Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Confined water in imidazolium based ionic liquids: a supramolecular guest@host complex case

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School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD (UK).

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1. Characterization of Ionic Liquids

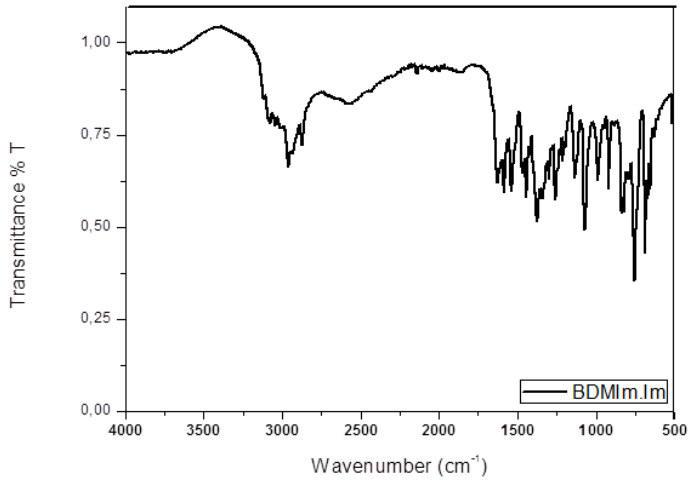

Figure S1. IR-ATR spectrum of BMMI·Im.

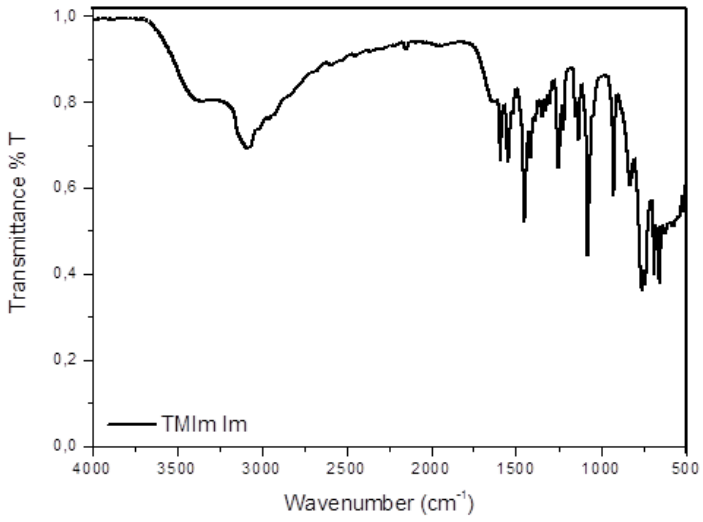

Figure S2. IR-ATR spectrum of MMMI·Im.

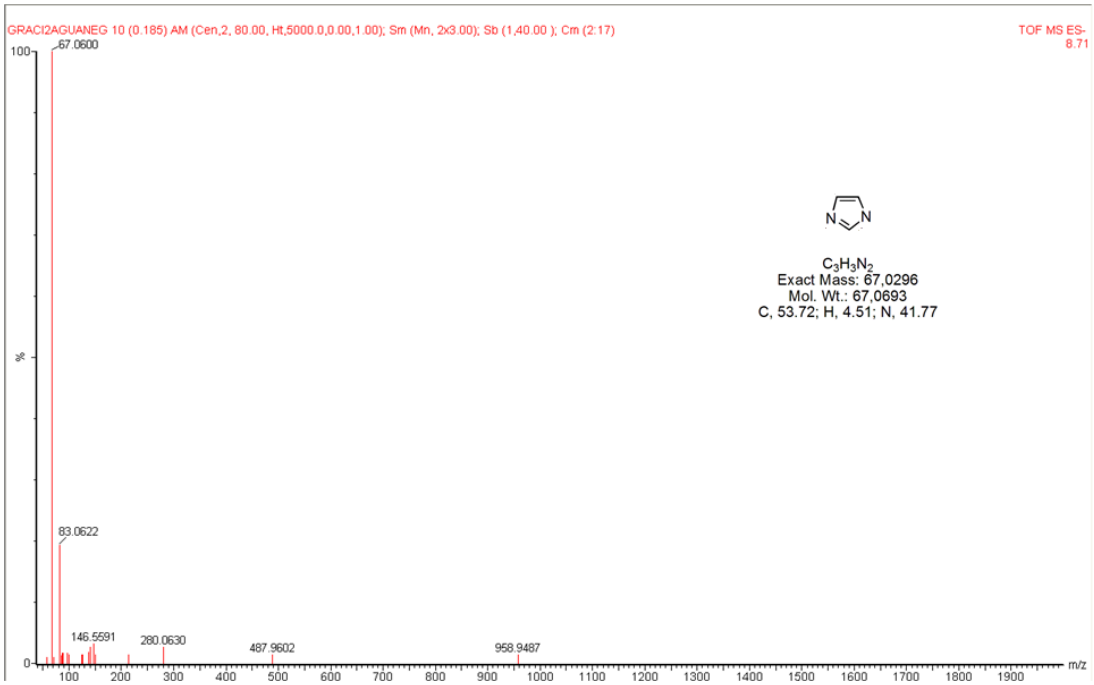

Figure S3. HRMS spectrum of MMMI·Im in water negative.

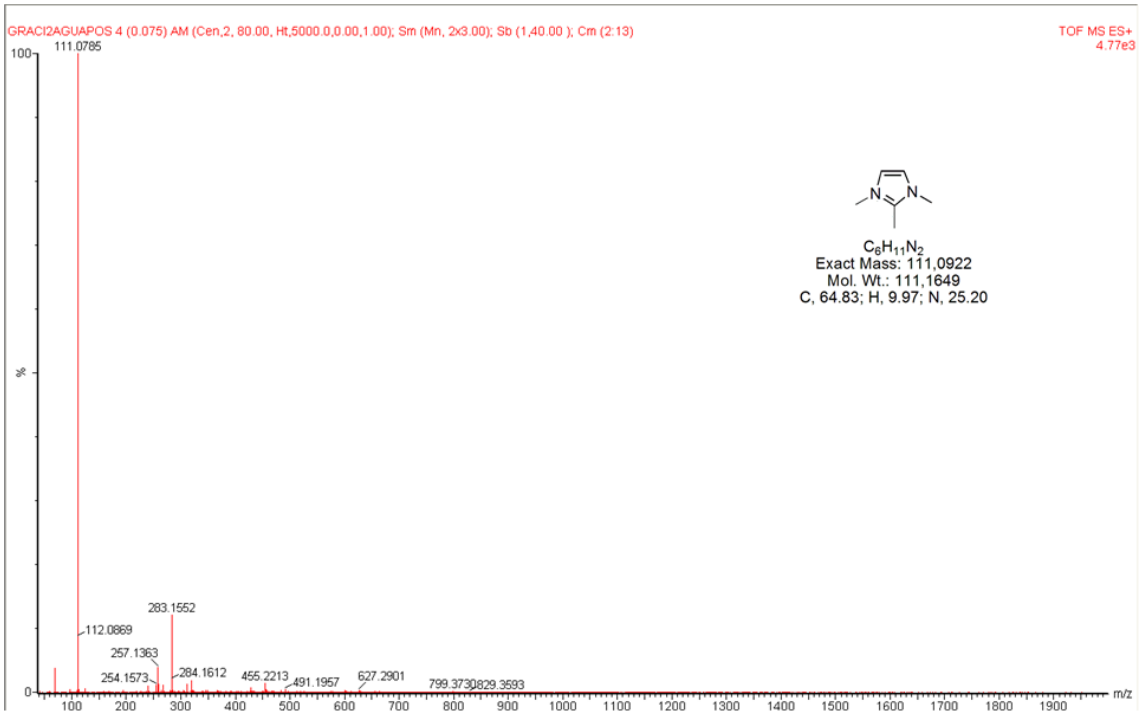

Figure S4. HRMS spectrum of MMMI·Im in water positive.

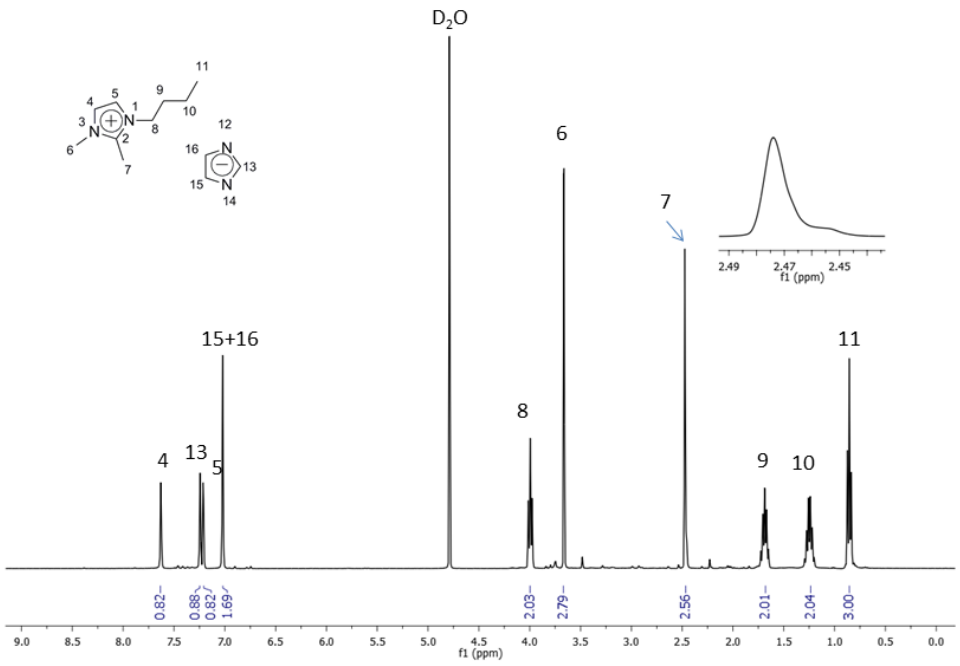

Figure S5. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (1 M).

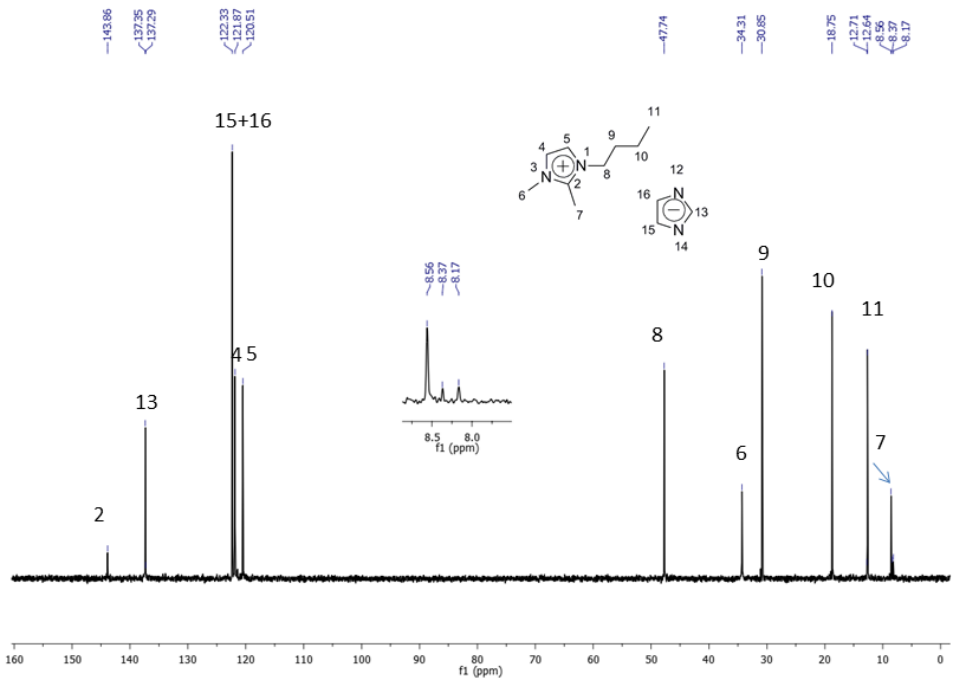

Figure S6. ^{13}C{^{1}H}-NMR (100.6 MHz, 25 °C) spectrum of BMMI·Im in D_2O (1 M).

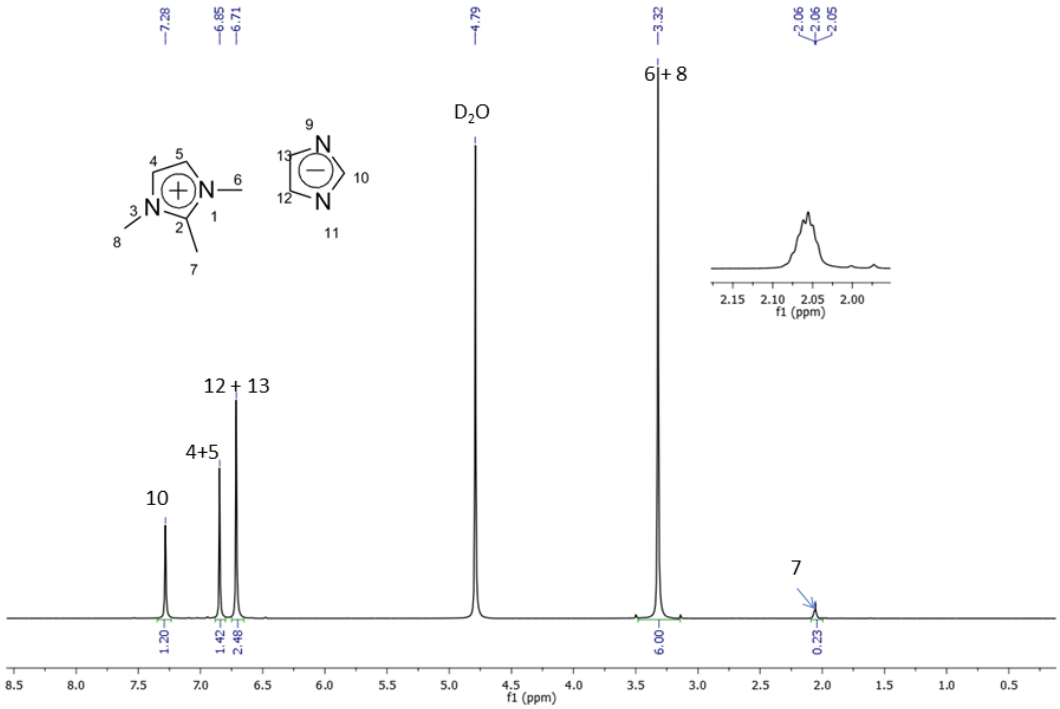

Figure S7. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in D_2O (1 M).

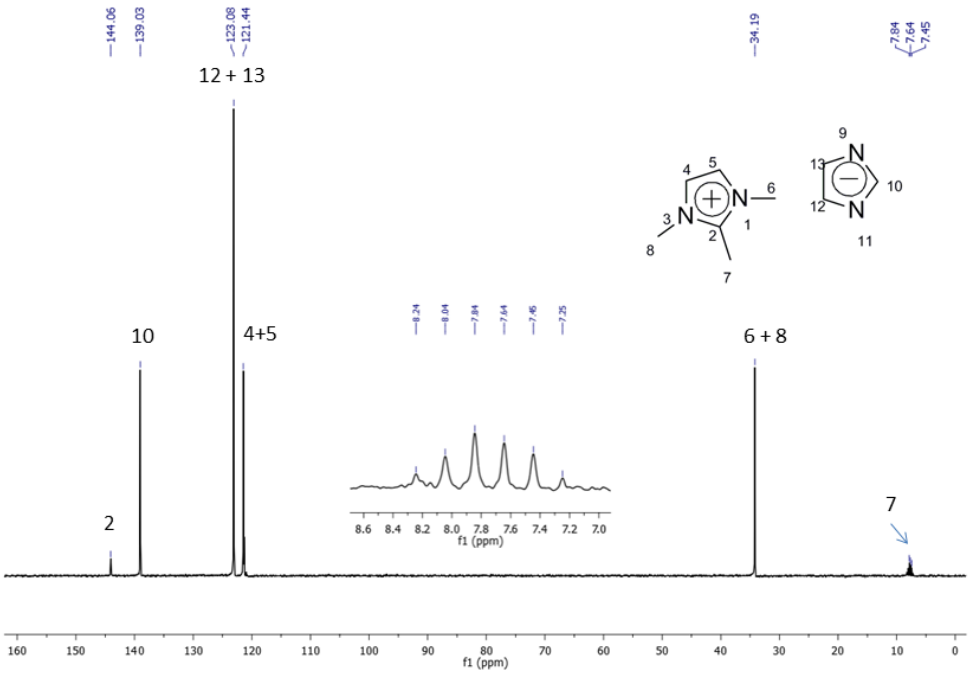

Figure S8. $^{13}C\{^{1}H\}$-NMR (100.6 MHz, 25 °C) spectrum of MMMI·Im in D_2O (1 M).

2. NMR-Spectral Data

2.1. Deuteration after 1h

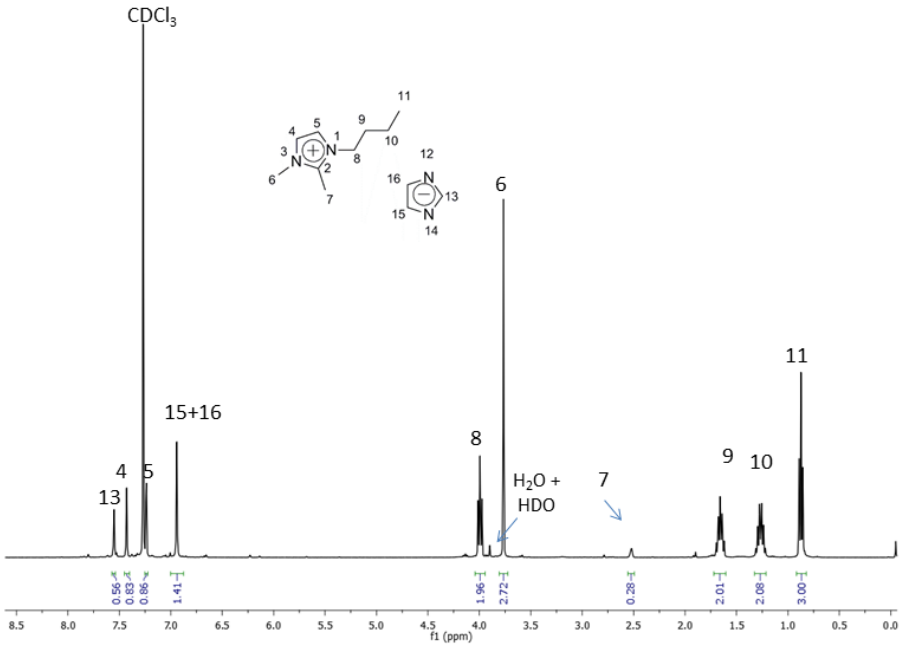

Figure S9. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in $CDCl_3$ (0.2 M) after 1h.

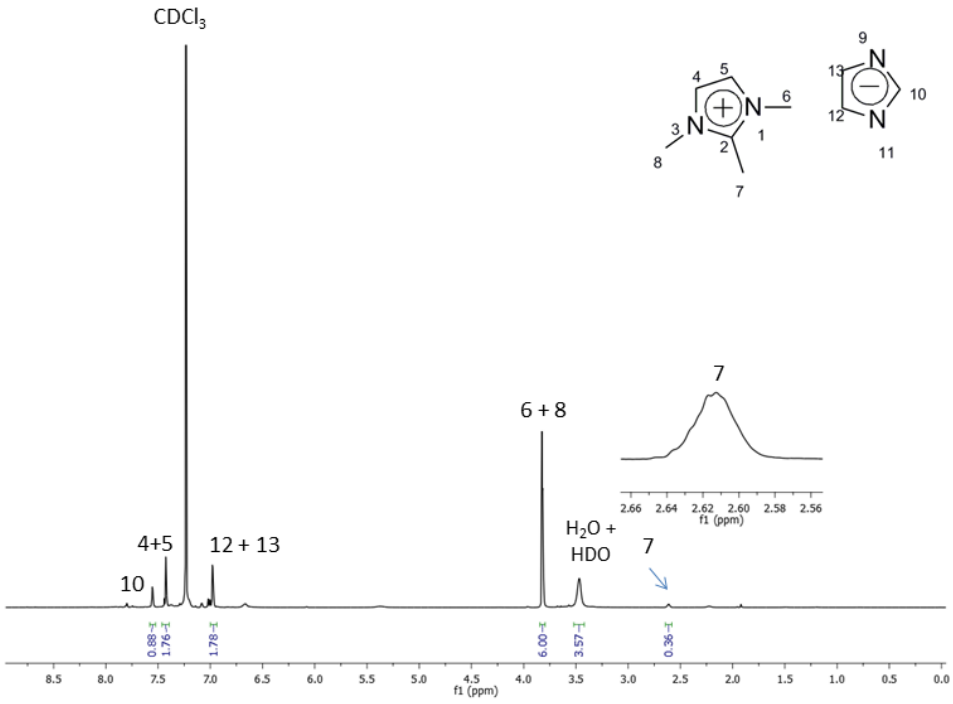

Figure S10. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in $CDCl_3$ (0.2 M) after 1h.

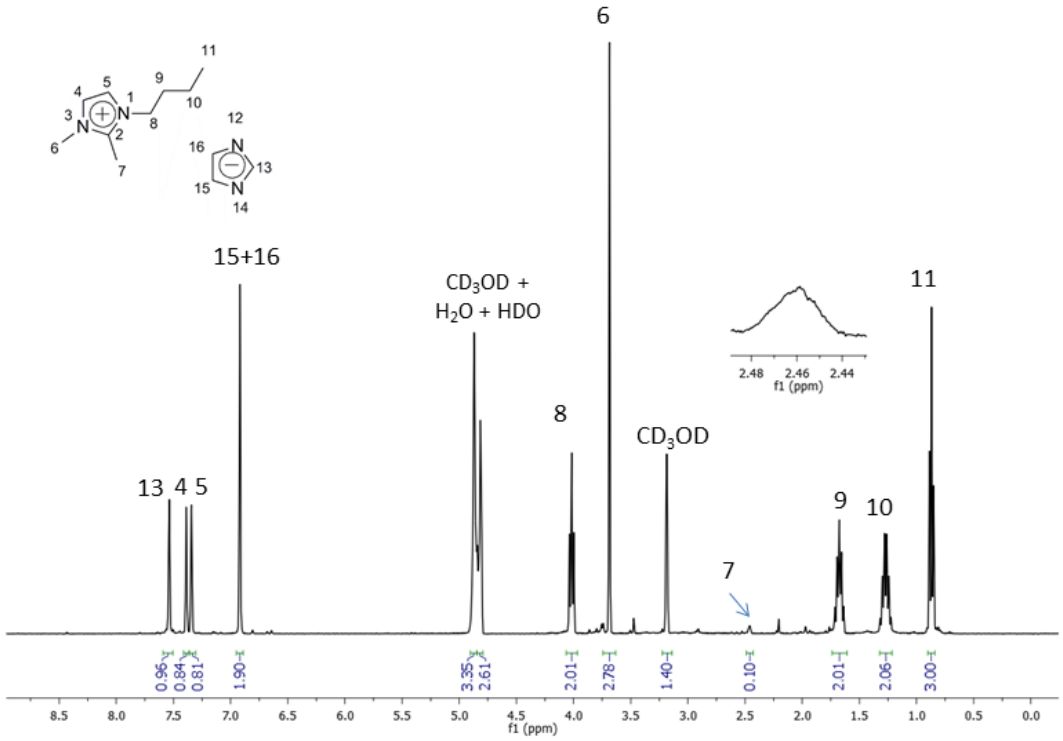

Figure S11. ^{1}H-NMR (100.6 MHz, 25 °C) spectrum of BMMI·Im in CD_3OD (0.2 M) after 1h.

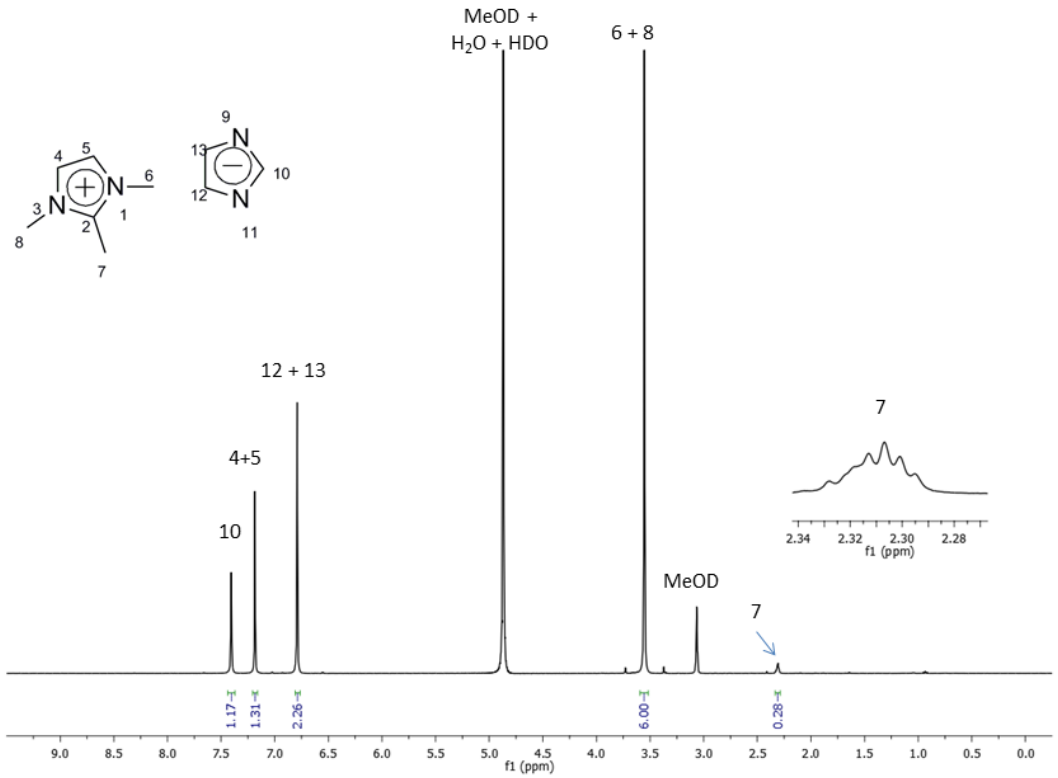

Figure S12. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in CD_3OD (0.2 M) after 1h.

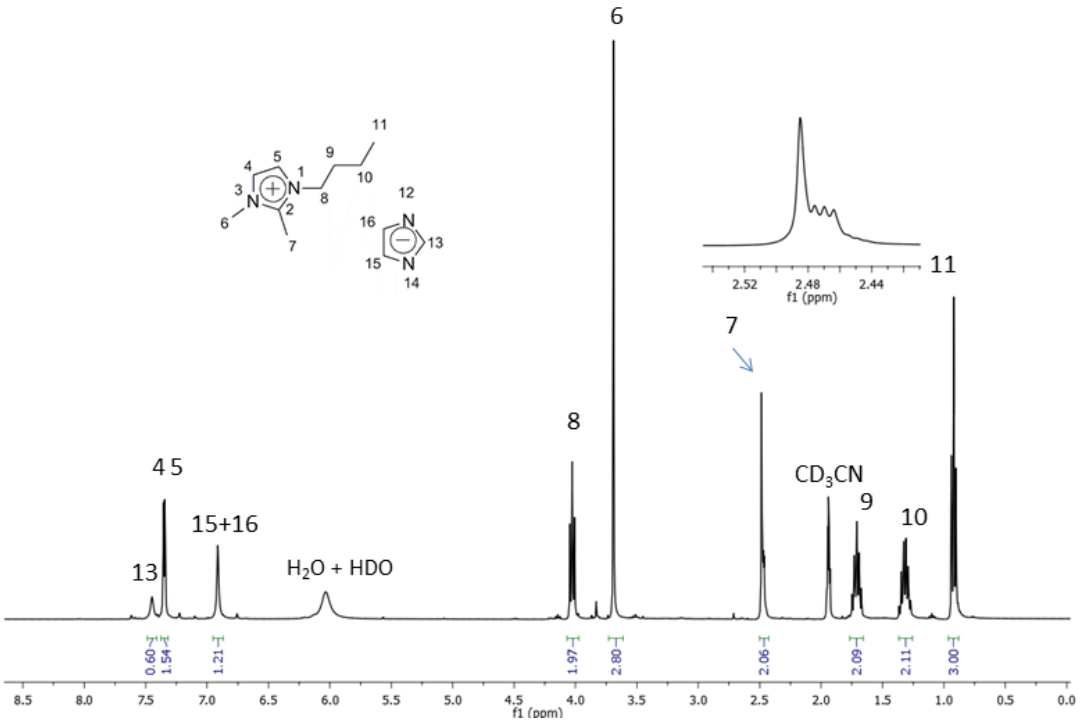

Figure S13. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in CD_3CN (0.2 M) after 1h.

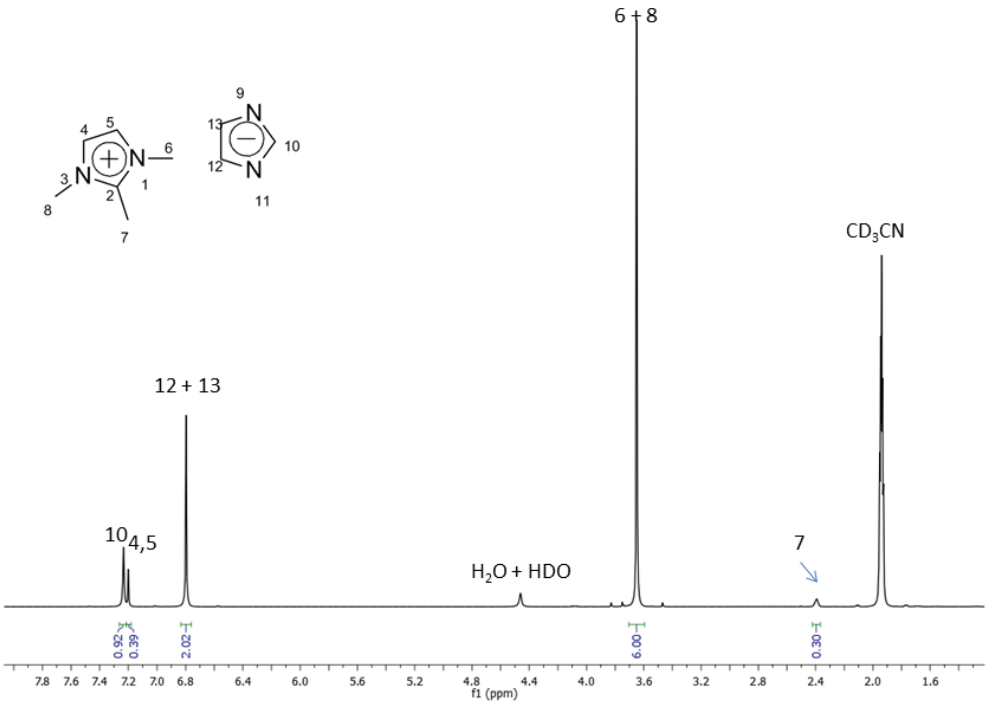

Figure S14. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in CD_3CN (0.2 M) after 1h.

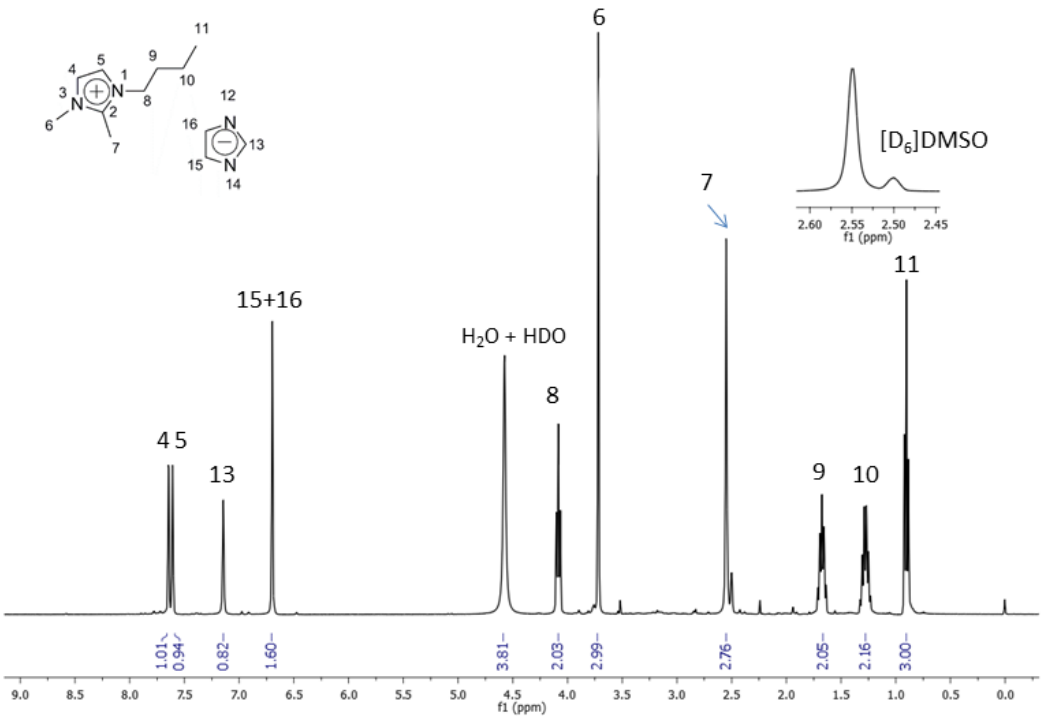

Figure S15. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in [D_6]DMSO (0.2 M) after 1h.

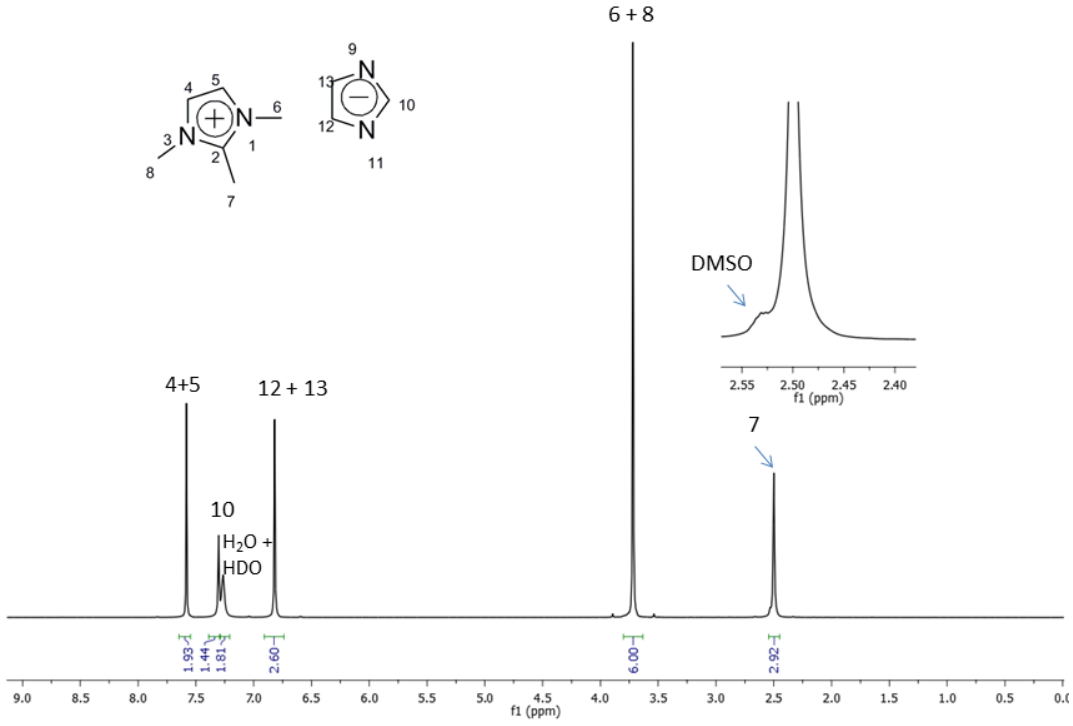

Figure S16. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (0.2 M) after 1h.

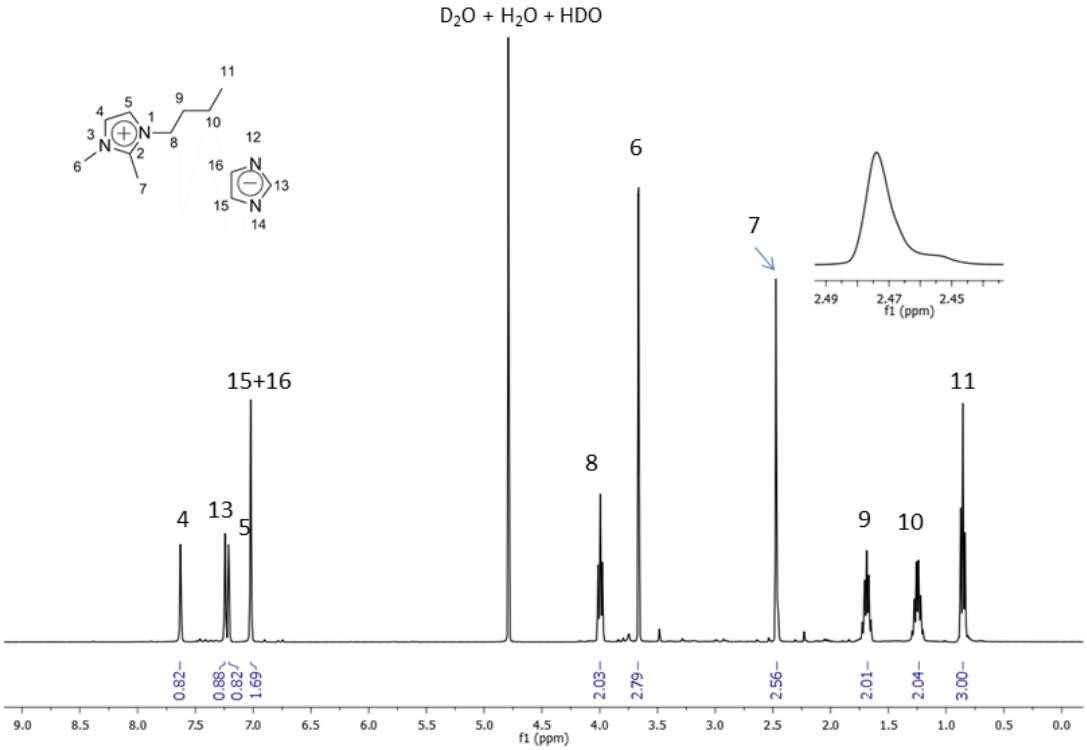

Figure S17. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (0.2 M) after 1h.

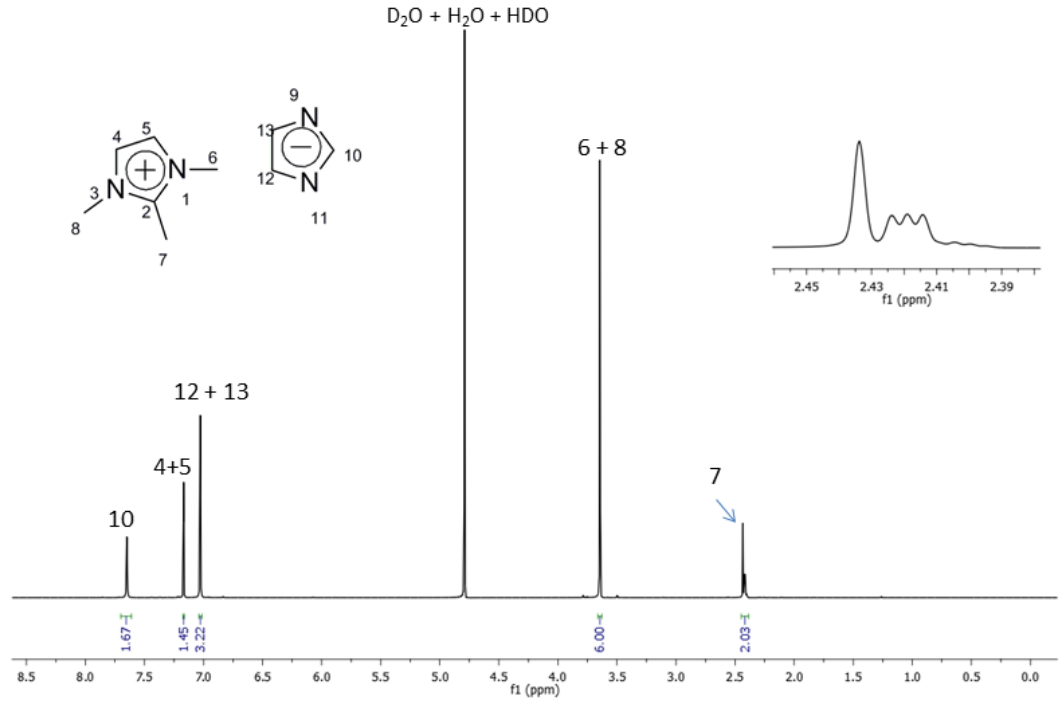

Figure S18. ^{1}H-NMR (400 MHz, 25 °C) spectrum of MMMI·Im in D_2O (0.2 M) after 1h.

2.2. Deuterium transfer test and water confined prove

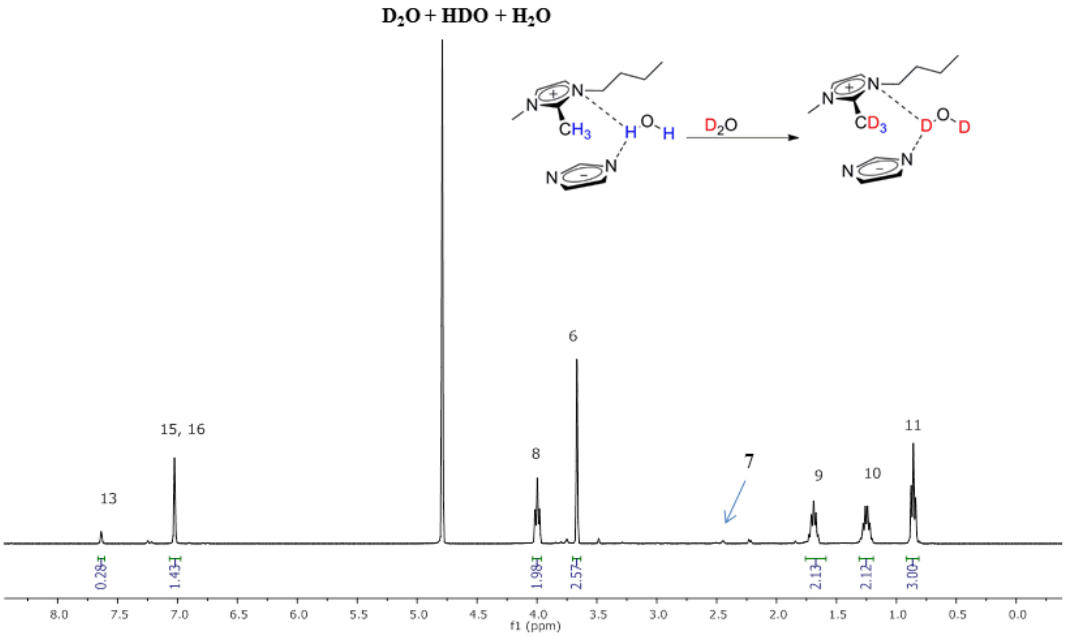

Figure S19. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (2 M) after 2h.

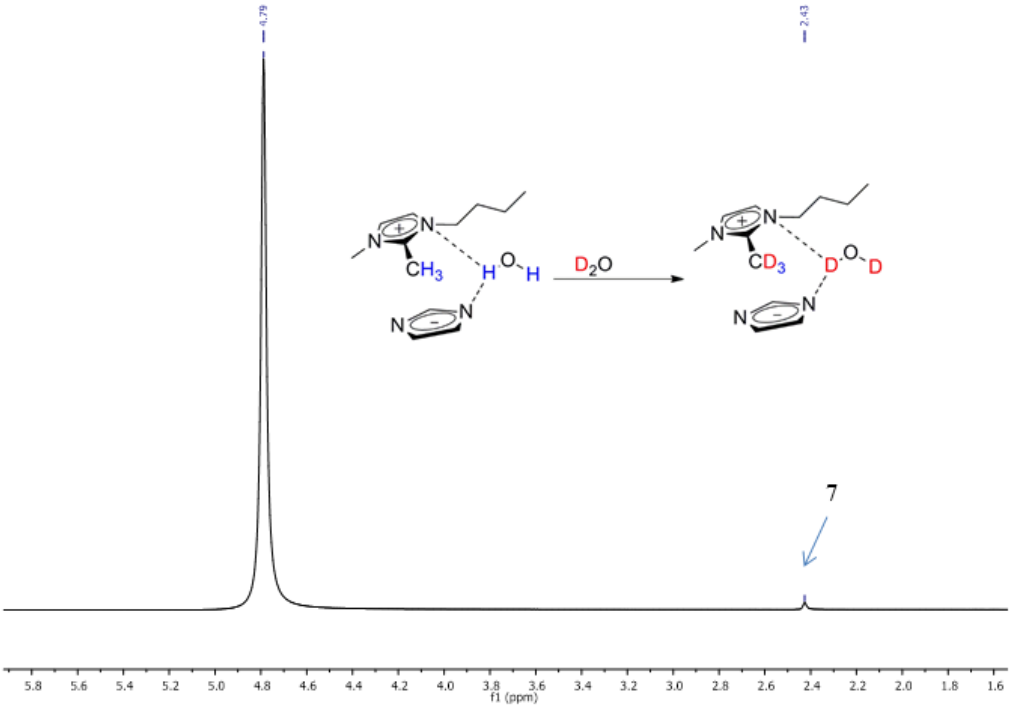

Figure S20. ^{2}H-NMR (61.4 MHz, 25 °C) spectrum of BMMI·Im in D_2O (2 M) after 2h.

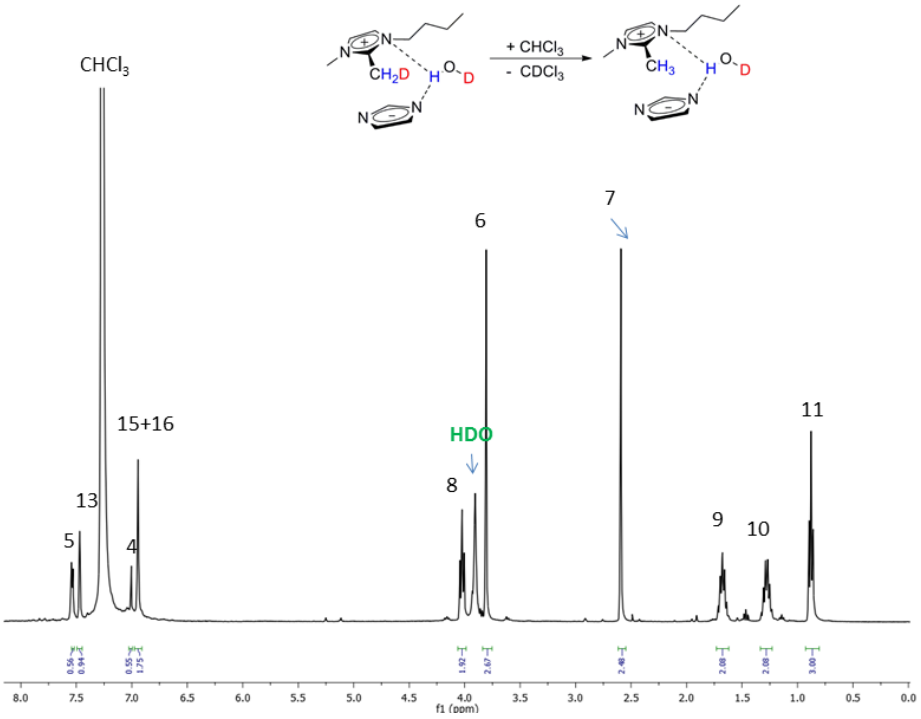

Figure S21. ^{1}H-NMR (400 MHz, 25 °C) spectrum of BMMI·Im in $CHCl_3$ (0.5 M) ([D_6]DMSO capillary).

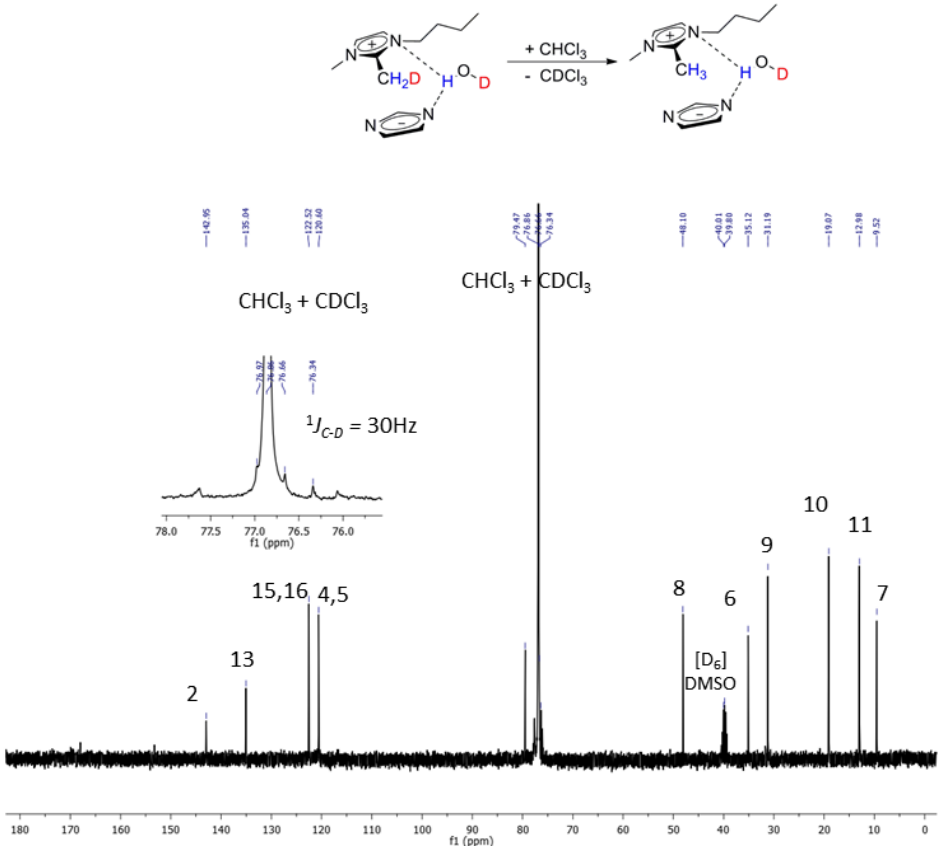

Figure S22. ^{13}C{^{1}H}-NMR (100.6 MHz, 25 °C) spectrum of BMMI·Im in $CHCl_3$ (0.5 M) ([D_6]DMSO capillary).

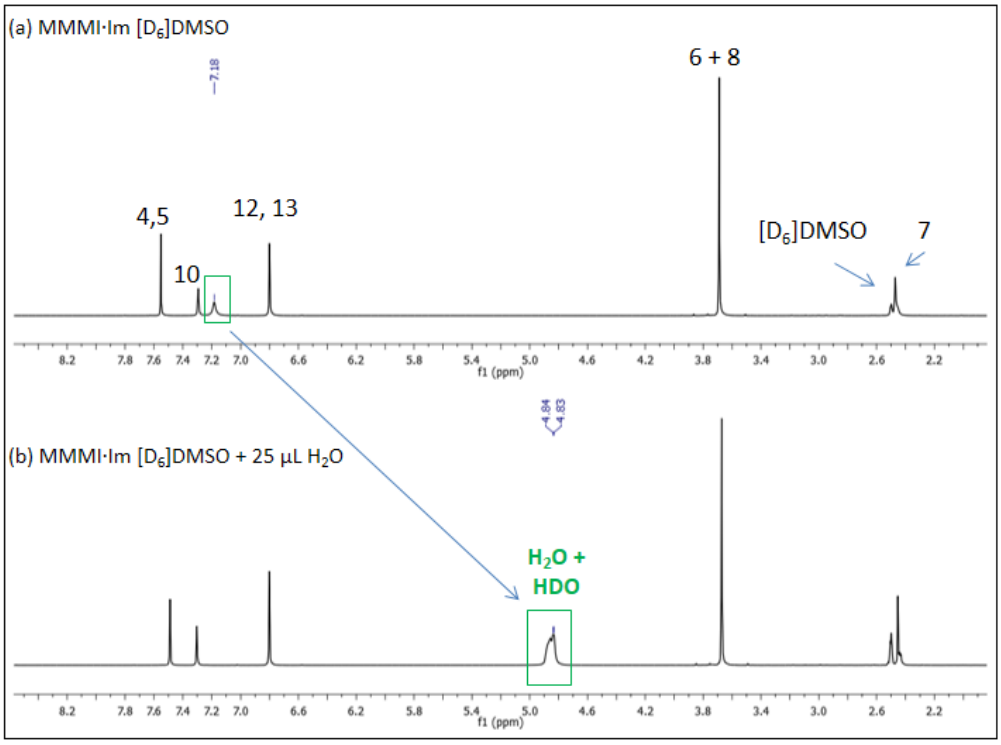

Figure S23. ^{1}H NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) after 72h: without water (***a***), addition of 25 µL H_2O (***b***).

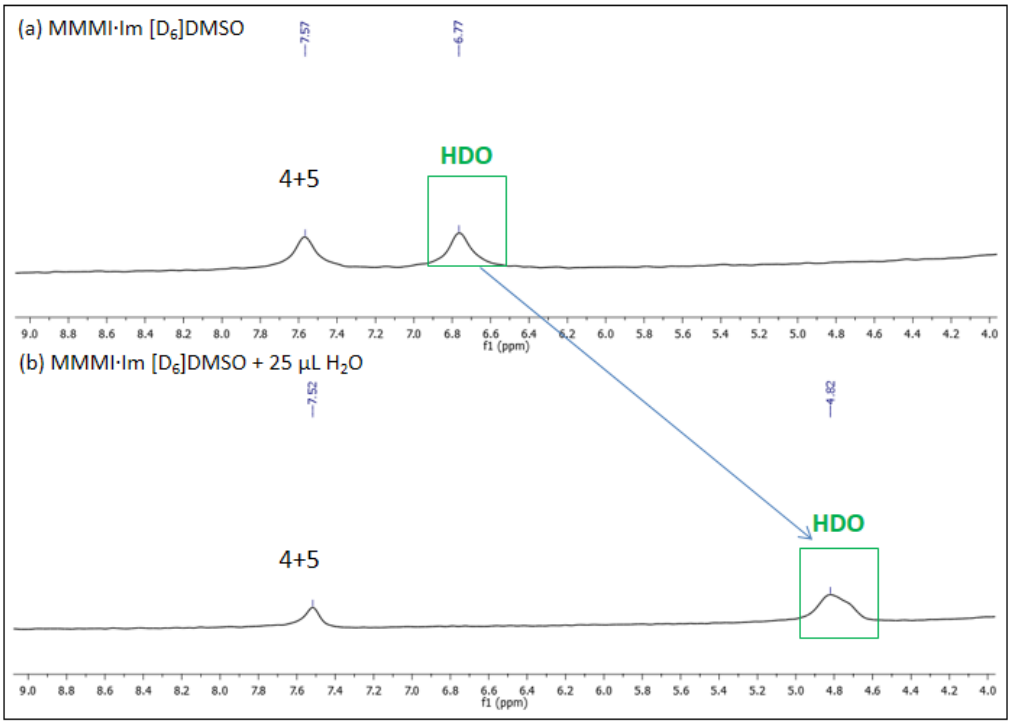

Figure S24. ^{2}H-NMR (61.4 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) after 72h: without water (***a***), addition of 25 µL H_2O (***b***).

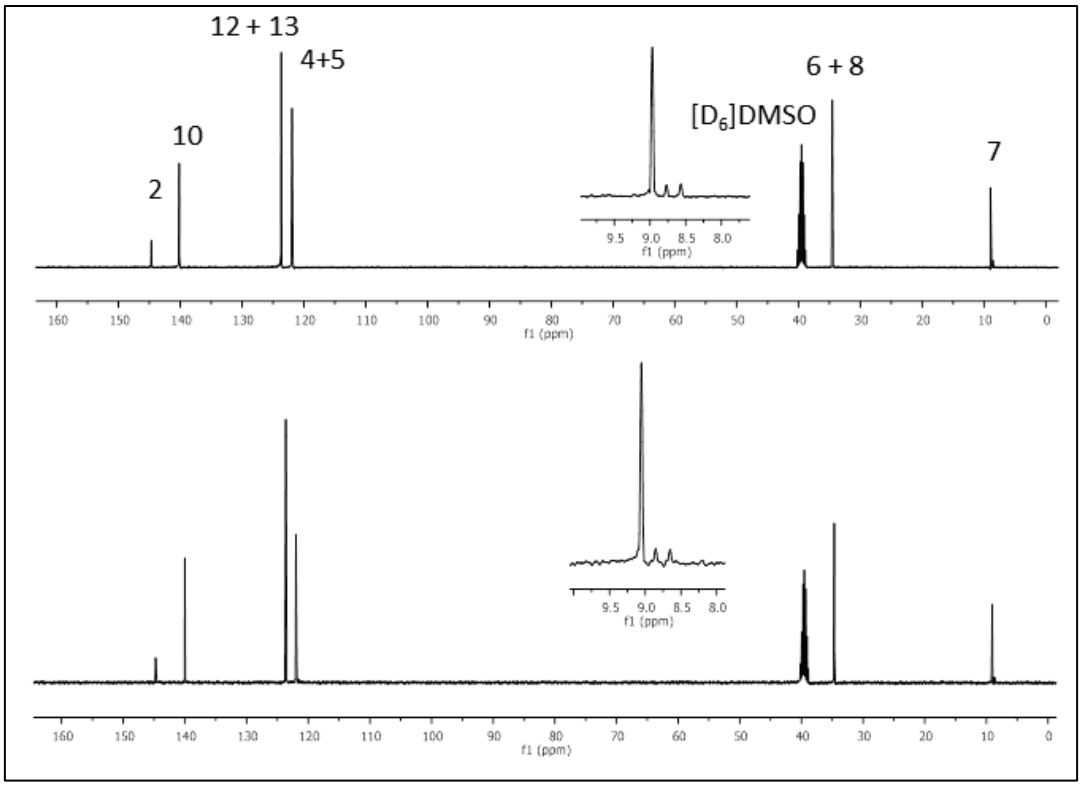

Figure S25. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, 25 °C) spectrum of MMMI·Im in $[D_6]$DMSO (1 M) after 72h: without water (top), addition of 25 µL H_2O (bottom).

2.3. NMR-Spectra ^{1}H-^{1}H NOESY

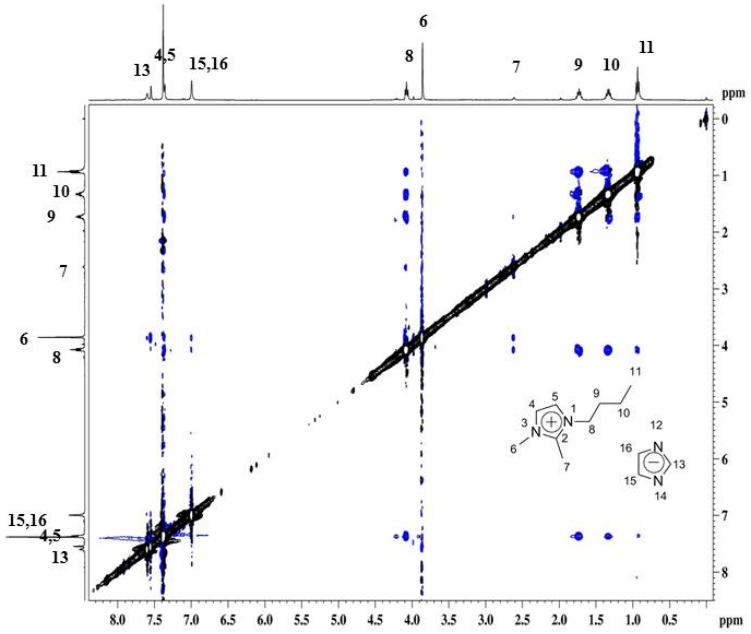

Figure S26. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in $CDCl_3$, (0.2 M) after 1h.

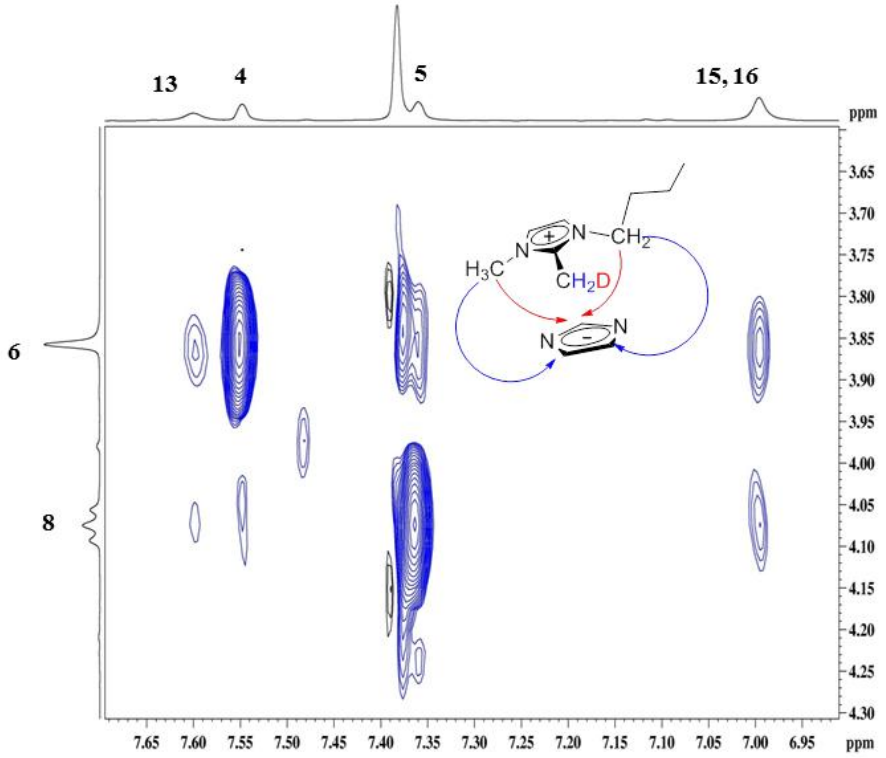

Figure S26.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in $CDCl_3$, (0.2 M) after 1h, expansion of H6 and H8.

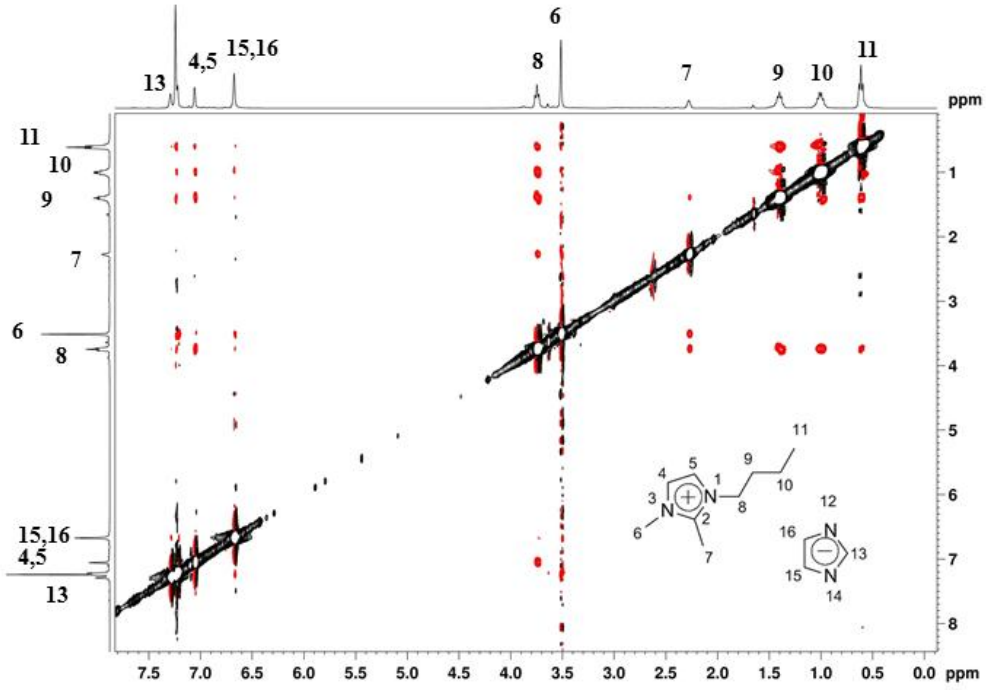

Figure S27. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in $CDCl_3$, (1 M) after 1h.

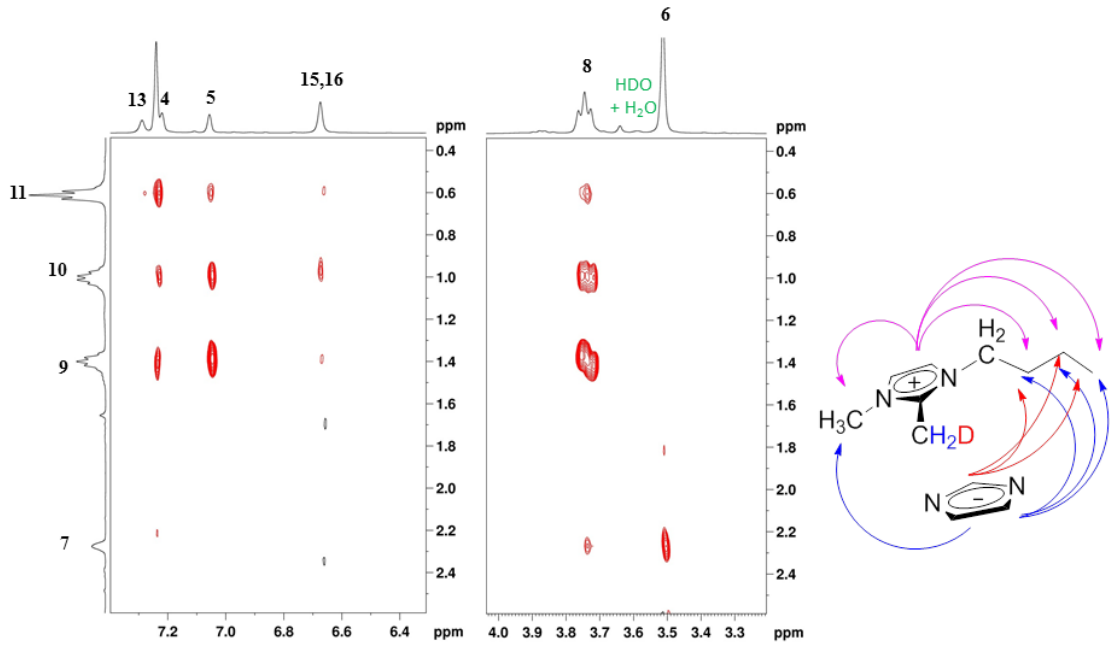

Figure S27.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·m expansion in $CDCl_3$, (1 M) after 1h.

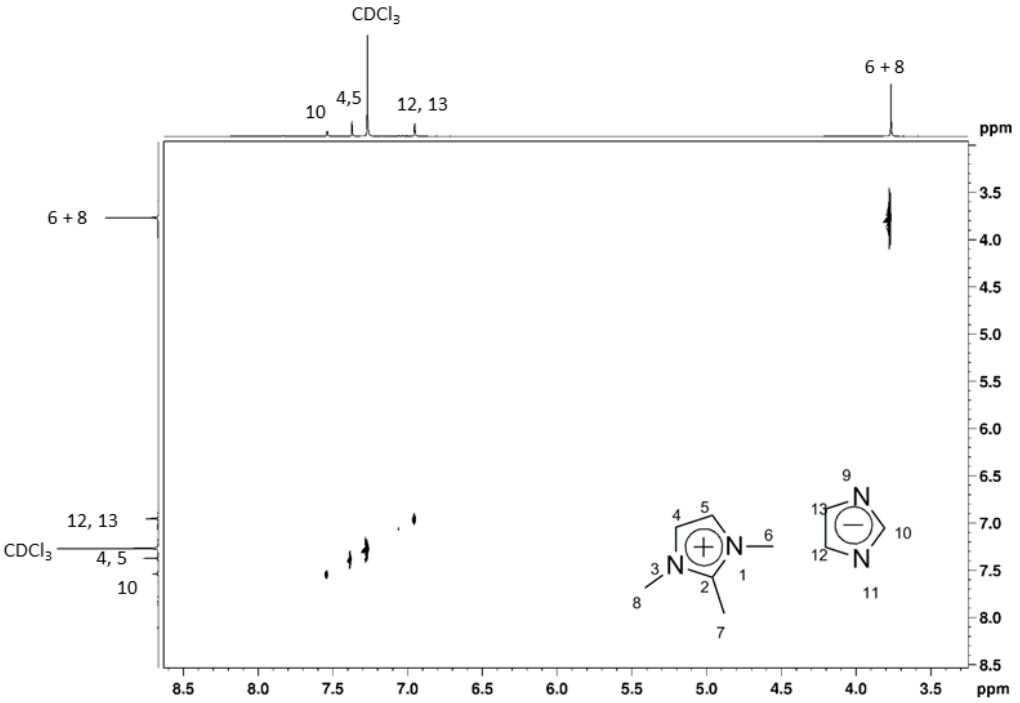

Figure S28. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in $CDCl_3$, (0.2 M) after 1h.

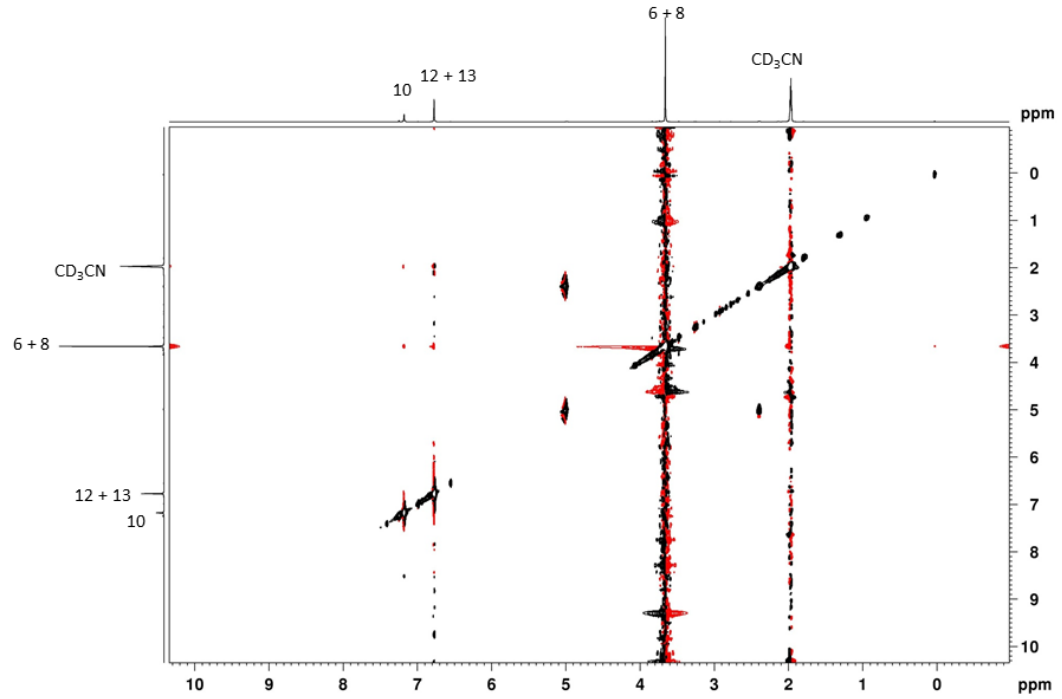

Figure S29. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in CD_3CN (0.2 M) after 1h.

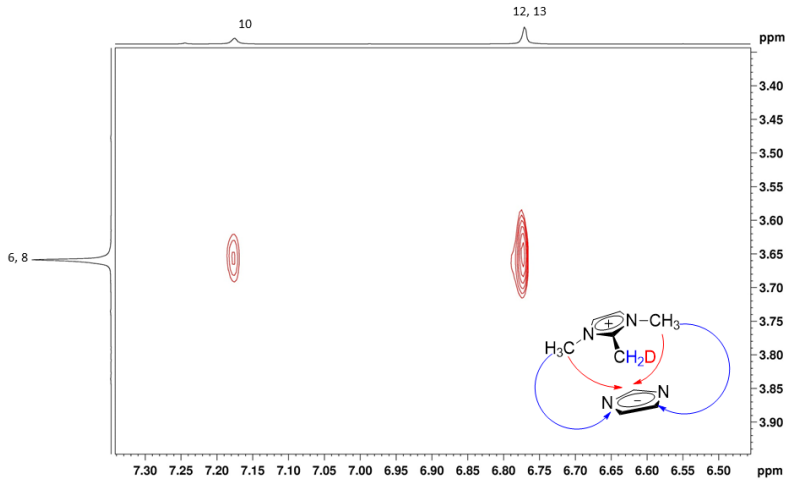

Figure S29.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in CD_3CN (0.2 M) after 1h, expansion of H6/H8.

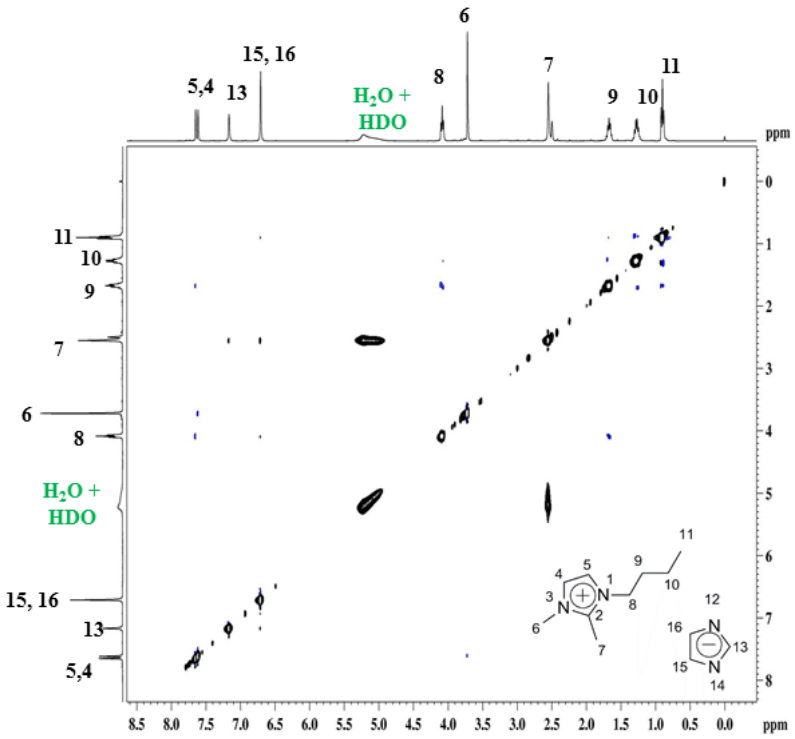

Figure S30. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in [D_6]DMSO (0.2 M) after 1h.

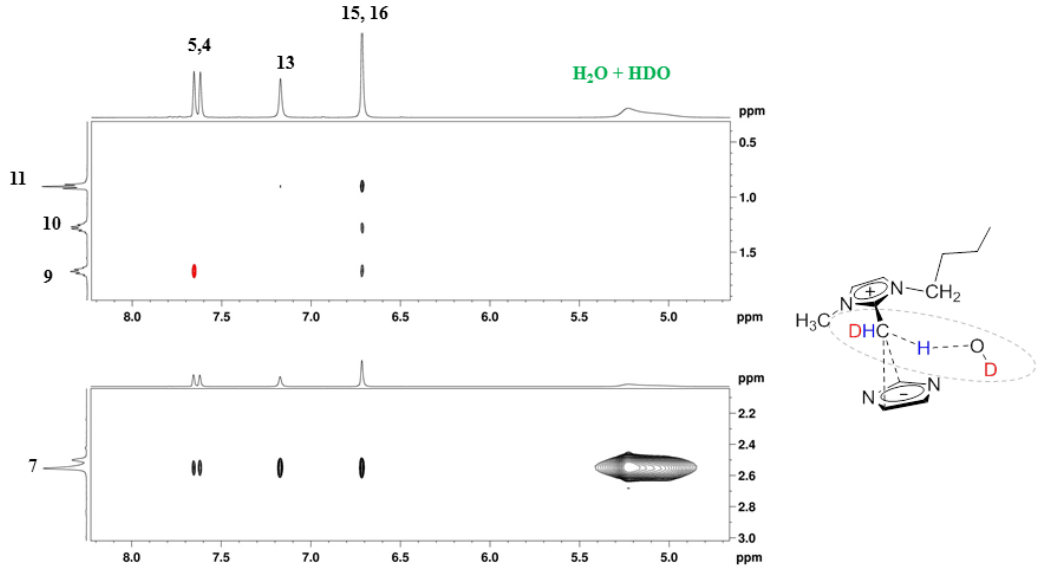

Figure S30.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in [D_6]DMSO (0.2 M) after 1h, expansion (water exchange).

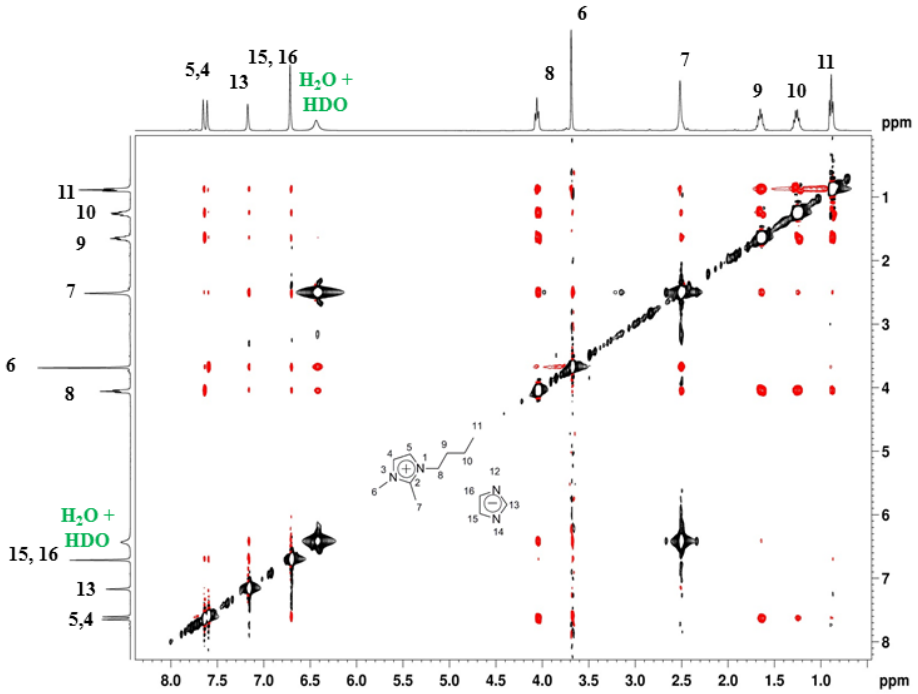

Figure S31. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in [D_6]DMSO (1 M) after 1h.

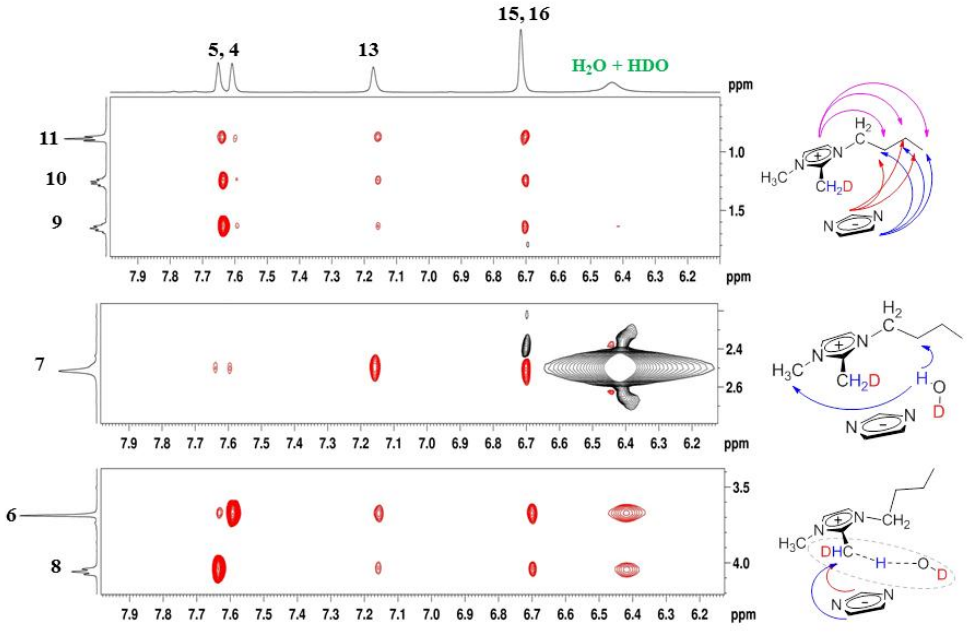

Figure S31.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in [D_6]DMSO (1 M), expansion (water exchange).

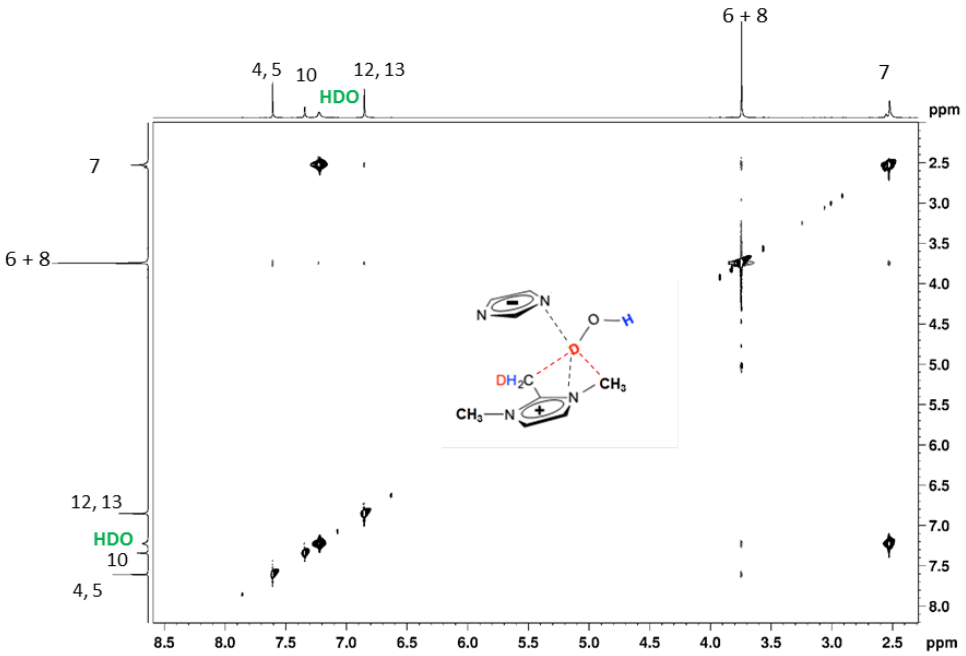

Figure S32. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) after 72h.

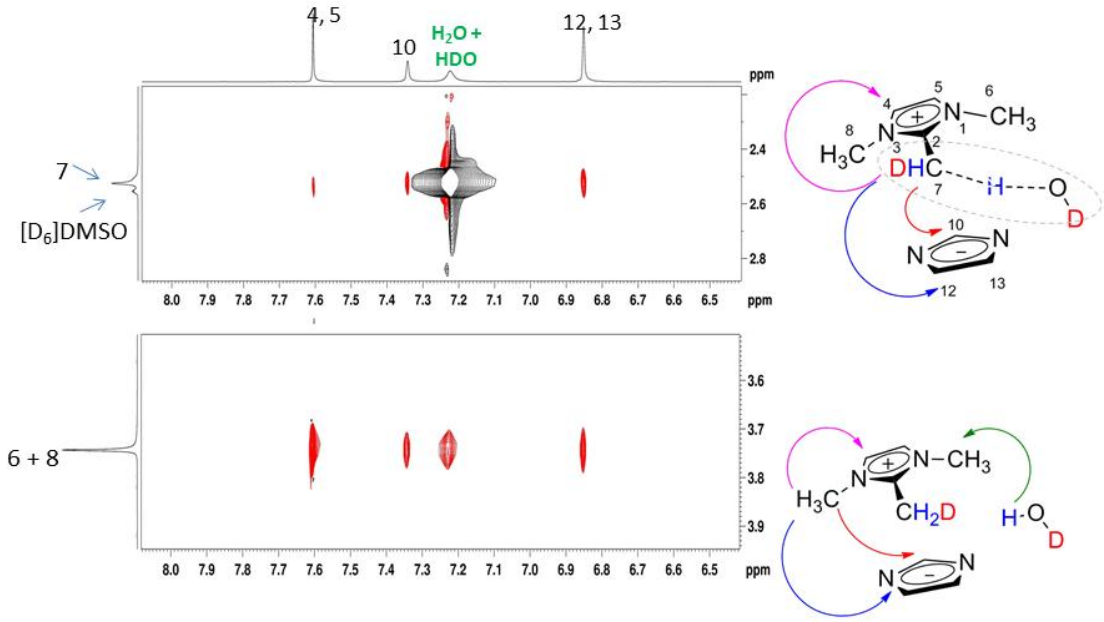

Figure S32.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) after 72h, expansion of H6/H8 and H7 (water exchange).

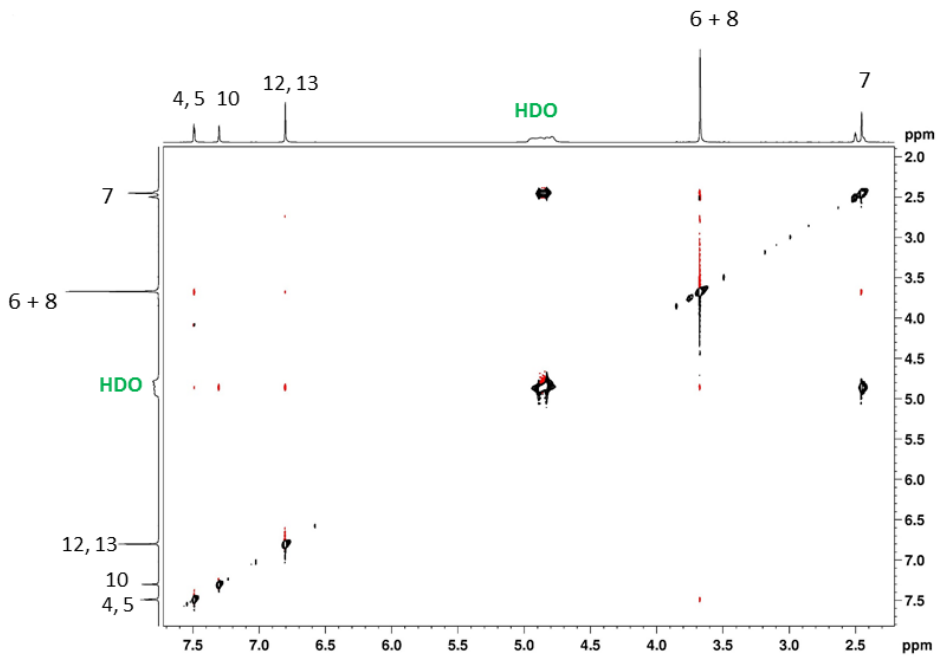

Figure S33. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) and 25 µL H_2O after 72h.

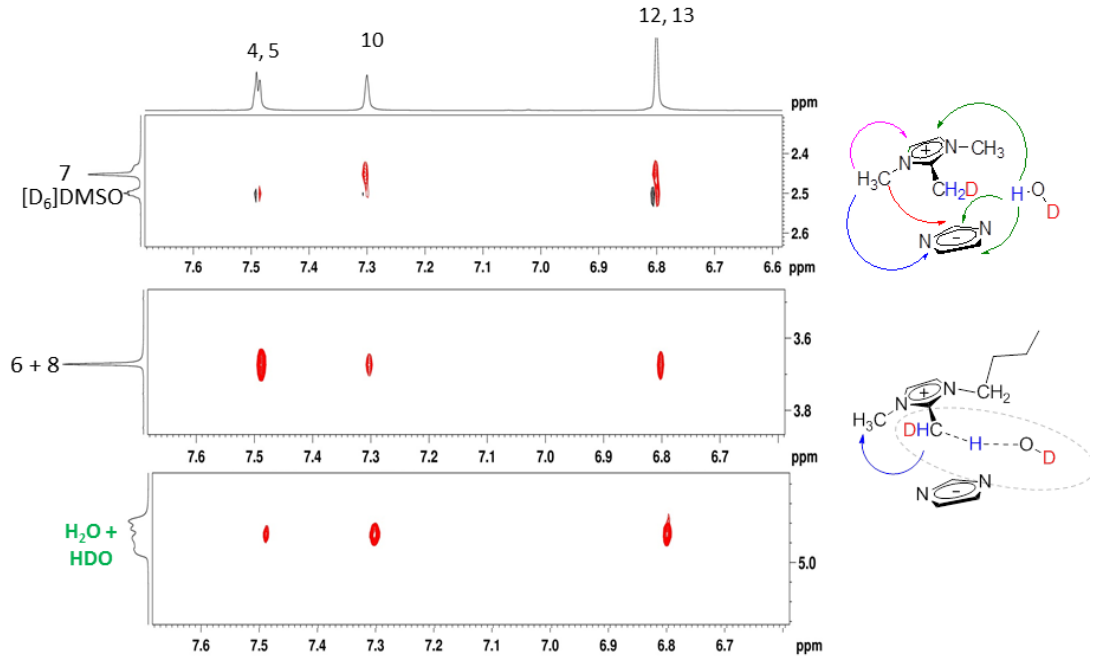

Figure S33. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of MMMI·Im in [D_6]DMSO (1 M) and 25 µL H_2O after 72h, expansion of H6/H8 (water exchange).

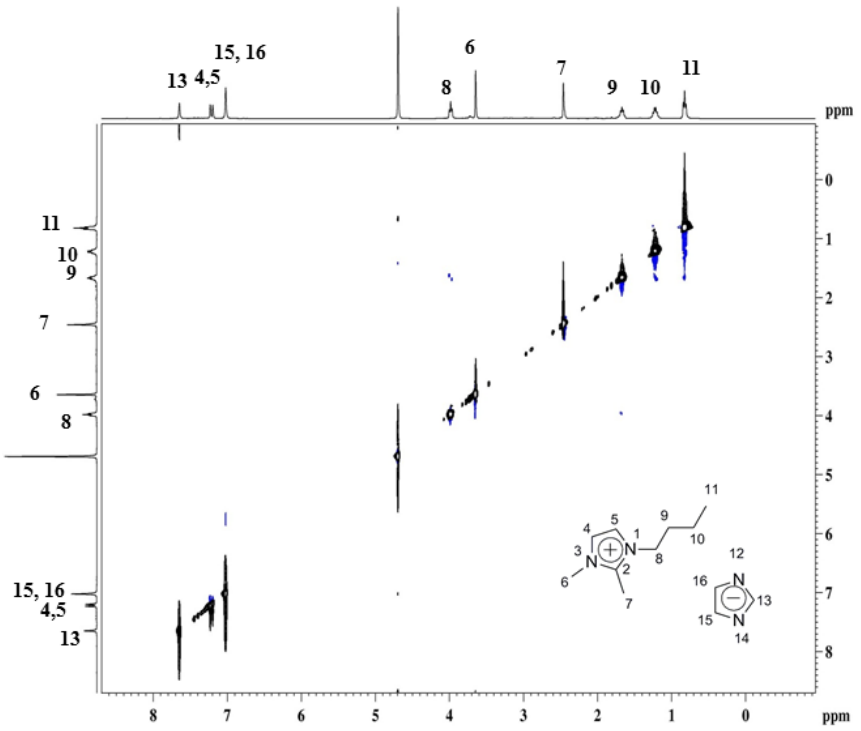

Figure S34. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (0.2 M) after 1h.

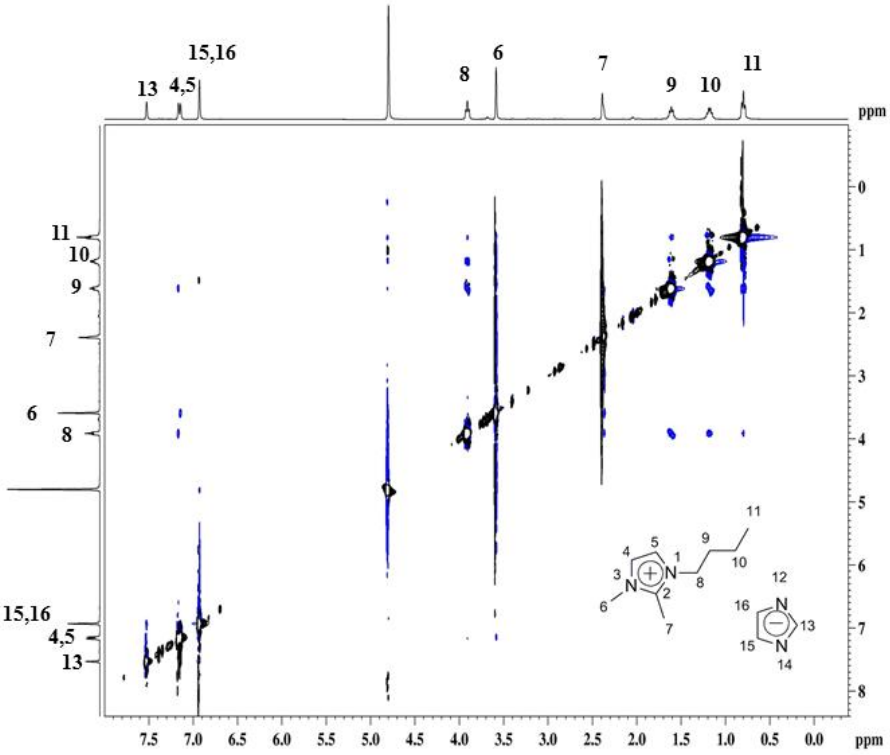

Figure S35. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (1 M) after 1h.

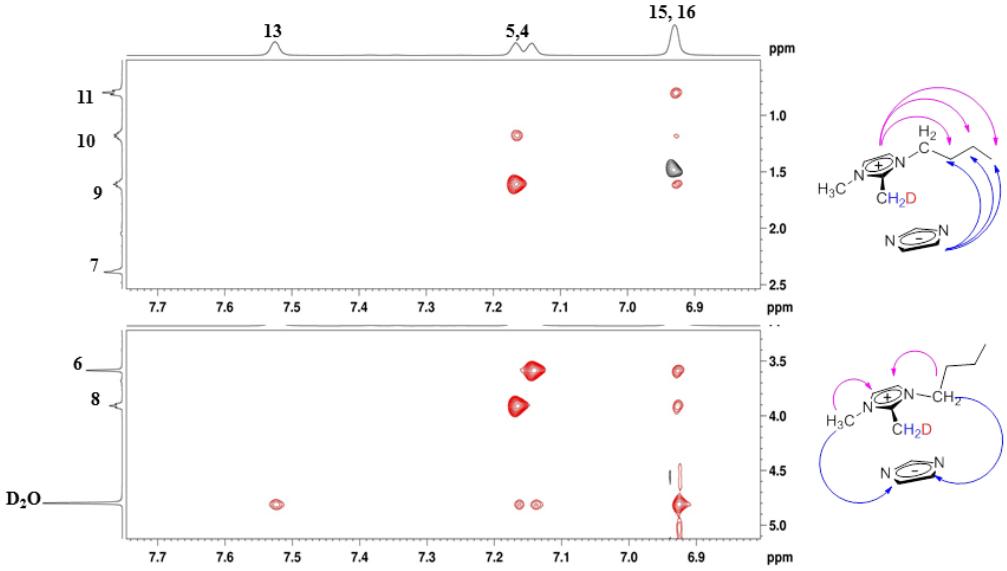

Figure S35.1. ^{1}H-^{1}H NOESY NMR (400 MHz, 25 °C) spectrum of BMMI·Im in D_2O (1 M) after 1h, expansion of H4/H5, H13 and H15/H16.

3. X-Ray Diffraction Analysis for MMMI·Im

Table S1. Crystal data and structure refinement for MMMI·Im

Identification code	OJDULA
Empirical formula	$C_9H_{16}N_4O$
Formula weight	196.26
Temperature/K	120(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.3864(4)
b/Å	12.0203(7)
c/Å	12.5938(7)
α/°	90
β/°	103.725(6)
γ/°	90
Volume/Å^3	1086.24(11)
Z	4
ρ_{calc}g/cm^3	1.200
μ/mm^{-1}	0.669
F(000)	424.0
Crystal size/mm^3	0.9416 × 0.63 × 0.5186
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.316 to 149.746
Index ranges	-9 ≤ h ≤ 6, -14 ≤ k ≤ 12, -14 ≤ l ≤ 15
Reflections collected	4439
Independent reflections	2149 [R_{int} = 0.0296, R_{sigma} = 0.0272]
Data/restraints/parameters	2149/0/136
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.1423
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.1456
Largest diff. peak/hole / e Å^{-3}	0.23/-0.26

4. DFT Calculations

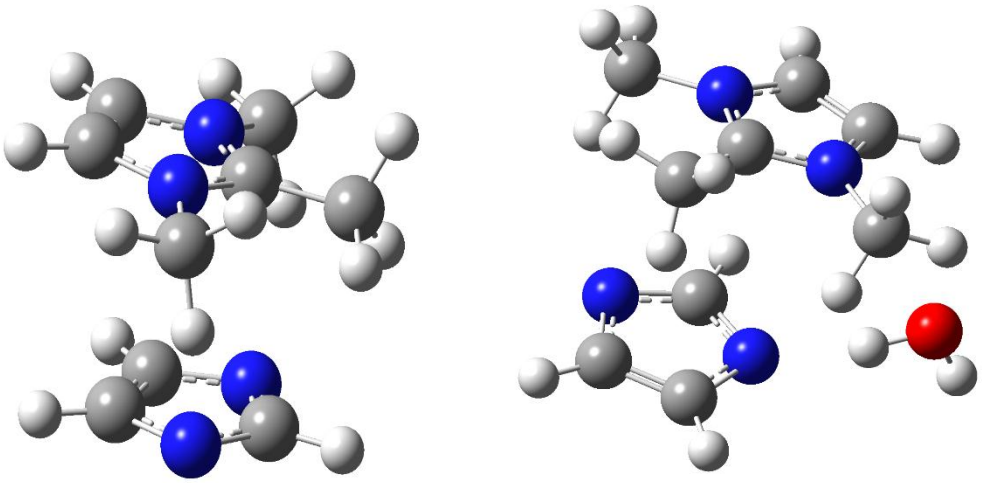

Figure S36. Optimized structure obtained by DFT calculation of the ionic pair of MMMI·Im (left) and the ionic pair MMMI·Im (parallel displaced) with water.

Table S2. Water

	Coordinates (Å)		
Atomic Number	X	Y	Z
1	0.000000	0.759537	-0.466331
8	0.000000	0.000000	0.116583
1	0.000000	-0.759537	-0.466331
Theory Level: wB97XD//spAug-cc-pVTZ Total Molecular Energy: -76.4396415 Ha			

Table S3. 1,2,3-trimethyl-1*H*-imidazol-3-ium

	Coordinates (Å)		
Atomic Number	X	Y	Z
6	0.046597	-0.032631	-0.016606
6	0.025605	-0.034840	1.332487
6	2.138510	-0.100722	0.691906
7	1.366880	-0.072501	-0.397435
1	-0.752772	-0.006147	-0.733679
1	-0.795996	-0.010226	2.024001
7	1.333918	-0.076772	1.756960
6	3.617624	-0.143952	0.690768
1	3.973663	-0.969046	0.074465
1	4.026779	0.781657	0.283984
1	4.005615	-0.276375	1.696218
6	1.764121	-0.097401	3.151890
1	2.288051	-1.025269	3.367611
1	2.407695	0.753667	3.358911
1	0.881984	-0.034974	3.780515
6	1.858717	-0.100127	-1.769684
1	1.019048	0.045221	-2.441204
1	2.579079	0.699708	-1.922605
1	2.323979	-1.060733	-1.979386
Theory Level: wB97XD//spAug-cc-pVTZ Total Molecular Energy: -344.5638538 Ha			

Table S4. Imidazol-1-ide

	Coordinates (Å)		
Atomic Number	X	Y	Z
6	1.969476	-2.897942	0.690783
6	3.970586	-3.288968	1.237980
6	3.867334	-3.302384	-0.140605
7	2.574668	-3.049741	-0.496038
1	0.909697	-2.683183	0.768948
1	4.843035	-3.450942	1.857780
1	4.638045	-3.476776	-0.880200
7	2.745014	-3.027933	1.777101
Theory Level : wB97XD//spAug-cc-pVTZ Total Molecular Energy: -225.6471675 Ha			

Table S5. 1,2,3-trimethyl-1*H*-imidazol-3-ium imidazol-1-ide (MMMI·Im) near anti-parallel displaced conformation

	Coordinates (Angstroms)		
Atomic Number	X	Y	Z
6	0.049079	0.041674	-0.017592
6	0.025972	0.021333	1.330896
6	2.137516	0.016178	0.692845
7	1.368668	0.057967	-0.398715
1	-0.747674	0.040756	-0.736878
1	-0.795417	0.000174	2.021608
7	1.332557	0.024389	1.758960
6	3.608759	-0.019141	0.698760
1	3.949975	-1.028938	0.435368
1	4.007641	0.691844	-0.023338
1	3.996961	0.218864	1.684236
6	1.772666	-0.223388	3.125011
1	2.218826	-1.222791	3.156538
1	2.487890	0.536056	3.432389
1	0.904413	-0.174690	3.775313
6	1.862811	-0.146603	-1.752207
1	1.045627	0.025819	-2.446264
1	2.663251	0.558176	-1.965261
6	1.969408	-2.890887	0.690218
6	3.972885	-3.283797	1.237806
6	3.870645	-3.294580	-0.140080
7	2.578188	-3.033254	-0.494318
1	0.904063	-2.708147	0.769046
1	4.839580	-3.463170	1.856397
1	4.633799	-3.491160	-0.878228
7	2.749286	-3.012874	1.774908
1	2.219578	-1.179143	-1.822553
Theory Level: wB97XD//spAug-cc-pVTZ Total Molecular Energy: -570.3606343 Ha			

Table S6. 1,2,3-trimethyl-1*H*-imidazol-3-ium imidazol-1-ide (MMMI·Im) near parallel displaced conformation

	Coordinates (Å)		
Atomic Number	X	Y	Z
6	0.013099	0.516021	0.075165
6	0.009948	0.404827	1.418873
6	2.025152	-0.126917	0.705532
7	1.274489	0.184686	-0.351206
1	-0.771082	0.765524	-0.613553
1	-0.777736	0.536868	2.135428
7	1.269683	0.008726	1.794756
6	3.463646	-0.463520	0.659776
1	3.652614	-1.131726	-0.176523
1	4.056803	0.447306	0.550776
1	3.757944	-0.981830	1.566517
6	1.661729	-0.390045	3.140017
1	1.757056	-1.480311	3.150485
1	2.594385	0.096582	3.414929
1	0.882647	-0.075123	3.827389
6	1.688539	-0.012087	-1.731147
1	0.884516	0.318053	-2.381432
1	2.582247	0.571246	-1.942023
6	2.222649	-3.284471	0.749519
6	0.368633	-2.866020	-0.176530
6	0.171068	-3.008726	1.180322
7	1.368798	-3.271738	1.780654
1	3.277212	-3.490170	0.883618
1	-0.359030	-2.675426	-0.953403
1	-0.750342	-2.958992	1.742895
7	1.694685	-3.033127	-0.457360
1	1.876750	-1.079070	-1.873265
Theory Level: wB97XD//spAug-cc-pVTZ Total Molecular Energy: -570.3577295 Ha			

Table S7. Hydrated 1,2,3-trimethyl-1H-imidazol-3-ium imidazol-1-ide [MMMI·Im]·[H_2O] near anti-parallel displaced conformation

	Coordinates (Å)		
Atomic Number	X	Y	Z
6	0.140387	-0.549890	-0.122112
6	0.038714	-0.134172	1.157152
6	2.166361	-0.046200	0.589663
7	1.466699	-0.469983	-0.463004
1	-0.589967	-0.943322	-0.802536
1	-0.811209	-0.062289	1.808682
7	1.308009	0.188957	1.582563
6	3.632766	0.089307	0.632151
1	4.075851	-0.909994	0.711985
1	3.999122	0.571567	-0.272784
1	3.945915	0.666060	1.497015
6	1.690574	0.462140	2.960193
1	2.248644	-0.397562	3.340543
1	2.291042	1.367664	3.010665
1	0.784165	0.608986	3.539499
6	2.056523	-0.911038	-1.717064
1	1.289206	-1.417985	-2.291247
1	2.455424	-0.057846	-2.263130
6	2.094435	-2.836887	1.785219
6	4.195486	-2.955739	1.987593
6	3.845547	-3.424234	0.738695
7	2.488333	-3.340032	0.606597
1	1.047814	-2.674410	2.007310
1	5.174366	-2.886794	2.437090
1	4.471487	-3.825327	-0.043850
7	3.069689	-2.566389	2.655618
1	2.838256	-1.633782	-1.495215
8	0.470596	-3.426542	-1.233257
1	0.112161	-4.311148	-1.284947
1	1.236447	-3.490294	-0.596468
Theory Level: wB97XD//spAug-cc-pVTZ Total Molercular Energy: -646.8268967 Ha			

Table S8. Hydrated 1,2,3-trimethyl-1H-imidazol-3-iumimidazol-1-ide [MMMI·Im]·[H_2O] near parallel displaced conformation

	Coordinates (Å)		
Atomic Number	X	Y	Z
6	-2.169168	-1.173654	0.264367
6	-2.323801	-1.536966	1.552840
6	-0.326769	-0.622368	1.343144
7	-0.929675	-0.595789	0.153013
1	-2.812429	-1.300969	-0.585033
1	-3.133416	-2.034470	2.051562
7	-1.170399	-1.186389	2.210019
6	0.998504	-0.060610	1.676112
1	1.599418	0.033898	0.777036
1	0.884584	0.921443	2.140191
1	1.523453	-0.723692	2.364212
6	-0.902773	-1.404434	3.624344
1	0.072234	-1.876796	3.751321
1	-0.934412	-0.455903	4.158108
1	-1.674564	-2.061317	4.013869
6	-0.343054	-0.118346	-1.093054
1	-1.144046	0.000120	-1.816711
1	0.129691	0.846779	-0.930125
6	1.804627	-2.766324	-0.042725
6	0.028122	-3.659450	-0.766787
6	0.113356	-3.890841	0.587761
7	1.256676	-3.310758	1.055514
1	2.747005	-2.235917	-0.008010
1	-0.728005	-3.984820	-1.465652
1	-0.549969	-4.443793	1.235714
7	1.112867	-2.934258	-1.169652
1	0.373555	-0.861183	-1.451199
1	1.778099	-2.977758	2.597775
8	2.006207	-2.595503	3.504605
1	2.700407	-3.145372	3.863742
Theory Level: wB97XD//spAug-cc-pVTZ Total Molecular Energy: -646.8250085 Ha			

Table S9. Bond Lengths in Å.

Entry	Atom	Atom	Crystallographic	Theoretical
1	N1	C2	1.3321(17)	1.3334
2	N1	C5	1.3772(17)	1.3771
3	N1	C6	1.4642(18)	1.4556
4	C2	N3	1.3360(17)	1.3407
5	C2	C7	1.4793(18)	1.4733
6	N3	C4	1.3804(18)	1.3717
7	N3	C8	1.4641(19)	1.4543
8	C4	C5	1.342(2)	1.3489
9	N9	C10	1.343(2)	1.3401
10	N9	C13	1.374(2)	1.3662
11	C10	N11	1.3320(19)	1.3349
12	N11	C12	1.3688(18)	1.3657
13	C12	C13	1.360(2)	1.3790

Table S10. Bond Angles in º.

Entry	Atom	Atom	Atom	Crystallographic	Theoretical
1	C2	N1	C5	109.28(11)	108.78
2	C2	N1	C6	125.48(12)	124.66
3	C5	N1	C6	125.04(12)	125.34
4	N1	C2	N3	107.38(11)	107.83
5	N1	C2	C7	126.97(12)	127.09
6	N3	C2	C7	125.62(13)	124.36
7	C2	N3	C4	109.25(11)	109.25
8	C2	N3	C8	125.03(12)	124.36
9	C4	N3	C8	125.72(12)	125.45
10	C5	C4	N3	106.84(12)	106.89
11	C4	C5	N1	107.24(12)	107.21
12	C10	N9	C13	102.69(12)	103.30
13	N11	C10	N9	115.73(13)	115.76
14	C10	N11	C12	103.08(12)	103.03
15	C13	C12	N11	109.36(13)	109.31
16	C12	C13	N9	109.15(13)	108.58

Table S11. Torsion Angles (degree)

				Crystallographic	Theoretical
A	B	C	D	Angles (°)	
N1	C2	N3	C4	-0.62(14)	-0.26
N1	C2	N3	C8	178.66(12)	-175.92
C2	N1	C5	C4	0.29(15)	-0.98
C2	N3	C4	C5	0.80(15)	1.42
N3	C4	C5	N1	-0.65(15)	-0.26
C5	N1	C2	N3	0.21(14)	1.87
C5	N1	C2	C7	-177.90(13)	-176.41
C6	N1	C2	N3	-174.90(12)	169.84
C6	N1	C2	C7	7.0(2)	-0.34
C6	N1	C5	C4	175.43(13)	-168.54
C7	C2	N3	C4	177.52(13)	176.28
C7	C2	N3	C8	-3.2(2)	2.40
C8	N3	C4	C5	-178.47(13)	175.17
N9	C10	N11	C12	-0.15(16)	-1.28
C10	N9	C13	C12	-0.15(16)	-0.50
C10	N11	C12	C13	0.05(16)	0.86
N11	C12	C13	N9	0.07(17)	-0.24
C13	N9	C10	N11	0.07(17)	1.15

5. Molecular Dynamics Simulations

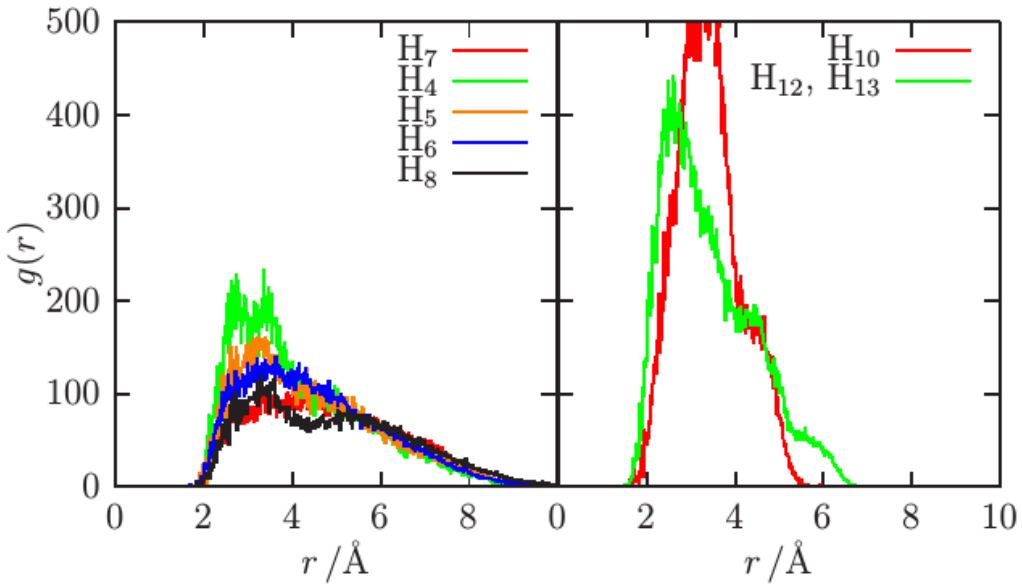

Figure S37. Radial distribution functions for distances between the water protons and the hydrogens of the cation (left panel) and the anion (right panel) for the BMMI system.

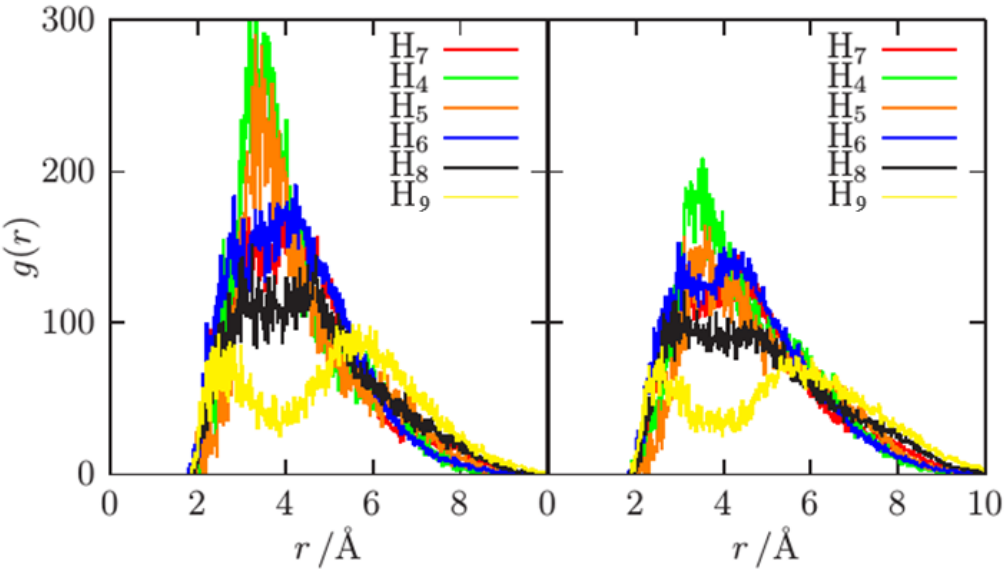

Figure S38. Radial distribution functions for distances between the cation's hydrogens and the anion's H10 (left panel) and the anion's H12 and H13 (right panel) in the BMMI system.