Supporting Information

Ionic liquid mediated sol-gel synthesis in the presence of water or formic acid : which synthesis for which material?

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Experimental section

Stability of $[C_4MIm][PF_6]$ in HCOOH :

Sample preparation

The stability was tested using the same molar ratio as those used in the ionogel synthesis. In a Vial, 238 mg (0.84 mmol) of $[C_4MIm][PF_6]$ were dissolved in 0.5 mL HCOOH (13.2 mmol). The mixture was stirred for 48h at room temperature while samples for NMR measurements were taken periodically.

NMR spectroscopy

The ^{19}F and ^{31}P spectra were recorded using a Bruker Avance 400 MHz (9.4 T) spectrometer using CD_3CN or D_2O as solvents at a frequency of 376.5 MHz (^{19}F) and 161.97 MHz (^{31}P).

Small angle X Ray scattering (SAXS) experiments were performed with an in-house setup of the *Laboratoire Charles Coulomb, "Réseau X et gamma", Université Montpellier 2,*

France. A high brightness low power X- ray tube, coupled with aspheric multilayer optic (GeniX^{3D} from Xenocs) was employed. It delivers an ultralow divergent beam (0.5mrad). Scatterless slits were used to give a clean 0.8mm beam diameter (35 Mphotons/s) at the sample. We worked in a transmission configuration and scattered intensity was measured by a Schneider 2D imageplate detector prototype, at a distance of 1,9m from the sample. Intensities were corrected by transmission and the empty cell contribution was substracted.

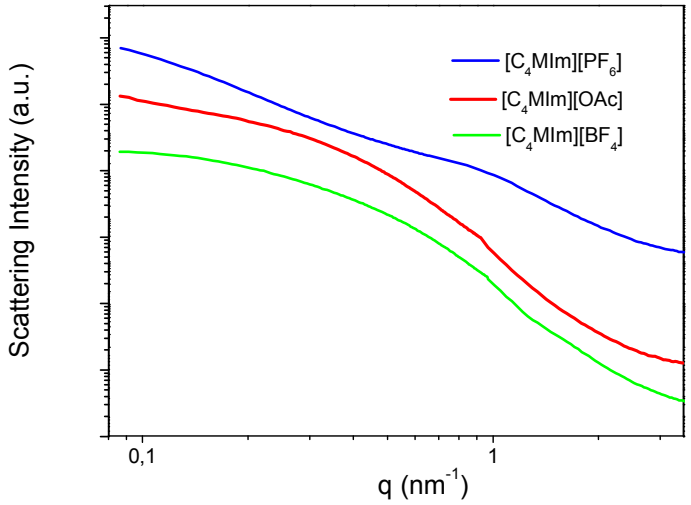

Figure S1. Small-angle X-ray scattering (SAXS) pattern of the washed gels obtained by the hydrolysis way.

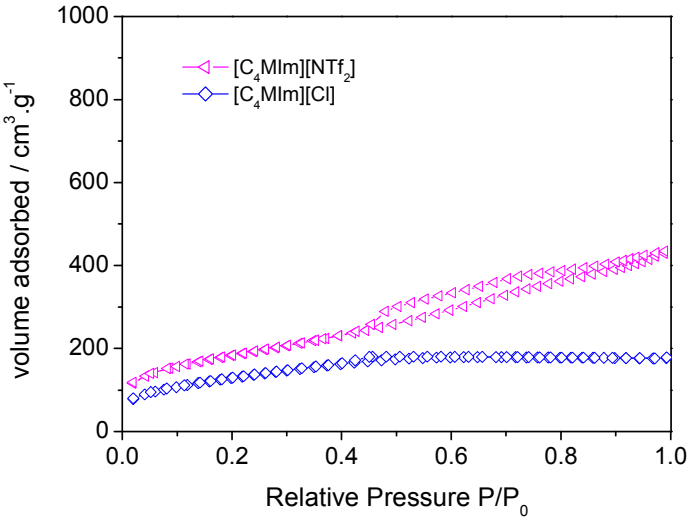

Figure. S2. Influence of anion in hydrolysis way: N_2 sorption isotherms of washed gels arising from $[C_4MIm][NTf_2]$ and $[C_4MIm][Cl]$ ILs.

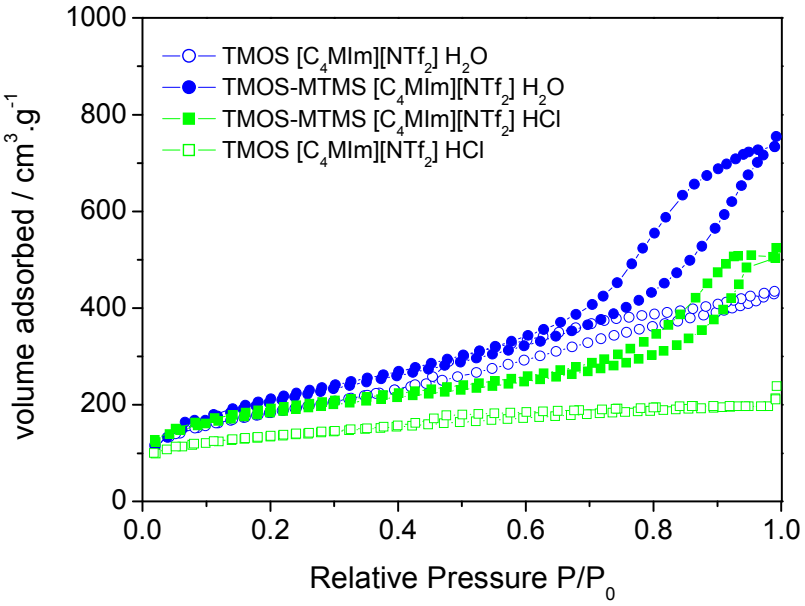

Figure S3. Effect of the addition of a methylated precursor in hydrolysis way: N_2 sorption isotherms of washed gels arising from $[C_4MIm]$ $[NTf_2]$ and 50/50 TMOS-MTMS precursor mixture.

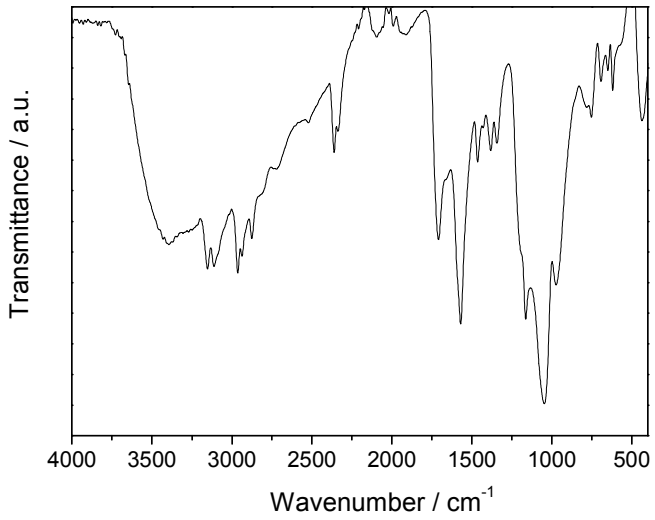

Figure S4. FT-IR psectra of ionogel obtained using $[C_4MIm][OAc]$ and the formic acid solvolysis

Table S1. Condensation extent (^{29}Si MAS NMR) hydrolysis way

Anion	C %	Q_2 % (-92 ppm)	Q_3 % (-101 ppm)	Q_4 % (- 110 ppm)
[BF_4]	97	-	12	88
[OAc]	90	-	40	60
[PF_6]	95	-	20	80
[Cl]	89	4	35	61
[NTf_2]	87	-	35	55

Table S2. Condensation extent (^{29}Si MAS NMR) formic acid solvolysis way

Anion	C %	Q_2 % (-92 ppm)	Q_3 % (-101 ppm)	Q_4 % (- 110 ppm)
[BF_4]	NA			
[OAc]	87	2	45	53
[PF_6]	NA			
[Cl]	90	-	40	60
[NTf_2]	89	1	42	57

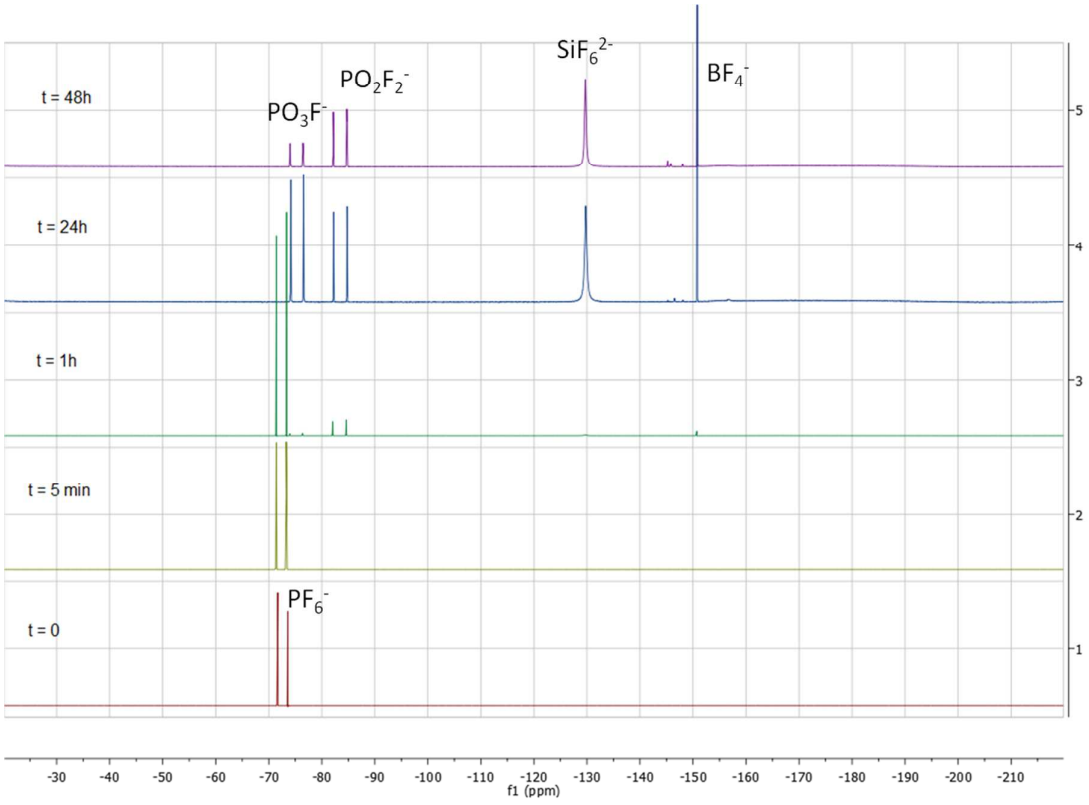

Figure S5. ^{19}F NMR spectra of $[C_4MIm][PF_6]$ at different time. The spectrum at t = 0 was obtained in CD_3CN while the others were recorded in D_20.

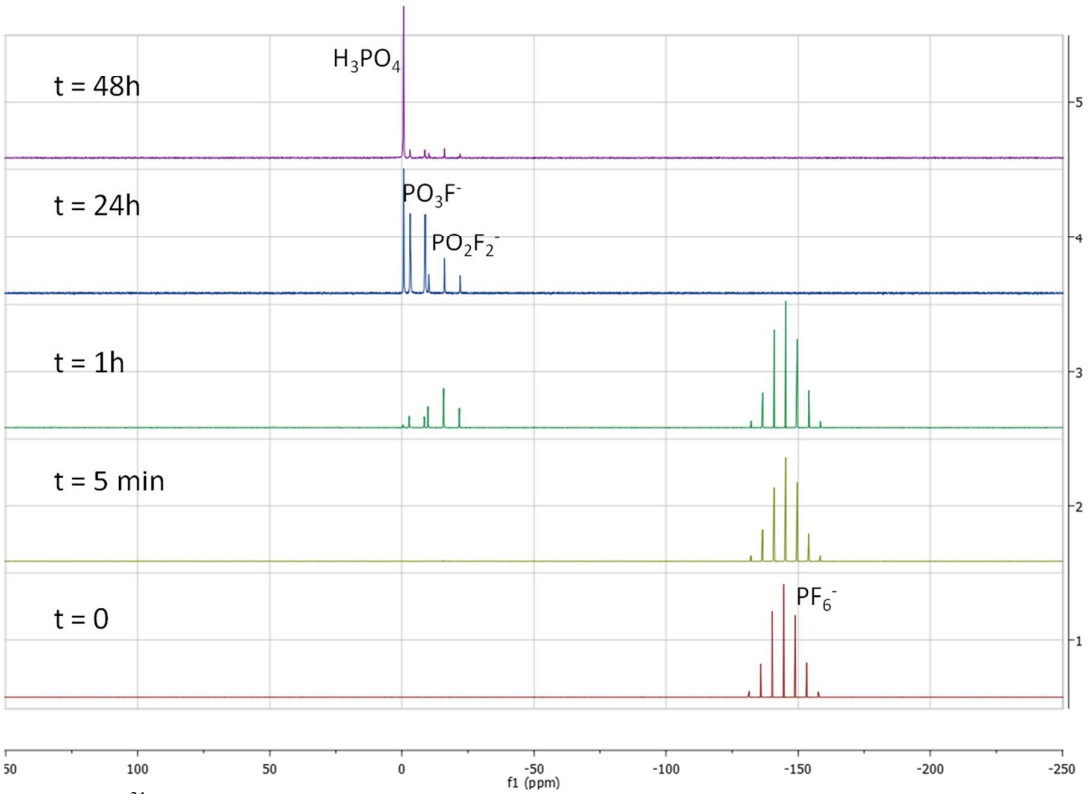

Figure S6. ^{31}P NMR spectra of $[C_4MIm][PF_6]$ at different time. The spectrum at t = 0 was obtained in CD_3CN while the others were recorded in D_20.

Table S3. Chemical shifts attribution of the species formed during the reaction of $[C_4MIm][PF_6]$ and HCCOH[1]

product	^{19}F δ (ppm)	^{31}P δ (ppm)
PF_6^-	-72.6 (d, J_{F-P} = 707 Hz)	-144.3 (sept, J_{P-F} = 707 Hz)
PO_3F^{2-}	-75.2 (d, J_{F-P} = 911 Hz)	-5.6 (d, J_{P-F} = 911 Hz)
$PO_2F_2^-$	-83.3 (d, J_{F-P} = 960 Hz)	-15.9 (t, J_{P-F} = 960 Hz)
SiF_6^{2-}	-129.7 (s)	
BF_4^-	-150.8 (s)	
H_3PO_4		0

1 Plakthotnyk, A. V.; Ernst, L.; Schmutzler, R. *J. Fluorine Chem.* **2005**, *126*, 27-31

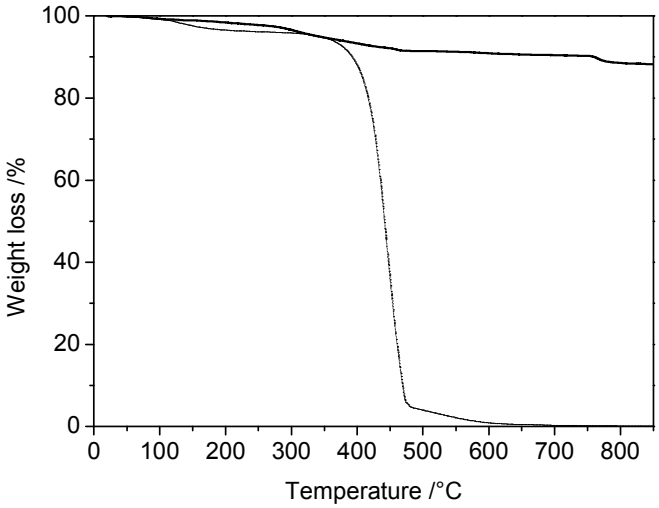

Figure S7. TGA of $[C_4MIm][BF_4]$ (dotted lines) and washed gel after extraction of $[C_4MIm][BF_4]$ (straight line) in CH_3CN