Electronical Supplementary information

Controlled grafting of dialkylphosphonate-based ionic liquids on γ -alumina: design of hybrid materials with high potential for CO₂ separation applications

MA. Pizzoccaro-Zilamy, S. Muñoz Piña, B. Rebiere, C. Daniel, D. Farrusseng, M. Drobek, G. Silly, A. Julbe and G. Guerrero

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1. Characterizations

Solution NMR experiments: ¹H, ¹³C, ³¹P, and ¹⁹F NMR spectra were recorded using a Bruker 300 MHz NMR spectrometer at respective frequencies of 300.13, 75.42, 121.49 and 282.4 MHz, equipped with a 5 mm QNP probe. Chemical shift data were given in δ ppm and were calibrated to TMS (¹H, ¹³C), or CFCl₃ (¹⁹F) or H₃PO₄ (85% in H₂O, ³¹P) on the basis of the relative chemical shift of the solvent as an internal standard.

Solid state NMR experiments:

¹⁹F MAS NMR experiments: the spinning frequency was 20 kHz, and the single pulse experiments were performed with a ~90° solid pulse of 4 μ s. A recycle delay of 5 s was used (corresponding in both cases to full relaxation of ¹⁹F) and number of scans was 16. ¹⁹F chemical shifts were referenced to external PTFE at -122 ppm (used as a solid reference).

2. Synthesis and characterizations of the γ-alumina powder

The γ -alumina powder was prepared from the boehmite by a sol-gel process based on colloid chemistry in aqueous media according to the method reported elsewhere [1]. The boehmite (5 wt%) was placed in a beaker containing a mixture of ultrapure water and nitric acid (HNO₃/boehmite molar ratio ~0.042) as the peptizing agent. The suspension was sonicated during 15 minutes and then vigorously stirred for 2 days at room temperature. The resulting sol was centrifuged at 8500 rpm during 30 minutes in order to remove any unhydrolyzed particles. The as-obtained stable sol was first concentrated by removing the water at temperatures under 150°C, followed by thermal treatment at 600°C/3h under ambient air (*), leading to the formation of γ -alumina powder (specific surface area of S_{BET} =220 m²/g).

 27 Al solid state NMR (600 MHz, 24 kHz): δ (ppm) 10.2 (Al_{VI}); 68.2 (Al_{IV})

It must be noted that before each NMR measurement the powder was re-calcined at 450°C/3h under nitrogen atmosphere for removing any physisorbed water on the powder surface.

(*) Details of the thermal treatment in air: heating ramp 10°C/min until 150°C, 1h dwelling at 150°C, second heating ramp 1°C/min until 600°C, 3h of dwell, natural cooling down to 25°C.

3. Organic synthesis

diethyl(3-bromopropyl)phosphonate

The diethyl(3-bromopropyl)phosphonate was synthesized via an Arbuzov reaction from triethylphosphite and 1,3-dibromopropane, as described in [2]; its physicochemical constants were in a good agreement with the literature data.

¹H NMR (300 MHz, CDCl₃, δ(ppm)): 4.05 (m, 4H, –PO(CH₂CH₃)₂); 3.41 (t, 2H, Br–CH₂–CH₂); 2.07 (m, 2H, –CH₂– CH₂–P); 1.80 (m, 2H, –CH₂–CH₂–P); 1.27 (t, 6H, –PO(CH₂CH₃)₂).

³¹P NMR (121.442 MHz, CDCl₃): δ(ppm) 30.8.

Elemental analysis calculated for $H_{16}C_7O_3PBr$ (%): C (32.5); H (6.2); found: C (32.5); H (6.7). Exact mass calculated for ESI(+), (m/z): 259.0099; found: 259.0101.



1-bromo-2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethane

In a 100 mL bottom flask, 0.0857 g (0.04 mol) of tetraethylene glycol was mixed in 60 mL of methylene chloride and placed in an ice bath. Then, 269.9 g (0.09mol) of triphenylphosphine was added under stirring. The addition of N-bromosuccinimide (172.6 g, 0.09 mol) was realized by fractions of 50 mg in order to maintain the temperature below 10°C. At the end, the reaction mixture was warm up to room temperature and afterwards it was stirred during 2 days. The methylene chloride was removed under reduced pressure and the crude product was crystallized with pentane. The resulting salts were grinded and pentane was added. The obtained suspension was filtered. The pentane was removed under reduced pressure and the crude product purified over a chromatography column using 70 mL of dichloromethane as eluant. After removal of the solvent under vacuum, the product was isolated as yellow oil with 62 % yield (8.50 g) and dried under vacuum (70 mbar) overnight.

 ^{1}H NMR (300 MHz, CDCl₃, δ (ppm)) 3.84 (4H, t); 3.70 (8H, s); 3.50 (4H, t). ^{13}C NMR (75.432 MHz, CDCl₃, δ (ppm)): 71.64; 70.97-71.09; 30.77.



diethyl 2–(2–(2–(2–bromoethoxy)ethoxy)ethoxy)ethylphosphonate

In a 100 mL three necked bottom flask under an argon atmosphere, 2.38 g (7.43 mmol) of 1-bromo-2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethane was heated to 140°C. With an addition funnel, 0.97 g (0.584 mmol) of triethylphosphite was added in 3 portions. The diethyl(ethyl)phosphonate and the bromoethane generated from the reaction was removed by a recovery still head during all the addition of triethylphosphite. At the end of the addition, the reaction mixture was stirred and heated to 140°C overnight. After cooling to room temperature, the crude product was purified on a 400 mL silica chromatography column, eluting first with dichloromethane then increasing the solvent polarity with methanol (v/v 1% then 3% of methanol) (Rf = 0.13, methanol 5%, KMnO₄ stain used for TLC). A second purification process was performed in similar condition on an 200 mL silica chromatography column in order to obtain the pure product as a translucent liquid (Rf=0.13, methanol 5%, KMnO₄ stain used for TLC) (36.47 g, 16.56% yield).

¹H NMR (500 MHz, $CDCl_{3,}\delta$ (ppm)): 4.16 (q, ³J_{H-H} = 7.11 Hz, 4H, OCH_2CH_3); 3.868 (t, 2H, $BrCH_2CH_2$); 3.79 (m, 2H, PCH_2CH_2); 3.74 – 3.66 (m, 8H, OCH_2CH_2O -); 3.532 (t, 2H, $BrCH_2CH_2$); 2.19 (m, 2H, PCH_2CH_2); 1.254 (t, 6H, OCH_2CH_3).

 ^{13}C NMR (125.721 MHz, CDCl_{3,} δ (ppm)): 71.23; 70.63 - 70.2; 65.16; 61.66, 61.61; 30.29; 26.46; 27.56; 16.42; 16.45.

³¹P (202.404 MHz, CDCl₃, δ (ppm)): 28.61.

Elemental analysis calculated for H₂₆C₁₂O₆PBr (%): C (38.2); H (6.90); found: C (37); H (7.1).

Exact mass calculated for ESI(+), (m/z): 377.0729; found: 377.0728.



1-methyl-3-(3-(diethylphosphinyl)propyl)imidazolium bromide [ImPE][Br]

The 1-methyl-3-(3-(diethylphosphinyl)propyl)imidazolium bromide was obtained as a yellow oil in high yield from the coupling reaction of 1-methylimidazole with diethyl(3-bromopropyl)phosphonate adapted from the procedure published by Mu *et al.* [4]. The diethyl(3-bromopropyl)phosphonate precursor (27.00 g, 107 mmol) was dissolved in 50 mL of dry THF. Then, 1-methylimidazole (8.80 g, 107 mmol) was added dropwise and the mixture was heated to reflux at 70°C during 3 days under argon. After cooling to room temperature and decanting, two phases could be distinguished: a yellow oil phase and a translucent liquid phase. The two phases were separated and the yellow oil part was washed twice with 50 mL of THF, followed by liquid-liquid extraction with CH₂Cl₂ and H₂O. The aqueous fractions were concentrated under vacuum to afford **[ImPE][Br]** as a yellow oil with a 88% yield (32 g).

¹H NMR (300 MHz, CDCl₃, δ (ppm)): 10.53 (s, 1H, N–CH–N); 7.54 (s, 1H, N–CH); 7.36 (s, 1H, N–CH); 4.57 (t, 2H, CH₂–N); 4.06 (m, 4H, O–CH₂–CH₃); 4.06 (s, 3H,CH₃–N); 2.17-1.77 (m, 4H, CH₂–CH₂–P); 1.34 (t, 6H,O–CH₂–CH₃). ¹³C NMR (75.432 MHz, CDCl₃, δ (ppm)): 137.5; 123.7; 122.5; 62.0; 49.3; 36.7; 23.9; 22.8; 20.9; 16.5.

³¹P NMR (121.442 MHz, CDCl₃, δ(ppm)): 29.8.

Exact mass calculated for ESI(+), (m/z): 261.1368; found: 261.1367. Exact mass calculated for ESI(-), (m/z): 78.9183; found: 78.9186.



Tf₂N

1-methyl-3-(3-(diethylphosphinyl)propyl)-imidazolium bis(trifluoromethanesulfonimide) [ImPE][Tf₂N]

18.8 g (55.13 mmol) of 1-methyl-3-(3-(diethylphosphinyl)propyl)imidazolium bromide were dissolved in 50 mL of absolute ethanol. Lithium bis(trifluoromethanesulfonimide) (23 g, 80 mmol) was then added and rapidly a white precipitate appeared. The reaction mixture was stirred for 24 h, and then concentrated via rotary evaporation. 30 mL of distilled water was added under stirring to the remaining suspension in order to solubilize the solid part and finally the product was extracted with 30 mL of CH_2Cl_2 . The CH_2Cl_2 phase was washed three times with distilled water (3 x 30 mL) and the organic phase extracted and concentrated under reduced pressure (0.1 bar) at 60°C for 2h yielding 20.82 g (38.5 mmol, 70%) of **[ImPE][Tf_2N]** as a light yellow viscous oil.

¹H NMR (300 MHz, DMSO, δ (ppm)): 9.07 (s, 1H, N–CH–N); 7.76 (s, 1H, N–CH); 7.69 (s, 1H, N–CH); 4.20 (t, 2H, CH₂–N); 3.98 (m, 4H, O–CH₂–CH₃); 3.831 (s, 3H,CH₃–N); 2.1-1.68 (m, 4H, CH₂–CH₂–P); 1.22 (t, 6H,O–CH₂–CH₃).

¹³C NMR (75.432 MHz, DMSO, δ(ppm)): 136.87; 126; 123.78; 122.23; 121.73; 117.47; 113.2; 61.29; 61.2; 49.07; 48.81; 35.78; 23.27; 23.22; 22.36; 20.5; 16.23; 16.15.

³¹P RMN (121.442 MHz, DMSO, δ(ppm)): 30.39.

¹⁹F NMR (170.385 MHz, DMSO, δ(ppm)): -78.71.

Elemental analysis calculated (%): C (38.7); H (6.5); N (8.0); S (12.2); found: C (26.29); H (3.54); N (9.16); S (13.35).

Exact mass calculated for ESI(+), (m/z): 261.1368; found: 261.1368. Exact mass calculated for ESI(-), (m/z): 279.9173; found: 279.9178.



1-methyl-3-(3-(diethylphosphinyl)dodecyl)imidazolium bromide [ImC12PE][Br]

The diethyl(3-bromododecyl)phosphonate precursor (93.1 g, 242 mmol) was dissolved in 300 mL of dry THF. Then 1-methylimidazole (20.6 g, 251 mmol) was added rapidly and the mixture was heated at 70°C during 17h under argon. After cooling to room temperature, the THF was evaporated and an orange oil was obtained. The mixture was purified using distillation under reduced pressure (0.05 mbar) at 120°C to remove 1-methylimidazole (introduced in excess) in order to obtain **[ImC₁₂PE][Br]** as an orange oil with a 88.5% yield (100 g, 214 mmol).

¹H NMR (300 MHz, MeOD, δ(ppm)): 8.96 (s, 1H, N–CH–N); 7.65 (s, 1H, N–CH); 7.58 (s, 1H, N–CH); 4.22 (t, 2H, CH₂–N); 4.08 (m, 4H, O–CH₂–CH₃); 3.94 (s, 3H,CH₃–N); 1.9 – 1.73 (m, 4H, CH₂–CH₂–P); 1.56 – 1.22 (m, 24H). ¹³C NMR (75.432 MHz, CDCl₃, δ(ppm)): 137.5; 123.7; 122.5; 62.0; 49.3; 36.7; 23.9; 22.8; 20.9; 16.5.

³¹P NMR (121.442 MHz, DMSO, δ(ppm)): 32.07.

Elemental analysis calculated (%): C (51.4); H (8.6); N (6.0); found: C (48.60); H (8.78); N (7.95). Exact mass calculated for ESI(+), (m/z): 387.2777; found: 387.2780. Exact mass calculated for ESI(-), (m/z): 78.9183; found: 78.9184.



1-methyl-3-(3-(diethylphosphinyl)dodecyl)imidazolium bis(trifluoromethanesulfonimide) [ImC₁₂PE][Tf₂N]

10.35 g (22.14 mmol) of 1-methyl-3-(3-(diethylphosphinyl)dodecyl)imidazolium bromide were dissolved in 30 mL of distilled water. 6.9 g (24 mmol) of lithium bis(trifluoromethanesulfonimide) was then added, and rapidly a white oil appeared. The reaction mixture was stirred for 1h at room temperature. After decanting, two phases could be distinguished: an orange white oil phase and a white aqueous phase. The two phases were separated and the orange oil part was dissolved in dichloromethane (15 mL). The purification was realized by adding 15 mL of water followed by a centrifugation of the mixture at 8500 rpm during 5 min. The resulting two phases were separated. The CH₂Cl₂ phase was evaporated under reduced pressure (0.1 bar, at 60°C for 2h) yielding 11.15 g (16.7 mmol, 70%) of **[ImC₁₂PE][Tf₂N]** as a yellow liquid.

¹H NMR (300 MHz, DMSO, δ (ppm)): 9.08 (s, 1H, N–CH–N); 7.75 (s, 1H, N–CH); 7.69 (s, 1H, N–CH); 4.13 (t, 2H, CH₂–N); 3.95 (m, 4H, O–CH₂–CH₃); 3.83 (s, 3H,CH₃–N); 1.76 – 1.6 (m, 4H, CH₂–CH₂–P); 1.45 – 1.18 (m, 24H). ¹³C NMR (75.432 MHz, CDCl₃, δ (ppm)): 136.7; 124; 122.7; 122.7; 122; 117.8; 113.2; 61.2; 61.1; 49.2; 36.2, 30.2; 30.; 29.8; 29.4; 29.3; 28.9; 28.8; 25.9; 25.8; 24; 22.5; 22.4; 16.8; 16.7. ³¹P NMR (121.442 MHz, DMSO, δ(ppm)): 32.07.
¹⁹F NMR (270.385 MHz, DMSO, δ(ppm)): -78.71.
Elemental analysis calculated (%): C (39.6); H (6.0); N (6.3); S (9.6); found: C (39.2); H (5.87); N (8.15); S (10.34).
Exact mass calculated for ESI(+), (m/z): 387.2777; found: 387.2779.
Exact mass calculated for ESI(-), (m/z): 279.9173; found: 279.9175.



1-methyl-3-(3-(diethylphosphinyl) 2–(2–(2–ethoxy)ethoxy)ethoxy)ethyl)imidazolium bromide [ImPEGPE][Br]

The diethyl-(2-{2-[2-(2-bromo-ethoxy)-ethoxy]-ethoxy}-ethyl)phosphonate precursor (6.12 g, 16.2 mmol) was mixed under argon with 1-methylimidazole (1.25 g, 15.2 mmol) without any solvent. The mixture was heated under stirring at 110°C for 40 minutes to obtain the **[ImPEGPE][Br]** ionic liquid as a yellow liquid with a 99% yield (15.2 mmol, 6.96g).

¹H NMR (300 MHz, CDCl₃, δ (ppm)): 10.4 (s, 1H, N⁺-CH-N); 7.69 (s, 1H, =CH); 7.4 (s, 1H, =CH); 4.63 (t, 2H, N⁺-CH₂); 4.12 (q, ³J_{H-H} = 9.81 Hz, 4H, OCH₂CH₃); 4.07 (s, 3H, CH₃-N⁺); 3.90 (m, 2H, N⁺CH₂CH₂); 3.75 – 3.63 (massif, 12H, CH₂-O); 2.11 (m, 2H, PCH₂CH₂); 1.35 (t, 6H, OCH₂CH₃).

¹³C NMR (75.432 MHz, CDCl₃, δ (ppm)): 137.917; 123.601; 122.605; 70.35; 70.284; 70.245; 70.148; 69.031; 65.105; 61.75; 49.75; 36.586; 27.844; 25.996; 16.476; 16.397.

³¹P NMR (121.442 MHz, CDCl₃, δ (ppm)): 28.54.



 Tf_2N

1-methyl-3-(3-(diethylphosphinyl) 2–(2–(2–(2–ethoxy)ethoxy)ethoxy)ethyl)imidazolium bis(trifluoromethanesulfonimide) [ImPEGPE][Tf₂N]

9.77 g (21.25 mmol) of 11-methyl-3-(3-(diethylphosphinyl) 2-(2-(2-(2-ethoxy)ethoxy)ethoxy)ethyl) imidazolium bromide were dissolved in 30 mL of distilled water. Lithium bis(trifluoromethane-

-sulfonimide) (6.6 g, 22.93 mmol)) was then added, and rapidly a white precipitate appeared. The reaction mixture was stirred for 1 h. After decantation, two phases could be distinguished: a yellow oil phase and a white aqueous phase. The two phases were separated and the yellow oil was washed three times with distilled water (3 x 20 mL). Traces of water were removed under reduced pressure (0.1 bar) at 80°C for 3h yielding 10.45 g (15.8 mmol, 74%) of **[ImPEGPE][Tf₂N]** as a light yellow viscous oil.

¹H NMR (300 MHz, DMSO, δ (ppm)): 9.04 (s, 1H, N⁺-CH-N); 7.71 (s, 1H, =CH); 7.69 (s, 1H, =CH); 4.33 (t, 2H, N⁺-CH₂); 3.98 (q, ³J_{H-H} = 9.81 Hz, 4H, OCH₂CH₃); 3.86 (s, 3H, CH₃-N⁺); 3.76 (t, 2H, N⁺CH₂CH₂); 3.61 – 3.48 (massif, 12H, CH₂-O); 2.11 (m, 2H, PCH₂CH₂); 1.21 (t, 6H, OCH₂CH₃).

¹³C NMR (75.432 MHz, CDCl₃, δ(ppm)): 135.95; 124.98; 122.52; 121.83; 120.76; 116.49; 112.27; 69.81; 69.70; 69.53; 67.28; 63.56; 60.15; 60.07; 47.91; 34.87; 26.04; 24.23; 15.42; 15.34

³¹P NMR (121.442 MHz, DMSO, δ(ppm)): 28.66.

 ^{19}F NMR (270.385 MHz, DMSO, $\delta(\text{ppm})):$ -78.73.

Elemental analysis calculated (%): C (33.5); H (5.0); N (4.0); S (9.9); found: C (30.97); H (4.29); N (8.65); S (10.61).

Exact mass calculated for ESI(+), (m/z): 379.1998; found: 379.1995. Exact mass calculated for ESI(-), (m/z): 279.9173; found: 279.9177.

4. FTIR spectrum of [ImPE][Tf₂N] ionic liquid in ATR mode and DFT calculated spectrum



Figure S1. Portion of the FTIR spectra of [ImPE][Tf₂N]: a) experimental, b) model.

Computational Method:

The calculations were performed applying Density Functional Theory (DFT) with B3LYP level, using 6-311G(2d,p) as basis set on Gaussian 09 program package. Geometry optimization and harmonic vibrational frequencies were calculated at the same level DFT. The predicted wavenumbers correspond to the isolated molecular state (the experimental wavenumbers correspond to a liquid state spectrum). No scaling factors were applied. A detailed interpretation of the vibrational spectra of these compounds has been made.

5. ¹⁹F NMR



Figure S2. ¹⁹F NMR spectra of **I.** pure liquid phase IL [ImPE][Tf₂N] (liquid NMR), **II.** grafted ImPE-Tf₂N(1) powder sample (MAS solid-state NMR).



Figure S3. ¹⁹F NMR spectra of **I.** pure liquid phase IL [ImC₁₂PE][Tf₂N] (liquid NMR), **II.** grafted ImC₁₂PE-Tf₂N powder sample (MAS solid-state NMR).

6. Stability of ILs phosphonate functions toward hydrolysis under forcing reaction conditions

Procedure

All the hydrothermal-assisted hydrolysis of dialkylphosphonate ester ILs was carried out by following the same experimental protocol. 100 mg of the IL were dissolved in 20 mL of the selected solvent (either H_2O or (1/1) H_2O :EtOH v/v mixture). Then, the solution was placed in a 90 mL Teflon[®] autoclave and heated at 130°C for 20h, 48h or 92h (except for [ImPEGPE][Tf₂N] which was not investigated after 92h reaction time). At the end, the solvent was removed under reduced pressure (0.1 bar) at 80°C for 2h and a viscous liquid was recovered.

Determination of the % of residual –PO(OEt)₂ coupling function

The ³¹P liquid NMR spectra were used to estimate quantitatively the remaining percentage of dialkylphosphonate ester coupling functions after the different forcing condition treatments. All the signals were integrated and the percentage was calculated according to the following equation: Integration of the – $PO(OEt)_2$ signal

% of residual $-PO(OEt)_2$ coupling function = $\frac{1}{\sum Integr}$

 $-x\,100$

Cations	Anions	Abbreviations	Solvents	т (°С)	δ (<i>-P(O)(OEt)₂</i>) / ppm	Deuteriated solvents	Samples
	Br-	ImPE-Br	H ₂ O	130	33.83	D ₂ O	ImPE-Br/H ₂ O
N N P(OCH ₂ CH ₃) ₂			H₂O:EtOH				ImPE-Br/H ₂ O:EtOH
	Tf₂N ⁻	ImPE-Tf ₂ N*	H ₂ O:EtOH	130	30.41	DMSO	ImPE- TfaN/HaO:EtOH
N N (O)3 PlocH2	Tf₂N⁻	ImPEGPE-Tf ₂ N*	H₂O:EtOH	130	28.68	DMSO	ImPEPEG- Tf ₂ N/H ₂ O:EtOH
N () () () () () () () () () () () () ()	Tf₂N⁻	ImC ₁₂ PE-Tf ₂ N*	H ₂ O:EtOH	130	32.08	DMSO	ImC ₁₂ PE- Tf ₂ N/H ₂ O:EtOH

Table S1. Details of the reaction tests carried out (*not soluble in water)



Figure S4. ¹H liquid NMR spectra of ImPE-Br/H2O after 20h in forcing reaction condition.



Figure S5. ³¹P liquid NMR spectra of ImPE-Br/H2O after 20h in forcing reaction condition.



Figure S6. ¹H liquid NMR spectra of ImPE-Br/H2O after 48h in forcing reaction condition.







Figure S8. ¹H liquid NMR spectra of ImPE-Br/H2O after 92h in forcing reaction condition.







Figure S10. ¹H liquid NMR spectra of ImPE-Br/H2O:EtOH after 20h in forcing reaction condition.



Figure S11. ³¹P liquid NMR spectra of ImPE-Br/H2O:EtOH after 20h in forcing reaction condition.



Figure S12. ¹H liquid NMR spectra of ImPE-Br/H2O:EtOH after 48h in forcing reaction condition.







Figure S14. ¹H liquid NMR spectra of ImPE-Br/H2O:EtOH after 92h in forcing reaction condition.



Figure S15. ³¹P liquid NMR spectra of ImPE-Br/H2O:EtOH after 92h in forcing reaction condition.



Figure S16. ¹H liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 20h in forcing reaction condition.



Figure S17. ³¹P liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 20h in forcing reaction condition.



Figure S18. ¹H liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 48h in forcing reaction condition.



Figure S19. ³¹P liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 48h in forcing reaction condition.

DMSO ImPE-NTf2 (48h, 130 C)_SMP/GG P31-dec1H DMSO /opt/topspin cmos 22



Figure S20. ¹H liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 92h in forcing reaction condition.



Figure S21. ³¹P liquid NMR spectra of ImPE-Tf₂N/H2O:EtOH after 92h in forcing reaction condition.



Figure S22. ¹H liquid NMR spectra of ImPEGPE-Tf₂N/H₂O:EtOH after 20h in forcing reaction condition.



Figure S23. ³¹P liquid NMR spectra of ImPEGPE-Tf₂N/H₂O:EtOH after 20h in forcing reaction condition.



Figure S24. ¹H liquid NMR spectra of ImPEGPE-Tf₂N/H2O:EtOH after 48h in forcing reaction condition.



Figure S25. ³¹P liquid NMR spectra of ImPEGPE-Tf₂N/H2O:EtOH after 48h in forcing reaction condition.



Figure S26. ¹H liquid NMR spectra of ImC₁₂PE-Tf₂N/H₂O:EtOH after 20h in forcing reaction condition.



Figure S27. ³¹P liquid NMR spectra of ImC₁₂PE-Tf₂N/H₂O:EtOH after 20h in forcing reaction condition.



Figure S28. ¹H liquid NMR spectra of $ImC_{12}PE-Tf_2N/H_2O$:EtOH after 48h in forcing reaction condition.



Figure S29. ³¹P liquid NMR spectra of ImC₁₂PE-Tf₂N/H₂O:EtOH after 48h in forcing reaction condition.



Figure S30. ¹H liquid NMR spectra of ImC₁₂PE-Tf₂N/H₂O:EtOH after 92h in forcing reaction condition.



Figure S31. ³¹P liquid NMR spectra of ImC₁₂PE-Tf₂N/H₂O:EtOH after 92h in forcing reaction condition.

7. FTIR spectra of the pure ionic liquid [ImC₁₂PE][Tf₂N] and grafted sample ImC₁₂PE-Tf₂N between 2600 and 4000 cm⁻¹



Figure S32. FTIR spectra of the pure ionic liquid $[ImC_{12}PE][Tf_2N]$ (on the top) and grafted sample $ImC_{12}PE-Tf_2N$ (on the bottom) between 2600 and 4000 cm⁻¹.

8. ²⁷AI MAS NMR



Figure S33. ^{27}Al MAS NMR spectra of pristine $\gamma\text{-alumina}$ and grafted $Tf_2N^{\text{-}}$ samples.

9. Schematic representation of the chemisorbed and physisorbed CO_2 on a pristine γ -Al₂O₃



Figure S34. Possible configurations of species resulting from the reaction of CO_2 with the pristine γ -Al₂O₃, depending on the equilibrium pressure.

10. References

[1] Leenaars, A.F.M; Keizer, K. & Bruggraaf, A.J. The reparation and characterization of alumina membrane with ultra-fine pores, *J.Mater.Sci.* **1984**, 19, 1077-1088. doi: 10.1007/BF01120016

[2] Hewitt, D.W. & Newland, G.L. Organophosphorus compounds. P-Arylated perhydro-1,2-azaphosphorines, Aust. J. Chem., **1977**, 30, 579. doi:10.1071/CH9770579