH][Thy]:EG (1:3)	263	Not observed	124
[DBUH][Thy]:EG (1:4)	179	Not observed	120

Table S2. Comparison of CO_2 capacity by DESs used in this work with other DESs.

Absorbents	T/ ℃	P/bar	Capacity (mol CO_2/mol solvent)	References
[DBUH][Car]:EG (1:4)	25	1.0	0.99	This work
[DBUH][Car]:EG (1:3)	25	1.0	0.99	This work
[DBUH][Car]:EG (1:2)	25	1.0	0.97	This work
[DBUH][Thy]:EG (1:4)	25	1.0	1.00	This work
[DBUH][Thy]:EG (1:3)	25	1.0	0.99	This work
[DBUH][Thy]:EG (1:2)	25	1.0	0.97	This work
[DBUH][Im]:EG (7:3)[a]	40	1.0	1.01[b]	[2]
[DBUH][Im]:EG (6:4)[a]	40	1.0	0.98[b]	[2]
[DBUH][MLU]:EG (1:2)	40	1.0	0.95	[3]
[DBUH][MLU]:EG (1:1)	40	1.0	0.90	[3]
DBN−BmimCl−Im (1:1:2)	25	1.0	0.97	[4]
[N_{2222}][Im]–EG (1:2)	25	1.0	0.94	[1]
[N_{2222}][Triz]–EG (1:2)	25	1.0	0.92	[1]
[P_{2222}][Im]–EG (1:2)	25	1.0	0.91	[1]
[P_{2222}][Triz]–EG (1:2)	25	1.0	0.91	[1]
[EMIM][2-Npyr]-EG (1:2)	25	1.0	0.85	[5]
[MEAH][Im]:EG (1:1)	25	1.0	0.62	[6]
L-arginine: glycerol (1:5)	80	1.0	0.403	[7]
L-arginine: glycerol (1:6)	80	1.0	0.457	[7]
MEA:BmimCl (1:1)	25	1.0	0.45	[8]
DBN-DMLU (2:1)	45	1.0	0.36	[9]

[a] Compositions in parentheses are mass ratios, [b] mol CO_2/mol [DBUH][Im]

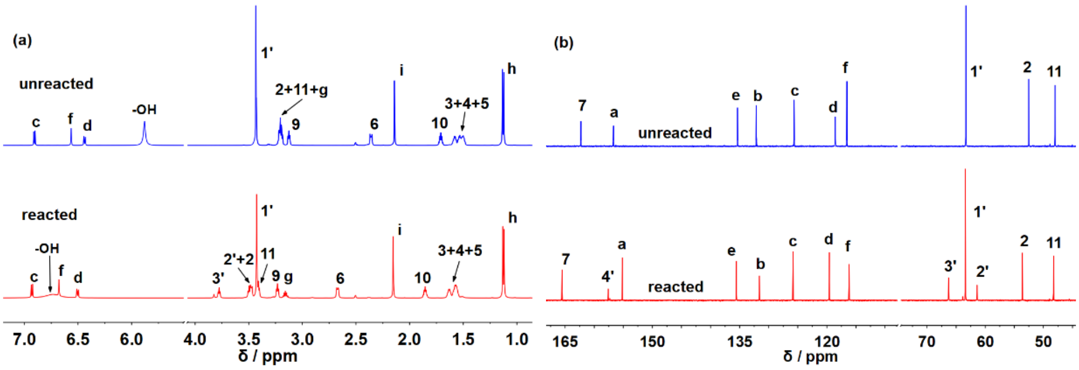

Fig. S1 The [1]H (a) and [13]C (b) NMR spectra of [DBUH][Thy]:EG (1:2) before and after CO_2 uptake.

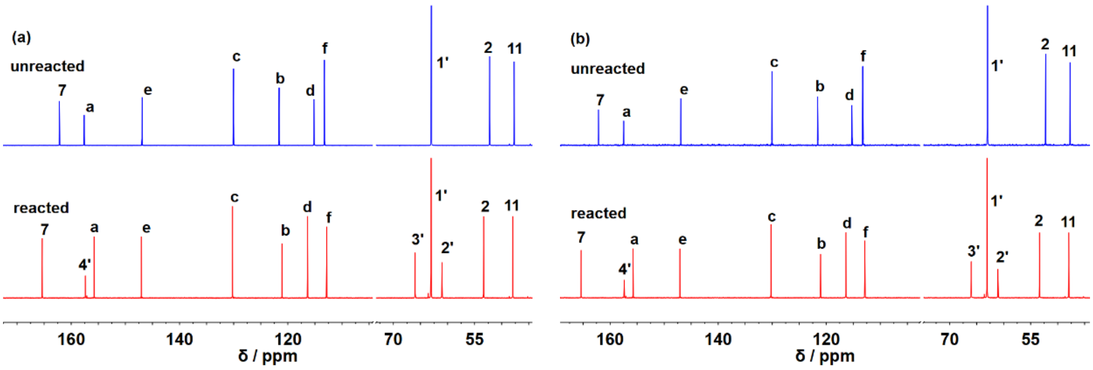

Fig. S2 [13]C NMR spectra of [DBUH][Car]:EG (1:3) (a) and [DBUH][Car]:EG (1:4) (b) before and after CO_2 uptake.

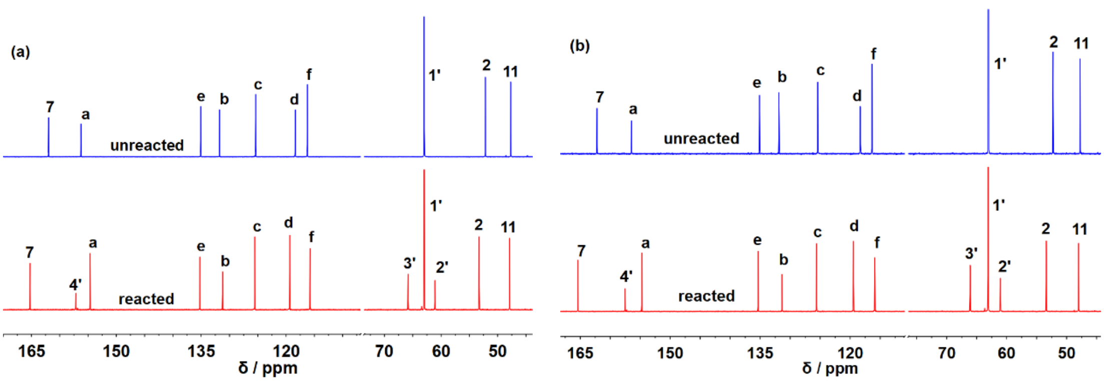

Fig. S3 [13]C NMR spectra of [DBUH][Thy]:EG (1:3) (a) and [DBUH][Thy]:EG (1:4) (b) before and after CO_2 uptake.

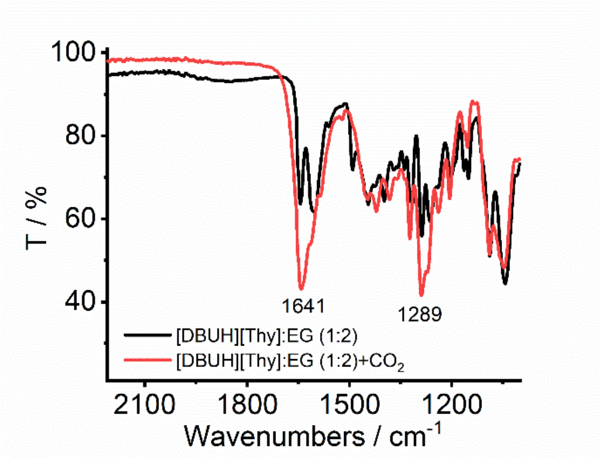

Fig. S4 The FTIR spectra of [DBUH][Thy]:EG (1:2) with and without CO_2.

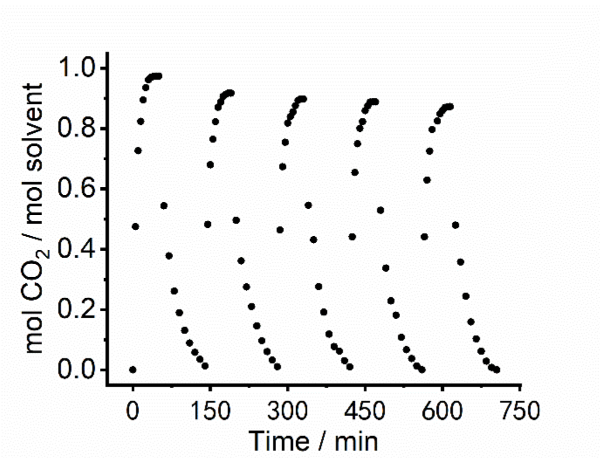

Fig. S5 The CO_2 absorption-desorption cycles by [DBUH][Car]:EG (1:2). Absorption: 25 °C, CO_2 (1.0 atm); Desorption: 70 °C, N_2 (1.0 atm).

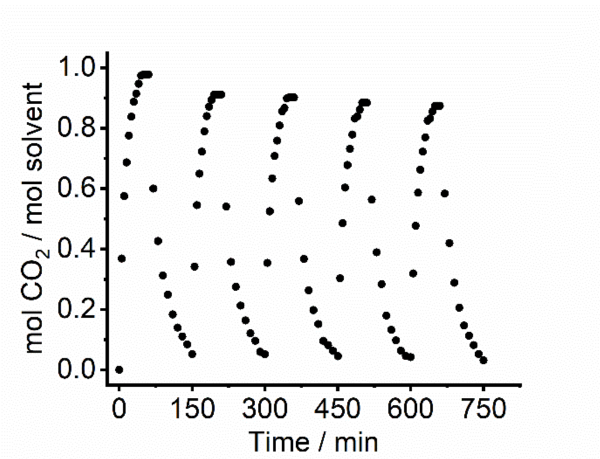

Fig. S6 The CO_2 absorption-desorption cycles by [DBUH][Thy]:EG (1:2). Absorption: 25 °C, CO_2 (1.0 atm); Desorption: 70 °C, N_2 (1.0 atm).

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