Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Robust Ionic liquid@MOF composite as a versatile superprotonic conductor

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SEM-EDX

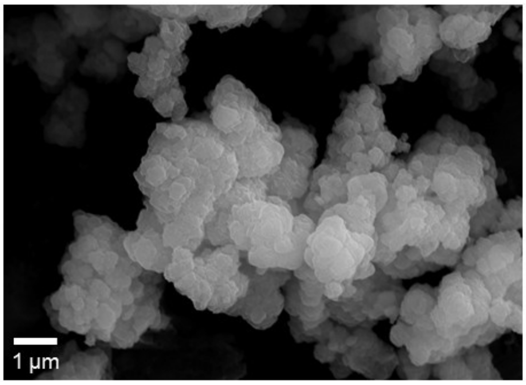

Figure S1: SEM image of MIL-101(Cr)-SO_3H

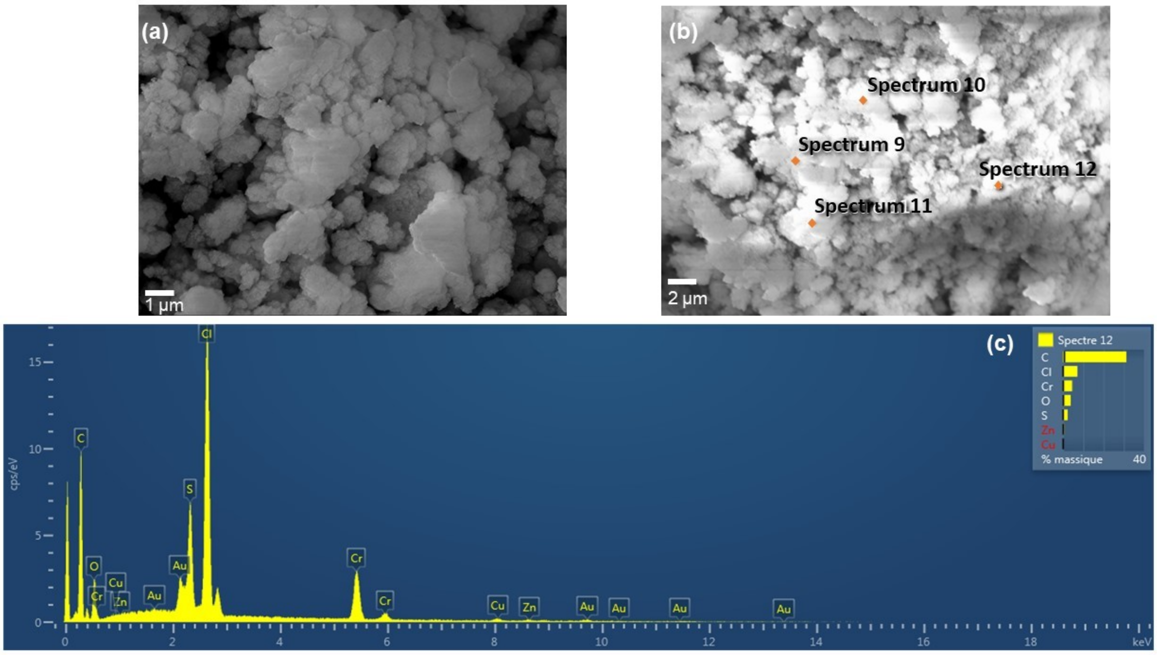

Figure S2. (**a and b**) SEM images of EMIM@MIL-101-SO_3H and (**c**) XEDS spectrum of EMIM@MIL-101-SO_3H in the case of (b).

Elemental Analysis

Table S1. EA results of MIL-101(Cr)-SO_3H and EMIM@MIL-101-SO_3H.

MIL-101(Cr)-SO_3H		
	%exp (wt%)	Weight ratio, m(C)/m(S) = 4.34 -SO_3H functionalization degree= 68.6 %
C	27.93	
S	6.43	
EMIM@MIL-101-SO_3H before PC measurements		
	%exp (wt%)	Weight ratio, m(C)/m(N) = 3.61
C	34.7	
N	9.6	
EMIM@MIL-101-SO_3H after PC measurements recorded at 298K-473K / 0% RH		
	%exp (wt%)	Weight ratio, m(C)/m(N) = 3.66
C	37.4	
N	10.2	
EMIM@MIL-101-SO_3H after PC measurements recorded at 343K / 80% RH for 6 days		
	%exp (wt%)	Weight ratio, m(C)/m(N) = 3.67
C	35.6	
N	9.7	

Thermogravimetric analysis (TGA)

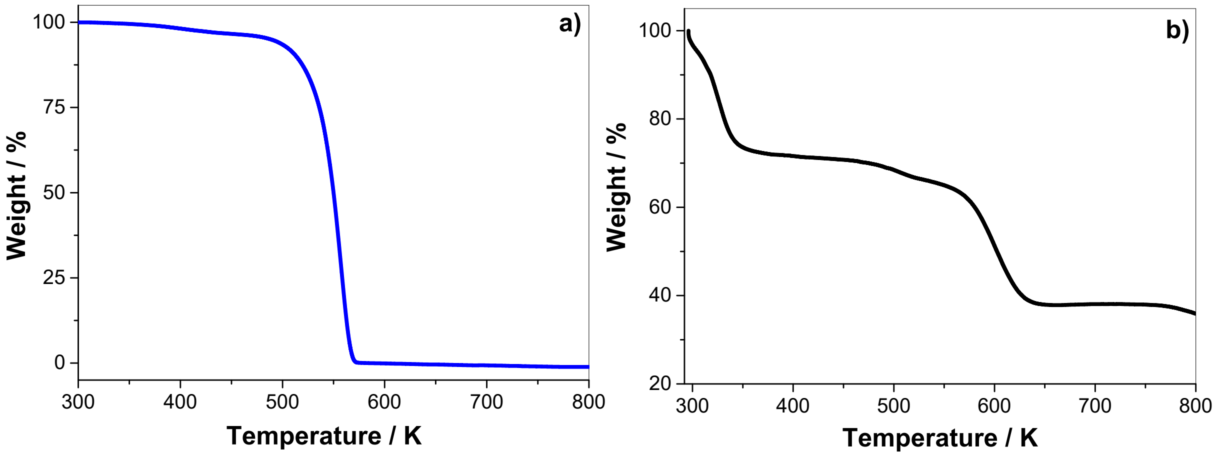

Figure S3 TGA curve (wt %) of (**a**) bulk EMIMCl and (**b**) MIL-101(Cr)-SO_3H.

FT-IR spectroscopy

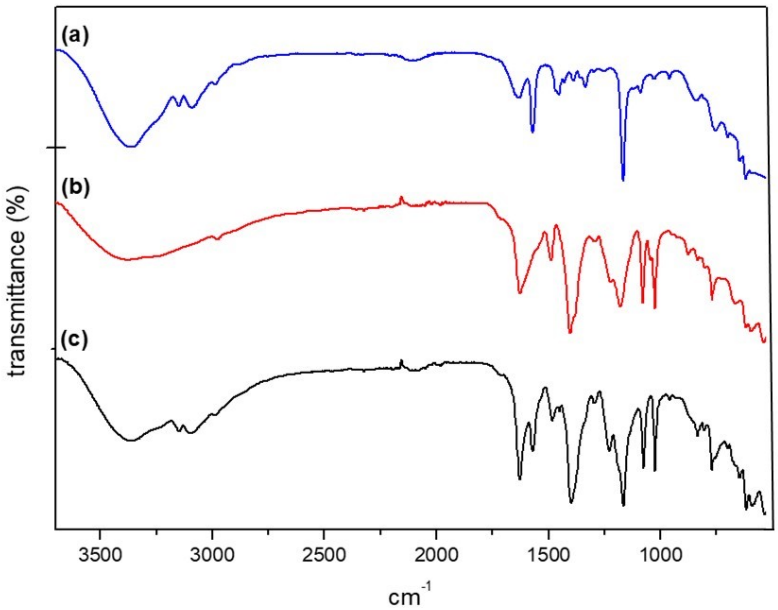

Figure S4: FT-IR spectra of (**a**) EMIMCl, (**b**) MIL-101(Cr)-SO_3H and (**c**) EMIM@MIL-101-SO_3H.

Table S2: Main FT-IR vibration bands of EMIMCl, MIL-101(Cr)-SO_3H and EMIM@MIL-101-SO_3H with the corresponding assignment.

MIL-101(Cr)-SO_3H	EMIMCl	EMIM@MIL-101-SO_3H	Assignment
	3151	3148	ν(C-H)
	3083	3088	ν (C-H)
1628	1630	1628	ν(C-O) as + δ(H-O-H)
	1574	1568	Imidazole skeleton
1485		1479	ν(C-O)s
	1448	1450	Imidazole skeleton
1403		1397	ν(S=O) as
	1330		Imidazole skeleton
1178	1167	1166	ν(S=O) s + Imidazole skeleton
1077		1077	ν(S-O)
1026		1026	ν(S-O)
840		840	ν(Cr-O)
773		773	ν(C-S)

Impedance measurements of the anhydrous EMIM@MIL-101-SO_3H

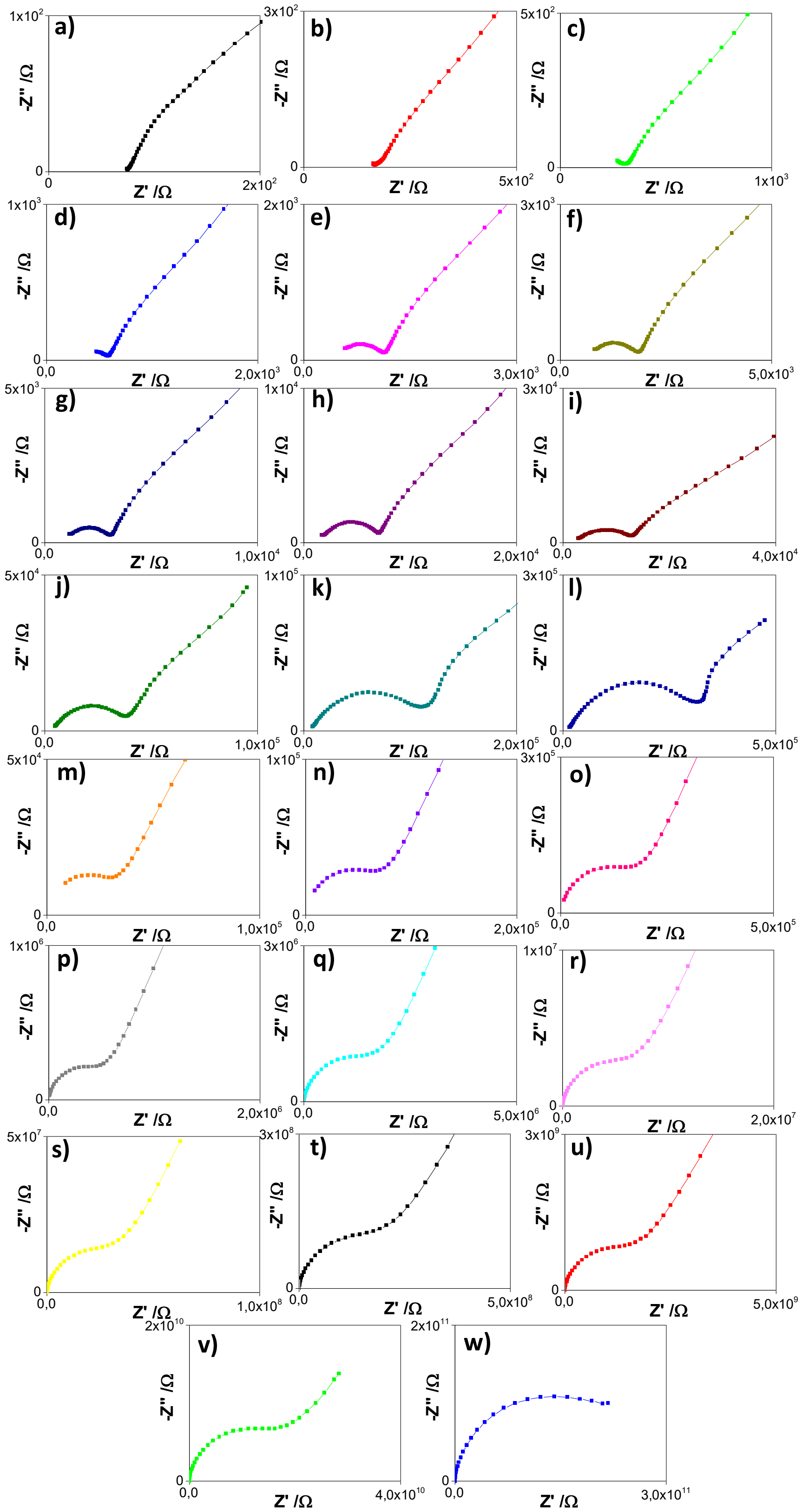

Figure S5: Nyquist plots of the impedance for the dehydrated EMIM@MIL-101-SO_3H powder recorded under 0% RH, at 473 K (**a**), 463 K (**b**), 453 K (**c**), 443 K (**d**), 433 K (**e**), 423 K (**f**), 413 K (**g**), 403 K (**h**), 393 K (**i**), 383 K (**j**), 373 K (**k**), 363 K (**l**), 353 K (**m**), 343 K (**n**), 333 K (**o**), 323 K (**p**), 313 K (**q**), 303 K (**r**), 293 K (**s**), 283 K (**t**), 273 K (**u**), 263 K (**v**) and 253 K (**w**).

Impedance measurements of the bulk EMIMCl

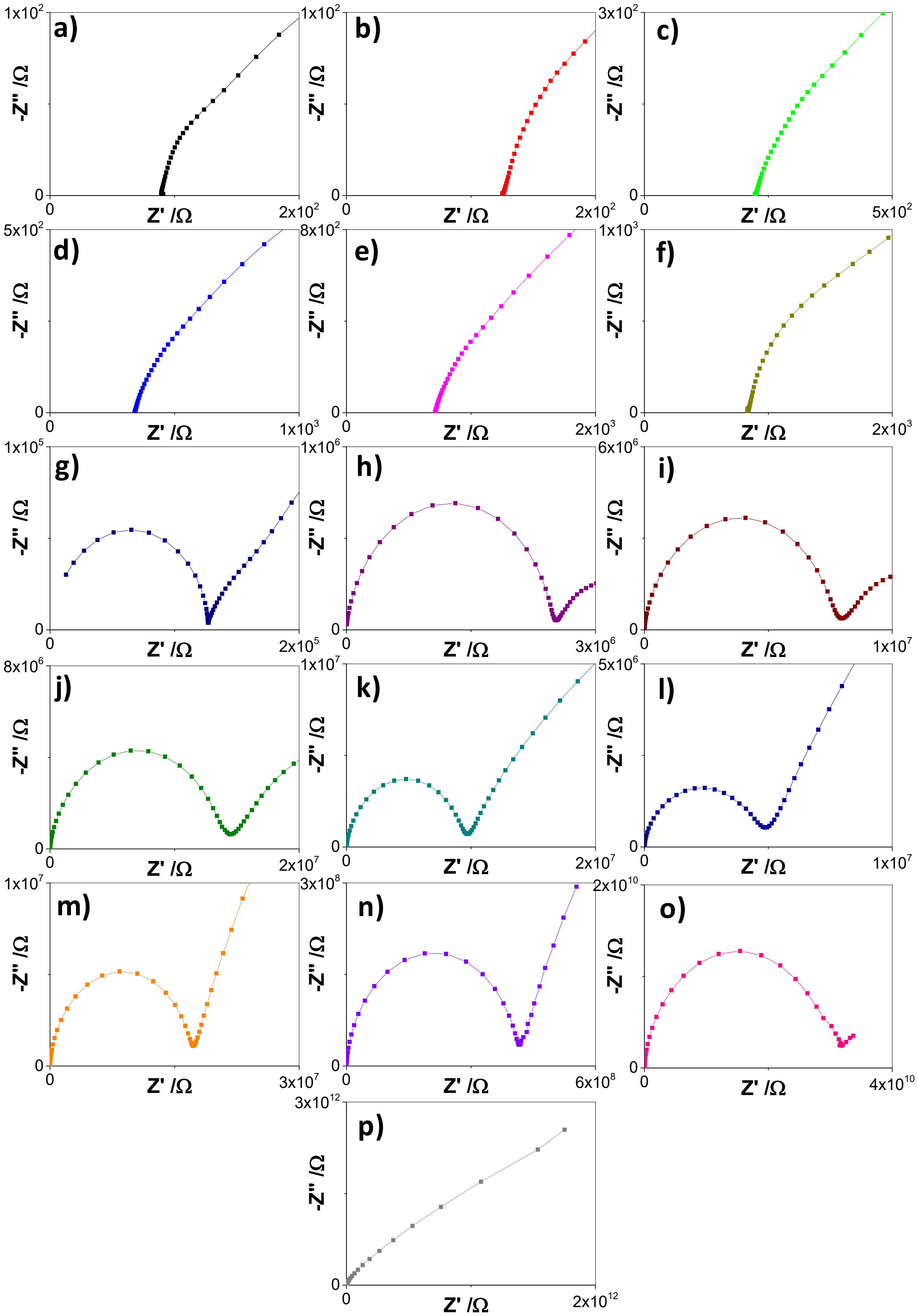

Figure S6: Nyquist plots of the impedance for the bulk EMIMCl recorded under 0% RH, at 323 K (**a**), 313 K (**b**), 303 K (**c**), 293 K (**d**), 283 K (**e**), 273 K (**f**), 263 K (**g**), 253 K (**h**), 243 K (**i**), 233 K (**j**), 223 K (**k**), 213 K (**l**), 203 K (**m**), 193 K (**n**), 183 K (**o**) and 173 K (**p**).

Impedance measurements of the anhydrous MIL-101(Cr)-SO_3H

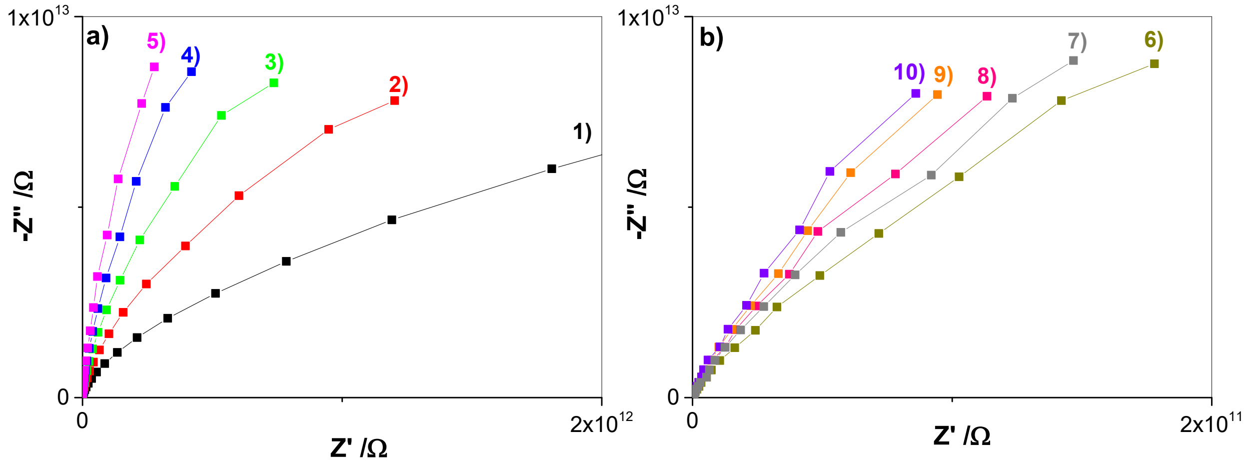

Figure S7: Nyquist plots of the impedance for the dehydrated MIL-101(Cr)-SO_3H recorded under 0% RH, at 393 K (**1**), 383 K (**2**), 373 K (**3**), 363 K (**4**), 353 K (**5**), 343 K (**6**), 333 K (**7**), 323 K (**8**), 313 K (**9**) and 303 K (10).

Impedance measurements of the hydrated EMIM@MIL-101-SO_3H for RH varying from 35 % to 80 %

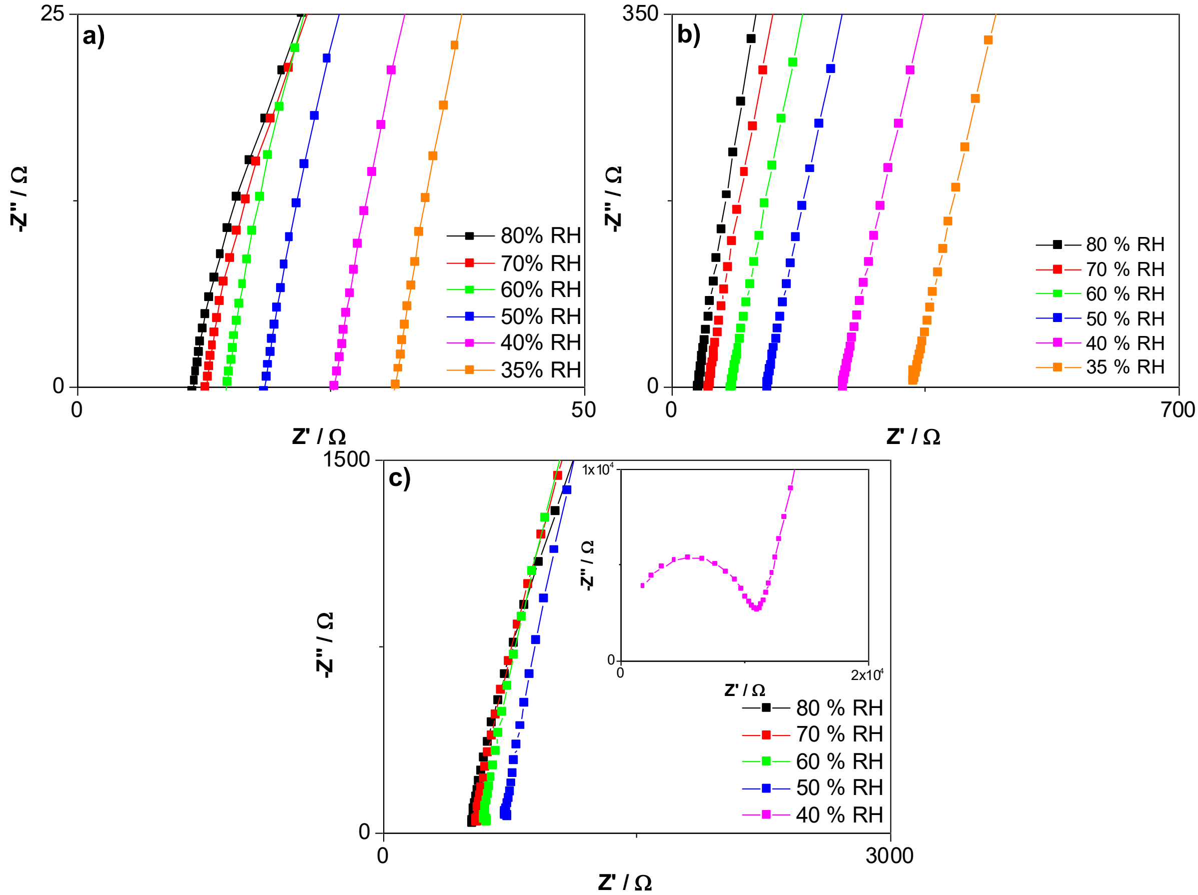

Figure S8: Nyquist plots of the impedance for EMIM@ MIL-101-SO_3H recorded at 343 K (**a**) and 303 K (**b**) and for MIL-101(Cr)-SO_3H recorded at 343 K (**c**) for RH varying from 35% to 80%.

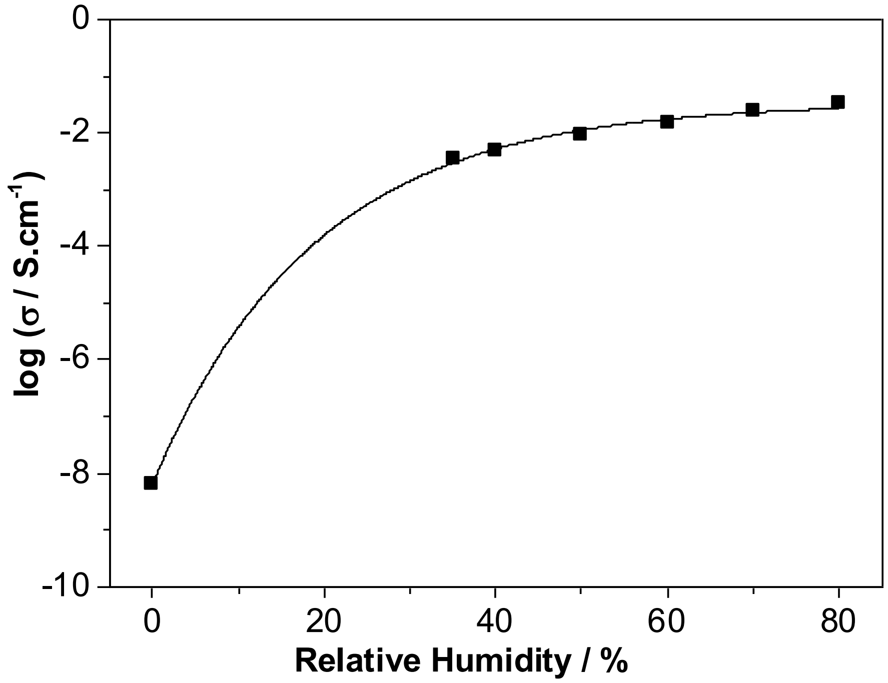

Figure S9: Humidity dependence of the conductivity for EMIM@MIL-101-SO_3H recorded at 303 K. The exponential line is a guide for the eyes.

Water sorption isotherm of EMIM@MIL-101-SO_3H

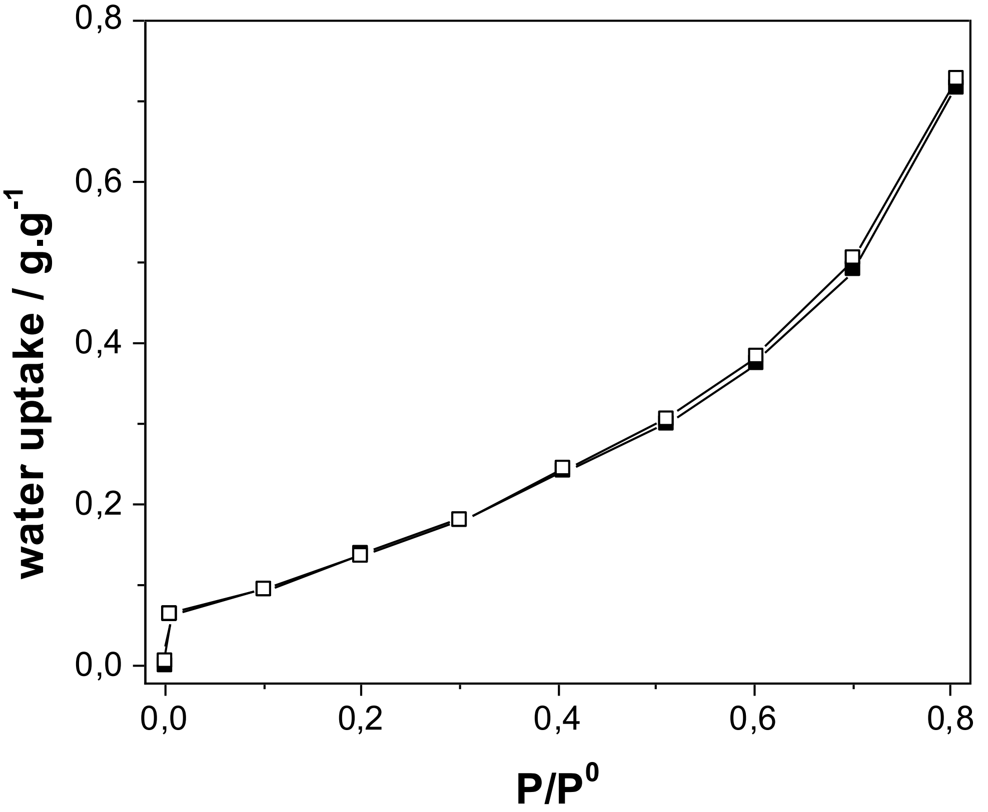

Figure S10: Water sorption isotherm of EMIM@MIL-101-SO_3H recorded at 303 K. Full and empty squares refer to the adsorption and desorption branches, respectively.

Additional impedance measurements

Impedance measurements of the hydrated EMIM@MIL-101-SO_3H and MIL-101(Cr)-SO_3H at RH = 80 % for T varying from 343 K to 298 K

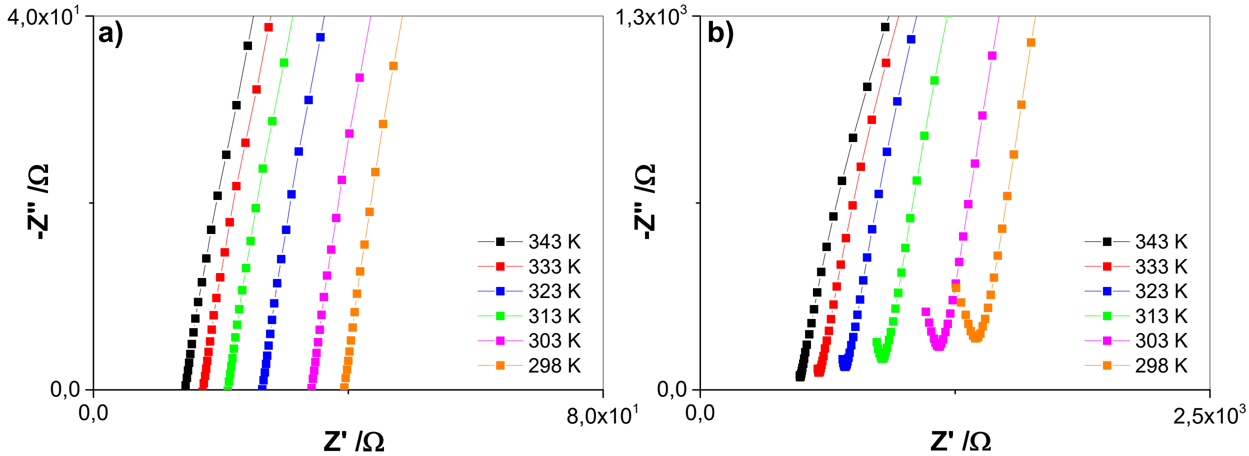

Figure S11: Nyquist plots of the impedance for EMIM@MIL-101-SO_3H (**a**) and MIL-101(Cr)-SO_3H (**b**) recorded under 80% RH, for T varying from 343 K to 298 K.

Impedance measurements of the hydrated EMIM@MIL-101-SO_3H recorded at RH = 80 % and T = 343 K

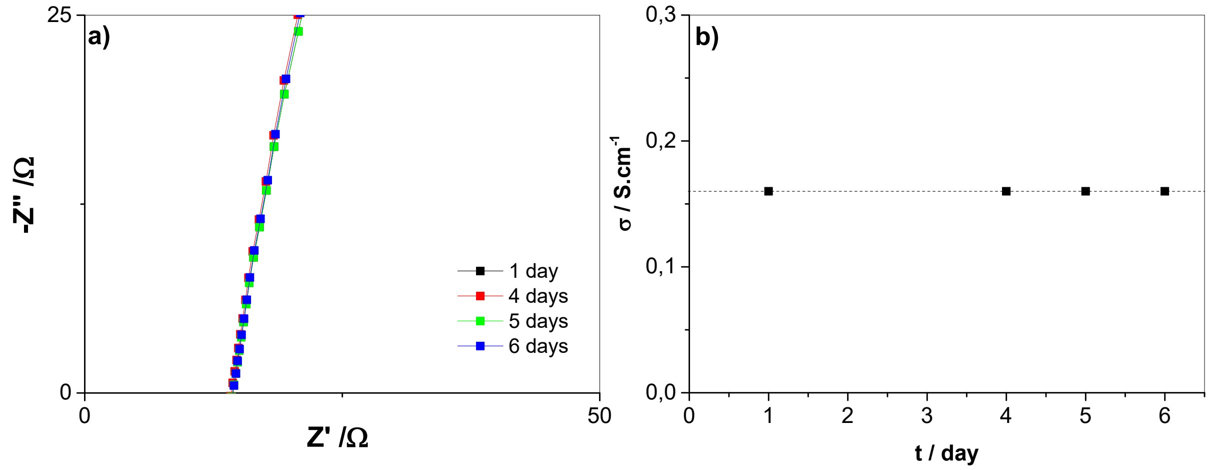

Figure S12: Time dependence of the conductivity of EMIM@MIL-101-SO_3H recorded at 343 K under 80% RH.

Table S3. Conductivity values deduced from the Nyquist plots, for EMIMCl, MIL-101(Cr)-SO_3H and EMIM@MIL-101-SO_3H powders at different RH/T conditions. l and S are the sample thickness and surface.

Anhydrous EMIM@MIL-101-SO₃H RH = 0% (l = 0.044 cm, S = 0.3631 cm²)							
T / K	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***
473	1.6×10^{-3}	463	7.2×10^{-4}	453	4.0×10^{-4}	443	3.0×10^{-4}
433	2.0×10^{-4}	423	1.4×10^{-4}	413	9.8×10^{-5}	403	6.4×10^{-5}
393	4.1×10^{-5}	383	2.4×10^{-5}	373	1.4×10^{-5}	363	7.4×10^{-6}
353	3.5×10^{-6}	343	1.4×10^{-6}	333	5.1×10^{-7}	323	2.0×10^{-7}
313	6.6×10^{-8}	303	1.5×10^{-8}	293	2.9×10^{-9}	283	4.8×10^{-10}
273	6.0×10^{-11}	263	6.0×10^{-12}	253	5.1×10^{-13}	243	5.9×10^{-14}
Bulk EMIMCl RH = 0% (l = 0.098 cm, S = 0.3631 cm²)							
T / K	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***
323	3.0×10^{-3}	313	2.1×10^{-3}	303	1.2×10^{-3}	293	7.9×10^{-4}
283	5.0×10^{-4}	273	3.2×10^{-4}	263	2.1×10^{-6}	253	1.4×10^{-7}
243	2.8×10^{-8}	233	2.5×10^{-8}	223	2.8×10^{-8}	213	5.5×10^{-8}
203	1.9×10^{-8}	193	6.5×10^{-10}	183	8.5×10^{-12}		
Hydrated EMIM@MIL-101-SO₃H							
T = 343 K (l =0.186 cm, S = 0.1256 cm²)				***T = 298 K (l =0.148 cm, S = 0.1256 cm²)***			
RH / %	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***
80	1.4×10^{-1}	70	1.2×10^{-1}	80	3.2×10^{-2}	70	2.3×10^{-2}
60	1.0×10^{-1}	50	8.4×10^{-2}	60	1.4×10^{-2}	50	9.0×10^{-3}
40	6.0×10^{-2}	35	4.8×10^{-2}	40	5.0×10^{-3}	35	3.5×10^{-3}
Hydrated MIL-101(Cr)-SO₃H T = 343 K (l =0.376 cm, S = 0.1256 cm²)							
RH / %	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***	***RH / %***	***σ / S cm⁻¹***
80	5.6×10^{-3}	70	5.4×10^{-3}	60	5.0×10^{-3}	50	4.2×10^{-3}
40	2.7×10^{-4}						
Hydrated EMIM@MIL-101-SO₃H RH = 80% (l = 0.270 cm, S = 0.1256 cm²)							
T / K	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***
343	1.4×10^{-1}	333	1.3×10^{-1}	323	1.0×10^{-1}	313	8.3×10^{-2}
303	6.4×10^{-2}	298	5.5×10^{-2}				
Hydrated MIL-101(Cr)-SO₃H RH = 80% (l = 0.313 cm, S = 0.1256 cm²)							
T / K	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***	***T / K***	***σ / S cm⁻¹***
343	5.1×10^{-3}	333	4.3×10^{-3}	323	3.5×10^{-3}	313	2.8×10^{-3}
303	2.1×10^{-3}	298	1.8×10^{-3}				