SUPPORTING INFORMATION

Carbonyl-functionalized metallic ionic liquids via coordination for efficient hydrogen sulfide separation and conversion by α, β-unsaturated carboxylate esters

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selectivity in five CMILs with other absorbents at 1.0 bar.

Table S8. The H_2S solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K.

Table S9. The CO_2 solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K.

Table S10. The CH_4 solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K.

Table S11. Cartesian coordinates of [Na-15C][LA] from Gaussian 09 program.

Table S12. Cartesian coordinates of [Na-15C][LA] + H_2S from Gaussian 09 program.

Table S13. Cartesian coordinates of [Na-15C][LA] + 2 H_2S from Gaussian 09 program.

Gas solubility measurements

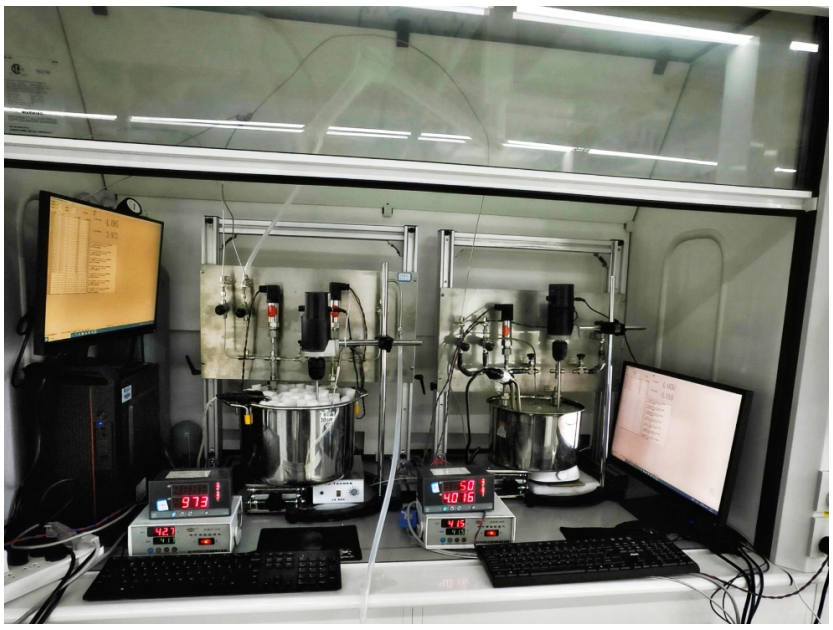
The solubility of CMILs for H_2S (the determination of CO_2 and CH_4 solubility is the same with H_2S) was determined using a test setup built by the group in the previous stage[1, 2], as shown in **Scheme S1**. The device consists of four main components: (1) a water bath system for maintaining a constant temperature; (2) a pressure sensor for real-time monitoring of pressure changes; (3) a magnetic stirrer to ensure adequate mixing; (4) a two-compartment glass reaction vessel, with a large compartment volume of V_1 = 192.009 cm^3 and a small compartment volume of V_2 = 40.748 cm^3. The volumes of each compartment were calibrated using the standard volume method. The experiments were carried out by temperature control in a thermostatic water bath (with an uncertainty of 0.1 K), and the chamber pressure was measured by a Wideplus-8 type pressure. In order to verify the reliability of the device, the solubility of CO_2 in PEG-200 at 313.2 K was measured and compared with literature data[3]. As demonstrated in **Scheme S2**, the two solubility curves largely coincide with minimal error, proving that the device has an accurate volumetric capability and excellent gas tightness.

After accurately weighed (w, weighing uncertainty 0.0001 g on an electronic balance) CMILs were placed in the equilibrium chamber, the initial residual pressure of the equilibrium chamber was measured by evacuation P_0. Subsequently, the H_2S was charged into the storage chamber to the pressure P_1, and the valve between the two chambers was opened to allow the H_2S to enter the equilibrium chamber. When the system pressure is stabilized for half an hour to reach absorption equilibrium, the equilibrium chamber pressure P_2 and the gas storage chamber pressure P_3 are recorded respectively. At this time, the partial pressure of H_2S is dented as P_{H_2S}, $P_{H_2S} = P_2 - P_0$.

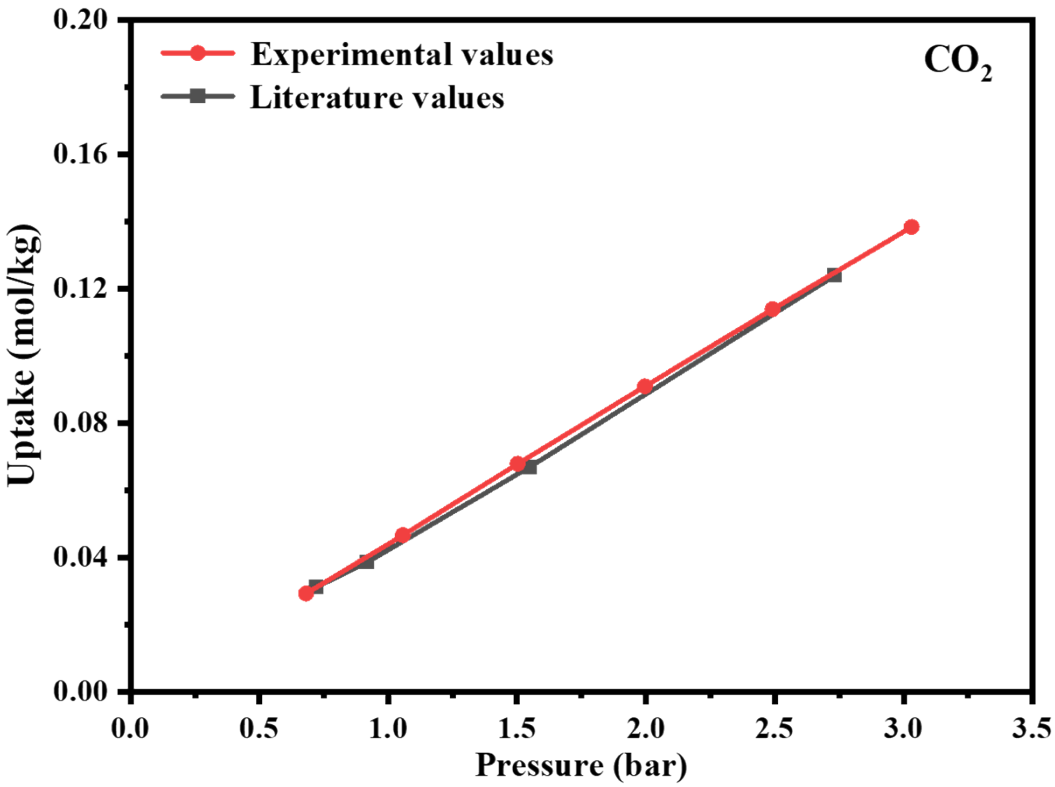
The data acquisition system recorded the pressure change in real time during the experiment, and the absorption equilibrium was deemed to have been reached when the system pressure remained stable (with a change of less than 0.1 kPa) for 30 minutes. Finally, the amount of H_2S absorbed can be calculated by the following equation:

$$m_{(H_2S)} = [\rho_{(H_2S)}^{(P_1,T)} V_1 - \rho_{(H_2S)}^{(P_3,T)} V_1 - \rho_{(H_2S)}^{(P_{(H_2S)},T)} (V_2 - w/\rho_{CMILs})]/w$$

where V_1 and V_2 are the volumes of the storage and equilibrium chambers, respectively (cm^3); w is the mass of the absorbent (g); ρ_{CMILs} is the density of the CMILs at the experimental temperature ($g \cdot cm^{-3}$); T is the experimental temperature (K); and m_{H_2S} is the amount of H_2S absorbed (g)；$\rho_{(H_2S)}^{(P_1,T)}$、$\rho_{(H_2S)}^{(P_2,T)}$和$\rho_{(H_2S)}^{(P_3,T)}$are the densities ($g \cdot cm^{-3}$) of H_2S at different temperatures and pressures, respectively. NIST Chemistry WebBook was cited for the gas densities used in this article. To ensure the reliability of the data, all experiments were carried out three times in parallel and the results were taken as the arithmetic mean.



Scheme S1 | Apparatus for measurement of gas absorption.



Scheme S2 | CO_2 absorption in PEG-200 at 313.2 K.

Reaction details

To ensure the equimolar reaction between H_2S and the substrate, the molar of H_2S was calculated based on its density (mol/L) using data from the NIST Standard Reference Database Number 69 (DOI: https://doi.org/10.18434/T4D303). The experiment was conducted using a dual-chamber volumetric setup, with the large and small vessels having volumes of 192.009 cm^3 and 40.748 cm^3, respectively. According to the molar amount of substrate, the corresponding amount of H_2S was precisely controlled by regulating the volume of gas released from the large vessel. The density of H_2S under different pressures was obtained from the isothermal property data provided by NIST. The experimental procedure was as follows: first, the small tank containing the reactant was evacuated to remove excess air and prevent side reactions. Then, both chambers were placed in a thermostatic water bath to maintain a stable temperature. H_2S from the large vessel was introduced into the small vessel by opening the valve. The amount of H_2S transferred was determined based on the substrate quantity, and the target molar ratio was achieved by controlling the pressure drop (ΔP) in the large vessel.

$$\rho_{H_2S}(\mathrm{mol \cdot L^{-1}}) = \frac{n_{H_2S}(\mathrm{mol})}{V_{vessel}(\mathrm{L})} = \frac{\frac{m_{Substrate}(\mathrm{g})}{M_{Substrate}(\mathrm{g \cdot mol^{-1}})}}{V_{vessel}(\mathrm{L})} \qquad \text{Eq. S1}$$

$$\rho_{H_2S}(\mathrm{mol \cdot L^{-1}}) \Rightarrow p_{H_2S}(\mathrm{bar}) \qquad \text{Eq. S2}$$

where ρ_{H_2S} denotes the density of H_2S in the unit of $mol \cdot L^{-1}$, n_{H_2S} denotes the molar of H_2S in the unit of mol, $m_{Substrate}$ and $M_{Substrate}$ denote the mass and molecular weight of the substrate in the units of g and $g \cdot mol^{-1}$, respectively, and V_{vessel} denotes the volume of the tank in the unit of L.

Synthesis of [Na][LA]

[Na][LA] was prepared by a one-step acid-base neutralization method. The specific steps were as follows: equimolar amounts of Levulinic acid (LA) and sodium hydroxide (NaOH) were dissolved in deionized water and stirring until complete dissolution. Subsequently, the excess water in the system was removed by distillation under reduced pressure, and then dried under vacuum at 343.2 K to remove the residual trace water, ensuring that the product was dry, eventually obtaining white powdery [Na][LA].

Table S1. The specifications and sources of the chemicals used in this work

Chemicals	Abbr./(number)	CAS number	MW. (g/mol)	Mass purity	Source
Levulinic acid	LA	123-76-2	116.12	0.980	Macklin
4-Oxocyclohexanecarboxylic acid	OCHCA	874-61-3	142.15	0.980	Macklin
4-Formylbenzoic acid	CBA	619-66-9	150.13	0.980	Macklin
4\'-Hydroxyacetophenone	HAP	99-93-4	136.15	0.980	Macklin
Hexanoic acid	CA	142-62-1	116.16	0.980	Macklin
Sodium hydroxide	NaOH	1310-73-2	40	0.960	Aladdin
Potassium hydroxide	KOH	1310-58-3	56.11	0.999	Aladdin
15-Crown-5	15-C-5	33100-27-5	220.26	0.970	Aladdin
18-Crown-6	18-C-6	17455-13-9	264.32	0.990	Aladdin
n-Butyl acrylate	BA	141-32-2	128.17	0.990	Innochem
Ethyl acrylate	EA	140-88-5	110.12	0.990	Innochem
Methyl acrylate	MA	96-33-3	86.09	0.990	Innochem
Butyl methacrylate	BMA	97-88-1	142.2	0.990	Innochem
Ethyl methacrylate	EMA	97-63-2	114.14	0.990	Innochem
Methyl methacrylate	MMA	80-62-6	100.12	0.990	Innochem
Methyl crotonate	MCA	623-43-8	100.12	0.980	Innochem
Cyclohexyl Acrylate	CA	3066-71-5	154.21	0.980	Macklin
Methyl-3,3-dimethylacrylate	MDA	924-50-5	114.14	0.980	Macklin
H_2S	–	7783-06-4	34.08	0.9999	Shanghai Tongchen Specialty Gas Co., Ltd
CO_2	–	124-38-9	44.01	0.9999	Jinhong Gas Co., Ltd
CH_4	–	74-82-8	16.04	0.9999	Jinhong Gas Co., Ltd

Figures S1–S14

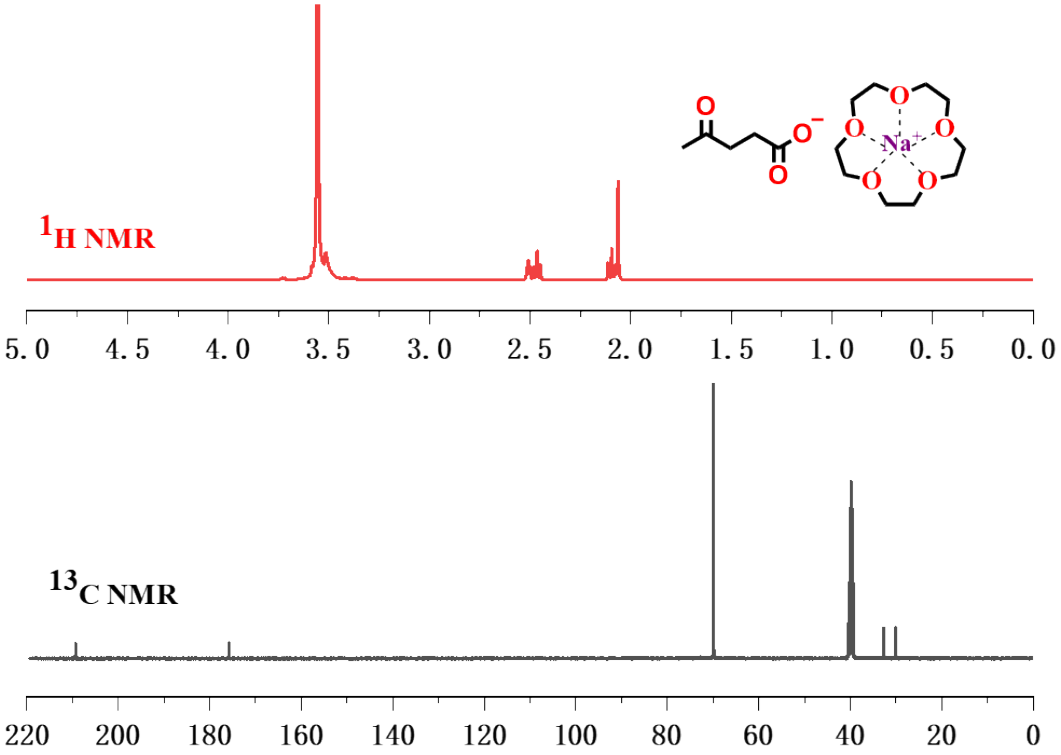


Figure S1. ^{1}H and ^{13}C NMR of [Na-15C][LA].

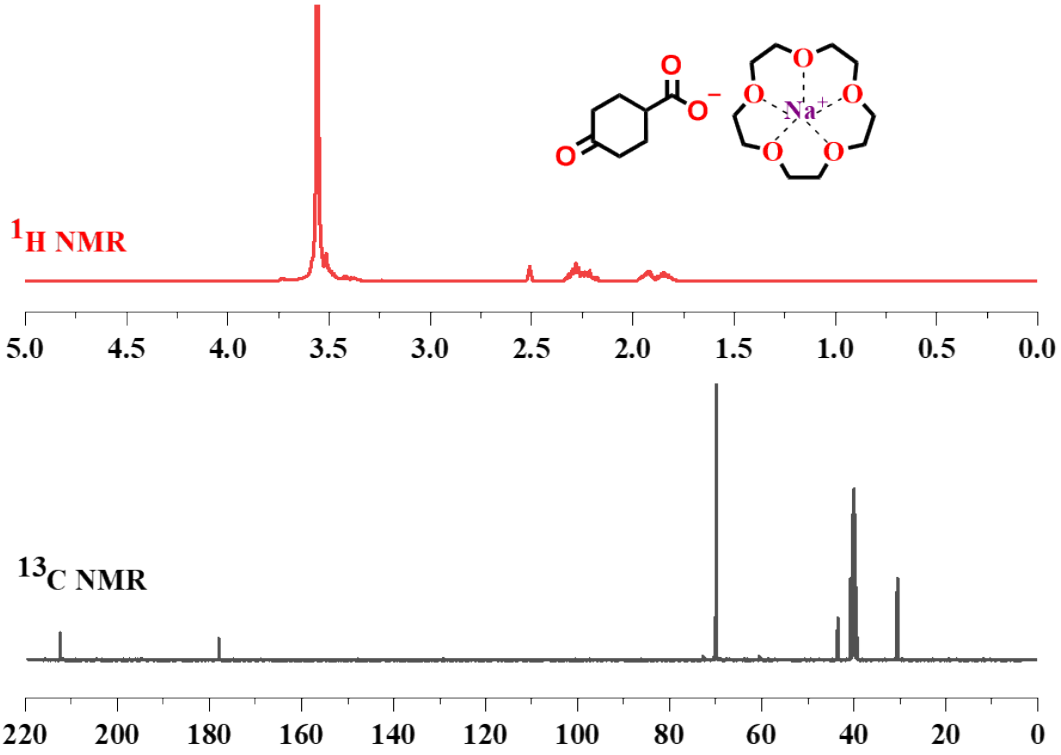


Figure S2. ^{1}H and ^{13}C NMR of [Na-15C][OCHCA].

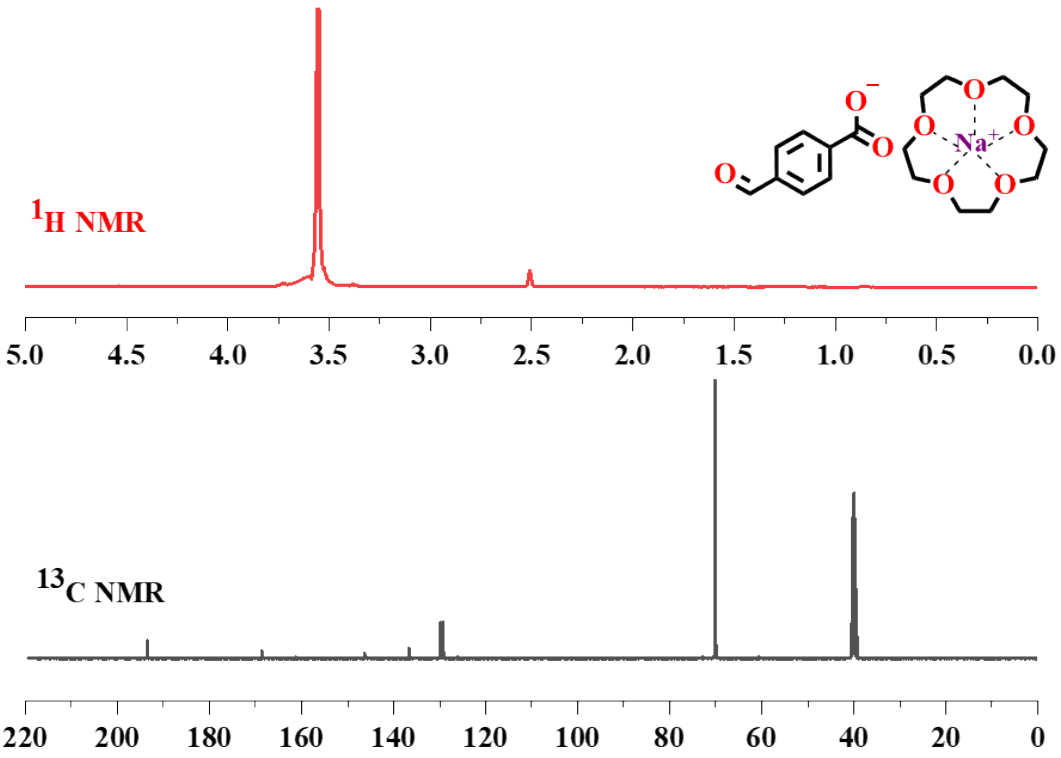


Figure S3. ^{1}H and ^{13}C NMR of [Na-15C][CBA].

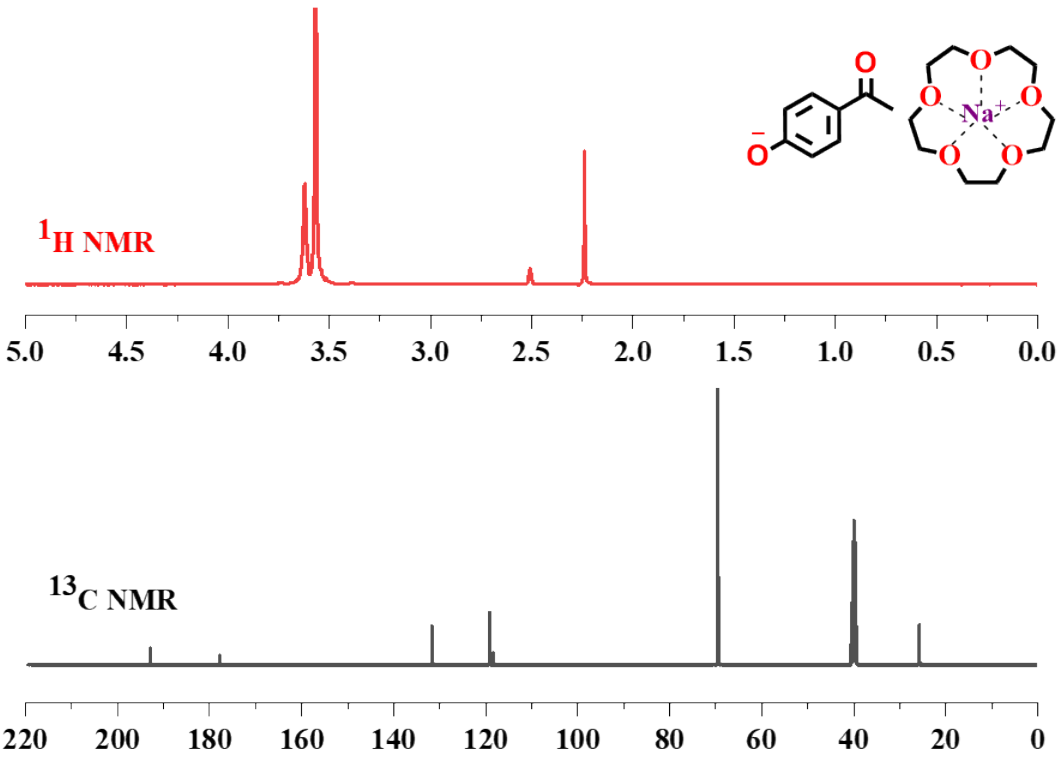


Figure S4. ^{1}H and ^{13}C NMR of [Na-15C][HAP].

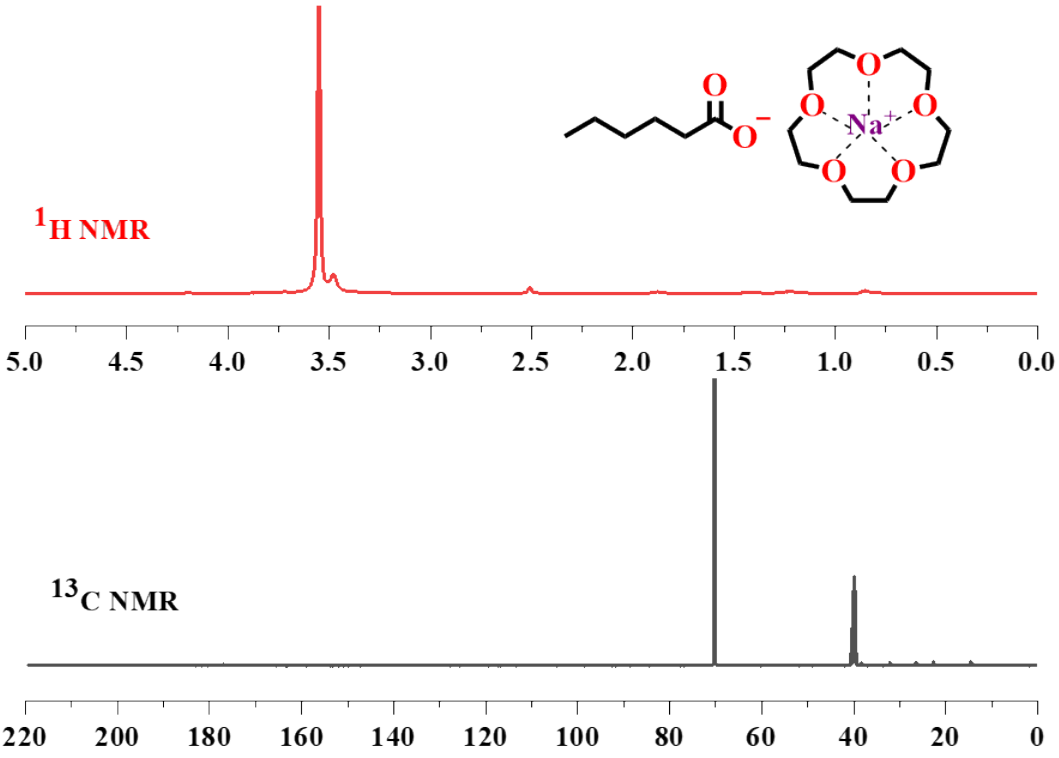


Figure S5. ^{1}H and ^{13}C NMR of [Na-15C][CA].

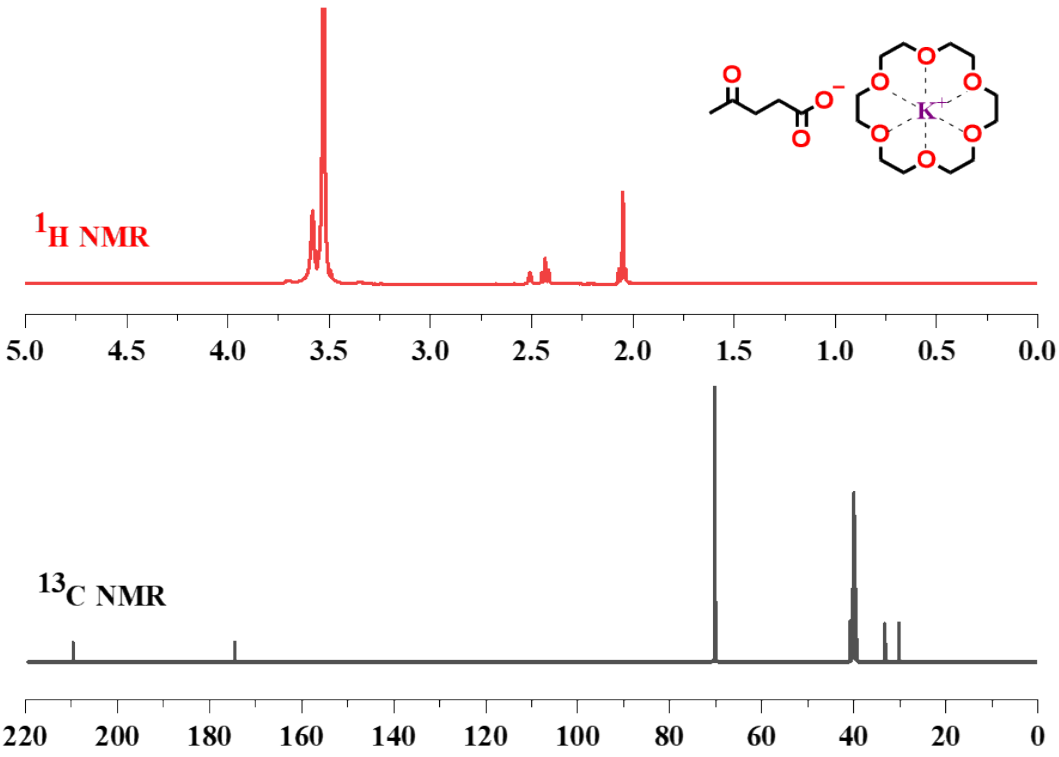


Figure S6. ^{1}H and ^{13}C NMR of [K-18C][LA].

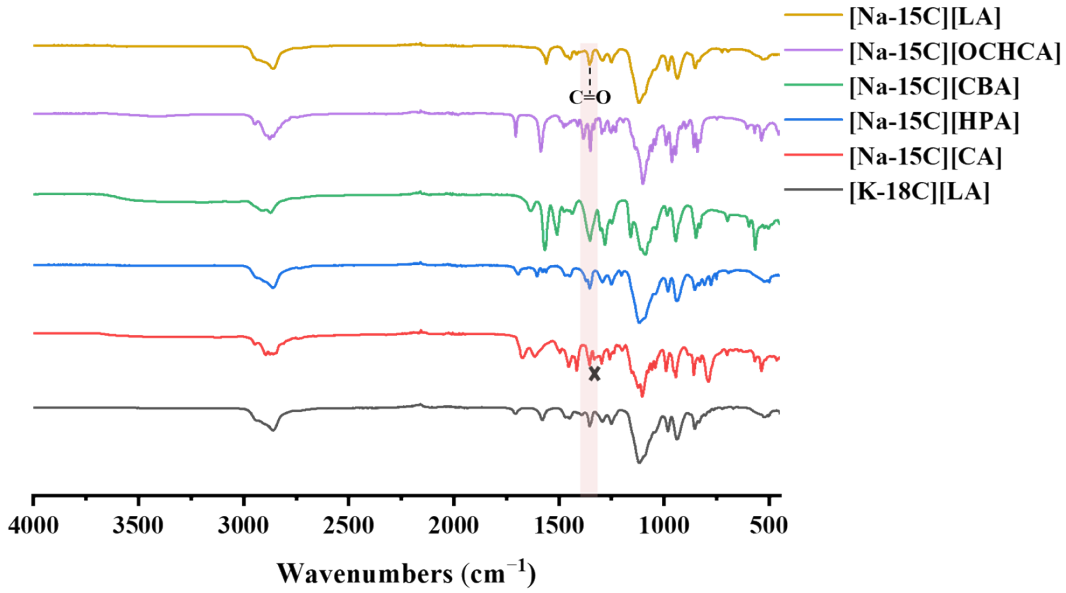


Figure S7. FT-IR spectra of CMILs.

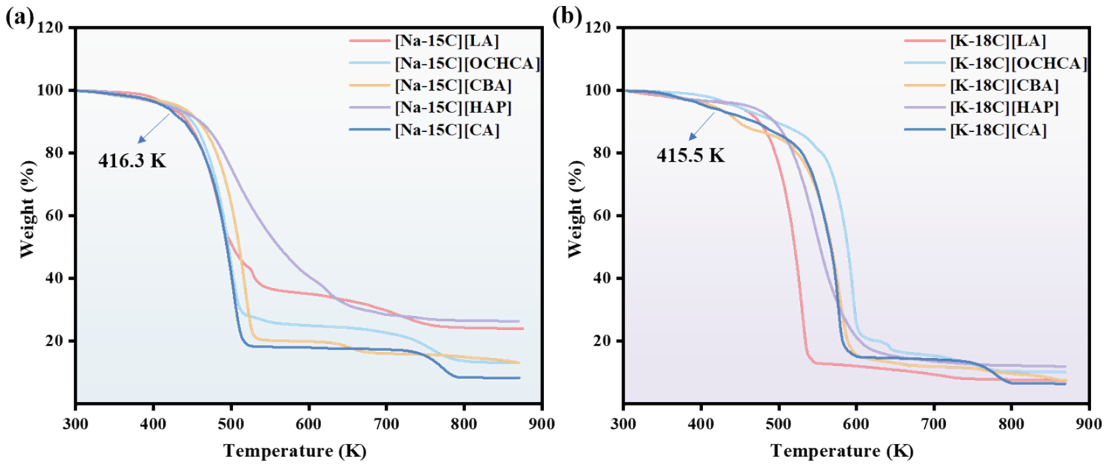


Figure S8. TGA carve of all CMILs. (a) 15-C-5-based CMILs; (b) 18-C-6-based CMILs.

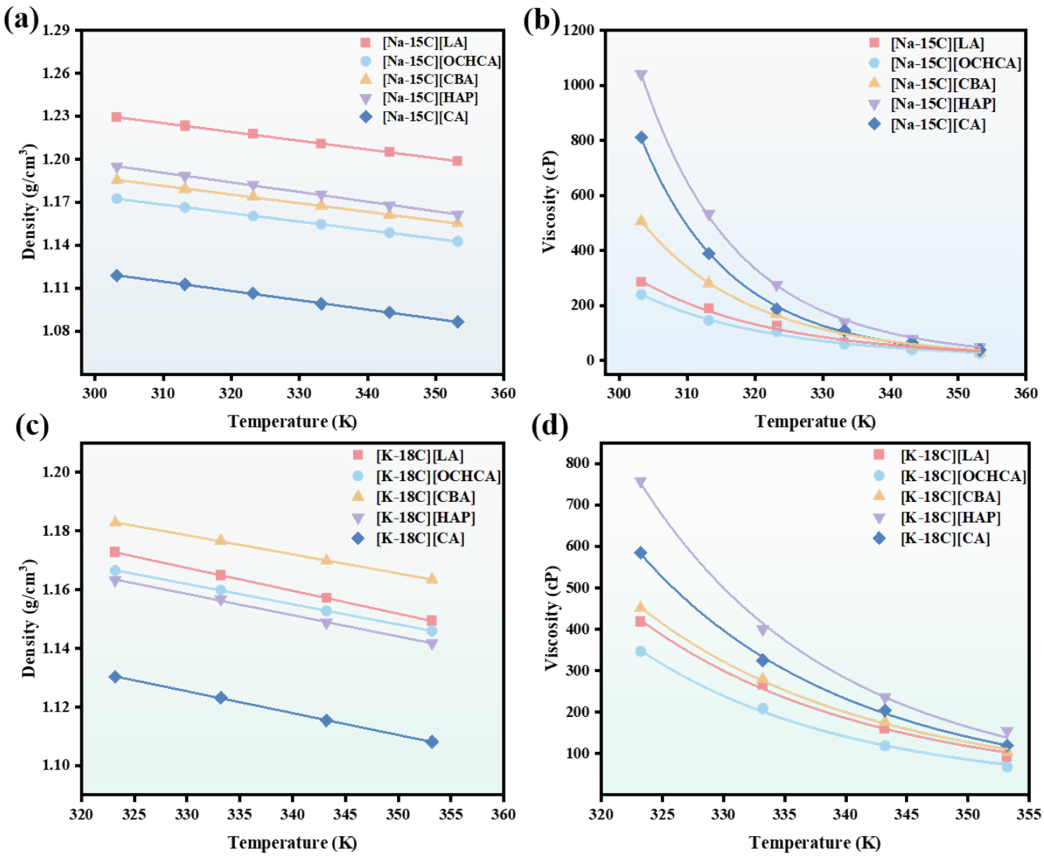


Figure S9. Property of all CMILs. (a) Density and (b) Viscosity curves of 15-C-5-based CMILs (measured from 303.2 K to 353.2 K); (c) Density and (d) Viscosity curves of 18-C-6-based CMILs (measured from 323.2 K to 353.2 K).

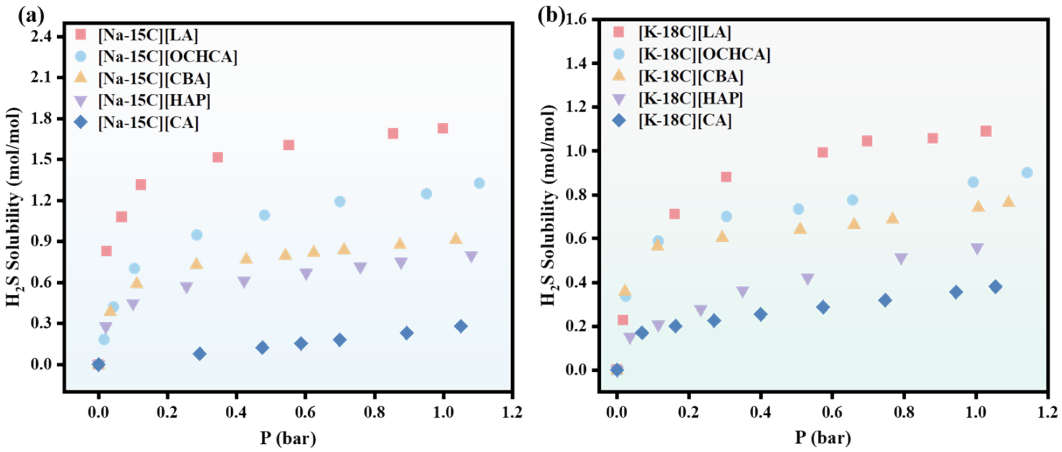


Figure S10. H_2S solubility of all CMILs. (a) 15-C-5-based CMILs (measured at 313.2 K); (b) 18-C-6-based CMILs (measured at 323.2 K).

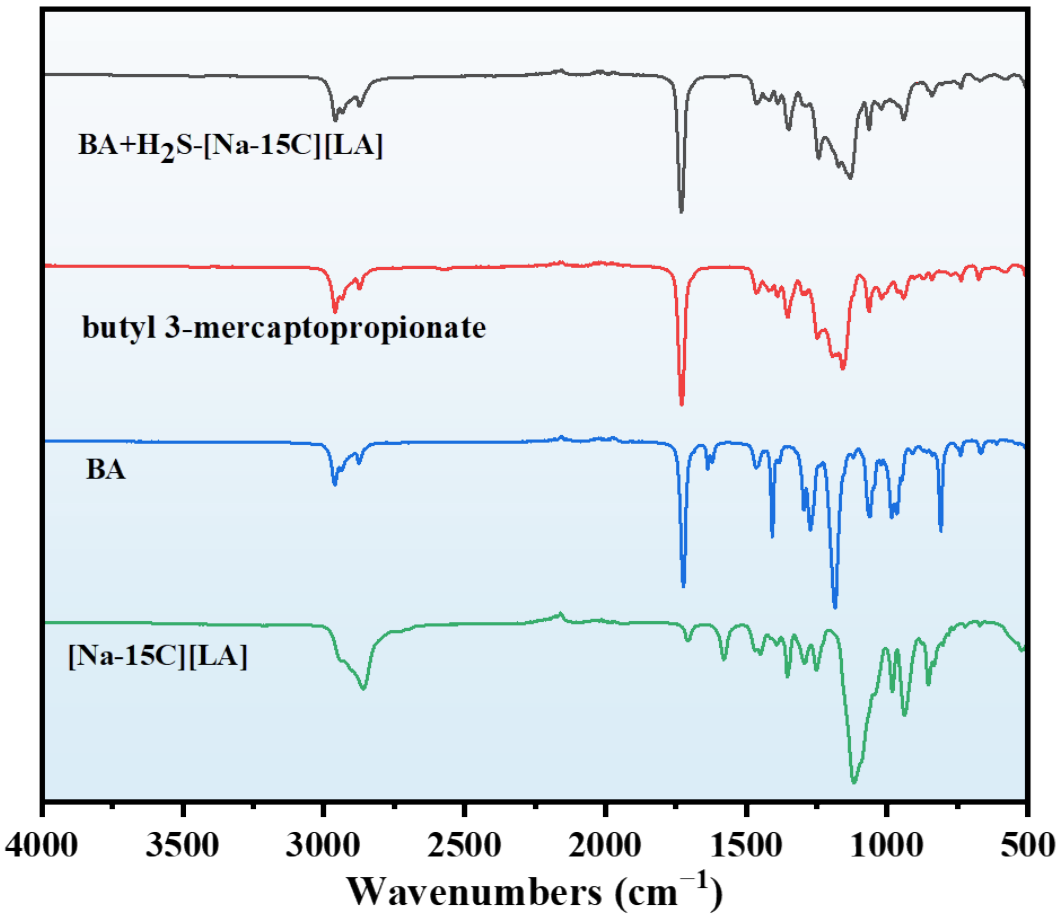


Figure S11. FT-IR spectra monitoring the reaction of H_2S with BA catalyzed by [Na-15C][CA].

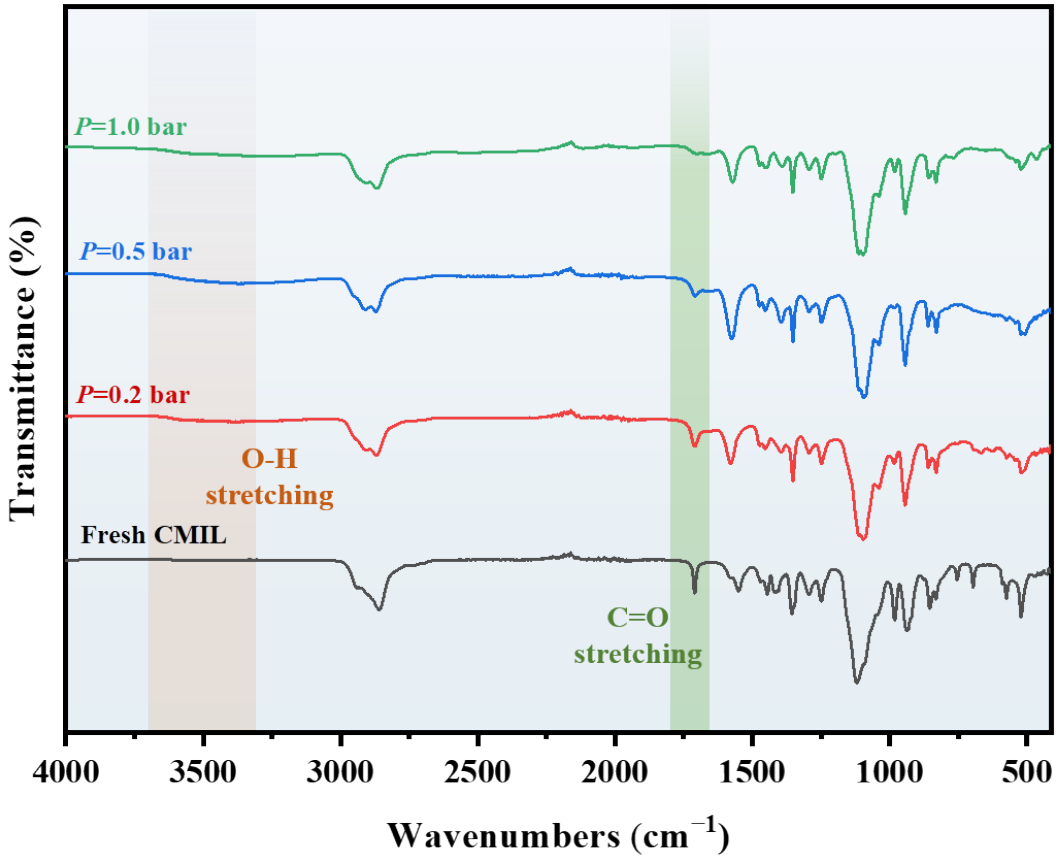


Figure S12. FT-IR spectra before and after H_2S absorption in [Na-15C][LA] in different partial pressures.

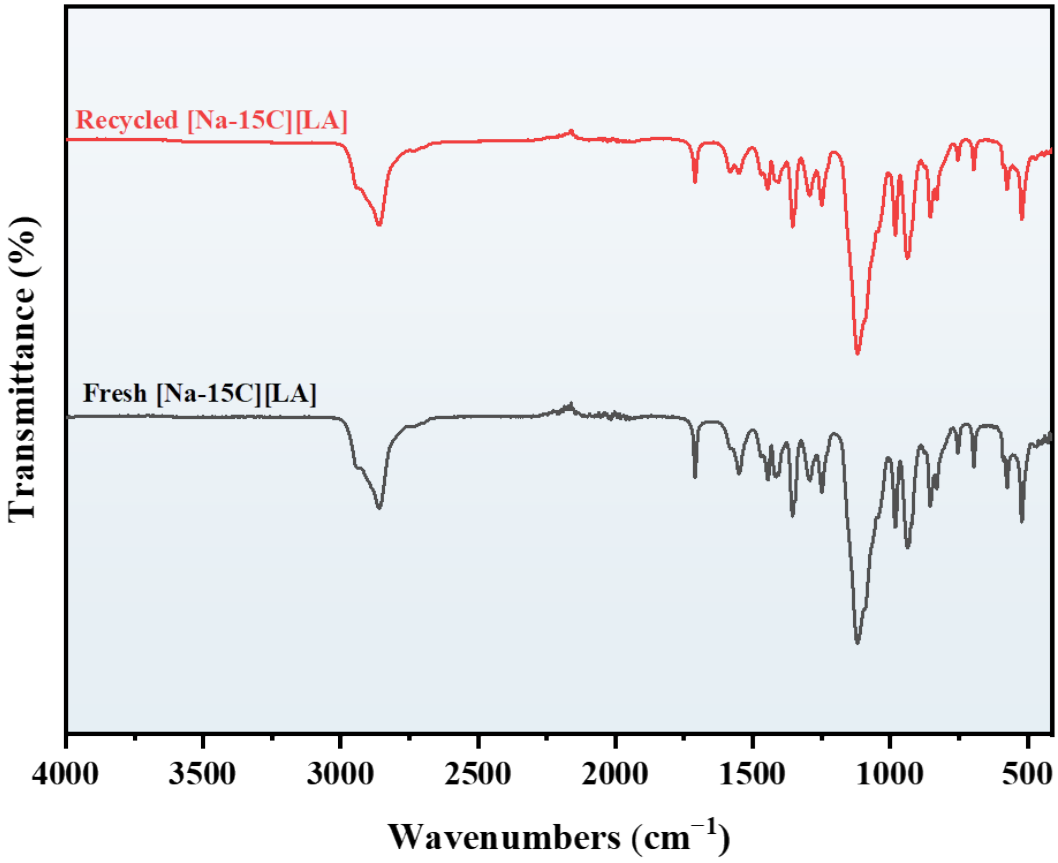


Figure S13. FT-IR spectra of fresh [Na-15C][LA] and after five reaction cycles.

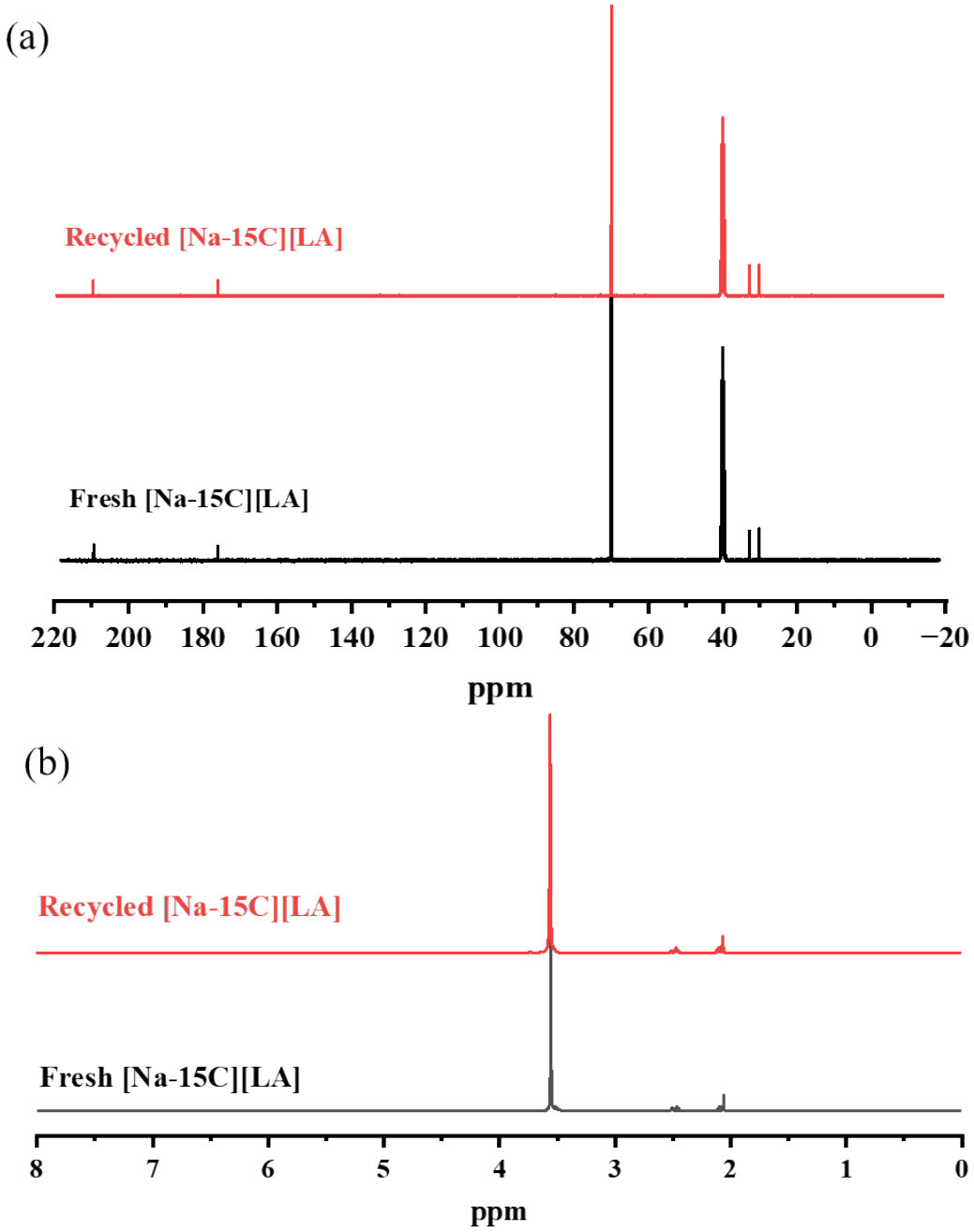


Figure S14. NMR spectra of fresh [Na-15C][LA] before and after five reaction cycles: (a) ^{13}C NMR spectrum, (b) ^{1}H NMR spectrum.

Table S2–Table S11

Table S2. Densities ρ (g·cm^{-3}) of the CMILs studied in this work.[a]

T/K	[Na-15C][LA]	[Na-15C][OCHCA]	[Na-15C][CBA]	[Na-15C][HAP]	[Na-15C][CA]
303.2	1.2293	1.1726	1.1905	1.1949	1.119
313.2	1.2232	1.1665	1.1794	1.1884	1.1127
323.2	1.2175	1.1604	1.174	1.1824	1.1066
333.2	1.2108	1.1547	1.1676	1.1755	1.1992
343.2	1.2049	1.1487	1.1611	1.1679	1.0932
353.2	1.1988	1.1428	1.1552	1.1615	1.0866
***T*/K**	**[K-18C][LA]**	**[K-18C][OCHCA]**	**[K-18C][CBA]**	**[K-18C][HAP]**	**[K-18C][CA]**
323.2	1.1727	1.1665	1.1828	1.1632	1.1303
333.2	1.1649	1.1599	1.1767	1.1567	1.1232
343.2	1.1571	1.1527	1.1698	1.1487	1.1154
353.2	1.1493	1.1459	1.16343	1.1417	1.1081

[a] Standard uncertainties u are u(T) = 0.02 K for temperature, and u(ρ_{CMILs}) = 0.0001 g·cm^{-3} for density. Relative standard uncertainty u_r is 0.027 for pressure.

Table S3. Viscosities η (cP) of the CMILs studied in this work.[a]

T/K	[Na-15C][LA]	[Na-15C][OCHCA]	[Na-15C][CBA]	[Na-15C][HAP]	[Na-15C][CA]
303.2	284.9	240.4	506.9	1040	811
313.2	188.6	145.7	281.2	532.2	389.1
323.2	124.3	105.4	170	275.2	187.8
333.2	66.3	59.3	104.6	138.5	109.7
343.2	45.2	39.5	49.1	79.2	65.4
353.2	29.1	26.4	30.3	48.7	39.1
***T*/K**	**[K-18C][LA]**	**[K-18C][OCHCA]**	**[K-18C][CBA]**	**[K-18C][HAP]**	**[K-18C][CA]**
323.2	418.6	347	451.3	758.3	584.8
333.2	266.8	208.4	279.8	399.9	325.1
343.2	160.6	118.9	175.8	235.6	204.2
353.2	92.3	67.3	103.7	155	119.9

[a] Standard uncertainties u are u(T) = 0.02 K for temperature, and u (η_{CMILs}) = 0.02 cP for viscosity.

Relative standard uncertainty u_r is 0.027 for pressure.

Table S4. Fitted parameters for Equation 3.

parameters	*a*	*b* ×10^4	r^2
[Na-15C][LA]	1.415	–6.120	0.999
[Na-15C][OCHCA]	1.354	–5.98	0.999
[Na-15C][CBA]	1.364	–5.91	0.999
[Na-15C][HAP]	1.389	–6.44	0.999
[Na-15C][CA]	1.318	–6.55	0.998
[K-18C][LA]	1.424	–7.80	0.999
[K-18C][OCHCA]	1.389	–6.90	0.999
[K-18C][CBA]	1.393	–6.50	0.998
[K-18C][HAP]	1.397	–7.25	0.997
[K-18C][CA]	1.371	–7.45	0.999

Table S5. Fitted parameters for Equation 4.

parameters	η_0	D	T_0	r^2
[Na-15C][LA]	0.009	4548.8	4.628	0.989
[Na-15C][OCHCA]	0.008	4531.9	4.703	0.993
[Na-15C][CBA]	0.002	5558.0	5.974	0.997
[Na-15C][HAP]	0.104	6558.8	7.208	0.999
[Na-15C][CA]	0.052	6910.1	7.935	0.999
[K-18C][LA]	0.0041	5394.1	5.162	0.996
[K-18C][OCHCA]	0.0015	5943.4	6.041	0.997
[K-18C][CBA]	0.0046	5358.2	5.084	0.998
[K-18C][HAP]	9.7842	6430.6	6.343	0.997
[K-18C][CA]	0.017	6012.9	5.876	0.998

Table S6. Comparison of H_2S absorption uptake, CO_2 absorption uptake, and H_2S/CO_2 selectivity in carbonyl CMILs with other absorbents.

Absorbents	T/K	S_{H_2S} (mol/mol)		S_{CO_2} (mol/mol)		S_A		References
		1.0 bar	0.1 bar	1.0 bar	0.1 bar	$S_{1/1}$	$S_{0.1/0.1}$	
[Na-15C][LA]	313.2	1.728	1.216	0.017	0.002	101.2	608	This work
[Na-15C][OCHCA]	313.2	1.274	0.684	0.087	0.008	14.6	85.5	
[Na-15C][CBA]	313.2	0.905	0.559	0.017	0.001	53.2	559	
[K-18C][LA]	323.2	1.085	0.545	0.160	0.013	6.8	41.9	
[TMHDA][Tf_2N]	313.2	0.673	0.234	0.023	0.0023	29.5	101.7	[4]
ChCl/urea (1:1.5)	313.2	0.028	0.0028	0.005	0.0005	5.6	5.6	[5]
[C_1-TMHDA]Ac-Pyrol (1:2)	313.2	1.17	0.445	0.13	0.013	9	34.2	[6]
[C_1-TMHDA]Ac-AA (1:2)	313.2	1.09	0.396	0.12	0.012	9.1	33.0	[6]
[C_1-TMHDA]Ac-Im (1:2)	313.2	1.02	0.306	0.11	0.011	9.3	27.8	[6]
[DBNH][1,2,4-triaz]	313.2	1.20	0.771	0.26	-	4.6	-	[2]
[DBNH][Im]	313.2	1.26	0.98	0.65	0.36	1.9	2.7	[7]
[TMGH][PhO]	313.2	0.85	0.56	0.090	0.067	9.4	8.3	[8]
[DBUH][PhO]	313.2	0.80	0.60	0.21	0.182	3.8	3.3	[8]
[MDEAH][Ac]	313.2	0.131	0.018	0.0156	0.002	8.4	9	[9]
[emim][FAP]	313.2	0.054	-	0.029	-	1.9	-	[10, 11]
[bmim][PF_6]	313.2	0.046	-	0.0146	-	3.2	-	[12, 13]
[bmim][BF_4]	313.2	0.052	-	0.0133	-	3.9	-	[12, 14]
[bmim][TF_2N]	313.2	0.061	-	0.023	-	2.7	-	[12, 15]
N-Formyl Morpholine	313.2	0.0617	-	0.0112	-	5.5	-	[16]
Sulfolane	313.2	0.043	-	0.009	-	4.8	-	[17]
Propylene carbonate	313.2	0.031	-	0.0088	-	3.5	-	[18, 19]
[DBNH][MP]	303.2	1.42	1.00[a]	0.95	0.81[a]	1.5	1.2	[20]

Table S6. Continued.

Absorbents	T/K	S_{H_2S} (mol/mol)		S_{CO_2} (mol/mol)		S_A		References
		1.0 bar	0.1 bar	1.0 bar	0.1 bar	$S_{1/1}$	$S_{0.1/0.1}$	
[DBUH][MP]	303.2	1.34	1.02 a	0.93	0.82 a	1.4	1.2	[20]
[TMGH][MP]	303.2	1.27	1.00 a	0.97	0.90 a	1.3	0.9	[20]
[DMEAH][Ac]	303.2	0.195	0.025	0.02	0.002	9.8	12.5	[9]
[DMEAH][For]	303.2	0.112	0.018	0.01	0.001	11.2	18	[9]
[emim][Tf_2N]	303.2	0.072	0.0072	0.028	0.0028	2.6	2.6	[21, 22]
[hemim][BF_4]	303.2	0.0316	0.00316	0.01	0.001	3.1	3.16	[23]
[emim][$EtSO_4$]	303.2	0.015	0.0015	0.009	0.0009	1.6	1.7	[23]
[C_4-TMHDA][Cl]-Im (1:2)	303.2	0.996	0.239	0.082	0.0082	12.1	29.2	[24]
[C_4-TMPDA][Cl]-Im (1:2)	303.2	0.482	0.096	0.059	0.0059	8.2	16.3	[24]
[emim][Ac]	323.2	0.41	0.2	0.2987	0.1601	1.4	1.2	[25]
[N_{2224}][IMA]	298.2	0.846	0.292	0.091	0.0091	9.3	32.1	[26]
[N_{2224}][NIA]	298.2	0.867	0.212	0.07	0.007	12.3	30.3	[26]
TBAB/Pro (1:1)	298.2	0.272	0.0272	0.275	0.0275	1.0	1.0	[27]
[Emim]Cl-Im(2:1)	298.2	0.531	0.053	0.0171	0.0017	30.9	30.9	[28]
[Emim]Cl-Im(1:1)	298.2	0.265	0.027	0.0112	0.0011	23.7	23.7	[28]
[Emim]Cl-Im(1:2)	298.2	0.289	0.029	0.0168	0.0017	17.2	17.2	[28]
[TMPDA][Tf_2N]	298.2	0.158	-	0.026	-	6.1	-	[29]
[BDMAEE][Tf_2N]	298.2	0.546	0.167	0.015	0.004	36.4	41.7	[29]
50 wt% MDEA	298.2	0.93		0.91		1.0		[30]
Methanol	298.2	0.028		0.0067		4.2		[31, 32]

Table S7. Comparison of H_2S absorption uptake, CH_4 absorption uptake, and H_2S/CH_4 selectivity in five CMILs with other absorbents at 1.0 bar.

Absorbents	T/K	H_2S uptake (mol/mol)	CH_4 uptake (mol/mol)	H_2S/CH_4 selectivity	References
[Na-15C][LA]	313.2	1.728	0.0015	1122.2	This work
[Na-15C][OCHCA]	313.2	1.274	0.0056	227.5	
[Na-15C][CBA]	313.2	0.905	0.0072	125.7	
[Na-15C][CBA]	313.2	0.780	0.0050	156	
[K-18C][LA]	323.2	1.085	0.0018	602.8	
[Na-15C][CA]	313.2	0.264	0.0051	51.7	
ChCl-urea	313.2	0.023	0.0005	43.7	[5]
[bmim][TF_2N]	313.2	0.048	0.0026	18.3	[15, 33]
ChCl/urea (1:1.5)	313.2	0.028	0.00046	60.8	[5]
[C1-TMHDA]Ac-AA (1:2)	313.2	1.09	9.1	293	[6]
[emim][FAP]	313.2	0.054	0.0025	21.5	[11]
[bmim][PF_6]	313.2	0.046	0.0012	38.6	[12, 13]
[bmim][BF_4]	313.2	0.052	0.009	58.5	[12, 14]
[bmim][TF_2N]	313.2	0.061	0.0020	30.7	[12, 15, 34]
[C_4Py][BF_4]	313.2	0.058	0.0011	52.7	[35]
[C_2mim][eFAP]	303.2	0.067	0.0024	27.9	[10, 36]
[C_4-TMPDA][Cl]-Im (1:2)	303.2	0.48	0.0044	109	[24]
[DPLEH][NPhO]	298.2	0.85	0.0069	122	[37]
[DMAPAH][NPhO]	298.2	0.57	0.0049	115	[37]
[BDAEH][NPhO]	298.2	0.63	0.0078	80	[37]
TEGDME	313.2	0.162	0.0026	61.8	[38, 39]
N-Formyl Morpholine	313.2	0.0617	0.00056	110.2	[40]
Sulfolane	313.2	0.043	0.00046	93.5	[17]
Propylene carbonate	313.2	0.031	0.00070	44.3	[41, 42]

Table S8. The H_2S solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K .

[Na-15C][LA]			[Na-15C][OCHCA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.023	0.830 ± 0.016	2.462 ± 0.051	0.016	0.184 ± 0.003	0.477 ± 0.009
0.067	1.079 ± 0.021	3.013 ± 0.063	0.043	0.421 ± 0.008	1.095 ± 0.021
0.124	1.315 ± 0.032	3.670 ± 0.077	0.104	0.703 ± 0.014	1.830 ± 0.037
0.346	1.516 ± 0.030	4.231 ± 0.089	0.285	0.949 ± 0.019	2.468 ± 0.049
0.552	1.607 ± 0.033	4.483 ± 0.094	0.481	1.094 ± 0.022	2.847 ± 0.057
0.855	1.689 ± 0.037	4.714 ± 0.098	0.7	1.193 ± 0.024	3.105 ± 0.062
0.999	1.728 ± 0.038	4.822 ± 0.103	0.951	1.251 ± 0.025	3.253 ± 0.065
			1.104	1.328 ± 0.026	3.459 ± 0.069

[Na-15C][CBA]			[Na-15C][HPA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.034	0.384 ± 0.007	0.981 ± 0.019	0.021	0.278 ± 0.005	0.736 ± 0.015
0.111	0.588 ± 0.012	1.499 ± 0.030	0.101	0.449 ± 0.009	1.186 ± 0.022
0.284	0.730 ± 0.014	1.860 ± 0.039	0.255	0.573 ± 0.011	1.515 ± 0.030
0.428	0.767 ± 0.015	1.955 ± 0.039	0.422	0.613 ± 0.013	1.621 ± 0.032
0.542	0.799 ± 0.016	2.034 ± 0.040	0.602	0.670 ± 0.013	1.772 ± 0.034
0.624	0.819 ± 0.016	2.086 ± 0.042	0.759	0.715 ± 0.014	1.891 ± 0.037
0.712	0.839 ± 0.017	2.137 ± 0.043	0.877	0.751 ± 0.015	1.985 ± 0.040
0.874	0.876 ± 0.017	2.232 ± 0.045	1.081	0.780 ± 0.016	2.114 ± 0.042
1.036	0.914 ± 0.018	2.328 ± 0.046			

[Na-15C][CA]			[K-18C][LA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.293	0.079 ± 0.001	0.226 ± 0.004	0.017	0.227 ± 0.005	0.543 ± 0.011
0.475	0.125 ± 0.002	0.354 ± 0.007	0.161	0.712 ± 0.014	1.701 ± 0.035
0.587	0.154 ± 0.003	0.437 ± 0.008	0.304	0.881 ± 0.017	2.105 ± 0.044
0.699	0.181 ± 0.003	0.513 ± 0.010	0.574	0.993 ± 0.020	2.324 ± 0.050
0.893	0.231 ± 0.005	0.655 ± 0.013	0.696	1.045 ± 0.022	2.496 ± 0.052
1.051	0.281 ± 0.006	0.796 ± 0.016	0.88	1.058 ± 0.022	2.528 ± 0.0053
			1.028	1.091 ± 0.023	2.606 ± 0.054

[Na-15C][LA] + 5 wt% H_2O		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0
0.037	0.629 ± 0.013	1.754 ± 0.037
0.068	1.096 ± 0.023	3.057 ± 0.064
0.22	1.533 ± 0.032	4.277 ± 0.088
0.438	1.688 ± 0.035	4.711 ± 0.098
0.67	1.780 ± 0.037	5.022 ± 0.105
0.87	1.815 ± 0.036	5.065 ± 0.105
1.05	1.821 ± 0.039	5.082 ± 0.106

Table S9. The CO_2 solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K .

[Na-15C][LA]			[Na-15C][OCHCA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0

0.21	0.004 ± 0.000	0.014 ± 0.001	0.121	0.009 ± 0.000	0.030 ± 0.001
0.368	0.006 ± 0.000	0.025 ± 0.001	0.301	0.023 ± 0.001	0.076 ± 0.003
0.507	0.008 ± 0.000	0.032 ± 0.002	0.408	0.036 ± 0.002	0.117 ± 0.004
0.831	0.014 ± 0.001	0.054 ± 0.002	0.611	0.055 ± 0.002	0.177 ± 0.009
1.007	0.017 ± 0.001	0.064 ± 0.003	0.960	0.084 ± 0.002	0.272 ± 0.010
			1.115	0.097 ± 0.003	0.314 ± 0.015

[Na-15C][CBA]			**[Na-15C][HPA]**		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.183	0.002 ± 0.000	0.007 ± 0.000	0.076	0.125 ± 0.004	0.442 ± 0.012
0.309	0.003 ± 0.000	0.012 ± 0.000	0.339	0.161 ± 0.005	0.566 ± 0.016
0.478	0.006 ± 0.000	0.020 ± 0.001	0.511	0.165 ± 0.005	0.580 ± 0.016
0.61	0.009 ± 0.001	0.030 ± 0.001	0.65	0.170 ± 0.005	0.599 ± 0.017
0.803	0.012 ± 0.001	0.039 ± 0.002	0.833	0.180 ± 0.005	0.635 ± 0.018
0.928	0.015 ± 0.001	0.049 ± 0.002	1.012	0.189 ± 0.006	0.703 ± 0.020
1.019	0.017 ± 0.001	0.057 ± 0.002			

[Na-15C][CA]			**[K-18C][LA]**		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.107	0.013 ± 0.000	0.047 ± 0.001	0.201	0.024 ± 0.001	0.056 ± 0.015
0.207	0.025 ± 0.001	0.091 ± 0.003	0.438	0.060 ± 0.002	0.136 ± 0.004
0.431	0.047 ± 0.001	0.175 ± 0.005	0.707	0.108 ± 0.003	0.253 ± 0.007
0.626	0.058 ± 0.002	0.218 ± 0.006	0.861	0.134 ± 0.004	0.319 ± 0.009
0.855	0.074 ± 0.002	0.275 ± 0.008	1.052	0.169 ± 0.005	0.403 ± 0.011
1.072	0.090 ± 0.003	0.295 ± 0.008			

Table S10. The CH_4 solubility in CMILs at 313.2 K, with [K-18C][LA] tested at 323.2 K .

[Na-15C][LA]			[Na-15C][OCHCA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.621	0.0008 ± 0.0000	0.0027 ± 0.0001	0.501	0.0031 ± 0.0001	0.0101 ± 0.0004
0.910	0.0013 ± 0.0000	0.0046 ± 0.0001	1.029	0.0058 ± 0.0002	0.0189 ± 0.0005
1.702	0.0032 ± 0.0001	0.0113 ± 0.0003	1.523	0.0092 ± 0.0003	0.0299 ± 0.0009
2.442	0.0061 ± 0.0002	0.0209 ± 0.0007	2.005	0.0118 ± 0.0004	0.0384 ± 0.0011
3.058	0.0080 ± 0.0002	0.0278 ± 0.0008	2.532	0.0155 ± 0.0005	0.0503 ± 0.0015
			3.012	0.0195 ± 0.0006	0.0636 ± 0.0019

[Na-15C][CBA]			[Na-15C][HPA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.510	0.0032 ± 0.0001	0.0102 ± 0.0004	0.521	0.002 ± 0.0000	0.0065 ± 0.0002
1.028	0.0075 ± 0.0002	0.0238 ± 0.0007	1.001	0.0050 ± 0.0001	0.0164 ± 0.0005
1.537	0.0103 ± 0.0003	0.0329 ± 0.0010	1.540	0.0079 ± 0.0002	0.0260 ± 0.0008
2.008	0.0123 ± 0.0004	0.0392 ± 0.0011	1.984	0.0105 ± 0.0003	0.0343 ± 0.0010
2.511	0.0157 ± 0.0005	0.0501 ± 0.0015	2.559	0.0151 ± 0.0005	0.0494 ± 0.0014
3.001	0.0183 ± 0.0005	0.0583 ± 0.0017	3.003	0.0187 ± 0.0006	0.0609 ± 0.0018

[Na-15C][CA]			[K-18C][LA]		
Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)	Pressure (bar)	Solubility ($mol \cdot mol^{-1}$)	Solubility ($mol \cdot kg^{-1}$)
0	0	0	0	0	0
0.496	0.0027 ± 0.0001	0.0095 ± 0.0003	0.647	0.0011 ± 0.0000	0.0032 ± 0.0001
0.988	0.0050 ± 0.0001	0.0177 ± 0.0005	1.096	0.0021 ± 0.0000	0.0062 ± 0.0002

1.535	0.0092 ± 0.0003	0.0326 ± 0.0009	1.626	0.0036 ± 0.0001	0.0107 ± 0.0003
2.018	0.0112 ± 0.0003	0.0399 ± 0.0012	2.027	0.0045 ± 0.0001	0.0134 ± 0.0004
2.527	0.0138 ± 0.0004	0.0489 ± 0.0015	2.528	0.0063 ± 0.0002	0.0189 ± 0.0006
3.033	0.0173 ± 0.0005	0.0614 ± 0.0018	3.021	0.0080 ± 0.0002	0.0240 ± 0.0007

Table S11. Cartesian coordinates of [Na-15C][LA] from Gaussian 09 program.

Atoms	Coordinates (Angstroms)		
	X	Y	Z
O	-2.738036	1.672084	0.451309
C	-1.927892	2.89582	0.257359
C	-1.512587	2.93191	-1.205766
O	-0.573238	1.826323	-1.370787
C	-0.095522	1.579359	-2.729186
C	0.384168	0.135302	-2.724117
O	-0.855837	-0.659007	-2.580217
C	-0.662178	-2.109387	-2.699429
C	-0.325314	-2.750057	-1.357556
O	-1.501363	-2.481039	-0.508624
C	-1.303704	-2.879803	0.892808
C	-2.509012	-2.317397	1.636447
O	-2.327847	-0.872772	1.586206
C	-3.446808	-0.03797	2.005253
C	-2.934887	1.391819	1.888315
H	-1.025561	2.812081	0.871353
H	-2.515609	3.787142	0.511684
H	-1.032945	3.894374	-1.429456
H	-2.385672	2.795238	-1.858383
H	0.721112	2.264937	-2.988269
H	-0.914647	1.683029	-3.452605
H	1.035777	-0.034587	-1.858771
H	0.888021	-0.111628	-3.667451
H	0.118734	-2.336276	-3.438147
H	-1.620304	-2.499596	-3.05057
H	0.552727	-2.283296	-0.901067
H	-0.179524	-3.831996	-1.48534
H	-0.386491	-2.409395	1.268339
H	-1.258087	-3.972353	0.990681
H	-2.530418	-2.67656	2.673846
H	-3.43087	-2.617878	1.120959
H	-3.726159	-0.24561	3.0473
H	-4.316462	-0.194307	1.352599
H	-1.963554	1.450764	2.389204
H	-3.656416	2.096287	2.321848
Na	-1.165072	-0.041658	-0.167596
C	3.593189	-0.285364	1.234861
C	2.583732	0.849607	1.431339

C	4.893579	0.17011	0.593287
C	1.146868	0.420261	1.084018
C	6.043973	-0.827417	0.693252
O	5.011449	1.253182	0.008648
O	0.179502	1.108887	1.548422
O	0.998324	-0.596233	0.281268
H	3.105954	-0.993824	0.545123
H	3.806072	-0.829069	2.162729
H	2.864792	1.661753	0.745158
H	2.591572	1.255904	2.445381
H	6.879802	-0.491975	0.076157
H	6.369863	-0.902941	1.738773
H	5.71483	-1.824148	0.377358

Table S12. Cartesian coordinates of [Na-15C][LA] + H_2S from Gaussian 09 program.

Atoms	Coordinates (Angstroms)		
	X	Y	Z
O	-2.282322	-1.707778	-1.412461
C	-1.180232	-2.681823	-1.416971
C	-1.079275	-3.217702	0.004739
O	-0.708736	-2.060815	0.817321
C	-0.601435	-2.290771	2.256537
C	-0.316083	-0.927075	2.873166
O	-1.516906	-0.10928	2.609325
C	-1.445286	1.26454	3.137952
C	-1.126971	2.2549	2.018309
O	-2.256518	2.105562	1.085394
C	-2.142125	2.850686	-0.176287
C	-3.268496	2.305553	-1.054509
O	-3.045152	0.865289	-1.139505
C	-3.401314	0.178051	-2.376604
C	-2.314161	-0.86564	-2.621581
H	-0.235467	-2.183938	-1.667677
H	-1.376406	-3.49627	-2.125864
H	-0.302441	-3.988549	0.056882
H	-2.046817	-3.621869	0.329111
H	0.223845	-2.979344	2.473343
H	-1.545028	-2.687851	2.652793
H	0.55395	-0.481785	2.384475
H	-0.1543	-1.030566	3.953759
H	-0.696888	1.336455	3.937108
H	-2.435708	1.487471	3.541236
H	-0.189431	1.972473	1.522358
H	-1.071534	3.277408	2.416118
H	-1.189478	2.618726	-0.665746
H	-2.259067	3.930639	-0.016406
H	-3.212723	2.770651	-2.047994
H	-4.244661	2.514104	-0.602598
H	-3.422584	0.877949	-3.222881
H	-4.380885	-0.301426	-2.27157

H	-1.350234	-0.355741	-2.725223
H	-2.550303	-1.462506	-3.512629
Na	-1.406348	-0.017432	0.165451
C	3.458375	1.571659	-0.451943
C	2.437715	1.056927	-1.481513
C	4.801491	0.860165	-0.526022
C	1.046226	0.860301	-0.866331
C	5.983224	1.644489	0.02336
O	4.924239	-0.289195	-0.971577
O	0.008726	0.980983	-1.596749
O	0.992642	0.51196	0.393821
H	3.028808	1.339368	0.536103
H	3.60167	2.655337	-0.50836
H	2.781329	0.06867	-1.820859
H	2.352324	1.706999	-2.354215
H	6.867342	1.005827	0.061745
H	6.181137	2.507667	-0.625274
H	5.751472	2.030091	1.023357
S	2.339268	-2.367345	0.189654
H	3.556533	-1.909933	-0.256534
H	1.769378	-1.090146	0.342662

Table S13. Cartesian coordinates of [Na-15C][LA] + 2 H_2S from Gaussian 09 program.

Atoms	Coordinates (Angstroms)		
	X	Y	Z
O	2.857942	1.204096	-1.74183
C	1.867829	2.27549	-1.9254
C	1.883378	3.095413	-0.64142
O	1.44314	2.168732	0.396859
C	1.381091	2.695883	1.757976
C	0.95715	1.523204	2.633879
O	2.052234	0.53747	2.544513
C	1.831962	-0.68871	3.33202
C	1.387918	-1.83598	2.425358
O	2.511967	-2.0002	1.488242
C	2.299416	-2.97421	0.407275
C	3.451531	-2.7339	-0.5685
O	3.366292	-1.32645	-0.95085
C	3.734003	-0.95135	-2.31239
C	2.746924	0.130201	-2.74568
H	0.865172	1.847806	-2.0504
H	2.119502	2.902078	-2.79046
H	1.185805	3.936142	-0.72968
H	2.898219	3.457846	-0.43278
H	0.635872	3.497244	1.824274
H	2.366974	3.060668	2.074162
H	0.031829	1.09405	2.241653
H	0.827584	1.857812	3.671103
H	1.090994	-0.51696	4.122767
H	2.795868	-0.94021	3.78016

H	0.479782	-1.55348	1.877549
H	1.224031	-2.74811	3.015004
H	1.362485	-2.7561	-0.11736
H	2.318266	-4.00402	0.787469
H	3.327914	-3.38551	-1.44381
H	4.414484	-2.9382	-0.08751
H	3.646146	-1.80866	-2.99327
H	4.760462	-0.56866	-2.33311
H	1.733773	-0.28591	-2.71282
H	2.998152	0.499001	-3.74901
Na	1.884465	-0.03002	0.165654
C	-3.12964	-1.06505	-0.10031
C	-2.10551	-0.94782	-1.24962
C	-4.52875	-0.60574	-0.50825
C	-0.66931	-0.84334	-0.71733
C	-5.19625	-1.49784	-1.55663
O	-4.39387	0.756637	-0.97524
O	0.2946	-1.32359	-1.39637
O	-0.49372	-0.19887	0.408731
H	-2.763	-0.43167	0.710728
H	-3.19047	-2.09254	0.26999
H	-2.31731	-0.01595	-1.79055
H	-2.15659	-1.78164	-1.95253
H	-6.20533	-1.1394	-1.78819
H	-4.59624	-1.47637	-2.47147
H	-5.26586	-2.527	-1.19524
S	-1.64244	2.660866	-0.12938
H	-2.91571	2.203518	-0.38649
H	-1.11093	1.375101	0.147321
S	-5.70869	-0.64594	1.038884
H	-5.29654	1.092283	-1.22383
H	-4.95548	0.237944	1.773827

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