Integrated, one-pot carbon capture and utilisation using porous ionic liquids

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Supplementary Information

Materials

The ionic liquids tributyltetraoctylphosphonium chloride - $[P_{4,4,4,8}][Cl]$ - trihexyltetradecylphosphonium chloride - $[P_{6,6,6,14}][Cl]$ - and trihexyltetradecylphosphonium bromide - $[P_{6,6,6,14}][Br]$ - were supplied by Solvay, $> 95\%$pure. The ionic liquids were degassed for at least 72 hours under primary vacuum and were kept dried and degassed before the preparation of the porous liquids. The water content of the pure ionic liquids, estimated by the Karl Fischer coulometric titration method, was found to be 80 ppm ($x_{H_2O} = 0.001$), 155 ppm ($x_{H_2O} = 0.004$) and 280 ppm ($x_{H_2O} = 0.009$) for $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$ and $[P_{6,6,6,14}][Br]$, respectively.

ZIF-8, a 2-methylimidazole zinc salt $ZnIm_2$ with a pore aperture of 3.4 Å and a pore inner diameter of 11.6 Å - Basolite Z1200 (BASF product 691348) - was obtained from Sigma Aldrich, batch STBG590V. HKUST-1, a copper benzene-1,3,5-carboxylate ($Cu(BTC)_2$) with 9 Å main channels and tetrahedral-shaped 5 Å side-pockets, accessible through 3 Å triangular window — Basolite C300 (BASF product 688614) — was purchased from Sigma Aldrich, batch STBF5289V. Both solids were passed through a 11 µm pore-size Nylon Nitex to narrow particle size distribution in the porous liquid. Carbon dioxide, CO_2 4.5 was purchased from Messer with a mole fraction purity of 99.995 %. The gas was used as received.

Styrene oxide > 97 % was purchased from ACROS Organics and the NMR standard, 2,4-dibromomesitylene 98 %, by Alfa Aesar. Tetrabutylammonium chloride - NBu_4Cl - tetrabutylammonium bromide - NBu_4Br - and tetrabutylammonium iodide - NBu_4I were purchased from Sigma Aldrich, > 97 %, > 98 % and > 98 % pure, respectively.

Porous ionic liquids preparation

The porous ionic liquids, i.e. suspensions of ZIF-8 in $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$ and $[P_{6,6,6,14}][Br]$, were prepared at room temperature by weighing the components using a Mettler Toledo New Classic MS balance with an accuracy of ±0.01 mg, and by stirring the mixture at 430–540 rpm during 5 minutes. The porous ionic liquids were degassed under primary vacuum for up to 24 hours before use. The prepared samples are listed in Table S1 and the estimated uncertainty on the suspended solid concentration is ±0.0005 %.

Table S1: Sample nomenclature and composition

Sample	m_{IL} (g)	m_{MOF} (g)	MOF %w/w
$[P_{4,4,4,8}][Cl]$			
$[P_{4,4,4,8}][Cl]$ + ZIF-8	2.00498	0.10240	5.1073
$[P_{6,6,6,14}][Cl]$			
$[P_{6,6,6,14}][Cl]$ + ZIF-8	2.03615	0.10418	5.1165
$[P_{6,6,6,14}][Br]$			
$[P_{6,6,6,14}][Br]$ + ZIF-8	2.61641	0.13002	4.9694

Density and viscosity measurements

Density (of the pure ionic liquids and of the porous ionic liquids) and viscosity (of the pure ionic liquids) were measured in a coupled Anton Paar density meter (DMA 5000 M) and viscometer (LOVIS 2000 ME) in the temperature range 293–353 K at atmospheric pressure. The densimeter's measuring element is a U-shaped vibrating-tube, that is electronically excited to oscillate at its characteristic frequency whose value changes depending on the density of the filled sample. The calibration of the equipment was performed before the measurements with two substances of the precisely known densities, air and the Anton Paar ultra-pure water. Even if the densimeter is only recommended for the measurement of homogeneous fluid samples, we believe that in the present case, the density of the stable suspensions is also precise to within $5 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$ as a function of the temperature controlled to within 0.001 °C.

The viscometer is based on Hoeppler falling ball principle, measuring the rolling time of a ball through the liquid confined in a glass capillary. In order to cover the samples viscosity in the worked temperature range, two capillaries with different diameter, 1.8 and 2.5 mm, were calibrated with two different standard oils, APN26 and APN415 respectively, and two balls with known material, geometry and density. The precision of this module is 0.05 % in the viscosity and 0.02 °C in the temperature. Both the densimeter and viscometer cells were filled with *ca.* 1 mL of sample and the measurements were carried out simultaneously, using the temperature table scan mode.

The relative deviations of the density and viscosity from appropriate fitting functions, δ, were calculated using the following equation:

$$\delta = \frac{(Y_{exp} - Y_{calc})}{Y_{calc}} 100 \tag{S1}$$

where Y denotes the density (ρ) or the viscosity (η): Y_{exp} are the experimental and Y_{calc} are the calculated values obtained by the linear fitting of densities against temperature, and by the Vogel-Tammann-Fulcher (VTF) fitting of the viscosities against temperature, respectively.

Density and viscosity data

Table S2: Experimental densities of the pure ionic liquids, $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$, and the corresponding porous ionic liquids, $[P_{4,4,4,8}][Cl]$ + ZIF-8, $[P_{6,6,6,14}][Cl]$ + ZIF-8, $[P_{6,6,6,14}][Br]$ + ZIF-8, in the temperature range 293–353 K. The deviations indicated are relative to the fitting polynomials with coefficients listed in Table S3

T/K	ρ/g cm^{-3}	δ/%	T/K	ρ/g cm^{-3}	δ/%
$[P_{4,4,4,8}][Cl]$			$[P_{4,4,4,8}][Cl]$+ZIF-8		
293.149	0.92717	-0.009	293.149	0.939372	-0.0005
298.150	0.92430	-0.005	298.155	0.936568	-0.0009
303.151	0.92141	0.001	303.154	0.933759	-0.0003
313.149	0.91569	0.007	313.154	0.928142	0.0005
323.150	0.90998	0.01	323.154	0.922527	0.001
333.151	0.90436	0.007	333.154	0.916915	0.001
343.150	0.89877	-0.001	343.154	0.911316	0.0004
353.150	0.89320	-0.01	353.154	0.905730	-0.002
$[P_{6,6,6,14}][Cl]$			$[P_{6,6,6,14}][Cl]$+ZIF-8		
293.150	0.89404	-0.01	293.150	0.908005	-0.1
298.150	0.89089	-0.009	298.154	0.905113	-0.1
303.150	0.88818	-0.007	303.154	0.902223	-0.1
313.150	0.88221	-0.004	313.154	0.896451	-0.1
323.151	0.87649	0.06	323.154	0.890687	-0.05
333.150	0.87066	-0.006	333.154	0.884940	-0.1
343.150	0.86493	-0.01	343.155	0.879211	-0.1
353.150	0.85917	-0.01	353.154	0.873475	-0.1
$[P_{6,6,6,14}][Br]$			$[P_{6,6,6,14}][Br]$+ZIF-8		
293.150	0.95819	-0.02	293.150	0.974933	-0.002
298.150	0.9553	-0.03	298.150	0.971908	-0.001
303.151	0.95198	0.007	303.151	0.968880	0.0002
313.150	0.94597	0.01	313.150	0.962833	0.002
323.149	0.94008	0.007	323.149	0.956798	0.002
333.151	0.93360	0.06	333.151	0.950773	0.001
343.150	0.92777	0.05	343.150	0.944762	-0.0006
353.150	0.92315	-0.09	353.150	0.938747	-0.002

Table S3: Parameters A_0 and A_1 from linear functions used to fit the experimental densities, $\rho = A_0 + A_1 T$, as a function of temperature and absolute average deviation (AAD)

Sample	$A_0/\mathrm{g\,cm^{-3}}$	$A_1/\mathrm{g\,cm^{-3}\,K^{-1}}$	$AAD/\%$
$[P_{4,4,4,8}][Cl]$	1.0932	-5.6660×10^{-4}	0.007
$[P_{4,4,4,8}][Cl]$+ZIF-8	1.1038	-5.6090×10^{-4}	0.0009
$[P_{6,6,6,14}][Cl]$.	1.0645	-5.8346×10^{-4}	0.01
$[P_{6,6,6,14}][Cl]$+ZIF-8	1.0767	-5.7893×10^{-4}	0.01
$[P_{6,6,6,14}][Br]$	1.1324	-5.9503×10^{-4}	0.004
$[P_{6,6,6,14}][Br]$+ZIF-8	1.1517	-6.0314×10^{-4}	0.001

$AAD = \frac{100}{N} \sum_{i=1}^{N} \left(\frac{|\rho_{exp_i} - \rho_{cal_i}|}{\rho_{cal_i}} \right)$

Table S4: Experimental viscosities of the of the pure ionic liquids, $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$ in the temperature range 293–353 K. The deviations indicated are relative to the Vogel-Tammann-Fulcher (VTF) functions with coefficients listed in Table S5

T/K	$\eta/\mathrm{m\,Pa\,s}$	$\delta/\%$	T/K	$\eta/\mathrm{m\,Pa\,s}$	$\delta/\%$
	$[P_{4,4,4,8}][Cl]$			$[P_{6,6,6,14}][Cl]$	
293.149	12596	0.05	293.150	3566.7	0.06
298.150	7547.2	−0.4	298.150	2433.5	−0.2
303.151	4636.4	0.2	303.150	1685.6	0.1
313.149	1908.9	2.0	313.150	859.44	0.4
323.150	938.8	−3.8	323.151	470.33	0.2
333.151	466.59	−1.8	333.150	273.37	−0.3
343.150	251.49	−0.7	343.150	167.42	−1.1
353.150	144.99	−0.2	353.150	107.43	−2.0
	$[P_{6,6,6,14}][Br]$				
293.150	3948.4	−0.2			
298.150	2701.1	−0.6			
303.151	1873.1	−0.3			
313.149	949.13	0.5			
323.151	518.29	0.2			
333.151	302.22	−1.1			
343.150	184.60	−2.3			
353.150	117.83	−3.8			

Table S5: Parameters A, B and T_0 from VTF functions used to fit the experimental viscosity, $\eta = Ae^{(B/(T-T_0)}$, as a function of temperature and the corresponding absolute average deviation (AAD)

Sample	A/mPa s	B/K	T_0/K	AAD/%
$[P_{4,4,4,8}][Cl]$	5.2333×10^{-3}	2018.35	155.79	1.1
$[P_{6,6,6,14}][Cl]$	4.2720×10^{-3}	2346.19	121.09	0.6
$[P_{6,6,6,14}][Br]$	2.6320×10^{-3}	2567.15	112.60	1.1

$AAD = \frac{100}{N} \sum_{i=1}^{N} \left(\frac{|\eta_{exp_i} - \eta_{cal_i}|}{\eta_{cal_i}} \right)$

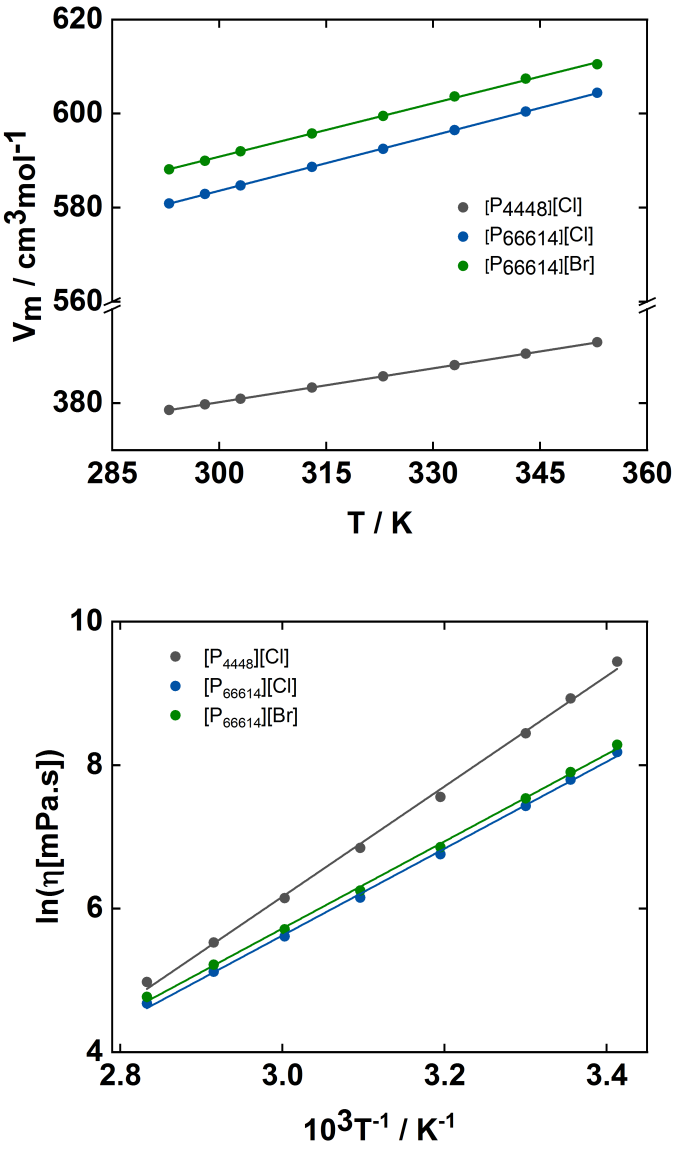

Figure S1: Molar volumes calculated from experimental densities (top) and viscosities (bottom) of the pure ionic liquids studied as a function of temperature: $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$.

Gas absorption measurements

Carbon dioxide absorption in the pure ionic liquids and in the porous ionic liquids was measured gravimetrically using an Intelligent Gravimetric Analyzer (IGA001) from Hiden Analytical in the 1–10 bar pressure range and 303–350 K temperature range. The CO_2 adsorption in the pure ZIF-8 was also measured gravimetrically in the 0.5–5 bar pressure range and 303–343 K temperature range. The detailed IGA001 working principle, measurement set up and data treatment are described in our previous work.[1]

We have followed the measurement procedure described before[1] and loaded an amount of 70–90 mg of liquid into the sample holder before sealing the stainless steel reactor vessel. The sample was degassed and dried by a turbo pump (Edwards, EXT75DX)during 24 hours before starting the absorption/desorption cycles at each temperature. The mass of the dry sample was recorded after obtaining a stable reading under vacuum to within ±0.015 mg.

The mass of gas absorbed, m_g, at a given temperature and pressure, is calculated from the raw weight data, m_{reading}, by:

$$\begin{aligned} m_{\text{reading}} &= m_0 + m_s + m_g + m_g^{\text{EP}} \\ &\quad - \sum_i \frac{m_i}{\rho_i}\rho_g(T_i,p) + \sum_j \frac{m_j}{\rho_j}\rho_g(T_j,p) - \frac{m_s}{\rho_s(T_s)}\rho_g(T_s,p) \end{aligned} \tag{S2}$$

where m_0 ($\approx \pm 10^{-4}$ to $\pm 10^{-3}$mg) is a small residual mass read after the tare with the empty pan at zero pressure, m_s is the mass of degassed sample, and m_g^{EP} is the mass effect resulting from adsorbed gas on the balance components (determined by performing a blank measurement with the empty pan). The sums over the i and j components account for the buoyancy effects due to the surrounding gas on the sample and counterweight sides, respectively. The last term in eq. (S2) is the buoyancy effect on the sample, which depends on the sample density. Additional buoyancy differences associated with changes in sample volume due to the (small) amount of dissolved gas are considered negligible. $\rho_g(T,p)$ is the gas density at the measurement temperature and pressure, calculated from an equation of state.

A blank measurement with the empty pan is performed in the same conditions as the ones with samples, in order to determine m_0, the adsorption correction m_g^{EP} and the buoyancy terms and in eq. (S2). The raw measurements of mass with the empty pan are observed to be linear with pressure along isotherms,

$$\begin{aligned} m_{\mathrm{reading}}^{\mathrm{EP}} &= m_0 + m_g^{\mathrm{EP}} - \sum_i \frac{m_i}{\rho_i}\rho_g(T_i, p) + \sum_j \frac{m_j}{\rho_j}\rho_g(T_j, p) \\ &= m_0 + Ap \end{aligned} \tag{S3}$$

Eq. (S3) allows determination of the third, forth and fifth terms on the right-hand side of eq. (S2), from which m_g, the mass of gas absorbed, is calculated.

From m_g the molality of the gas (quantity of gas absorbed per mass of solvent), $b(p, T)$, is then calculated at each temperature and pressure:

$$b(p, T) = \frac{n_g}{m_s} \tag{S4}$$

It is worth noting that the calculation of a mole fraction solubility is not practical in the presence of the suspended MOFs in the porous ionic liquids used as solvents.

The additional gas absorption capacity attributed to the MOFs in the porous ionic liquids can be calculated as:

$$n_g^{\mathrm{MOF}} = n_g^{\mathrm{PL}} - n_g^{\mathrm{IL}} \tag{S5}$$

where, n_g^{MOF}, n_g^{PL} and n_g^{IL} stand for the quantity of gas absorbed by the MOF, the porous liquid and the ionic liquid in the sample, respectively.

The absorption of the MOF in the porous liquid relative to that of the pure MOF (β) can be calculated as:

$$\beta = \frac{n_g^{\mathrm{MOF}}/w_{\mathrm{MOF}}}{b_g^{\mathrm{pureMOF}}} \tag{S6}$$

where w_{MOF} is the weight fraction of MOF in the porous liquid.

Gas absorption data

Table S6: Absorption and desorption of CO_2 in the ionic liquids, $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$ as function of pressure and temperature in the ranges 1–10 bar and 303–350 K, respectively.

$[P_{4,4,4,8}][Cl]$			$[P_{6,6,6,14}][Cl]$			$[P_{6,6,6,14}][Br]$		
$\frac{T}{K}$	$\frac{p}{10^2\,Pa}$	$\frac{b}{mmol\,kg^{-1}}$	$\frac{T}{K}$	$\frac{p}{10^2\,Pa}$	$\frac{b}{mmol\,kg^{-1}}$	$\frac{T}{K}$	$\frac{p}{10^2\,Pa}$	$\frac{b}{mmol\,kg^{-1}}$
CO_2 — Absorption								
303.78	0.0	0.0	304.40	0.0	0.0	303.08	0.0	0.0
303.16	998.8	58.8	303.14	999.6	64.6	303.15	999.3	50.0
303.14	1997.1	119.1	303.16	1997.8	128.8	303.16	1998.7	99.4
303.15	2998.7	179.9	303.16	2999.1	192.5	303.15	2998.8	149.7
303.15	4997.8	298.6	303.14	4998.4	321.7	303.15	4998.0	252.6
303.15	5999.3	362.5	303.16	5998.5	386.2	303.14	5998.3	307.0
303.14	7997.5	482.8	303.14	7998.9	514.7	303.15	7998.5	410.3
303.15	9997.7	612.0	303.14	9997.6	643.3	303.15	9998.4	517.0
322.27	0.0	0.0	322.61	0.0	0.0	321.69	0.0	0.0
323.16	998.8	36.3	323.17	999.3	45.7	323.13	998.1	37.3
323.15	1998.5	81.4	323.12	1998.8	95.7	323.16	1998.0	76.0
323.16	2998.3	125.6	323.16	2999.1	141.9	323.18	2998.7	118.9
323.17	4998.2	213.4	323.15	4998.0	238.1	323.16	4999.0	198.3
323.16	5997.5	260.3	323.18	5998.6	284.7	323.18	5998.7	236.4
323.16	8000.0	349.0	323.14	7998.4	380.5	323.18	7997.8	313.6
323.15	9998.0	439.3	323.18	9997.8	478.7	323.17	9999.8	390.5
332.56	0.0	0.0	333.43	0.0	0.0	333.38	0.0	0.000
333.23	999.0	37.0	333.15	999.1	39.3	333.13	998.9	32.4
333.08	1998.0	78.0	333.15	1998.1	88.7	333.15	1998.5	72.8
333.18	2996.3	119.7	333.16	2998.4	128.7	333.16	2998.4	104.9
333.15	4997.2	197.0	333.13	4997.9	206.6	333.17	4997.8	177.1
333.16	5999.6	240.5	333.14	5998.3	252.2	333.16	5998.7	210.8
333.12	7999.5	310.5	333.14	7996.8	338.0	333.15	7998.5	284.1
333.20	9999.0	399.7	333.18	9998.1	415.2	333.18	9999.0	349.8
348.49	0.0	0.0	349.22	0.0	0.0	348.813	0.0	0.0
351.43	999.0	31.7	351.71	998.1	33.3	351.648	999.7	26.7
350.70	1997.0	70.8	351.19	1996.9	72.5	351.122	1998.5	62.2
350.72	2998.9	101.1	351.13	2999.2	104.1	351.238	2997.9	82.0
350.60	4999.8	166.2	350.67	4995.3	173.9	351.001	4998.4	144.4
350.62	5999.0	197.8	350.56	5998.3	205.2	350.817	5997.4	175.9
350.45	7997.5	256.7	350.40	7998.1	277.2	350.629	7999.6	231.0
350.42	9999.1	322.9	350.44	9997.3	337.7	350.556	9999.4	288.6
CO_2 — Desorption								
303.15	9998.0	612.0	303.14	9997.6	643.3	303.15	9998.4	517.0
303.15	7997.5	496.9	303.15	7997.9	514.8	303.16	7999.6	409.7

$[P_{4,4,4,8}][Cl]$			$[P_{6,6,6,14}][Cl]$			$[P_{6,6,6,14}][Br]$		
T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}
303.14	5998.5	376.4	303.14	5998.9	384.2	303.14	5999.8	299.5
303.16	4998.0	311.4	303.14	4998.7	319.2	303.16	4998.4	245.6
303.15	2999.2	192.8	303.15	2999.4	191.3	303.15	2999.9	140.3
303.14	1998.9	129.0	303.15	1998.7	127.4	303.13	1999.4	87.0
303.15	998.5	68.1	303.15	997.9	63.6	303.14	999.9	34.6
303.11	0.0	0.0	303.16	0.0	0.0	303.16	0.0	0.0
323.15	9998.0	439.3	323.18	9997.8	478.7	323.17	9999.8	390.5
323.18	7998.5	343.4	323.16	8000.0	379.8	323.17	7997.8	310.0
323.14	5999.3	258.2	323.14	5999.0	284.8	323.16	5997.9	229.7
323.17	4998.7	213.7	323.18	4997.6	235.8	323.16	4999.8	194.3
323.18	2998.4	123.5	323.17	2999.1	140.0	323.17	2999.1	116.1
323.16	1998.0	78.1	323.17	1998.4	92.9	323.17	1998.2	73.4
323.17	998.2	33.1	323.17	999.2	45.0	323.15	999.5	35.0
319.82	0.000	0.0	323.17	0.0	0.0	323.20	0.0	0.0
333.20	9998.9	399.7	333.18	9997.8	415.2	333.18	9998.9	349.8
333.12	7994.2	322.1	333.14	8000.0	331.6	333.13	7997.9	282.2
333.05	5999.7	237.2	333.17	5999.0	252.8	333.16	5998.6	209.7
333.20	4998.4	196.1	333.14	4997.6	210.0	333.14	4998.2	175.0
333.26	2999.1	123.1	333.13	2999.1	125.0	333.14	2998.7	106.3
333.17	1997.6	80.4	333.16	1998.4	83.3	333.14	1996.4	68.0
333.22	999.3	37.2	333.14	999.2	37.7	333.14	999.9	30.8
331.48	0.0	0.0	332.30	0.0	0.0	332.04	0.0	0.0
350.42	9999.1	322.9	350.44	9997.3	337.7	350.56	9999.4	288.6
350.23	7997.8	257.4	350.44	7997.1	273.4	350.68	7999.7	230.2
350.54	5996.9	1920.2	350.80	5999.2	197.9	350.91	5998.7	170.4
350.17	4998.3	165.5	350.88	4997.8	165.8	350.98	4998.3	144.0
350.66	2998.5	97.6	350.91	2998.3	100.8	351.26	2999.4	82.6
350.40	1999.2	70.5	350.69	1997.4	71.0	350.88	1998.2	57.2
350.85	1000.2	30.5	351.45	1000.3	28.9	351.62	999.9	22.9
346.38	0.000	0.0	346.40	0.0	0.0	346.67	0.0	0.0

*Due to the instability in the temperature above 350 K the average data is reported in S8.

Table S7: Absorption and desorption of CO_2 in the porous ionic liquids, $[P_{4,4,4,8}][Cl]$+ZIF-8, $[P_{6,6,6,14}][Cl]$+ZIF-8 and $[P_{6,6,6,14}][Br]$+ZIF-8, as function of pressure and temperature in the ranges 1–10 bar and 303–350 K, respectively. The exact concentrations of ZIF-8 in the porous liquids are given in Table S1 of the Supplementary Information

$[P_{4,4,4,8}][Cl]$+ZIF-8			$[P_{6,6,6,14}][Cl]$+ZIF-8			$[P_{6,6,6,14}][Br]$+ZIF-8		
T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}
				CO_2 — Absorption				
303.13	0.0	0.0	303.73	0.0	0.0	303.14	0.0	0.0
303.05	998.3	77.2	303.30	999.1	82.6	303.16	1000.2	67.1
303.15	1998.9	148.3	303.20	1998.8	159.0	303.14	1997.8	131.1
303.13	2998.0	218.2	303.13	2998.3	235.2	303.15	2998.7	194.5
303.14	4998.7	352.3	303.14	4999.8	388.0	303.15	4996.9	322.3
303.15	5999.6	423.3	303.19	5999.8	464.4	303.15	5998.5	386.7
303.16	7997.0	550.9	303.12	7999.3	617.0	303.16	7998.9	515.1
303.14	9996.7	681.0	303.12	9998.3	769.6	303.14	9998.4	646.1
320.97	0.0	0.0	322.35	0.0	0.0	322.15	0.0	0.0
323.12	999.7	46.7	323.17	1000.1	61.2	323.21	999.3	45.4
323.16	1998.8	100.8	323.18	1998.2	121.5	323.16	1998.1	104.0
323.16	2999.8	152.5	323.17	2999.2	181.0	323.18	2999.4	144.9
323.15	4998.2	249.8	323.18	4998.2	301.3	323.19	4998.0	238.8
323.18	5998.5	302.3	323.14	5997.2	360.0	323.16	5998.5	291.7
323.18	7996.1	397.4	323.15	7998.4	482.4	323.14	7997.3	387.5
323.16	9997.7	495.6	323.16	9998.5	591.9	323.13	9998.1	481.5
332.98	0.0	0.0	333.24	0.0	0.0	333.44	0.0	0.0
333.07	999.0	42.6	333.15	999.3	53.3	333.14	998.9	38.9
333.16	1998.7	88.7	333.18	1998.1	115.8	333.16	1999.4	91.1
333.15	2999.0	139.8	333.16	2998.0	179.7	333.16	2998.7	133.1
333.14	4998.6	232.1	333.15	4998.0	280.3	333.17	4999.4	215.4
333.48	5997.1	277.0	333.13	5997.9	342.2	333.16	5998.2	246.4
333.22	7999.3	361.6	333.16	7998.6	437.6	333.12	7999.1	339.8
333.20	9998.7	449.9	333.13	9996.3	540.7	333.13	9999.6	414.0
348.71	0.0	0.0	348.74	0.0	0.0	348.36	0.0	0.0
351.47	999.3	47.0	351.45	996.4	61.1	351.48	999.6	37.3
350.96	1998.2	97.4	351.10	1999.1	113.8	351.11	1998.4	77.7
350.11	2999.5	136.2	351.14	2999.1	154.8	350.82	2997.2	114.3
350.85	4996.0	202.5	351.07	4996.5	240.7	350.55	4996.6	183.2
350.47	5998.7	244.4	350.97	5998.7	280.4	350.36	5999.2	215.2
350.44	7999.1	308.3	350.77	7998.2	365.4	350.18	7997.5	297.6
350.39	9995.5	384.8	350.46	9998.4	450.2	350.15	9998.5	358.0
				CO_2 — Desorption				
303.14	9996.7	681.0	303.12	9998.3	769.6	303.14	9998.4	646.1
303.15	7998.2	556.0	303.16	7998.1	616.9	303.15	7999.3	514.3

$[P_{4,4,4,8}][Cl]$+ZIF-8			$[P_{6,6,6,14}][Cl]$+ZIF-8			$[P_{6,6,6,14}][Br]$+ZIF-8		
T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}	T / K	p / 10^2 Pa	b / mmol kg^{-1}
303.16	5998.9	426.3	303.19	5999.2	464.3	303.14	5999.4	384.8
303.14	4998.7	358.7	303.18	4997.5	387.8	303.13	4999.1	322.0
303.14	2999.8	224.7	303.23	2998.1	235.2	303.14	2998.4	193.0
303.15	1998.1	152.3	303.14	1998.2	158.9	303.14	1998.2	129.6
303.16	997.8	78.2	303.18	999.3	82.7	303.15	998.9	63.0
303.27	0.0	0.0	303.70	0.0	0.0	303.12	0.0	0.0
323.16	9997.7	495.6	323.16	9998.5	591.9	323.13	9998.1	481.5
323.18	7997.3	401.4	323.16	7999.3	475.0	323.16	7998.6	378.6
323.16	5999.4	304.8	323.17	5997.9	364.9	323.16	5998.2	293.1
323.18	4999.0	255.3	323.16	4999.1	304.9	323.19	4999.1	240.1
323.16	2998.5	152.8	323.17	2999.5	181.8	323.17	2999.6	141.2
323.15	1996.7	102.3	323.15	1999.5	124.1	323.16	1998.2	94.0
323.16	999.2	51.2	323.16	999.1	61.5	323.17	998.9	45.0
322.66	0.0	0.0	323.17	0.0	0.0	323.14	0.0	0.0
333.20	9998.7	0.4499	333.13	9996.3	0.5407	333.13	9999.6	0.4140
333.12	7999.6	0.3552	333.19	7998.9	0.4387	333.15	7998.5	0.3336
333.07	5999.4	0.2711	333.11	5998.3	0.3472	333.14	5998.7	0.2510
333.20	4998.3	0.2337	333.15	4998.9	0.2878	333.14	4998.0	0.2084
333.10	2998.0	0.1520	333.13	2999.1	0.1819	333.16	2998.8	0.1289
333.11	1997.7	0.1063	333.12	1997.8	0.1388	333.16	1998.5	0.0888
333.18	999.1	0.0612	333.12	998.6	0.0727	333.14	999.2	0.0383
331.92	0.000	0.000	331.95	0.000	0.000	331.15	0.000	0.000
350.39	9995.5	384.8	350.46	9998.4	450.2	350.15	9998.5	358.0
350.37	7996.1	320.2	351.58	7998.1	368.7	350.43	7998.6	278.8
350.66	5998.9	248.1	351.09	5999.4	292.7	350.68	5999.4	204.5
350.91	4999.7	210.7	351.08	4998.3	247.2	350.81	4998.4	172.7
351.05	3000.1	138.8	351.00	2996.6	153.7	350.85	2999.8	101.0
350.84	1998.7	98.4	350.90	1997.6	115.0	350.96	1998.2	63.4
348.60	997.5	44.2	350.48	1000.3	54.9	351.36	998.8	22.1
344.24	0.0	0.0	346.35	0.0	0.0	345.60	0.0	0.0

*Due to the instability in the temperature above 350 K the average data is reported in S8.

Table S8: Average absorption of CO_2 by $[P_{4,4,4,8}][Cl]$, $[P_{4,4,4,8}][Cl]$+ ZIF-8, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Cl]$+ ZIF-8, $[P_{6,6,6,14}][Br]$ and $[P_{6,6,6,14}][Br]$+ ZIF-8 as function of pressure from 1–10 bar and at the temperature range 303–350 K. The uncertainties of temperature, pressure and gas absorption are also depicted in the table.

CO_2 — Average absorption					
$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$
	$[P_{4,4,4,8}][Cl]$			$[P_{4,4,4,8}][Cl]$+ZIF-8	
303.45 ± 0.47	0.0 ± 0.0	0.0 ± 0.0	303.20 ± 0.10	0.0 ± 0.0	0.0 ± 0.0
303.16 ± 0.01	998.6 ± 0.2	63.4 ± 6.6	303.11 ± 0.08	998.6 ± 1.1	77.7 ± 0.7
303.14 ± 0.00	1998.0 ± 1.3	124.1 ± 7.0	303.15 ± 0.01	1998.5 ± 0.6	150.3 ± 2.8
303.15 ± 0.00	2999.0 ± 0.4	186.3 ± 9.1	303.13 ± 0.01	2998.9 ± 1.3	221.4 ± 4.6
303.16 ± 0.00	4997.9 ± 0.2	305.0 ± 9.0	303.14 ± 0.00	4998.7 ± 0.0	355.5 ± 4.6
303.14 ± 0.01	5998.9 ± 0.6	369.4 ± 9.8	303.16 ± 0.00	5999.2 ± 0.5	424.8 ± 2.1
303.15 ± 0.01	7997.5 ± 0.0	489.9 ± 10.0	303.16 ± 0.01	7997.6 ± 0.9	553.5 ± 3.6
303.15 ± 0.00	9997.7 ± 0.0	612.0 ± 0.0	303.14 ± 0.00	9996.7 ± 0.0	681.0 ± 0.00
321.04 ± 1.73	0.0 ± 0.0	0.0 ± 0.0	321.82 ± 1.20	0.0 ± 0.0	0.0 ± 0.0
323.17 ± 0.00	998.5 ± 0.4	34.7 ± 2.2	323.14 ± 0.03	999.5 ± 0.4	48.9 ± 3.2
323.16 ± 0.01	1998.2 ± 0.4	79.8 ± 2.4	323.16 ± 0.00	1997.8 ± 1.5	101.6 ± 1.1
323.17 ± 0.01	2998.3 ± 0.1	124.5 ± 1.5	323.16 ± 0.00	2999.2 ± 0.9	152.7 ± 0.3
323.17 ± 0.00	4998.4 ± 0.4	213.5 ± 0.3	323.17 ± 0.02	4998.6 ± 0.6	252.6 ± 3.9
323.15 ± 0.01	5998.4 ± 1.3	259.3 ± 1.5	323.17 ± 0.01	5998.9 ± 0.7	303.5 ± 1.8
323.17 ± 0.01	7999.3 ± 1.1	346.2 ± 3.9	323.18 ± 0.00	7996.7 ± 0.8	399.4 ± 2.8
323.15 ± 0.00	9998.0 ± 0.0	439.3 ± 0.0	323.16 ± 0.00	9997.7 ± 0.0	495.6 ± 0.0
332.02 ± 0.76	0.0 ± 0.0	0.0 ± 0.0	332.45 ± 0.75	0.0 ± 0.0	0.0 ± 0.0000
333.22 ± 0.00	999.1 ± 0.3	37.1 ± 0.2	333.12 ± 0.08	999.1 ± 0.0	51.9 ± 13.1
333.12 ± 0.06	1997.8 ± 0.3	79.2 ± 1.7	333.14 ± 0.03	1998.2 ± 0.7	97.5 ± 12.4
333.22 ± 0.06	2997.7 ± 2.0	121.4 ± 2.4	333.12 ± 0.04	2998.5 ± 0.7	145.9 ± 8.7
333.17 ± 0.03	4997.8 ± 0.9	196.4 ± 0.4	333.17 ± 0.05	4998.4 ± 0.2	232.9 ± 1.1
333.10 ± 0.08	5999.6 ± 0.1	238.8 ± 2.3	333.28 ± 0.29	5998.2 ± 1.7	274.1 ± 4.1
333.12 ± 0.00	7996.8 ± 3.7	316.3 ± 8.2	333.17 ± 0.06	7999.5 ± 0.2	358.4 ± 4.5
333.20 ± 0.00	9999.0 ± 0.0	399.7 ± 0.0	333.20 ± 0.00	9998.7 ± 0.0	449.9 ± 0.0
347.43 ± 1.49	0.0 ± 0.0	0.0 ± 0.0	346.48 ± 3.16	0.0 ± 0.0	0.0 ± 0.0
351.14 ± 0.41	999.6 ± 0.8	31.1 ± 0.8	350.04 ± 2.04	998.4 ± 1.3	45.6 ± 2.0
350.55 ± 0.21	1998.1 ± 1.6	70.6 ± 0.2	350.90 ± 0.09	1998.4 ± 0.3	97.9 ± 0.7
350.69 ± 0.04	2998.7 ± 0.3	99.3 ± 2.5	351.08 ± 0.04	2999.8 ± 0.4	137.5 ± 1.9
350.38 ± 0.30	4999.1 ± 1.1	165.8 ± 0.5	350.88 ± 0.05	4999.6 ± 0.1	206.6 ± 5.8
350.58 ± 0.05	5998.0 ± 1.5	195.0 ± 4.0	350.57 ± 0.13	5998.8 ± 0.1	246.3 ± 2.7
350.34 ± 0.16	7997.7 ± 0.2	257.0 ± 0.5	350.40 ± 0.05	7997.6 ± 2.1	314.2 ± 8.4
350.42 ± 0.00	9999.1 ± 0.0	322.9 ± 0.0	350.39 ± 0.00	9995.5 ± 0.0	384.8 ± 0.0
	$[P_{6,6,6,14}][Cl]$			$[P_{6,6,6,14}][Cl]$+ZIF-8	
303.78 ± 0.88	0.0 ± 0.0	0.0 ± 0.0	303.72 ± 0.03	0.0 ± 0.0	0.0 ± 0.0
303.14 ± 0.01	998.8 ± 1.2	64.1 ± 0.7	303.23 ± 0.08	999.2 ± 0.2	82.7 ± 0.0

CO_2 — Average absorption					
$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$
303.16 ± 0.01	1998.2 ± 0.6	128.1 ± 1.0	303.17 ± 0.04	1998.5 ± 0.4	158.9 ± 0.0
303.16 ± 0.00	2999.2 ± 0.2	191.9 ± 0.9	303.18 ± 0.07	2998.2 ± 0.1	235.2 ± 0.0
303.14 ± 0.00	4998.6 ± 0.2	320.4 ± 1.7	303.16 ± 0.02	4998.6 ± 1.7	387.9 ± 0.1
303.15 ± 0.01	5998.7 ± 0.3	385.2 ± 1.4	303.19 ± 0.00	5999.5 ± 0.5	464.3 ± 0.0
303.15 ± 0.01	7998.4 ± 0.7	514.7 ± 0.1	303.14 ± 0.03	7998.7 ± 0.9	616.9 ± 0.1
303.14 ± 0.00	9997.6 ± 0.0	643.3 ± 0.0	303.12 ± 0.00	9998.3 ± 0.0	769.6 ± 0.0
322.89 ± 0.40	0.0 ± 0.0	0.0 ± 0.0	322.76 ± 0.60	0.0 ± 0.0	0.0 ± 0.0
323.17 ± 0.00	999.3 ± 0.1	45.4 ± 0.5	323.16 ± 0.01	999.6 ± 0.8	61.4 ± 0.2
323.14 ± 0.03	1998.6 ± 0.3	94.3 ± 2.0	323.17 ± 0.02	1998.9 ± 0.9	122.8 ± 2.0
323.17 ± 0.00	2999.1 ± 0.0	140.9 ± 1.4	323.17 ± 0.00	2999.4 ± 0.2	181.4 ± 0.6
323.17 ± 0.02	4997.8 ± 0.3	237.0 ± 1.7	323.17 ± 0.01	4998.6 ± 0.7	303.1 ± 2.5
323.16 ± 0.03	5998.8 ± 0.3	284.7 ± 0.1	323.16 ± 0.02	5997.6 ± 0.5	362.4 ± 3.6
323.15 ± 0.01	7999.2 ± 1.2	380.2 ± 0.5	323.16 ± 0.00	7998.8 ± 0.7	478.7 ± 5.2
323.18 ± 0.00	9997.8 ± 0.0	478.7 ± 0.0	323.16 ± 0.00	9998.5 ± 0.0	591.9 ± 0.0
332.86 ± 0.80	0.0 ± 0.0	0.0 ± 0.0	332.59 ± 0.91	0.0 ± 0.0	0.0 ± 0.0
333.15 ± 0.00	999.1 ± 0.1	38.5 ± 1.1	333.14 ± 0.02	999.0 ± 0.5	63.0 ± 13.7
333.15 ± 0.01	1998.3 ± 0.3	86.0 ± 3.8	333.15 ± 0.04	1998.0 ± 0.2	127.3 ± 16.3
333.15 ± 0.02	2997.9 ± 0.7	126.9 ± 2.6	333.14 ± 0.02	2998.5 ± 0.8	180.8 ± 1.6
333.13 ± 0.01	4998.7 ± 1.2	208.3 ± 2.4	333.15 ± 0.00	4998.6 ± 0.4	284.1 ± 5.3
333.16 ± 0.02	5997.6 ± 1.1	252.5 ± 0.4	333.12 ± 0.02	5998.1 ± 0.3	344.7 ± 3.5
333.14 ± 0.00	7998.3 ± 2.1	334.8 ± 4.5	333.17 ± 0.02	7998.8 ± 0.2	438.2 ± 0.8
333.18 ± 0.00	9998.1 ± 0.0	415.2 ± 0.0	333.13 ± 0.00	9996.3 ± 0.0	540.7 ± 0.0
347.81 ± 1.99	0.0 ± 0.0	0.0 ± 0.0000	347.54 ± 1.70	0.0 ± 0.0	0.0 ± 0.0
351.58 ± 0.18	999.2 ± 1.6	31.1 ± 0.0031	350.96 ± 0.69	998.4 ± 2.7	58.0 ± 4.3
350.94 ± 0.35	1997.1 ± 0.4	71.8 ± 0.0010	351.00 ± 0.14	1998.3 ± 1.1	114.4 ± 0.9
351.02 ± 0.16	2998.7 ± 0.7	102.5 ± 0.0023	351.07 ± 0.10	2997.8 ± 1.8	154.2 ± 0.8
350.77 ± 0.15	4996.5 ± 1.8	169.9 ± 0.0057	351.08 ± 0.01	4997.4 ± 1.3	244.0 ± 4.6
350.68 ± 0.17	5998.7 ± 0.6	201.5 ± 0.0051	351.03 ± 0.09	5999.1 ± 0.5	286.6 ± 8.7
350.42 ± 0.03	7997.6 ± 0.7	275.3 ± 0.0027	351.18 ± 0.57	7998.2 ± 0.1	367.0 ± 2.3
350.44 ± 0.00	9997.3 ± 0.0	337.7 ± 0.0000	350.46 ± 0.00	9998.4 ± 0.0	450.2 ± 0.0
	$[P_{6,6,6,14}][Br]$			$[P_{6,6,6,14}][Br]$+ZIF-8	
303.12 ± 0.57	0.0 ± 0.0	0.0 ± 0.0	303.13 ± 0.02	0.0 ± 0.0	0.0 ± 0.0
303.14 ± 0.01	999.6 ± 0.4	42.2 ± 10.9	303.15 ± 0.01	999.5 ± 0.9	65.1 ± 3.0
303.15 ± 0.02	1999.0 ± 0.5	93.2 ± 8.7	303.14 ± 0.00	1998.0 ± 0.3	130.4 ± 1.0
303.15 ± 0.00	2999.4 ± 0.8	145.0 ± 6.6	303.14 ± 0.01	2998.5 ± 0.2	193.7 ± 1.0
303.16 ± 0.01	4998.2 ± 0.3	2491.4 ± 4.9	303.14 ± 0.01	4998.0 ± 1.6	322.1 ± 0.2
303.14 ± 0.00	5999.1 ± 1.1	303.2 ± 5.3	303.15 ± 0.01	5998.9 ± 0.7	385.8 ± 1.4
303.15 ± 0.01	7999.0 ± 0.8	410.0 ± 0.5	303.16 ± 0.01	7999.1 ± 0.3	514.8 ± 0.6
303.15 ± 0.00	9998.4 ± 0.0	517.0 ± 0.0	303.14 ± 0.00	9998.4 ± 0.0	646.1 ± 0.0
322.45 ± 1.07	0.0 ± 0.0	0.0 ± 0.0	322.65 ± 0.70	0.0 ± 0.0	0.0 ± 0.0
323.14 ± 0.02	998.8 ± 1.0	36.1 ± 1.7	323.19 ± 0.03	999.1 ± 0.3	45.2 ± 0.3

CO_2 — Average absorption					
$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{p}{10^2\,\mathrm{Pa}}$	$\frac{b}{\mathrm{mmol\,kg^{-1}}}$
323.17 ± 0.00	1998.1 ± 0.2	74.7 ± 1.8	323.16 ± 0.00	1998.2 ± 0.1	99.0 ± 7.0
323.17 ± 0.01	2998.9 ± 0.3	117.5 ± 2.0	323.17 ± 0.01	2999.5 ± 0.2	143.1 ± 2.6
323.16 ± 0.00	4999.4 ± 0.6	196.3 ± 2.8	323.19 ± 0.01	4998.6 ± 0.8	239.4 ± 0.9
323.17 ± 0.01	5998.3 ± 0.6	233.1 ± 4.8	323.16 ± 0.00	5998.3 ± 0.2	292.4 ± 0.9
323.17 ± 0.00	7997.8 ± 0.0	311.8 ± 2.5	323.15 ± 0.01	7997.9 ± 1.0	383.0 ± 6.3
323.17 ± 0.00	9999.8 ± 0.0	390.5 ± 0.0	323.13 ± 0.00	9998.1 ± 0.0	481.5 ± 0.0
332.76 ± 0.95	0.0 ± 0.0	0.0 ± 0.0	332.29 ± 1.62	0.0 ± 0.0	0.0 ± 0.0
333.14 ± 0.01	999.4 ± 0.7	31.6 ± 1.1	333.14 ± 0.00	999.1 ± 0.2	38.6 ± 0.5
333.14 ± 0.01	1997.5 ± 1.5	70.4 ± 3.4	333.16 ± 0.00	1998.9 ± 0.6	89.9 ± 1.6
333.15 ± 0.01	2998.5 ± 0.2	105.6 ± 1.0	333.16 ± 0.00	2998.7 ± 0.1	131.0 ± 3.0
333.16 ± 0.02	4998.0 ± 0.3	176.1 ± 1.5	333.16 ± 0.02	4998.7 ± 1.0	211.9 ± 5.0
333.16 ± 0.00	5998.7 ± 0.1	210.2 ± 0.8	333.15 ± 0.01	5998.5 ± 0.4	248.7 ± 3.2
333.14 ± 0.01	7998.2 ± 0.4	283.2 ± 1.3	333.14 ± 0.02	7998.8 ± 0.4	336.7 ± 4.4
333.18 ± 0.00	9999.0 ± 0.0	349.8 ± 0.0	333.13 ± 0.00	9999.6 ± 0.0	414.0 ± 0.0
347.74 ± 1.52	0.0 ± 0.0	0.0 ± 0.0	346.97 ± 1.96	0.0 ± 0.0	0.0 ± 0.0
351.63 ± 0.02	999.8 ± 0.1	24.8 ± 2.7	351.42 ± 0.08	999.2 ± 0.6	29.7 ± 10.8
351.00 ± 0.17	1998.4 ± 0.2	59.7 ± 3.5	351.03 ± 0.11	1998.3 ± 0.1	70.6 ± 10.1
351.25 ± 0.02	2998.6 ± 1.1	82.3 ± 0.4	350.83 ± 0.02	2998.5 ± 1.9	107.7 ± 9.4
350.99 ± 0.02	4998.4 ± 0.1	144.2 ± 0.2	350.68 ± 0.02	4997.5 ± 1.3	177.9 ± 7.4
350.87 ± 0.07	5998.0 ± 1.0	173.1 ± 3.9	350.52 ± 0.23	5999.3 ± 0.2	209.9 ± 7.5
350.66 ± 0.04	7999.7 ± 0.1	230.6 ± 0.5	350.31 ± 0.02	7998.1 ± 0.8	288.2 ± 13.2
350.56 ± 0.00	9999.4 ± 0.0	288.5 ± 0.0	350.16 ± 0.00	9998.5 ± 0.0	358.0 ± 0.0

Table S9: Molality-based Henry's law constants, k_H, for CO_2 absorbed by the pure ionic liquids ($[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$ and $[P_{6,6,6,14}][Br]$) and the porous ionic liquids, ($[P_{4,4,4,8}][Cl]$+ ZIF-8, $[P_{6,6,6,14}][Cl]$+ ZIF-8 and $[P_{6,6,6,14}][Br]$+ ZIF-8). These are necessary for the calculation of the thermodynamic properties of absorption in Table 1 of the manuscript, as demonstrated in our previous work.[1]

T/K	k_H/MPa kg mol^{-1}	T/K	k_H/MPa kg mol^{-1}
$[P_{4,4,4,8}][Cl]$		$[P_{4,4,4,8}][Cl]$+ ZIF-8	
303.15	1.58 ± 0.02	303.14	1.19 ± 0.06
323.16	2.39 ± 0.02	323.16	1.7 ± 0.2
333.17	2.50 ± 0.09	333.17	1.84 ± 0.08
350.59	3.0 ± 0.1	350.61	2.05 ± 0.07
$[P_{6,6,6,14}][Cl]$		$[P_{6,6,6,14}][Cl]$+ ZIF-8	
303.15	1.3 ± 0.1	303.17	1.40 ± 0.02
323.16	1.8 ± 0.2	323.16	1.95 ± 0.01
333.15	2.1 ± 0.2	333.14	2.0 ± 0.1
350.83	2.6 ± 0.3	350.97	2.4 ± 0.2
$[P_{6,6,6,14}][Br]$		$[P_{6,6,6,14}][Br]$+ ZIF-8	
303.15	1.8 ± 0.3	303.15	1.78 ± 0.02
323.17	2.3 ± 0.3	323.16	2.42 ± 0.09
333.15	2.5 ± 0.3	333.15	2.8 ± 0.1
350.99	3.1 ± 0.4	350.71	3.4 ± 0.3

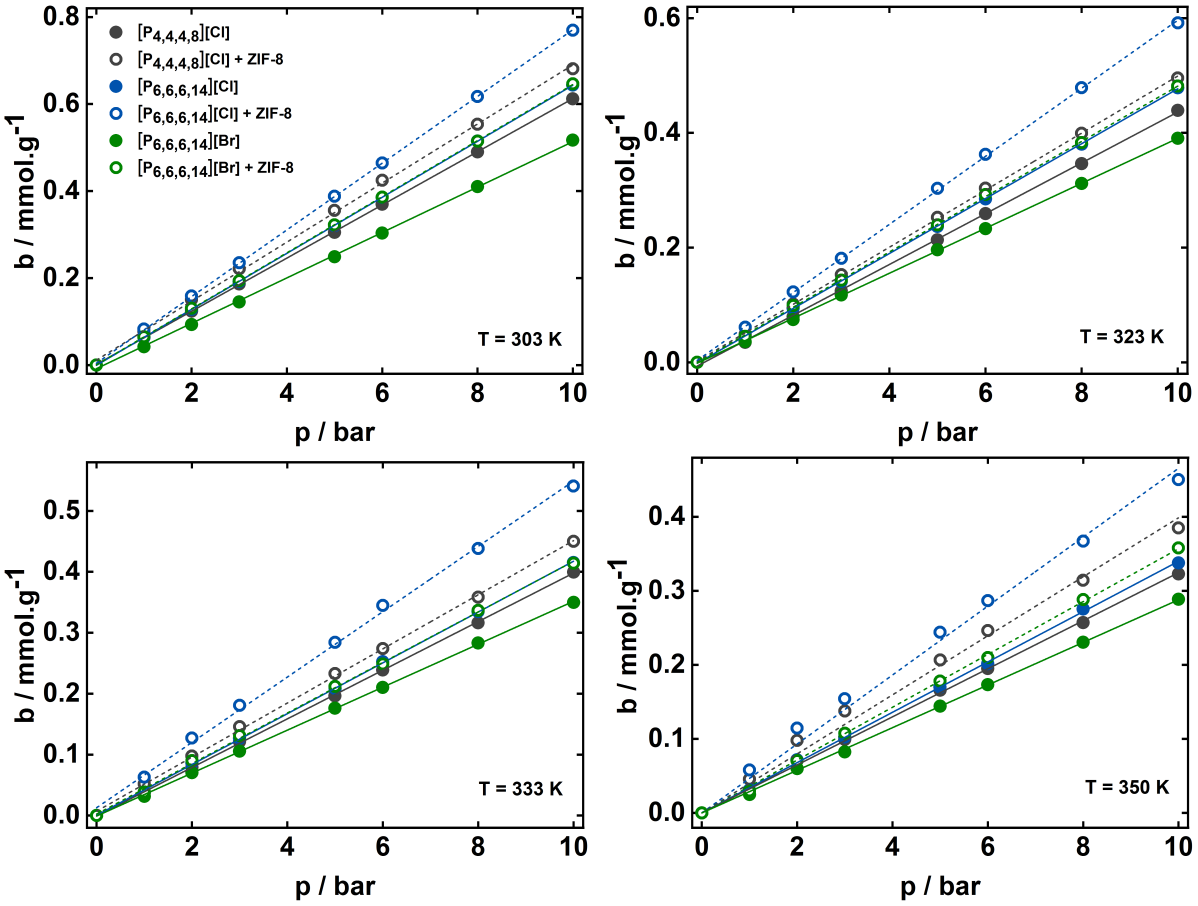

Figure S2: Average absorption of CO_2 in $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$, $[P_{4,4,4,8}][Cl]$+ZIF-8, $[P_{6,6,6,14}][Cl]$+ZIF-8 and $[P_{6,6,6,14}][Br]$+ZIF-8 as function of pressure and temperature in the ranges 0–10 bar and 303–353 K, respectively.

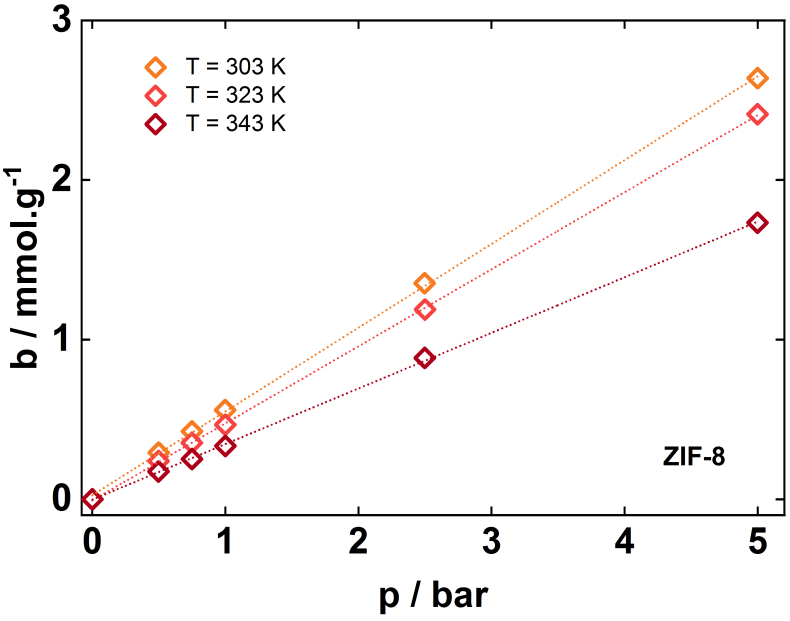

Figure S3: CO_2 adsorption by ZIF-8 as function of pressure (0.5–5 bar) and temperature (303–343 K). Data was taken from our previous work.[1]

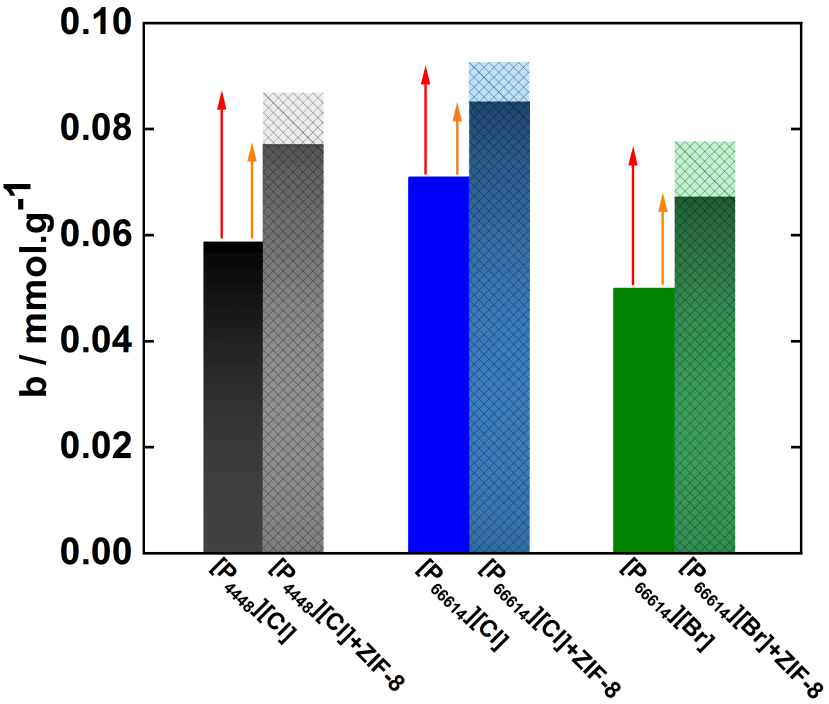

Figure S4: Absorption of CO_2 in $[P_{4,4,4,8}][Cl]$, $[P_{6,6,6,14}][Cl]$, $[P_{6,6,6,14}][Br]$, $[P_{4,4,4,8}][Cl]$ + $ZIF-_8$, $[P_{6,6,6,14}][Cl]$ + $ZIF-_8$ and $[P_{6,6,6,14}][Br]$ + $ZIF-_8$ at 1 bar and 303 K. The red and orange arrows represent 100 % (expected) and ≈ 80 % (measured) of the MOF capacity, respectively.

Coupling of CO_2 and styrene oxide to styrene carbonate

In a typical experiment, styrene oxide (SO) (2 mmol), (porous) IL (5.6 mL) and 2,4-dibromomesitylene (0.4 mmol, used as internal standard) were loaded into a 25 mL stainless steel autoclave. The reactor was flushed three times at room temperature with 5 bar of CO_2 to remove air from the vessel before being further charged to the working pressure, 10 bar, 5 bar or 2 bar of CO_2. The temperature was then raised to 25 °C, 50 °C or 80 °C. After the desired reaction time, 1 h, 3 h, 6 h or 18h, the reactor was cooled with an ice bath to stop the reaction and finally the excess of CO_2 was carefully released. In the case of using pure ionic liquids, the crude mixture was analyzed by ^1H NMR. In the case of porous ionic liquids, the solid (ZIF-8) was first separated from the reaction mixture by centrifuging the suspension and then thoroughly washed with acetonitrile. This procedure was repeated until the ^1H NMR of the washing solution did not show any residual peaks. Finally, the different fractions (containing the products, the remaining reactants and NMR standard) were gathered and analyzed by ^1H NMR as in a classical experiment.

The experiments at atmospheric pressure of CO_2 were carried out in a 50 mL Schlenk flask surmounted by a septum stopper with a folding skirt. The MOF (ZIF-8 or HKUST-1), 2,4-dibromomesitylene (0.4 mmol) and (porous) IL (5.6 mL) were loaded into the flask under argon atmosphere. Then, the solution was saturated with CO_2 by bubbling the gas inside the liquid, by immersing a needle that is directly connected to a CO_2 balloon. *ca.* 4 balloons were used to allow 4h bubbling. Styrene oxide (2 mmol) was added by a syringe directly into the (porous) IL/2,4-dibromomesitylene mixture and the heating was started. After the desired reaction time, 3 h or 18h, the Schlenk flask was cooled with an ice bath to stop the reaction. Thereafter the work-up was followed as previously described.

Fig. S5 shows an NMR spectrum that contains all the possible products obtained by the coupling of CO_2 and styrene oxide in the pure ionic liquid $[P_{6,6,6,14}][Cl]$ in which the fully conversion of the reactants is not achieved. The peaks assignment and integration are given as an example: ^{1}H NMR (400 MHz, CD_2Cl_2, δ / ppm); 7.2 - 7.4 (m, 28.3H),

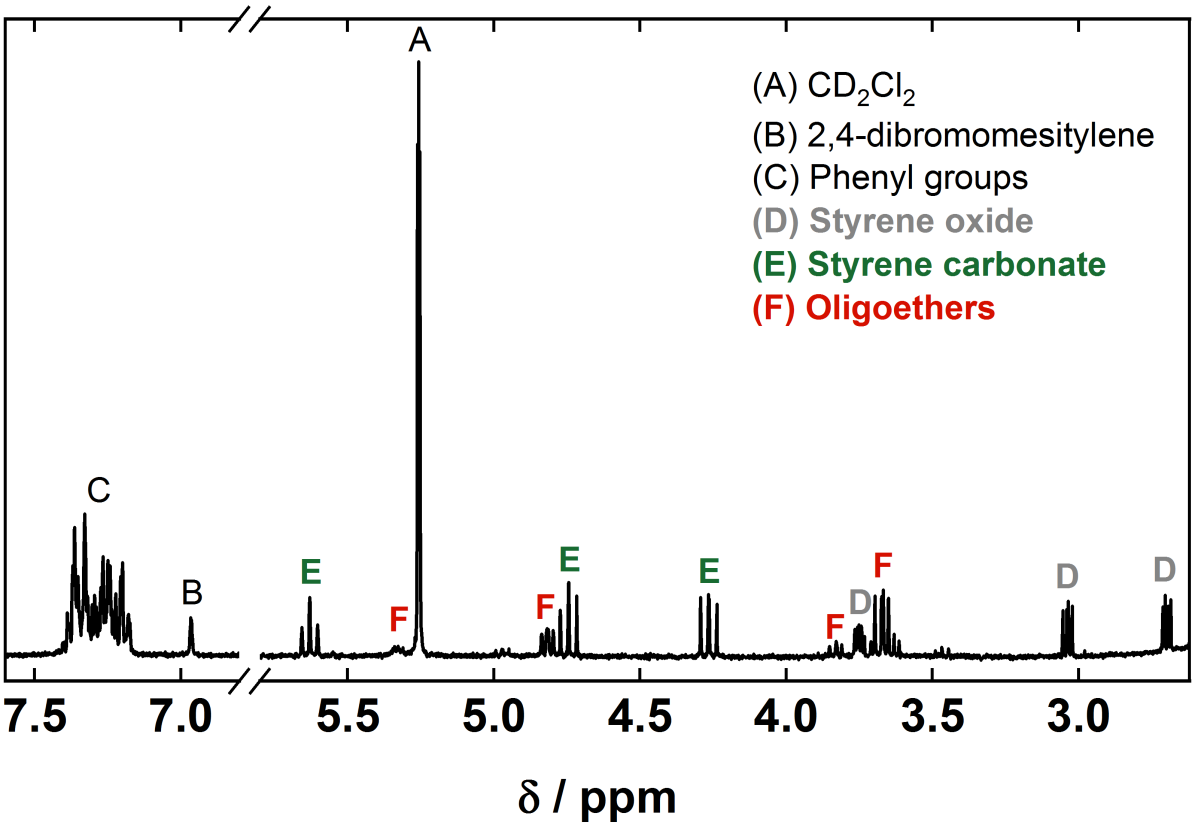

Figure S5: Trace of a reaction mixture analyzed by ^{1}H NMR. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), $[P_{P6,6,6,14}][Cl]$ (5.59 mL , 9.63 mmol), 1 h, 10 bar of CO_2.

5.7 (t, 1.8H), 5.4 (m, 0.4H), 4.9 (m, 1.5H), 4.8 (t, 2.0H), 4.3 (t, 2.0H), 3.9 (m, 0.4H), 3.8 (t, 1.6H), 3.7 (m, 3H), 3.1 (t, 2.0H), 2.8 (t, 1.9H). The error associated to the integration respect to the spectrum baseline vary within ±5 %.

By analysing the ^1H NMR spetra, the number of moles of styrene oxide (SO) and the different products (cyclic carbonates (CC) and aldehydes) at a certain time t, $n(A)_t$ and $n(B)_t$, respectively, can be determined relative to the internal standard (IS), 2,4-dibromomesitylene:

$$n(\text{A or B})_t = \frac{Area(\text{A or B})}{Area(IS)} n(IS) \tag{S7}$$

Knowing the number of moles of SO at the reaction time zero, $n(A)_0$, conversions of styrene oxide and the yields of the different products can be calculate:

$$Conversion(A) = \left(\frac{n(A)_0 - n(A)_t}{n(A)_0}\right) 100\% = \left(1 - \frac{n(A)_t}{n(A)_0}\right) 100\% \tag{S8}$$

$$Yield(B) = \left(\frac{n(B)_t}{n(A)_0}\right) 100\% \tag{S9}$$

The selectivity was then calculated by the ratio between each product yield and the SO conversion:

$$Selectivity(B) = \frac{Yield(B)}{Conversion(A)} \tag{S10}$$

Our hypothesis being that in the reaction mixture only SO, CC, oligoethers and aldehydes are present, we can access the yield of oligoethers by Eq. S11, while their chemical structure is uncertain (dimer, tetramer...).

$$Yield(oligoether) = \left(\frac{(n(\text{phenyl groups})_t - n(SO + CC + Aldehyde)_t}{n(A)_0}\right) 100\% \tag{S11}$$

Where $n(\text{phenyl groups})_t$ is obtained by the integration of the ^1H NMR signal in the range of 7.2–7.5 ppm.

Table S10: Coupling of styrene oxide and CO2 catalyzed by tetrabutylammonium halides. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol),NBu_4X (2 mol %), solvent MEK (6 mL), 10 bar of CO_2, 80 °C, 18 h.

	Conversion	Styrene carbonate yield (%)
NBu_4Cl	44	42
NBu_4Br	39	38
NBu_4I	23	24

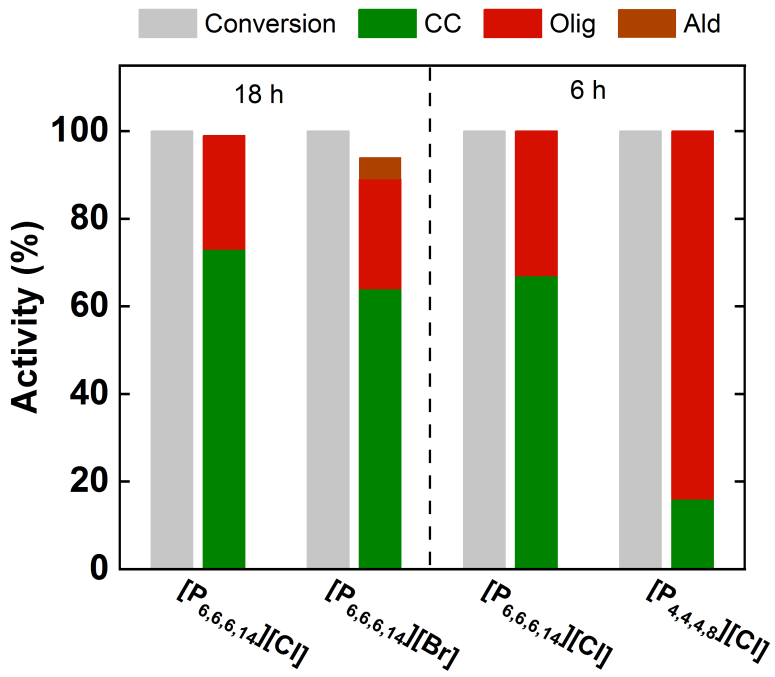

Figure S6: Influence of the nature of the IL salt: variation of the anion (left) and variation of the cation (right). Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), IL (5.59 mL), 80 °C, 10 bar of CO_2. SO stands for styrene oxide, CC for cyclic carbonate, Olig for oligoethers and Ald for aldehydes.

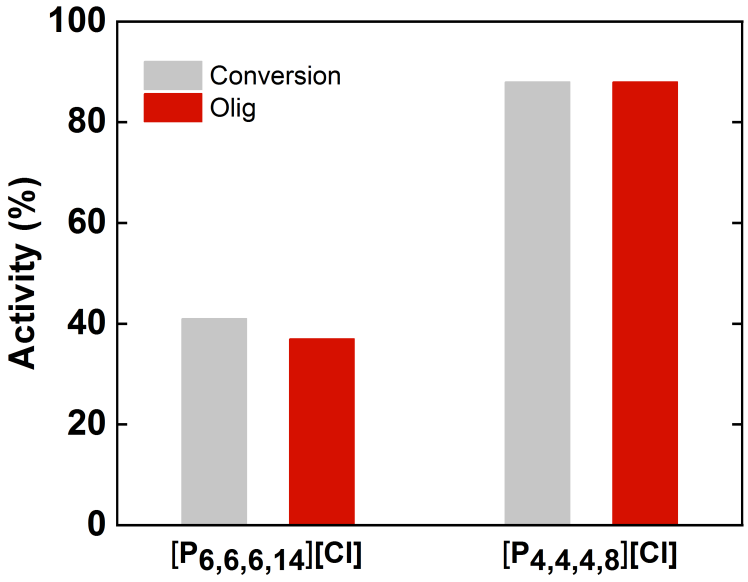

Figure S7: Control experiments to identify the side products in the coupling of styrene oxide and CO_2 catalyzed by $[P_{6,6,6,14}][Cl]$ and $[P_{4,4,4,8}][Cl]$ in the absence of CO_2. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), $[P_{6,6,6,14}][Cl]$ (5.59 mL , 9.63 mmol), 80 °C. Olig stands for oligoethers.

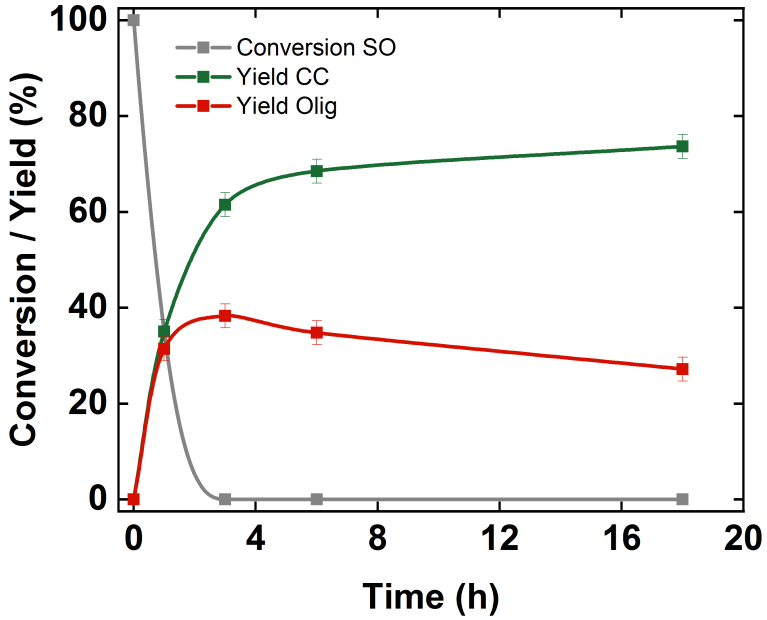

Figure S8: Time dependent profile of $[P_{6,6,6,14}][Cl]$ as a function of reaction time. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), $[P_{6,6,6,14}][Cl]$ (5.59 mL , 9.63 mmol), 80 °C, 10 bar of CO_2. SO stands for styrene oxide, CC for cyclic carbonate and Olig for oligoethers. The error bars correspond to ±5 %.

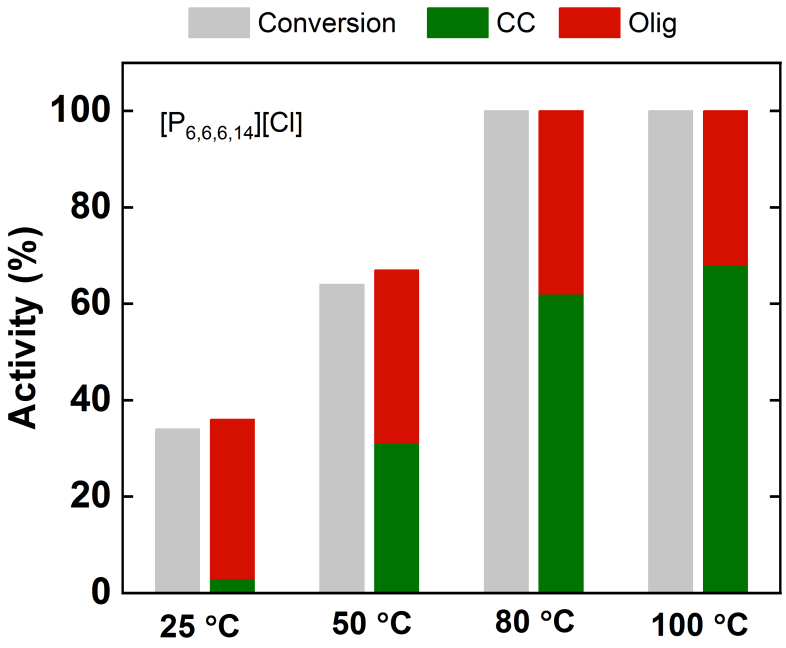

Figure S9: Influence of the reaction temperature on the performance of $[P_{6,6,6,14}][Cl]$. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), $[P_{6,6,6,14}][Cl]$ (5.59 mL , 9.63 mmol), 3 h, 10 bar of CO_2. CC stands for cyclic carbonate and Olig for oligoethers.

Table S11: Influence of the water in the side products yield. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), (porous) IL (5.59 mL), 80 °C, 10 bar of CO_2, 18 h.

(Po)IL	Water content / ppm	x_{H_2O}	Yield Olig %	Yield Aldehydes %
$[P_{4,4,4,8}][Cl]$	268	0.004	38	0
$[P_{4,4,4,8}][Cl]$	1200	0.02	84	0
$[P_{6,6,6,14}][Cl]$	190	0.005	27	0
$[P_{6,6,6,14}][Cl]$ + ZIF-8	190	0.005	0	0
$[P_{6,6,6,14}][Cl]$	1600	0.04	38	0
$[P_{6,6,6,14}][Cl]$ + ZIF-8	1600	0.04	11	0
$[P_{6,6,6,14}][Br]$	372	0.01	26	3

The water content showed to be important to the formation of oligoethers while the presence of ZIF-8 inhibit their formation (Table S11). In order to distinguish the role of the ZIF-8 in reducing the yield of oligoethers side-products formed: (1) ZIF-8 acts as a molecular sieve for water, which will not interfere in the epoxide opening or (2) ZIF-8 acts as a CO_2 reservoir, which allows the constant feeding to the catalytic reaction. The results presented in Figure S10 show the ZIF-8 do not trap the water from the IL neither from the organic solvent, heptane. The higher selectivity of the cyclic carbonate in the porous ionic liquids points towards the effect of the constant availability of the gas in the reaction media.

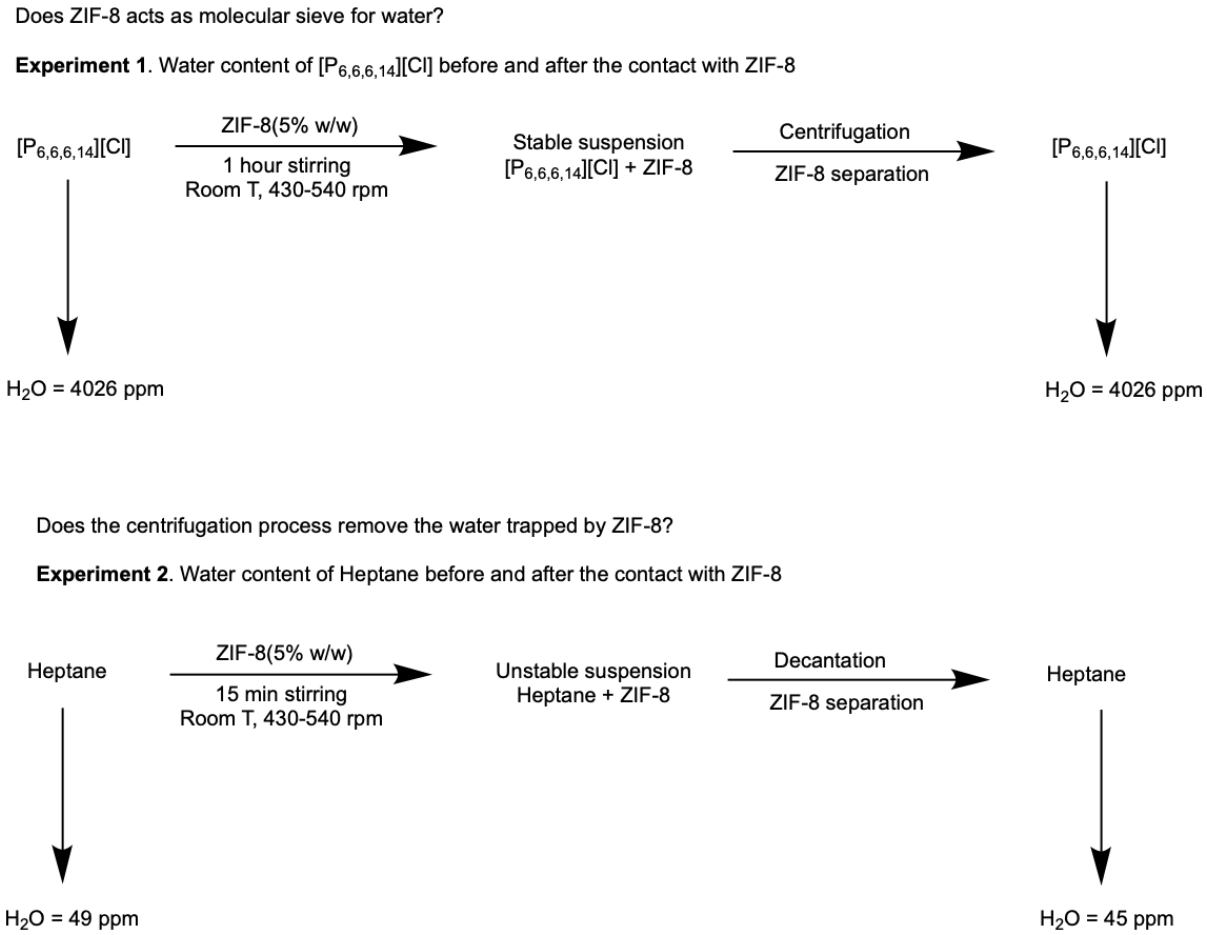

Figure S10: Role of the ZIF-8 as molecular sieve for water. The Experiment 2 was performed to avoid the centrifugation process and exclude the possibility of the water removal from the ZIF-8 cavities by this process.

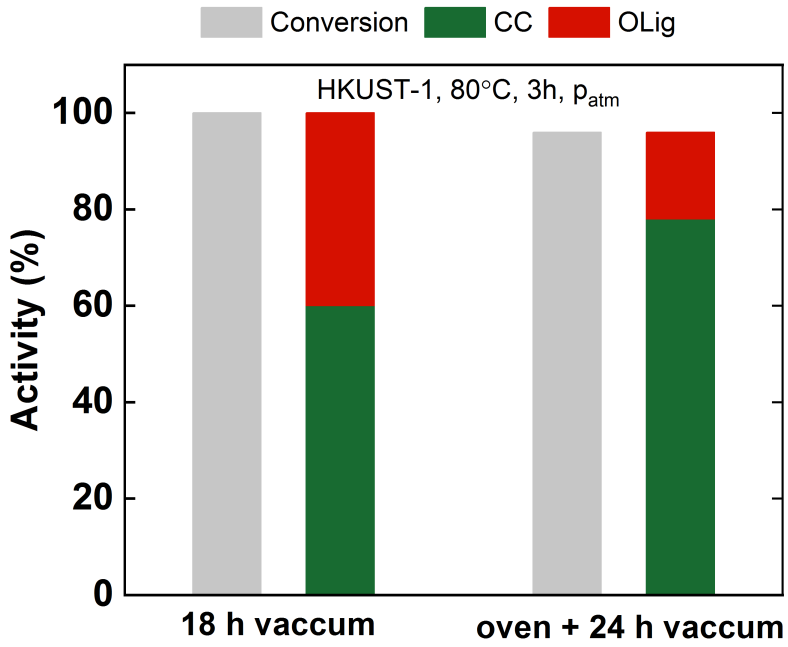

Figure S11: Coupling of CO_2 and styrene oxide using $[P_{6,6,6,14}][Cl]$ + HKUST-1 (5 %w/w) porous ionic liquid. The influence of the water content is also depicted in the picture: (18 h vacuum) the suspension was degassed under primary vacuum during 18 h; (oven + 7 h vacuum) HKUST-1 was first dried in an oven during 18 h and the suspension was degassed under primary and secondary vacuum during 2 h and 5 h, respectively. Reaction conditions: Styrene oxide (0.23 mL, 2 mmol), $[P_{6,6,6,14}][Cl]$ (5.59 mL , 9.63 mmol), 3 h, p_{atm} of CO_2. CC stands for cyclic carbonate and Olig for oligoethers.

References

(1) Avila, J.; Červinka, C.; Dugas, P.-Y.; Padua, A.; Costa Gomes, M. Porous ionic liquids: structure, stability and gas absorption mechanisms. *Adv. Mater. Interfaces* **2021**, *8*, 1001982.