

# Multifunctional polymers based on ionic liquid and Rose Bengal fragments for the conversion of CO<sub>2</sub> to carbonates.

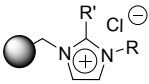
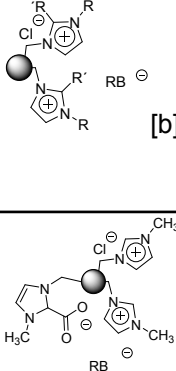
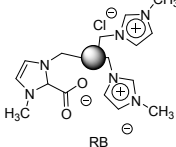
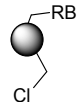
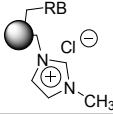
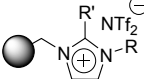
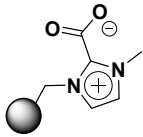
David Valverde,<sup>[a]</sup> Raúl Porcar,<sup>[a,c]</sup> Pedro Lozano,<sup>[b]</sup> Eduardo García-Verdugo,<sup>\*[a]</sup>  
Santiago V. Luis<sup>\*[a]</sup>

- [a] Dpt. of Inorganic and Organic Chemistry, Supramolecular and Sustainable Chemistry Group  
University Jaume I. Avda Sos Baynat s/nE-12071-Castellon  
E-mail: cepeda@uji.es luiss@uji.es
- [b] Dep. Bioquímica y Biología Molecular "B" e Inmunología. Universidad de Murcia. Campus  
de Espinardo, E-30.100. Murcia, Spain
- [c] Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, UNED, Paseo  
Senda del Rey, 9, E-28040, Madrid, Spain

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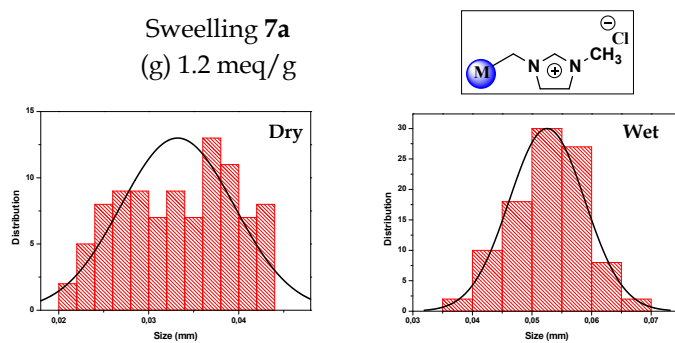
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**Table S1.** Structure and properties for the different SILLPs prepared.

Structure	Code	Type	Loading (meq/g)	R	R'	Water content [a] (%)	Swelling (%) <sup>[c]</sup>
	7a	Gel	1.01	CH <sub>3</sub>	H	1.81	56
	8a	Macroporous	1.09	CH <sub>3</sub>	H	3.46	-
	9a	Gel	0.97	CH <sub>4</sub> H <sub>9</sub>	H	1.27	69
	10a	Macroporous	1.94	CH <sub>4</sub> H <sub>9</sub>	H	2.62	-
	11a	Gel	0.88	CH <sub>10</sub> H <sub>21</sub>	H	1.27	81
	12a	Macroporous	0.95	CH <sub>10</sub> H <sub>21</sub>	H	2.10	-
	13b	Gel	3.18	CH <sub>3</sub>	H	11.35	-
	14b	Macroporous	3.79	CH <sub>3</sub>	H	15.14	-
	15b	Macroporous	3.71	CH <sub>3</sub>	CH <sub>3</sub>	-	-
 [b]	16a	Gel	1.01	CH <sub>3</sub>	H	2.01	-
	17a	Macroporous	1.09	CH <sub>3</sub>	H	3.50	-
	18a	Gel	0.97	CH <sub>4</sub> H <sub>9</sub>	H	-	-
	19a	Macroporous	1.94	CH <sub>4</sub> H <sub>9</sub>	H	2.60	-
	20a	Gel	0.88	CH <sub>10</sub> H <sub>21</sub>	H	1.17	-
	21a	Macroporous	0.95	CH <sub>10</sub> H <sub>21</sub>	H	2.10	-
	22b	Gel	3.18	CH <sub>3</sub>	H	-	-
	23b	Macroporous	3.79	CH <sub>3</sub>	H	-	-
	24b	Macroporous	3.71	CH <sub>3</sub>	CH <sub>3</sub>	-	-
	25b	Macroporous	3.68	CH <sub>3</sub>	H	-	-
	26	Macroporous	1.56	CH <sub>3</sub>	H	-	-
	27	Macroporous	2.23	CH <sub>3</sub>	H	-	-
	30a	Gel	1.1	CH <sub>3</sub>	H	-	-
	31b	Macroporous	3.67	CH <sub>3</sub>	H	-	-

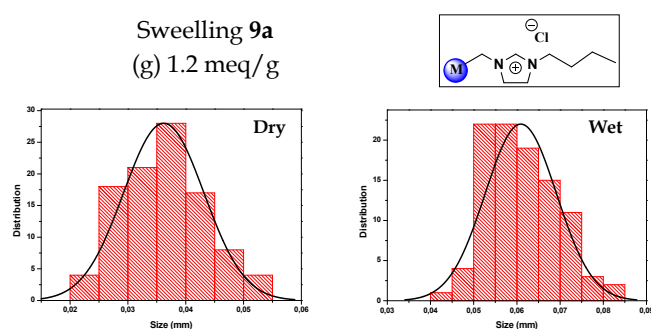
[a] Water content calculated from TGA, after equilibration at rt during 24 h. [b] RB loading  $3.92 \times 10^{-2}$   $\mu\text{mol RB / g}$  of polymer. [c]  $Swelling = \left( \frac{Wet\ size - Dry\ size}{Dry\ size} \right) \cdot 10^2$

a)



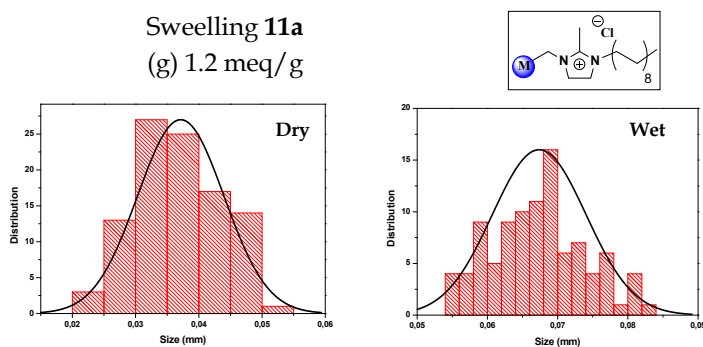
Swelling: 56%

b)



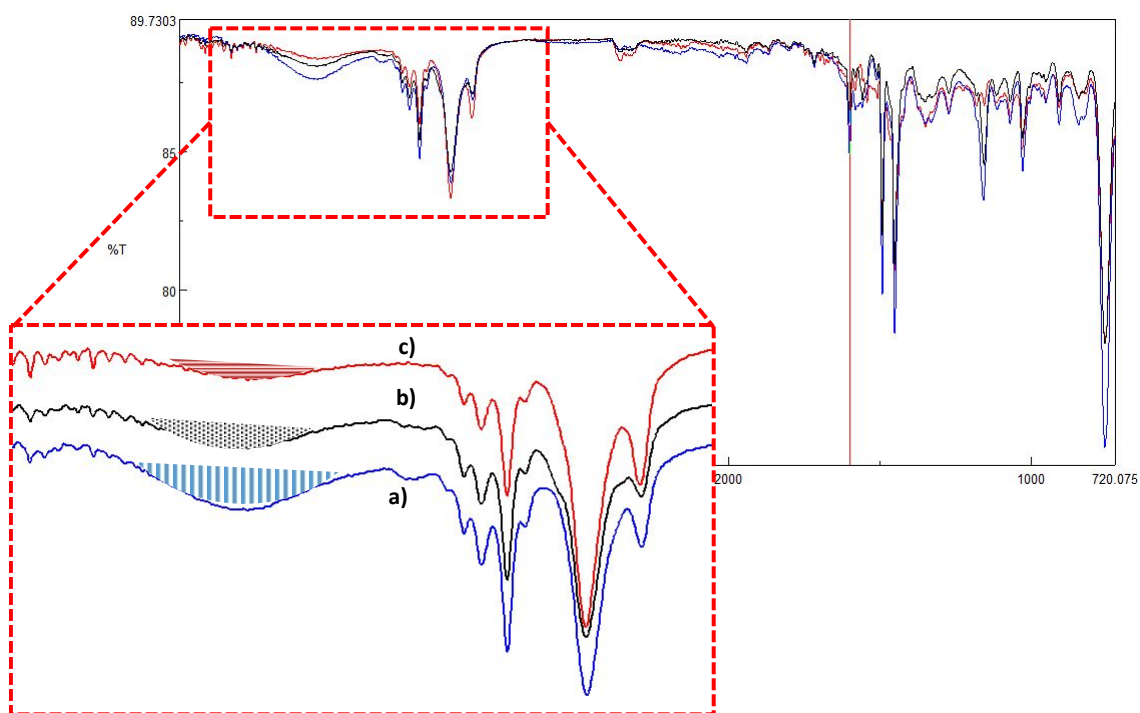
Swelling: 69%

c)

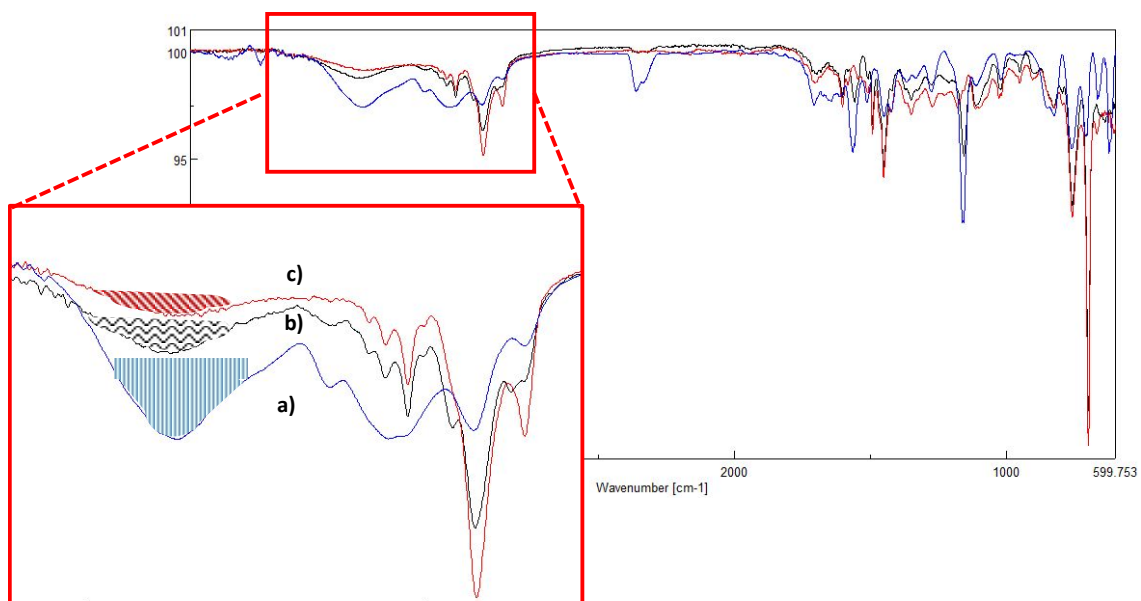


Swelling: 81%

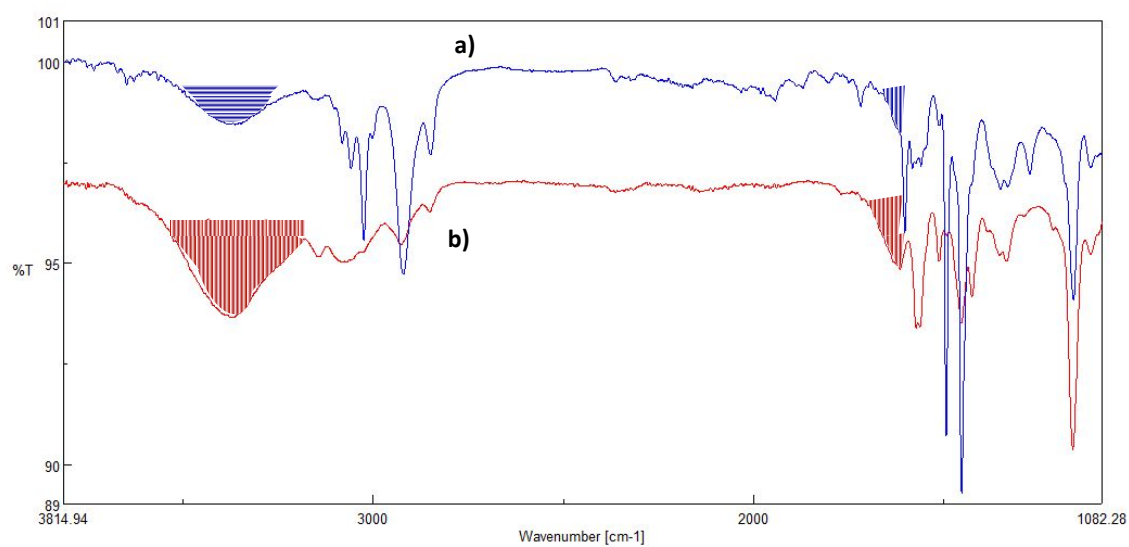
**Fig. S1.** Swelling of different RB-SILLPs resins in styrene oxide (SO) calculated as (a) **7a.** (b) **9a.** (c) **11a.**  $Swelling = \left( \frac{Wet\ size - Dry\ size}{Dry\ size} \right) \cdot 10^2$ . For each resin, the size distribution diagram on the left corresponds to the dry state, while the one on the right correspond the size distribution in the presence of SO.



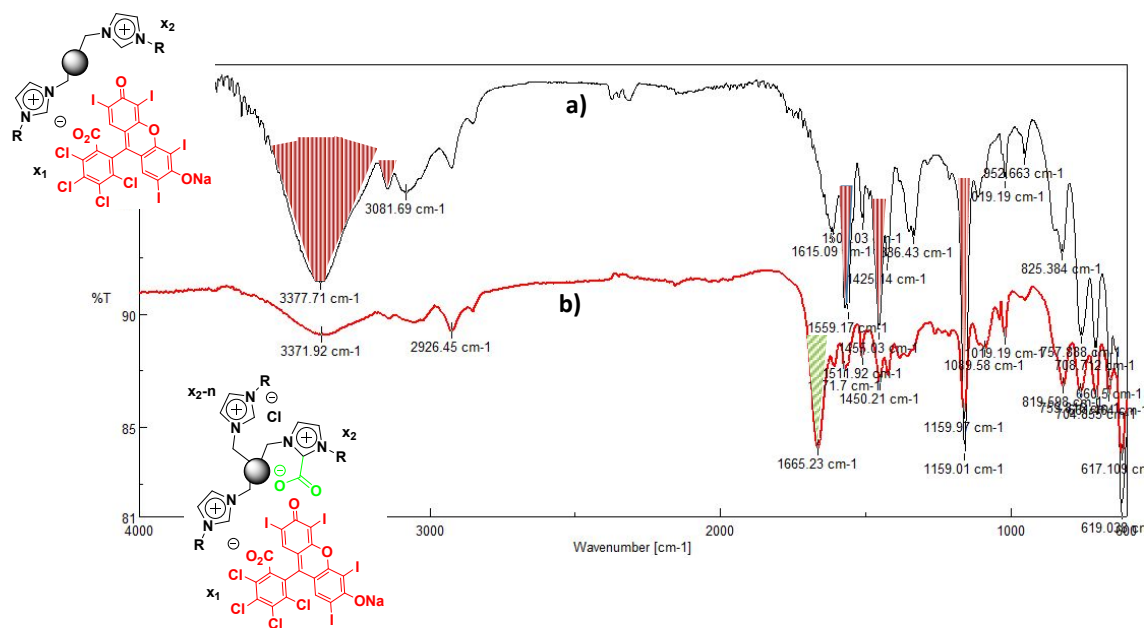
**Fig. S2.** FT-IR-ATR spectra obtained for the RB-SILLPs of  $\nu(\text{O-H})$  region showing the uptake of water from air as for the different low loading gel-type PS-DVB resin with different substitution pattern. a) **16a** (methyl). b) **18a** (butyl). c) **20a** (2-methyl-decyl).



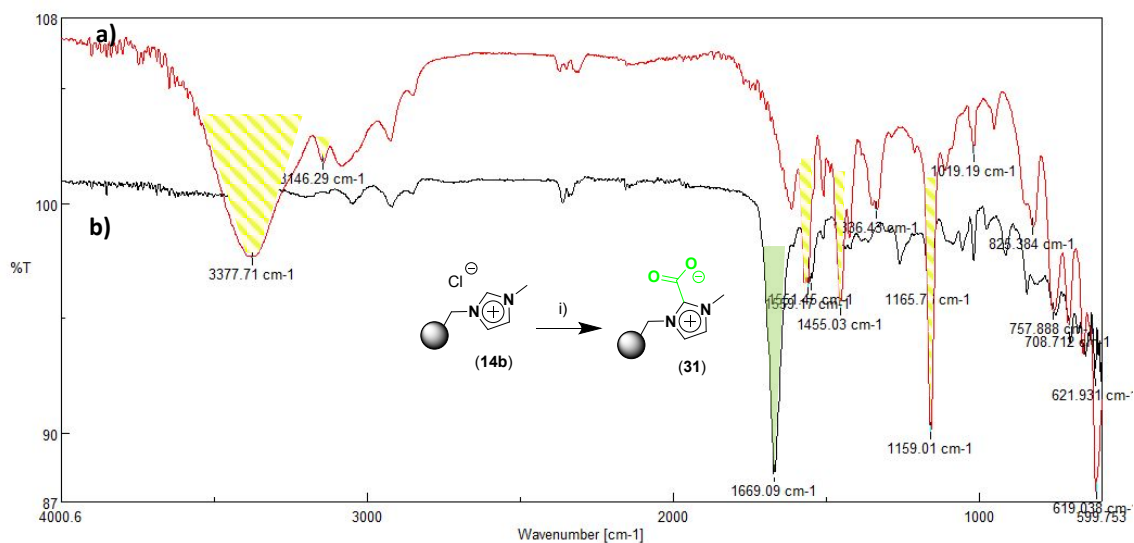
**Fig. S3.** FT- IR-ATR spectra obtained for the RB-SILLPs of  $\nu(\text{O-H})$  region showing the uptake of water from air as for the different of low loading macroporous type PS-DVB resin with different substitution pattern, a) **17a** (methyl). b) **19a** (butyl). c) **21a** (2-methyldecyl).



**Fig. S4.** FT-IR-ATR spectra obtained for the RB-SILLPs of  $\nu(\text{O-H})$  region showing the uptake of water from air as for the different for the RB-SILLPs of gel type PS-DVB resins with different loading. a) Low loading (**16a**). b) High loading (**22b**).

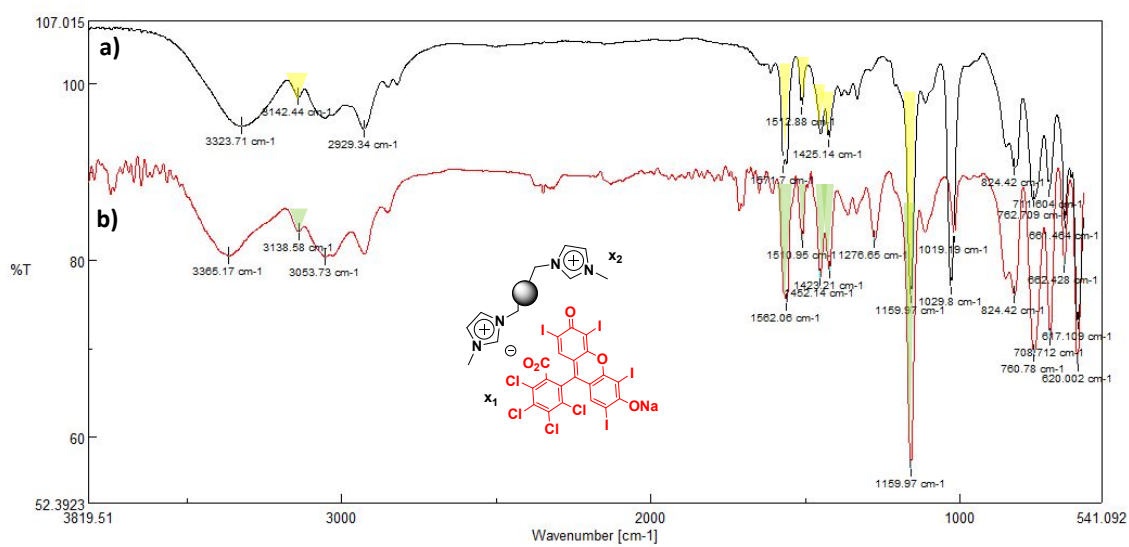


**Fig. S5.** FT-IR-ATR spectra obtained for the RB-SILLP **23b** a) before its use as catalyst. b) After its use in the catalytic reaction (36.7 mg RB-SILLP **23b**, for 5 h at 100 °C, 10 bar of CO<sub>2</sub> and using 1 mL epoxide).

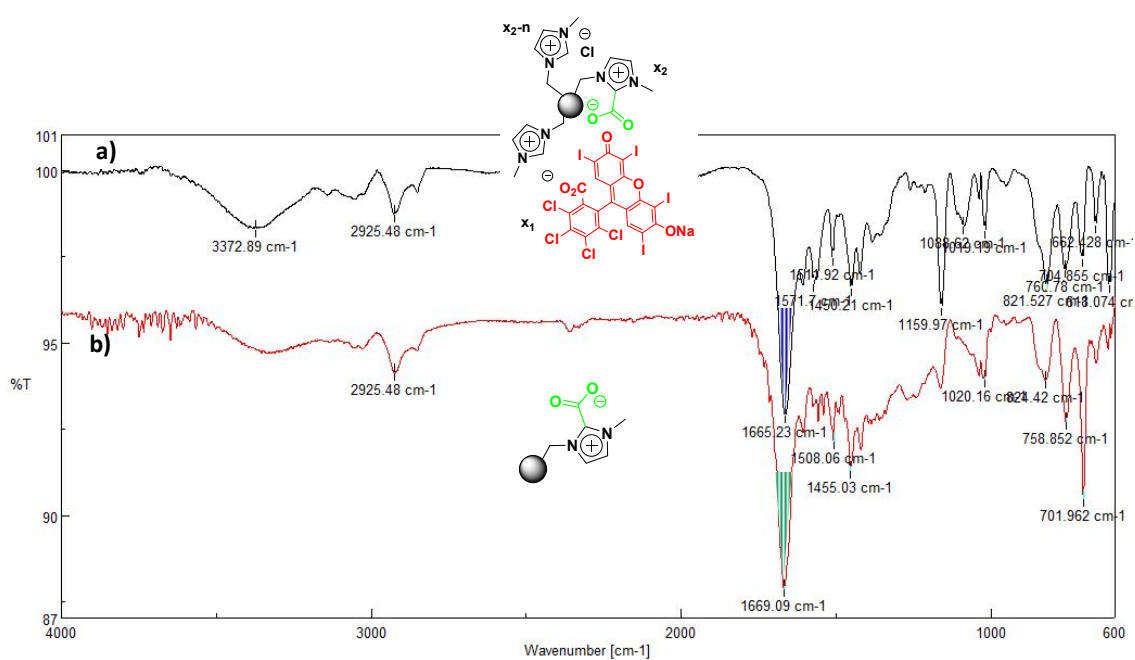


**Fig. S6.** FT-IR-ATR spectra for the synthesis of the zwitterionic NHC-CO<sub>2</sub> polymer **31** from **14b** (from a high loading chloromethylated resin, macroporous). i) Resin **14b** in 1,0 mL of dry THF, 8.5 equivalents of KHMDS at 80 °C and CO<sub>2</sub> (balloon). a) **14a**. b) **31**.

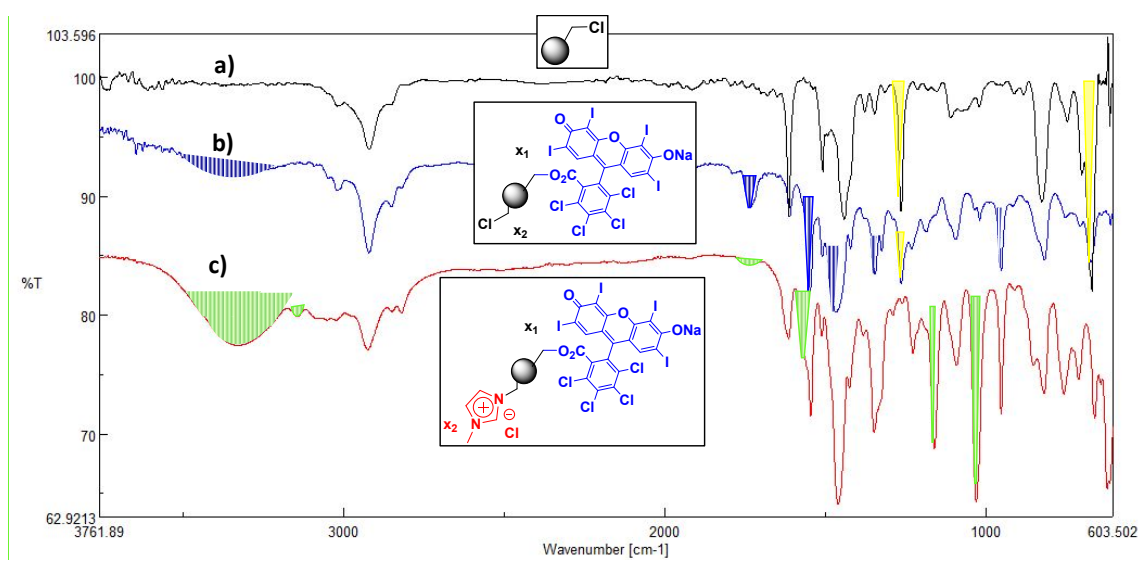




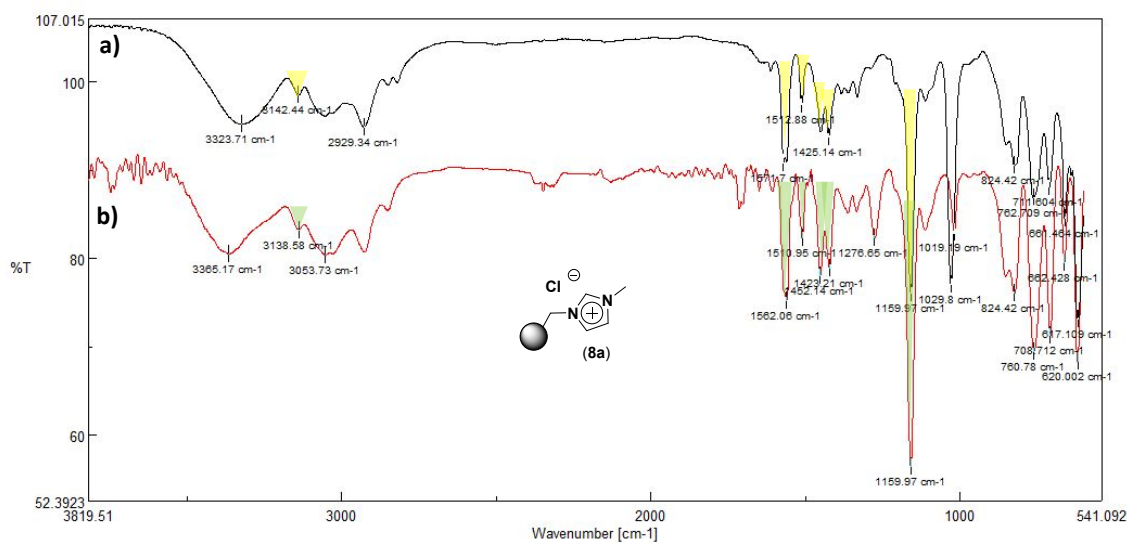
**Fig. S7.** FT-IR-ATR for RB-SILLP **17a**, a) before and b) after its use as catalyst (reaction conditions: solventless, 5 h, 100 °C, 10 bar CO<sub>2</sub>, 1, mL epoxide and 36.7 mg catalyst).



**Fig. S8.** FT-IR-ATR for RB-SILLP **25b** a) before and b) after its use as catalyst (reaction conditions: 5 h, 100 °C, 10 bar of CO<sub>2</sub> and using 1 mL epoxide and 36.7 mg of catalyst).



**Fig. S9.** FT-IR-ATR spectra obtained for a) Merrifield resin **2**. b) resin **26**. c) resin **27**.



**Fig. S10.** FT-IR-ATR for SILLP **8a** a) before and b) after its use as catalyst (reaction conditions: 5 h, 100 °C, 10 bar of CO<sub>2</sub> and using 1 mL epoxide and 36.7 mg of catalyst).

**Table S2.** Comparison of SILPs **27** with relevant catalysts reported in the literature for cycloaddition of CO<sub>2</sub> under flow continuous.

Entry	Catalyst	(g)	Cocatalyst	Solvent	Substrate <sup>a</sup>	Flow Substrate (mL/min)	Flow CO <sub>2</sub> (mL/min)	Flow N <sub>2</sub> (mL/min)	Pressure (bar)	Temp. (°C)	Time / Activity (h)	Yield (%)	Prod. <sub>T</sub> (g epoxide x g cat <sup>-1</sup> x h <sup>-1</sup> )	Prod. <sub>Exp</sub> (g epoxide x g cat <sup>-1</sup> x h <sup>-1</sup> )	Leaching <sup>b</sup>
1	<b>27</b>	1.9	RB/H <sub>2</sub> O	-	SO	0.005	0.05	-	140	150	234	57	1.9808	1.1291	X
2	MCM-41/[Co(II)(salen)]	4	<i>n</i> -Bu <sub>4</sub> NBr	-	EO	0.17	0.33	-	125	110	24	86	0.0901	0.775	X
3	Amorphous silica/[(salem)Al] <sub>2</sub> O <sub>t</sub> Bu	0.43	-	-	EO	0.0025	0.017	0.042	1.01	150	6	57	0.3159	0.1801	✓
4	MCM-41/[(salem)Al] <sub>2</sub> O <sub>t</sub> Bu	1.57	-	-	EO	0.0025	0.017	0.042	1.01	60	7	95	0.0865	0.0822	✓
5	Cs-P-Si-oxide	10	-	-	PO	0.05	0.2	-	140	200	3	50	0.0152	0.0076	✓
6	MOF MIL-101(Cr)	0.042	TBABr	Chlorobenzene	PO	0.25	4	-	50	100	5	80	1.0676	0.8541	✓
7	MOF MIL-101(Sc)	0.042	-	-	PO	0.25	4	-	50	100	5	57	1.0676	0.6085	✓

<sup>a</sup>: SO: Styrene oxide; EO = Ethylene Oxide; PO = Propylene Oxide.

<sup>b</sup>: X = No leaching; ✓ = Leaching

Entry (References):

2. Chemical fixation of CO<sub>2</sub> to ethylene carbonate under supercritical conditions: continuous and selective. X.-B. Lu, J.-H. Xiau, R. He, K. Jin, L.-M. Luo, X.-J. Feng, *Appl. Catal. Gen.* **2004**, 275, 73–78.

3 & 4. A Gas-phase flow reactor for ethylene carbonate synthesis from waste carbon dioxide. M. North, P. Villuendas, C. Young, *Chem. Eur. J.* **2009**, 15, 11454-11457.

5. T. Non-halogen catalysts for propylene carbonate synthesis from CO<sub>2</sub> under supercritical conditions. H. Yasuda, L.-H. He, T. Takahashi, T. Sakakura, *Appl. Catal. Gen.* **2006**, 298, 177-180.

6 & 7. Structure activity relationships in metal-organic framework catalysts for the continuous flow synthesis of propylene oxide carbonate from CO<sub>2</sub> and propylene oxide. B. R. James, J. A. Boissonault, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *RSC. Adv.* **2018**, 8, 2132-2137

