Supporting Information

Hydroxometalates from Anion Exchange Reaction of $[BF_4]^-$ based Ionic Liquids: Formation of $[M(OH)_6]^{2-}$ (M = Ti, Zr) and $[Zr(OH)_5]^-$

Hechun Lin,[1] Peter W. de Oliveira,[1] Volker Huch,[2] Michael Veith,[1,2*]*

[1]Leibniz Institute for New Materials, Campus D2 2, 66123 Saarbruecken, Germany

[2]Institute of Inorganic Chemistry, Saarland University, 66041 Saarbruecken, Germany

Contents

Experimental

1-Butyl-3-methyl-imidazolium chloride ([BMIM][Cl]). ^{1}H NMR (300 Hz, $CDCl_3$): δ = 0.81 (t, *J* = 7.2 Hz, 3H), 1.23 (m, 2H), 1.75 (m, 2H), 3.98 (s, 3H), 4.19 (t, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.62 (d, *J* = 1.5 Hz, 1H), 10.46 (s, 1H). ^{13}C NMR (300 Hz, $CDCl_3$): δ = 13.3, 19.3, 32.0, 36.3, 49.6, 122.0, 123.7, 137.6.

1-Butyl-3-methyl-imidazolium tetrafluroborate ([BMIM][BF_4]). ^{1}H NMR (300 Hz, CD_3CN): δ = 0.93 (t, *J* = 7.2 Hz, 3H), 1.31 (m, 2H), 1.80 (m, 2H), 3.83 (s, 3H), 4.13 (t, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 8.47 (s, 1H). ^{13}C NMR (300 Hz, CD_3CN): δ = 12.6, 18.9, 31.5, 35.7, 49.2, 122.2, 123.6, 136.0. ^{19}F NMR (300 Hz, CD_3CN): δ = -151.2.

Di(1-butyl-3-methyl-imidazolium) hexahydroxotitanate ($[BMIM]_2[Ti(OH)_6]$). 2.84 g $Ti(O^iPr)_4$ (10 mmol) was added dropwise to the solution of [BMIM][BF_4] (4.52 g, 20 mmol) and ethanol (11.4 g) under magnetic stirring at room temperature in an open flask (Relative Humidity: ~ 45%). After stirring for 1 hour at room temperature to obtain a turbid solution, the temperature was raised up to reflux, and the precipitates were solved to obtain a clear liquid. We continued stirring for 4 hours and distilled off the low boiling component to give rise to a clear liquid. The liquid was solved in CH_3CN and EtOAc under reflux, filtered and kept in a fridge to grow crystal (-10^{o}C). After several days, the product was collected via filter and washed with EtOAc/CH_3CN (1:1) to give rise to 1.55 g $[BMIM]_2[Ti(OH)_6]$ in 37% yield. Colorless needle-like crystal, Mp: 176-177^{o}C. IR: 525, 618, 775, 867, 1165, 1455, 2960, 3100 (cm^{-1}). ^{1}H NMR (300 Hz, CD_3CN): δ = 0.91 (t, *J* = 7.2 Hz, 6H), 1.29 (m, 4H), 1.79 (m, 4H), 2.45 (br, OH), 3.87 (s, 6H), 4.18 (t, *J* = 7.2 Hz, 4H), 7.34-7.39 (m, 4H), 9.18 (s, 2H). ^{13}C NMR (300 Hz, CD_3CN): δ = 12.7, 19.0, 31.7, 35.6, 49.0, 121.8, 123.4, 137.6. Anal. calcd for

$C_{16}H_{36}N_4O_6Ti \cdot H_2O$: C, 43.05; H, 8.58; N, 12.55; Found: C, 42.99, H: 6.75; N, 12.50. The product has been identified with single crystal X-ray diffraction.

Di(1-octyl-3-methyl-imidazolium) hexahydroxotitanate ($[OMIM]_2[Ti(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$. White solid, 4.50 g (83%); Mp: 69-72°C. IR: 548, 766, 865, 1165, 1460, 1565, 2925, 3105 (cm^{-1}). ^1H NMR (300 Hz, CD_3CN): δ = 0.86 (t, *J* = 6.6 Hz, 6H), 1.15-1.38 (m, 20H), 1.79 (t, *J* = 6.9 Hz, 4H), 3.29 (br, OH), 3.88 (s, 6H), 4.18 (t, *J* = 7.2 Hz, 4H), 7.36 (d, *J* = 1.8 Hz, 2H), 7.39 (d, *J* = 1.8 Hz, 2H), 9.26 (s, 2H). ^{13}C NMR (300 Hz, CD_3CN): δ = 13.4, 22.4, 25.8, 28.8, 28.9, 29.9, 31.5, 35.6, 49.2, 121.7, 123.3, 138.0. Anal. Calcd for $C_{24}H_{52}N_4O_6Ti \cdot H_2O$: C, 51.61; H, 9.74; N, 10.03; Ti, 8.57; Found: C, 51.28; H, 10.07; N, 10.07; Ti, 8.53 ± 0.12 (ICP).

Di(1-dodecyl-3-methyl-imidazolium) hexahydroxotitanate ($[DodMIM]_2[Ti(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$. White solid, 5.24 g (82%); Mp: 132-134°C. IR: 550, 768, 876, 1166, 1460, 1566, 2860, 2920, 3110 (cm^{-1}). ^1H NMR (300 Hz, CD_3CN): δ = 8.8 (t, *J* = 7.2 Hz, 6H), 1.17-1-38 (m, 36H), 1.79 (m, 4H), 2.58 (br, OH), 3.88 (s, 6H), 4.17 (t, *J* = 7.2 Hz, 4H), 7.32-7.37 (m, 4H), 9.12 (s, 2H). ^{13}C NMR (300 Hz, CD_3CN): δ = 13.4, 22.4, 25.8, 28.8, 29.08, 29.2, 29.29, 29.36, 29.37, 29.8, 31.6, 35.7, 49.3, 121.8, 123.3, 137.6. Anal. Calcd for $C_{32}H_{68}N_4O_6Ti \cdot HBF_4 \cdot H_2O$: C, 50.66; H, 9.43; N, 7.39; Found: C, 50.44; H, 8.47; N, 7.33.

Di(1-butyl-3-vinyl-imidazolium) hexahydroxotitanate ($[BVIM]_2[Ti(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$. The product was crystallized from EtOH/CH_3CN/EtOAc. White solid, 1.89 g (43%); Mp: 247-249°C. IR: 528, 600, 779, 859, 9176, 967, 1167, 1270, 1367, 1458, 1557, 1655, 2947, 3095 (cm^{-1}). ^1H NMR (300 Hz, D_2O):

δ = 0.78 (t, *J* = 7.2 Hz, 6H), 1.18 (m, 4H), 1.72 (m, 4H), 4.11 (t, *J* = 7.2Hz, 4H), 5.28 (dd, *J* = 2.7, 8.7 Hz, 2H), 5.66 (dd, *J* = 2.7, 15.6 Hz, 2H), 7.01 (dd, *J* = 8.7, 15.6 Hz, 2H), 7.44 (d, *J* = 1.5 Hz, 2H), 7.64 (d, *J* = 1.8 Hz, 2H), 8.91 (s, 2H). ^{13}C NMR (300 Hz, D_2O): δ = 12.5, 18.7, 31.0, 49.6, 109.0, 119.3, 122.8, 128.2, 134.3. Anal. Calcd for $C_{18}H_{36}N_4O_6Ti{\cdot}H_2O$: C, 45.96; H, 8.14; N, 11.91; Ti, 10.18; Found: C, 46.69; H, 7.06; N, 12.08; Ti, 9.87 ± 0.15 (ICP). The product has been identified with single crystal X-ray diffraction.

Di(1-(2-hydroxylethyl)-3-methyl-imidazolium)hexahydroxotitanate ($[HOEtMIM]_2[Ti(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$. The product was crystallized from acetone/EtOH to give rise to 2.29 g white solid (57%). Mp: 125-127^{o}C. IR: 517, 608, 774, 842, 1160, 1260, 1440, 1567, 2940, 3110, 3340 (cm^{-1}). ^{1}H NMR (300 Hz, D_2O): δ = 3.77 (s, 6H), 3.79 (t, *J* = 5.1 Hz, 4H), 4.19 (t, *J* = 5.1 Hz, 4H), 7.32 (d, *J* = 1.5 Hz, 2H), 7.38 (d, *J* = 1.5 Hz, 2H), 8.62 (s, 2H). ^{13}C NMR (300 Hz, D_2O): δ = 35.6, 51.4, 59.8, 122.4, 123.6, 136.4. Anal. Calcd for $C_{12}H_{28}N_4O_8Ti{\cdot}H_2O$: C, 34.13; H, 7.16; N, 13.27; Found: C, 34.48; H, 5.31; N, 13.46. The product has been identified with single crystal X-ray diffraction.

Di(1-butyl-pyridium) hexahydroxotitanate ($[BPM]_2[Ti(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$. White solid, 1.88 g (45%); Mp: 201-203 ^{o}C. IR: 542, 704, 990, 1470, 1657, 2915, 3065 (cm^{-1}). ^{1}H NMR (300 Hz, d^6-DMSO): δ = 0.89 (t, *J* = 7.2 Hz, 6H), 1.25 (m, 4H), 1.87 (m, 4H), 4.62 (t, *J* = 7.5 Hz, 4H), 8.14 (dd, *J* = 6.6, 7.5 Hz, 4H), 8.59 (d, *J* = 7.8 Hz, 2H), 9.16 (d, *J* = 5.4 Hz, 4H). ^{13}C NMR (300 Hz, d^6-DMSO): δ = 13.8, 19.2, 33.2, 60.9, 128.5, 145.4, 145.8. Anal. Calcd for $C_{18}H_{34}N_2O_6Ti{\cdot}H_2O$: C, 49.10; H, 8.24; N, 6.36; Found: C, 49.46; H, 6.35; N, 6.43. The product has been identified with single crystal X-ray diffraction.

Di(1-octyl-pyridium) hexahydroxotitanate ([OPM]$_2$[Ti(OH)$_6$]). The procedure was used as for [BMIM]$_2$[Ti(OH)$_6$]. White solid, 3.05 g (57%). There is no exact melting point; however the compound was decomposed above 193^{o}C. IR: 517, 878, 1470, 1651, 2928, 3084 (cm^{-1}). ^{1}H NMR (300 Hz, d^6-DMSO): δ = 0.82 (t, *J* = 6.9 Hz, 6H), 1.21 (m, 20H), 1.87 (m, 4H), 4.63 (t, *J* = 7.2 Hz, 4H), 8.15 (dd, *J* = 7.2, 6.3 Hz, 4H), 8.59 (t, *J* = 7.2 Hz, 2H), 9.20 (d, *J* = 5.7 Hz, 4H). ^{13}C NMR (300 Hz, d^6-DMSO): δ = 14.4, 22.5, 25.8, 28.88, 28.93, 31.3, 31.6, 61.1, 128.6, 145.5, 1445.7. Anal. Calcd for $C_{26}H_{50}N_2O_6Ti\cdot H_2O$: C, 56.51; H, 9.49; N, 5.07; Ti, 8.66; Found: C, 55.75; H, 10.84; N, 4.95; Ti, 7.84 ± 0.12 (ICP).

Poly-(1-ethyl-3-methyl-imidazolium) Poly-(pentahydroxozirconate) ([EMIM]$_\infty${[Zr(OH)$_5$]})$_\infty$. The procedure was used as for [BMIM]$_2$[Ti(OH)$_6$], except that 1.98 g [EMIM][BF$_4$] (10 mmol), 2.34 g Zr(OPr)$_4$ (5 mmol, 70% in PrOH) and 5.75 g EtOH were used. The product was crystallized from DMSO/EtOH. White solid, 1.1 g (76%); Mp: 252-253^{o}C. IR: 497, 765, 1152, 3133 (cm^{-1}). ^{1}H NMR (300 Hz, d^6-DMSO): δ = 1.39 (t, *J* = 7.2 Hz, 3H), 3.83 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 9.10 (s, 1H). ^{13}C NMR (300 Hz, d^6-DMSO): δ = 15.6, 36.1, 44.5, 122.4, 124.0, 136.7. Anal. Calcd for $C_6H_{16}N_2O_5Zr\cdot H_2O$: C, 23.59; H, 5.94; N, 9.17; Found: C, 23.15; H, 4.09; N, 9.05. The product has been identified with single crystal X-ray diffraction.

Poly-(1-butyl-3-methyl-imidazolium) Poly-(pentahydroxozirconate) ([BMIM]$_\infty${[Zr(OH)$_5$]})$_\infty$. The procedure was used as for [BMIM]$_2$[Ti(OH)$_6$], except that 4.68 g Zr(OPr)$_4$ (10.0 mmol, 70% in PrOH) was used. The product was crystallized from DMSO/EtOH. White solid, 2.03 g (91%); Mp: 181-183^{o}C. IR: 498, 853, 1159, 2953, 3127 (cm^{-1}). ^{1}H NMR (300 Hz, d^6-DMSO): δ = 0.88 (t, *J* = 7.2 Hz, 3H), 1.23 (m, 2H), 1.73 (m, 2H), 3.83 (s, 3H), 4.14 (t, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 9.10 (s, 1H). ^{13}C NMR (300 Hz, d^6-DMSO): δ = 13.7, 19.2, 31.8, 48.9, 122.7, 124.1, 137.0.

Anal. Calcd for $C_8H_{20}N_2O_5Zr \cdot H_2O$: C, 28.81; H, 6.65; N, 8.40; Found: C, 28.13; H, 4.75, N, 8.09. The product has been identified with single crystal X-ray diffraction.

Di(1-butyl-3-vinyl-imidazolium) hexahydroxozirconate ($[BVIM]_2[Zr(OH)_6]$). The procedure was used as for $[BMIM]_2[Ti(OH)_6]$, except that 2.33 g $[BVIM][BF_4]$ (10 mmol), 2.34 g $Zr(OPr)_4$ (5 mmol, 70% in PrOH) and 5.75 g EtOH were used. The product was crystallized from DMSO/EtOH. White solid, 1.68 g (68%); Mp: 197-198 ^oC. IR: 601, 765, 864, 921, 978, 1167, 1380, 1470, 1552, 1650, 2863, 2953, 3101, 3133 (cm^{-1}). ^1H NMR (300 Hz, d^6-DMSO): δ = 0.84 (t, J = 6.9 Hz, 6H), 1.25 (m, 4H), 1.79 (m, 4H), 4.19 (t, J = 7.2 Hz, 4H), 5.37 (dd, J = 8.7, 2.4 Hz, 2H), 5.94 (dd, J = 15.6, 2.4 Hz, 2H), 7.31 (dd, J = 8.7, 15.6 Hz, 2H), 7.91 (s, 2H), 8.19 (s, 2H), 9.58 (s, 2H). ^{13}C NMR (300 Hz, d^6-DMSO): δ = 13.7, 19.2, 31.6, 49.3, 108.9, 119.5, 123.6, 129.4, 136.1. Anal. Calcd for $C_{18}H_{36}N_4O_6Zr$: C, 43.61; H, 7.32; N, 11.30; Found: C, 44.46; H, 8.70; N, 11.51. The product has been identified with single crystal X-ray diffraction.

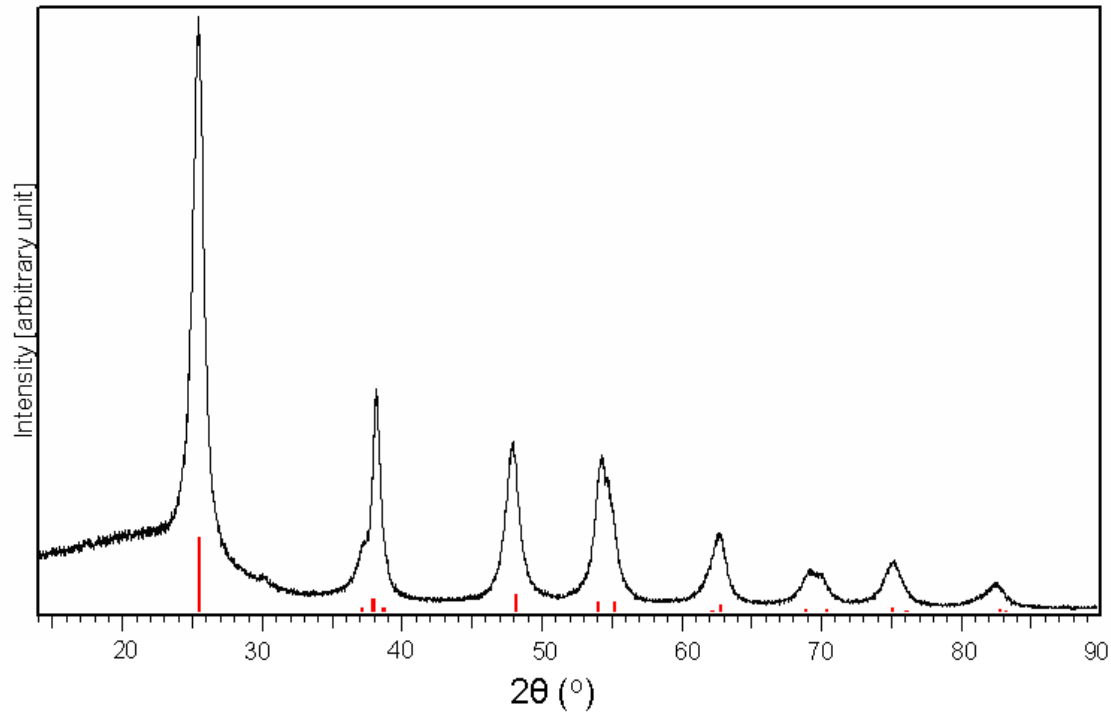
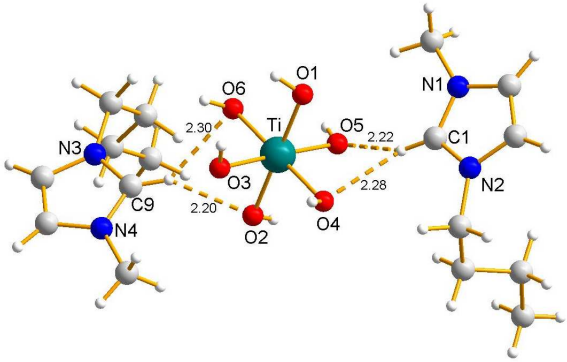


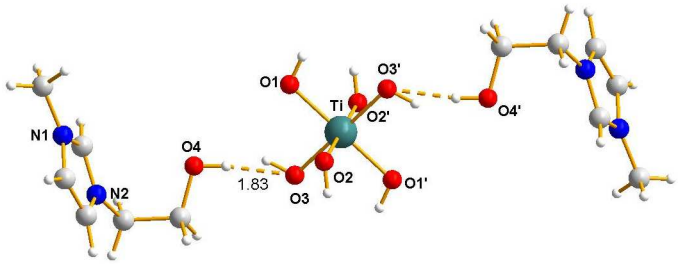
Fig. S1. The PXRD pattern of the obtained TiO_2 nanoparticles.

Fig. S2. ORTEP drawing: $[BMIM]_2[Ti(OH)_6]$



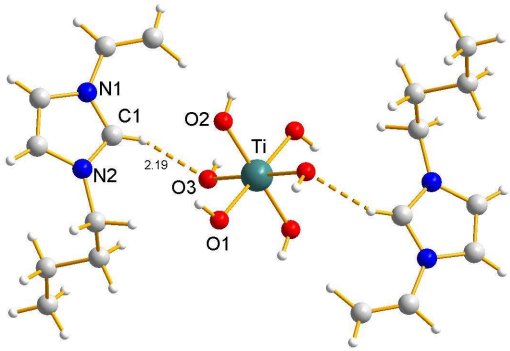
Empirical formula	C16 H36 N4 O6 Ti	
Formula weight	428.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.305(2) Å	α= 90°.
	b = 11.430(2) Å	β= 90°.
	c = 17.327(4) Å	γ = 90°.
Volume	2239.0(8) $Å^3$	
Z	4	
Density (calculated)	1.271 Mg/m^3	
Absorption coefficient	0.418 mm^{-1}	
F(000)	920	
Crystal size	0.36 x 0.2 x 0.13 mm^3	
Theta range for data collection	2.53 to 28.34°.	
Index ranges	-14<=h<=14, -15<=k<=15, -23<=l<=22	
Reflections collected	21512	
Independent reflections	5442 [R(int) = 0.1056]	
Completeness to theta = 28.34°	97.8 %	
Absorption correction	Multiscan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5442 / 0 / 250	
Goodness-of-fit on F^2	0.801	
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1090	
R indices (all data)	R1 = 0.1585, wR2 = 0.1417	
Absolute structure parameter	0.42(7)	
Largest diff. peak and hole	0.328 and -0.550 $e.Å^{-3}$	

Fig. S3. ORTEP drawing: $[HOEtMIM]_2[Ti(OH)_6]$



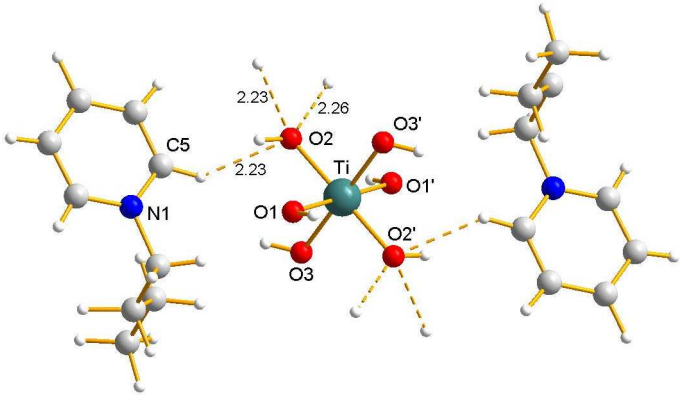
Empirical formula	C12 H28 N4 O8 Ti	
Formula weight	404.28	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 7.9680(3) Å	α= 90°.
	b = 9.6029(4) Å	β= 108.213(2)°.
	c = 11.7899(5) Å	γ = 90°.
Volume	856.92(6) $Å^3$	
Z	2	
Density (calculated)	1.567 Mg/m^3	
Absorption coefficient	0.549 mm^{-1}	
F(000)	428	
Crystal size	0.52 x 0.31 x 0.25 mm^3	
Theta range for data collection	2.69 to 42.35°.	
Index ranges	-15<=h<=14, -17<=k<=18, -21<=l<=22	
Reflections collected	22054	
Independent reflections	6039 [R(int) = 0.0208]	
Completeness to theta = 42.35°	98.8 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8767 and 0.7647	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6039 / 0 / 162	
Goodness-of-fit on F^2	1.877	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1885	
R indices (all data)	R1 = 0.0714, wR2 = 0.1948	
Largest diff. peak and hole	1.882 and -0.788 $e.Å^{-3}$	

Fig. S4. ORTEP drawing: $[BVIM]_2[Ti(OH)_6]$



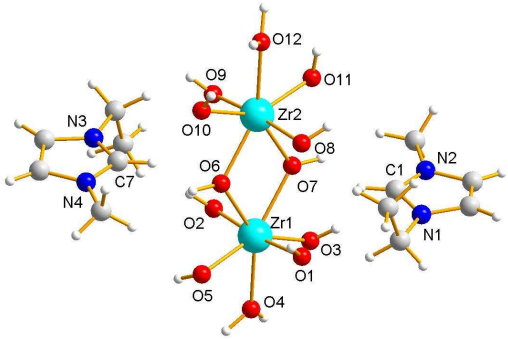
Empirical formula	C18 H36 N4 O6 Ti	
Formula weight	452.41	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.6718(17) Å	α= 90°.
	b = 11.695(2) Å	β= 98.89(3)°.
	c = 11.319(2) Å	γ = 90°.
Volume	1134.1(4) $Å^3$	
Z	2	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.417 mm^{-1}	
F(000)	484	
Crystal size	0.40 x 0.23 x 0.18 mm^3	
Theta range for data collection	3.27 to 27.94°.	
Index ranges	-11<=h<=11, -15<=k<=15, -14<=l<=14	
Reflections collected	13008	
Independent reflections	2630 [R(int) = 0.0656]	
Completeness to theta = 27.94°	96.4 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9288 and 0.8510	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2630 / 0 / 197	
Goodness-of-fit on F^2	2.155	
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1894	
R indices (all data)	R1 = 0.0649, wR2 = 0.1943	
Largest diff. peak and hole	0.721 and -0.624 $e.Å^{-3}$	

Fig. S5. ORTEP drawing: $[HOEtMIM]_2[Ti(OH)_6]$



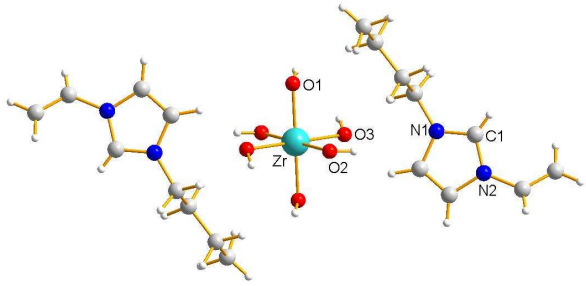
Empirical formula	C18 H34 N2 O6 Ti	
Formula weight	422.37	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 7.5574(13) Å	α= 90°.
	b = 12.356(2) Å	β= 91.936(6)°.
	c = 10.6617(18) Å	γ = 90°.
Volume	995.0(3) $Å^3$	
Z	2	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.467 mm^{-1}	
F(000)	452	
Crystal size	0.23 x 0.23 x 0.10 mm^3	
Theta range for data collection	2.52 to 26.81°.	
Index ranges	-9<=h<=9, -15<=k<=15, -12<=l<=13	
Reflections collected	7046	
Independent reflections	2081 [R(int) = 0.0483]	
Completeness to theta = 26.81°	97.6 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.9566 and 0.8986	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2081 / 0 / 183	
Goodness-of-fit on F^2	1.643	
Final R indices [I>2sigma(I)]	R1 = 0.0624, wR2 = 0.1641	
R indices (all data)	R1 = 0.1040, wR2 = 0.1792	
Largest diff. peak and hole	0.771 and -0.766 $e.Å^{-3}$	

Fig. S6. ORTEP drawing: $[EMIM]_2\{[Zr_2(OH)_{10}\cdot 2H_2O]^{2-}\}$



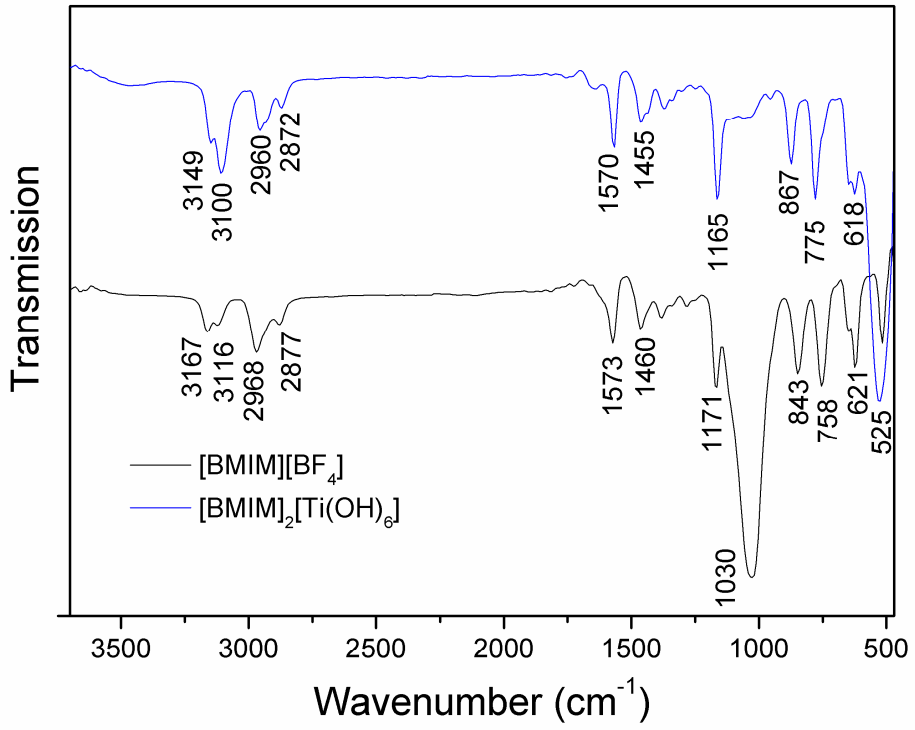
Empirical formula	C12 H36 N4 O12 Zr2	
Formula weight	610.89	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.7833(2) Å	α= 101.5310(10)°.
	b = 8.8355(2) Å	β= 102.0520(10)°.
	c = 9.3296(3) Å	γ = 115.0050(10)°.
Volume	537.74(3) $Å^3$	
Z	1	
Density (calculated)	1.886 Mg/m^3	
Absorption coefficient	1.036 mm^{-1}	
F(000)	312	
Crystal size	0.62 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.36 to 36.44°.	
Index ranges	-12<=h<=12, -14<=k<=14, -15<=l<=15	
Reflections collected	37836	
Independent reflections	10285 [R(int) = 0.0380]	
Completeness to theta = 36.44°	99.4 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8371 and 0.5675	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10285 / 10 / 299	
Goodness-of-fit on F^2	1.126	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.1033	
R indices (all data)	R1 = 0.0362, wR2 = 0.1044	
Absolute structure parameter	0.46(6)	
Largest diff. peak and hole	1.629 and -1.393 $e.Å^{-3}$	

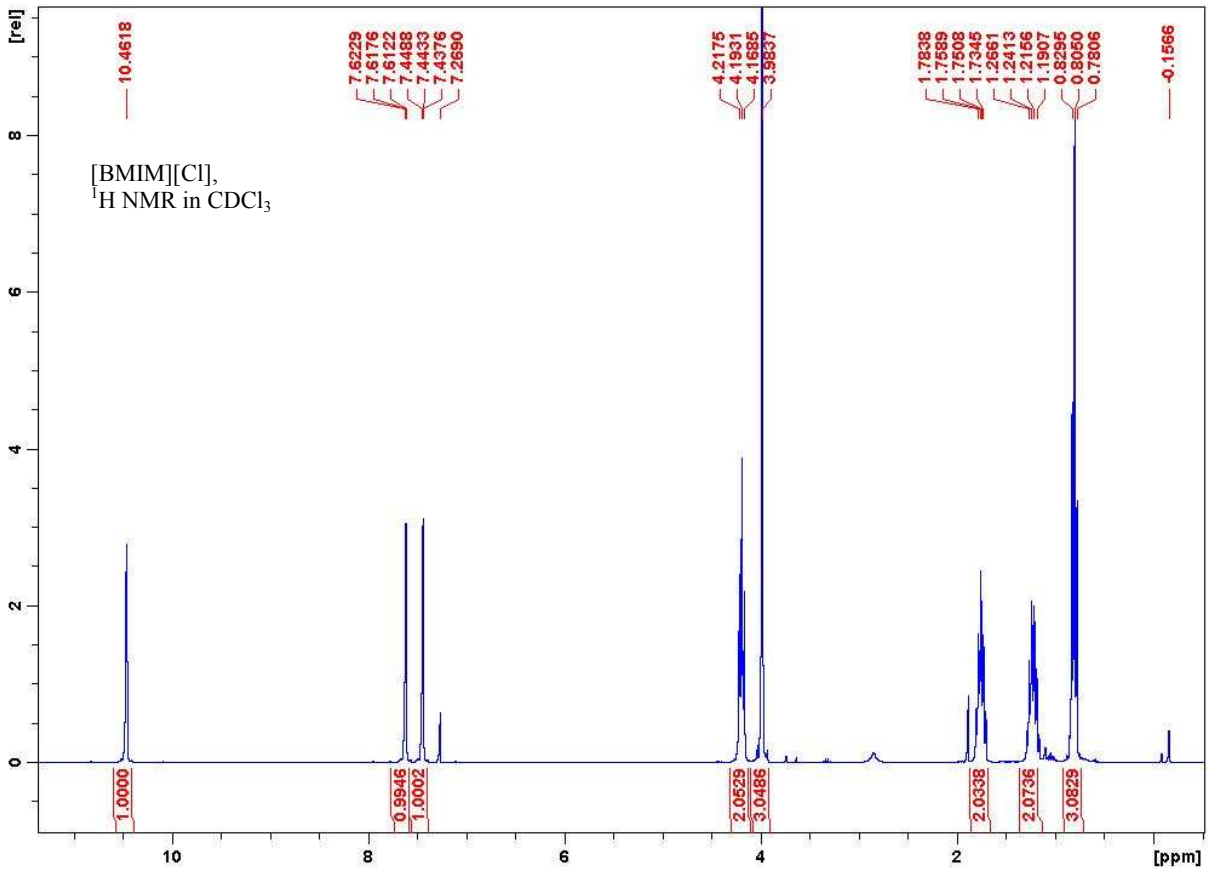
Fig. S7. ORTEP drawing: $[BVIM]_2[Zr(OH)_6]$

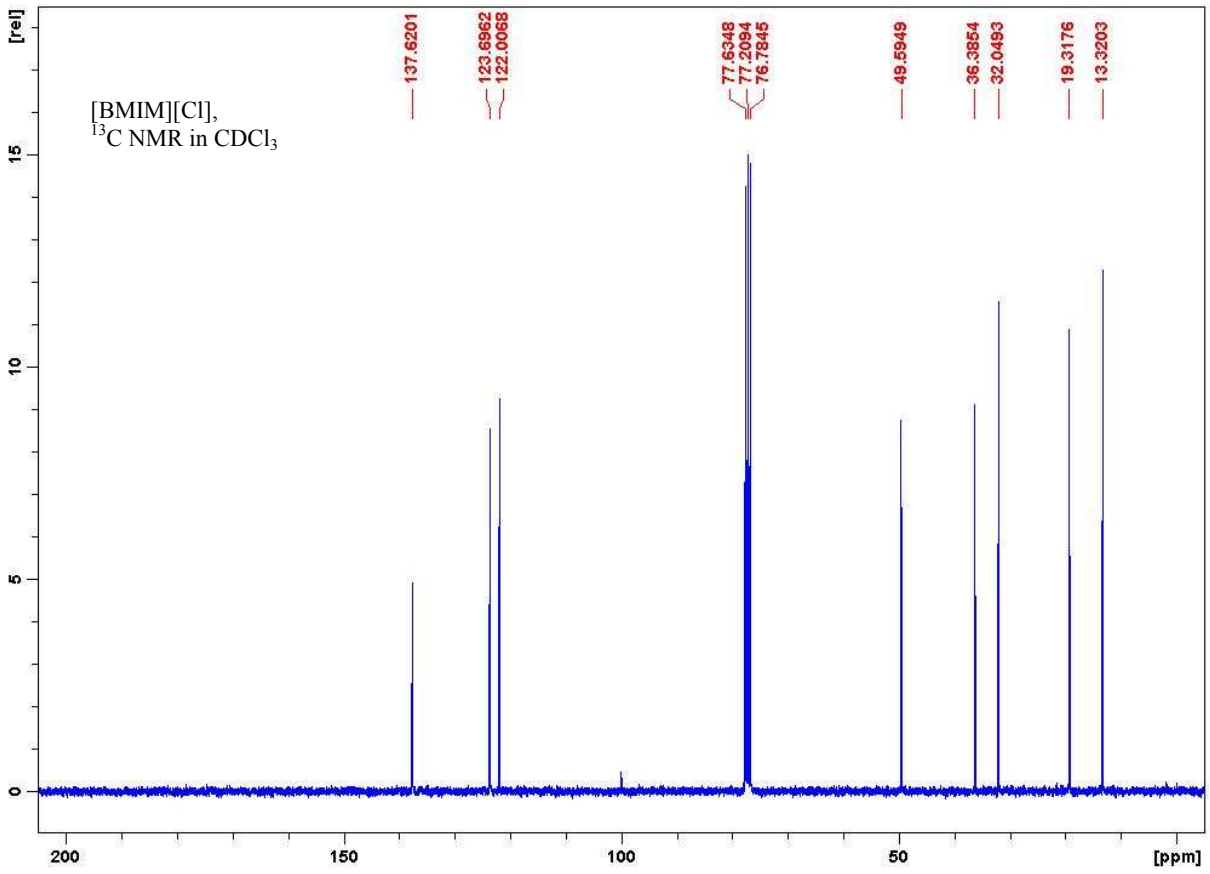


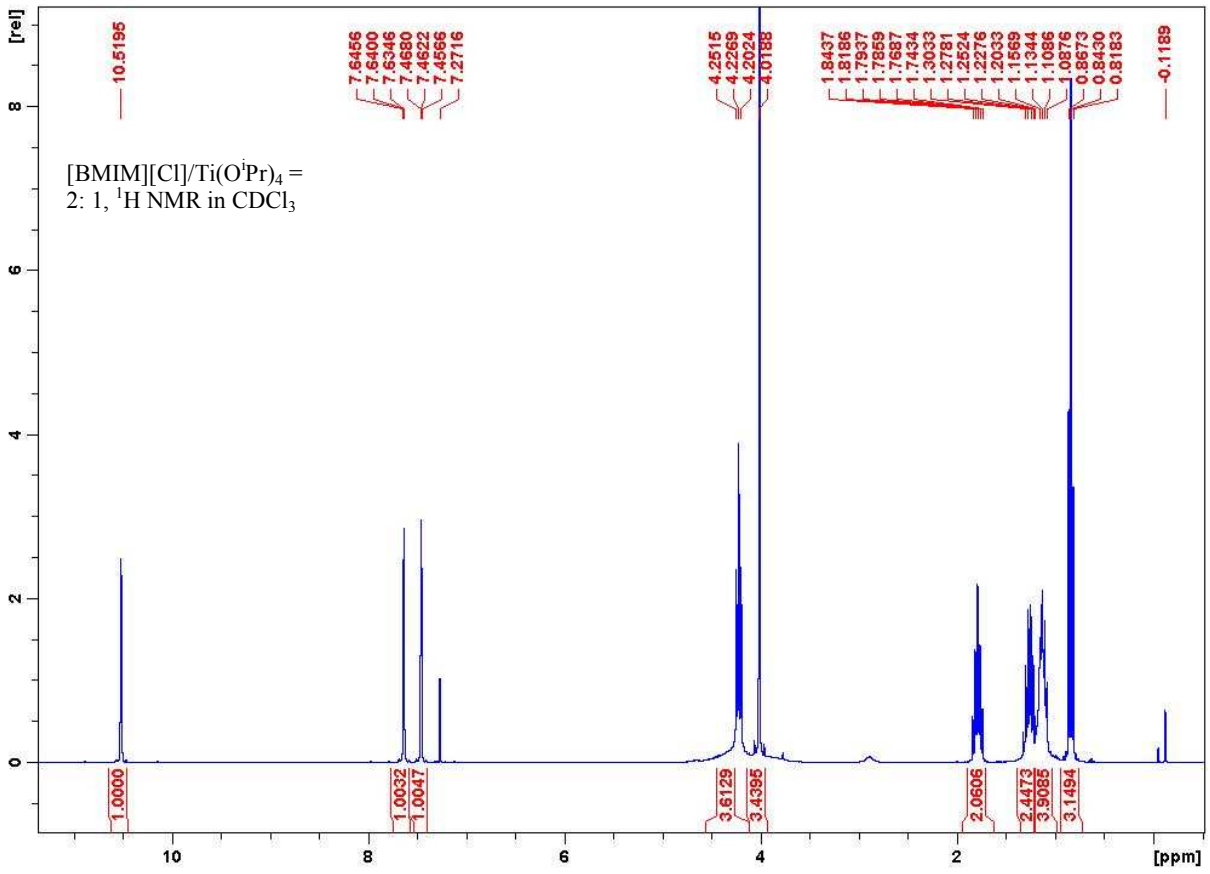
Empirical formula	C18 H36 N4 O6 Zr	
Formula weight	495.73	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.7890(3) Å	α= 90°.
	b = 11.4616(4) Å	β= 101.688(2)°.
	c = 11.4399(4) Å	γ = 90°.
Volume	1128.51(7) $Å^3$	
Z	2	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	0.527 mm^{-1}	
F(000)	520	
Crystal size	0.59 x 0.21 x 0.05 mm^3	
Theta range for data collection	2.54 to 35.09°.	
Index ranges	-10<=h<=14, -18<=k<=18, -18<=l<=18	
Reflections collected	17827	
Independent reflections	4981 [R(int) = 0.0482]	
Completeness to theta = 35.09°	99.5 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.9721 and 0.7445	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4981 / 0 / 196	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1337	
R indices (all data)	R1 = 0.0972, wR2 = 0.1606	
Largest diff. peak and hole	1.090 and -1.436 $e.Å^{-3}$	

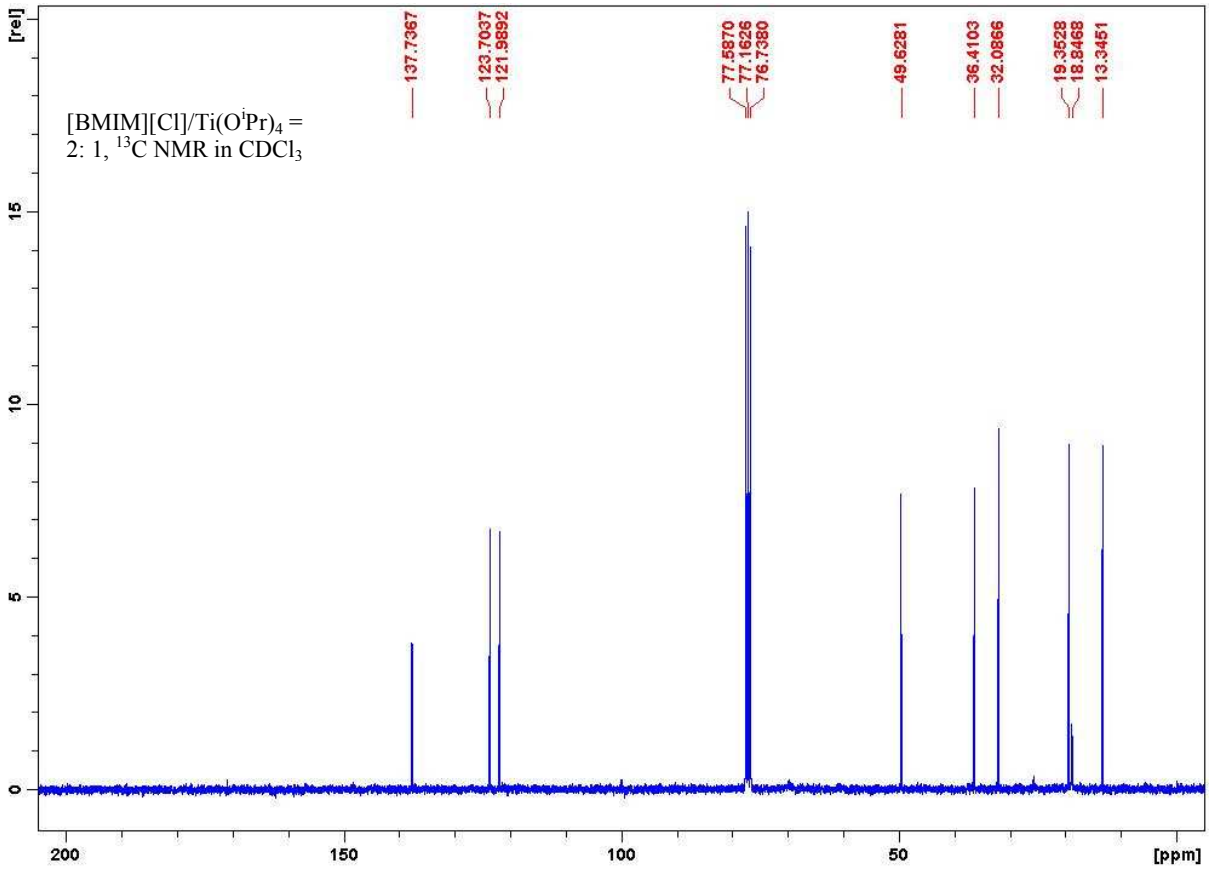
Fig. S8. FTIR spectra of $[BMIM][BF_4]$ and $[BMIM]_2[Ti(OH)_6]$

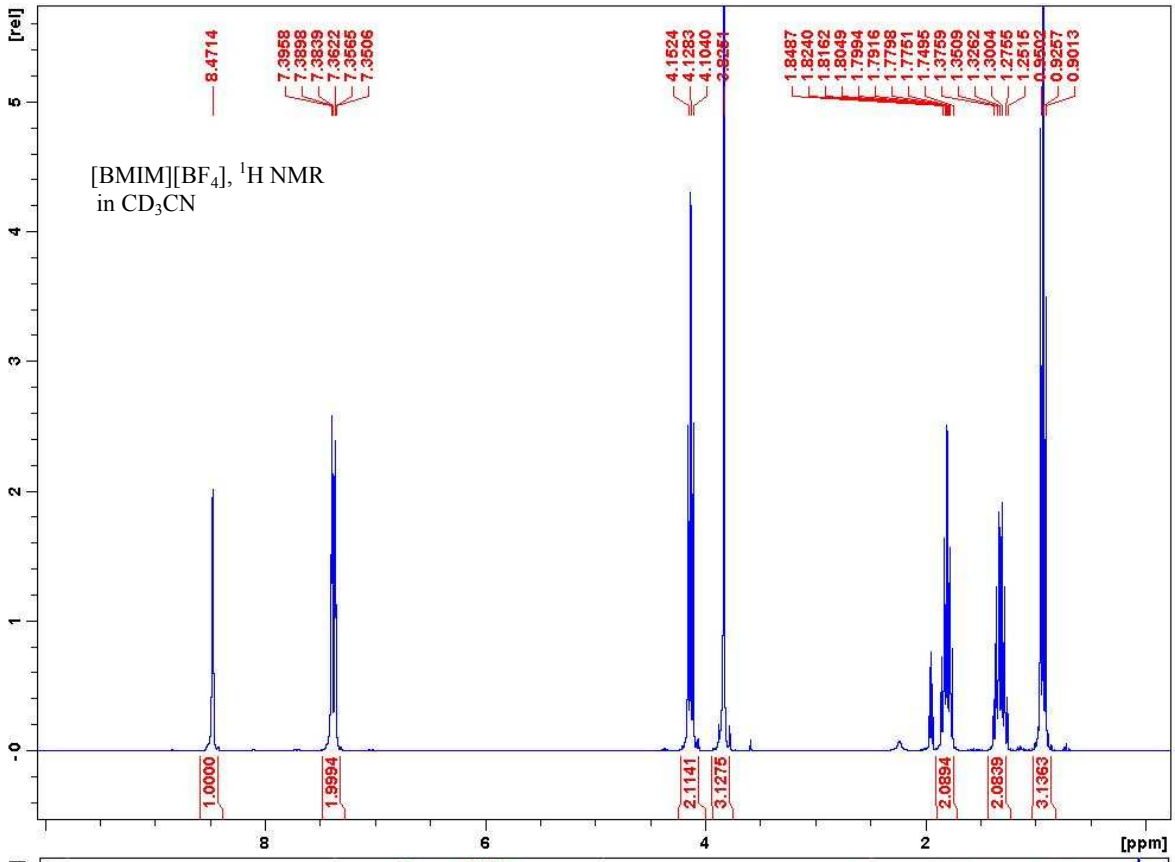


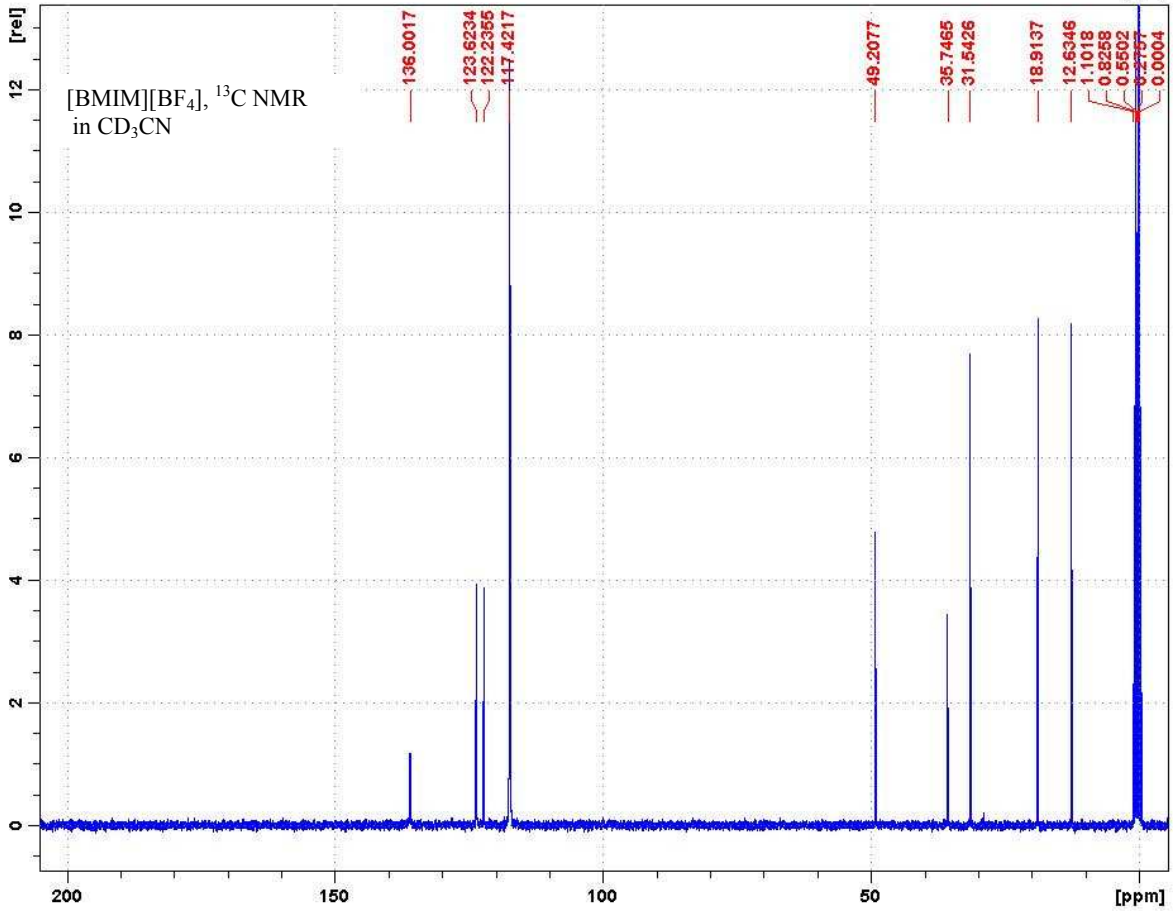

[rel]
10.4618
7.6229
7.6176
7.6122
7.4488
7.4433
7.4376
7.2690
4.2175
4.1931
4.1685
3.9837
1.7838
1.7589
1.7508
1.7345
1.2661
1.2413
1.2156
1.1907
0.8295
0.8050
0.7806
-0.1566
[BMIM][Cl],
1H NMR in CDCl3
1.0000
0.9946
1.0002
2.0529
3.0486
2.0338
2.0736
3.0829
[ppm]

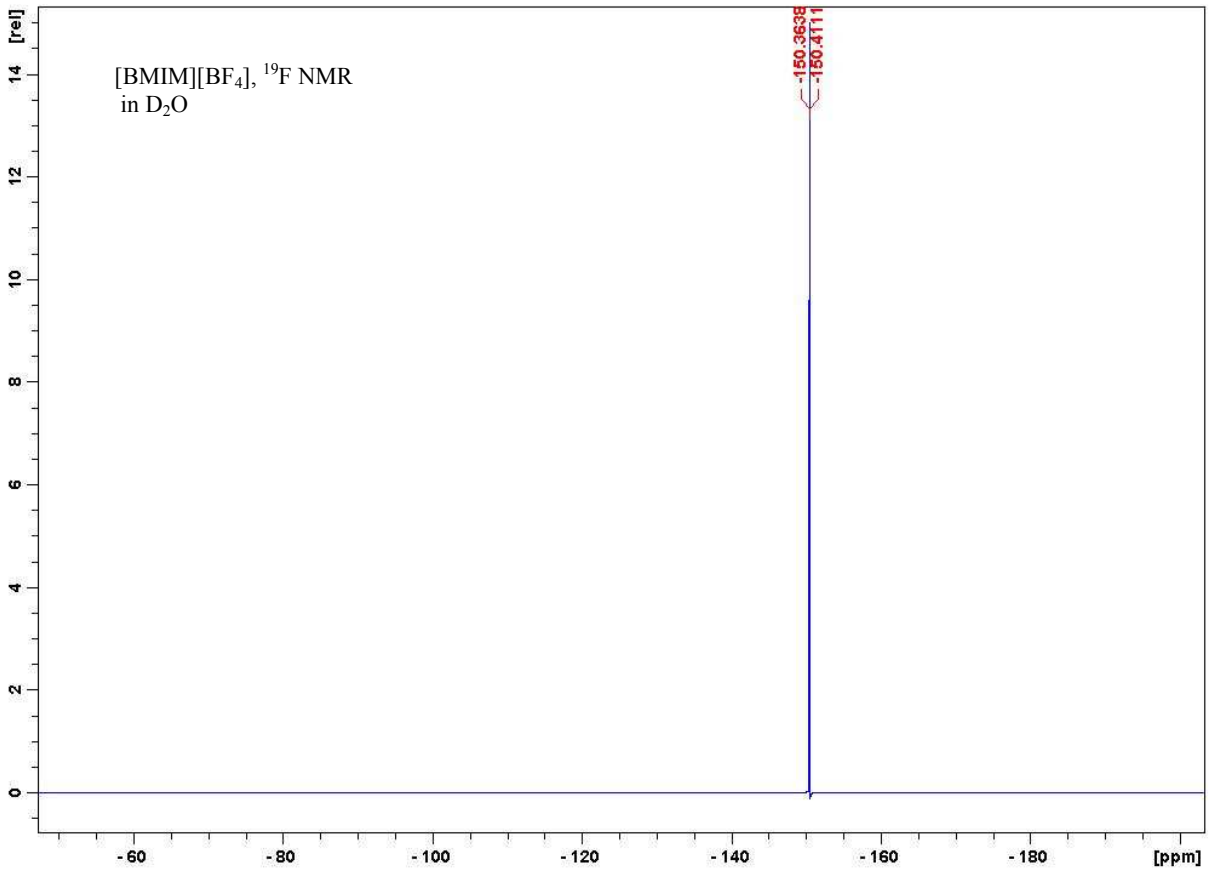

[rel]
137.6201
123.6962
122.0068
77.6348
77.2094
76.7845
49.5949
36.3854
32.0493
19.3176
13.3203
[BMIM][Cl],
13C NMR in CDCl3
[ppm]

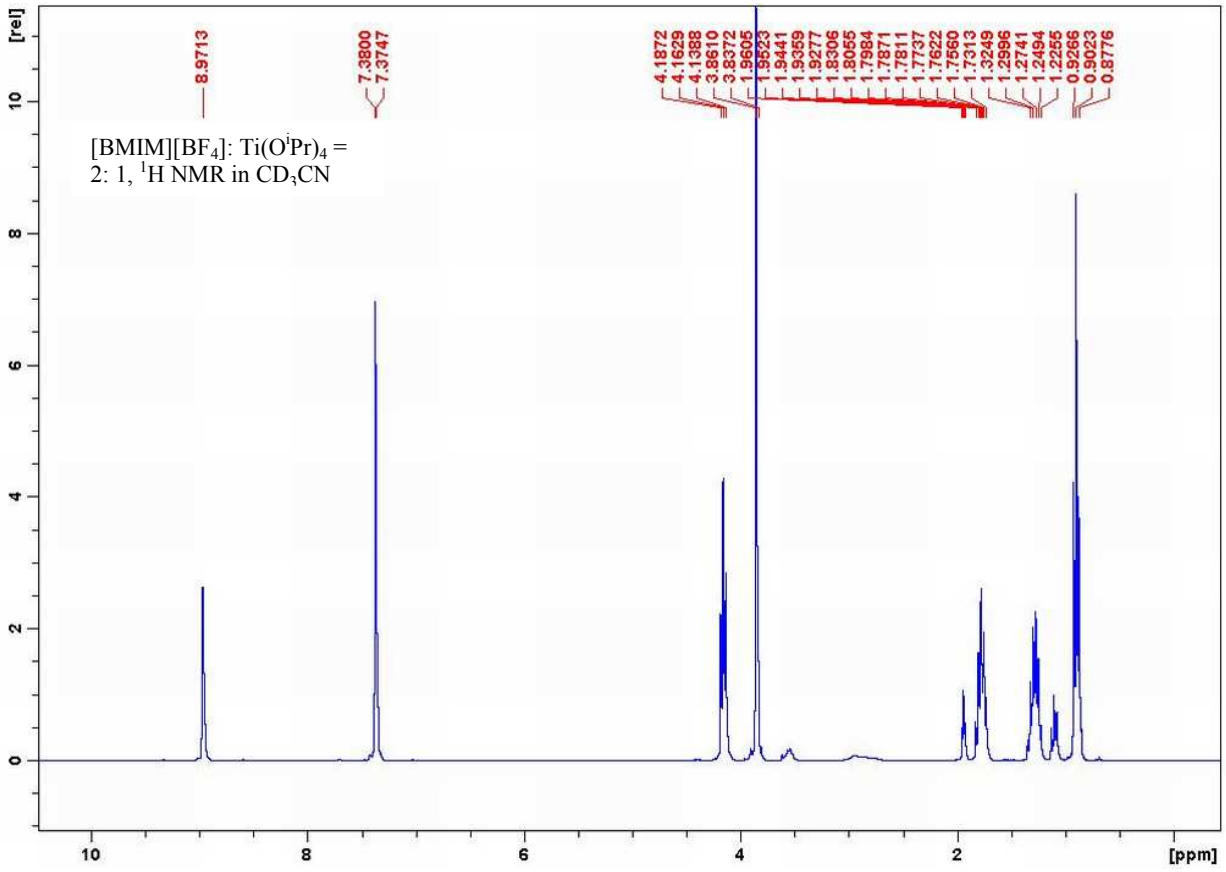

[rel]
10.5195
7.6456
7.6400
7.6346
7.4680
7.4622
7.4566
7.2716
4.2515
4.2269
4.2024
4.0188
1.8437
1.8186
1.7937
1.7859
1.7687
1.7434
1.3033
1.2781
1.2524
1.2276
1.2033
1.1569
1.1344
1.1086
1.0876
0.8673
0.8430
0.8183
-0.1189
[BMIM][Cl]/Ti(O^{i}Pr)$_4$ =
2: 1, ^{1}H NMR in CDCl$_3$
1.0000
1.0032
1.0047
3.6129
3.4395
2.0606
2.4473
3.9085
3.1494
[ppm]

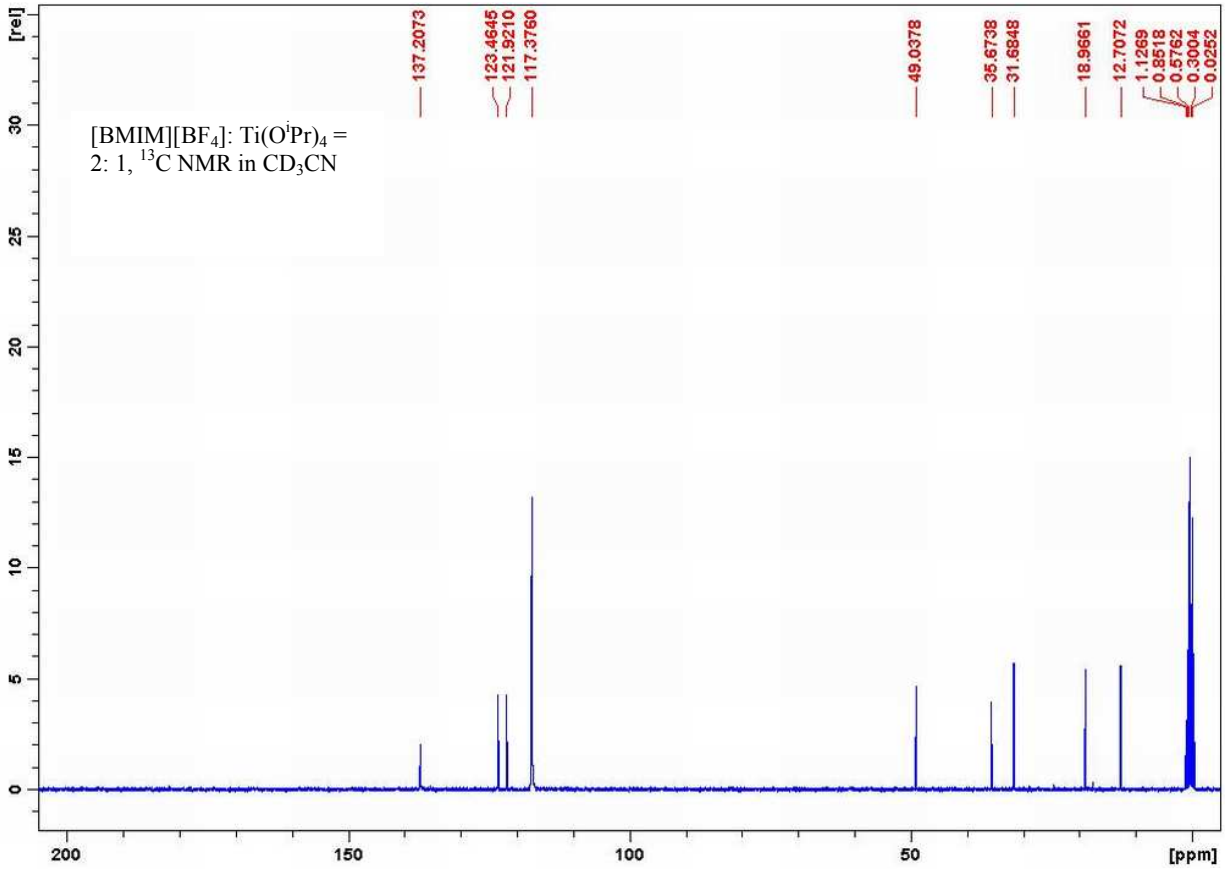

[rel]
137.7367
123.7037
121.9892
77.5870
77.1626
76.7380
49.6281
36.4103
32.0866
19.3528
18.8468
13.3451
[BMIM][Cl]/Ti(O^{i}Pr)$_4$ =
2: 1, ^{13}C NMR in CDCl$_3$
[ppm]

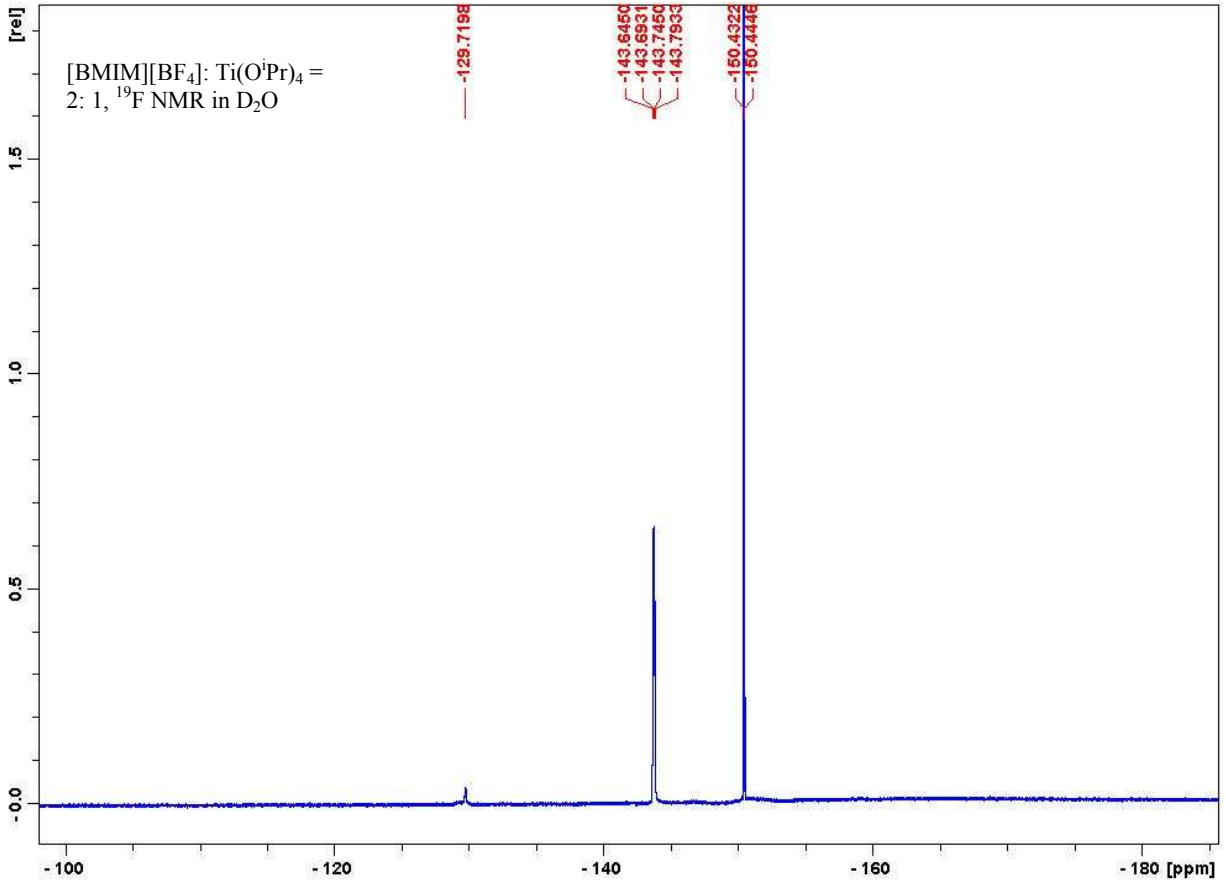

[BMIM][BF4], 1H NMR
in CD3CN
[rel]
[ppm]
8.4714
7.3958
7.3898
7.3839
7.3622
7.3565
7.3506
4.1524
4.1283
4.1040
1.8487
1.8240
1.8162
1.8049
1.7994
1.7916
1.7798
1.7751
1.7495
1.3759
1.3509
1.3262
1.3004
1.2755
1.2515
0.9502
0.9257
0.9013
1.0000
1.9994
2.1141
3.1275
2.0894
2.0839
3.1363

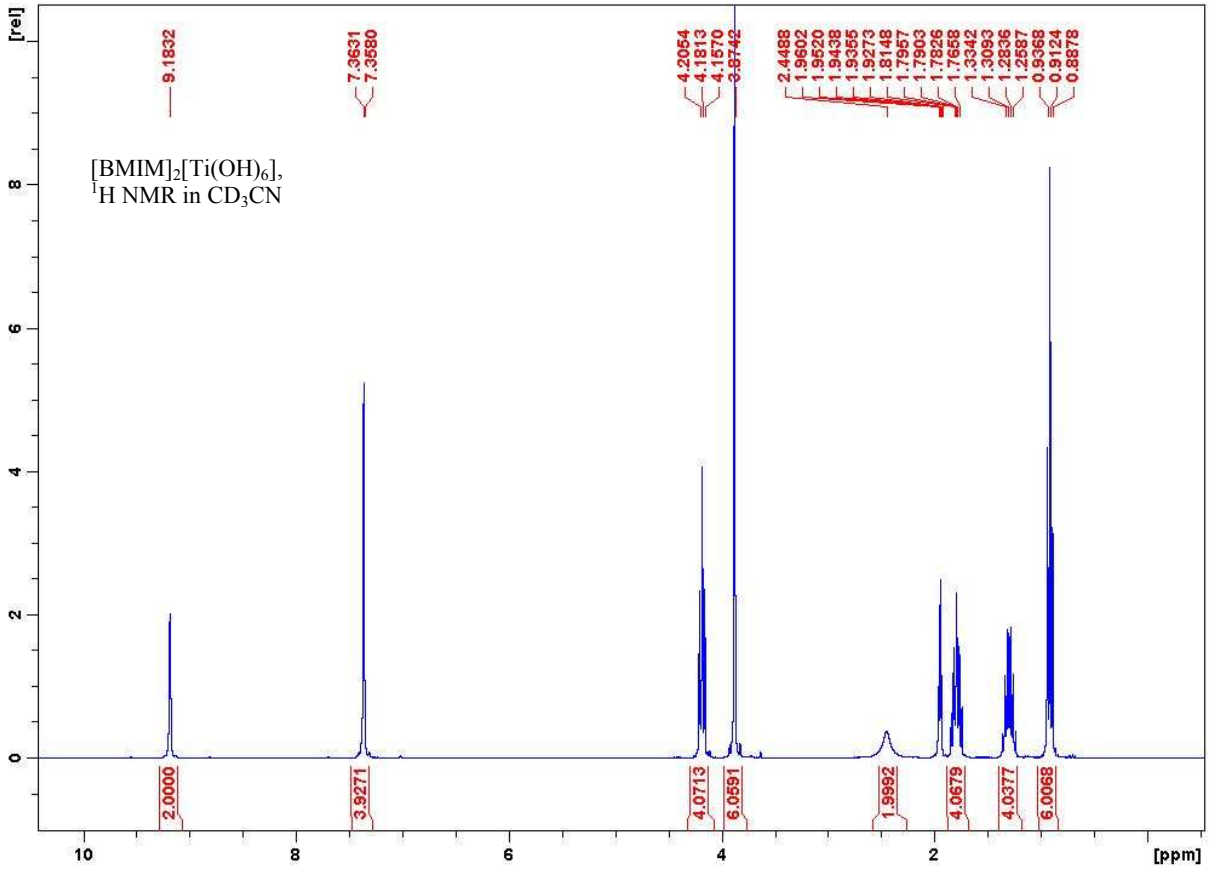

[BMIM][BF4], 13C NMR
in CD3CN
[rel]
[ppm]
136.0017
123.6234
122.2365
117.4217
49.2077
35.7465
31.5426
18.9137
12.6346
1.1018
0.8258
0.5502
0.0004

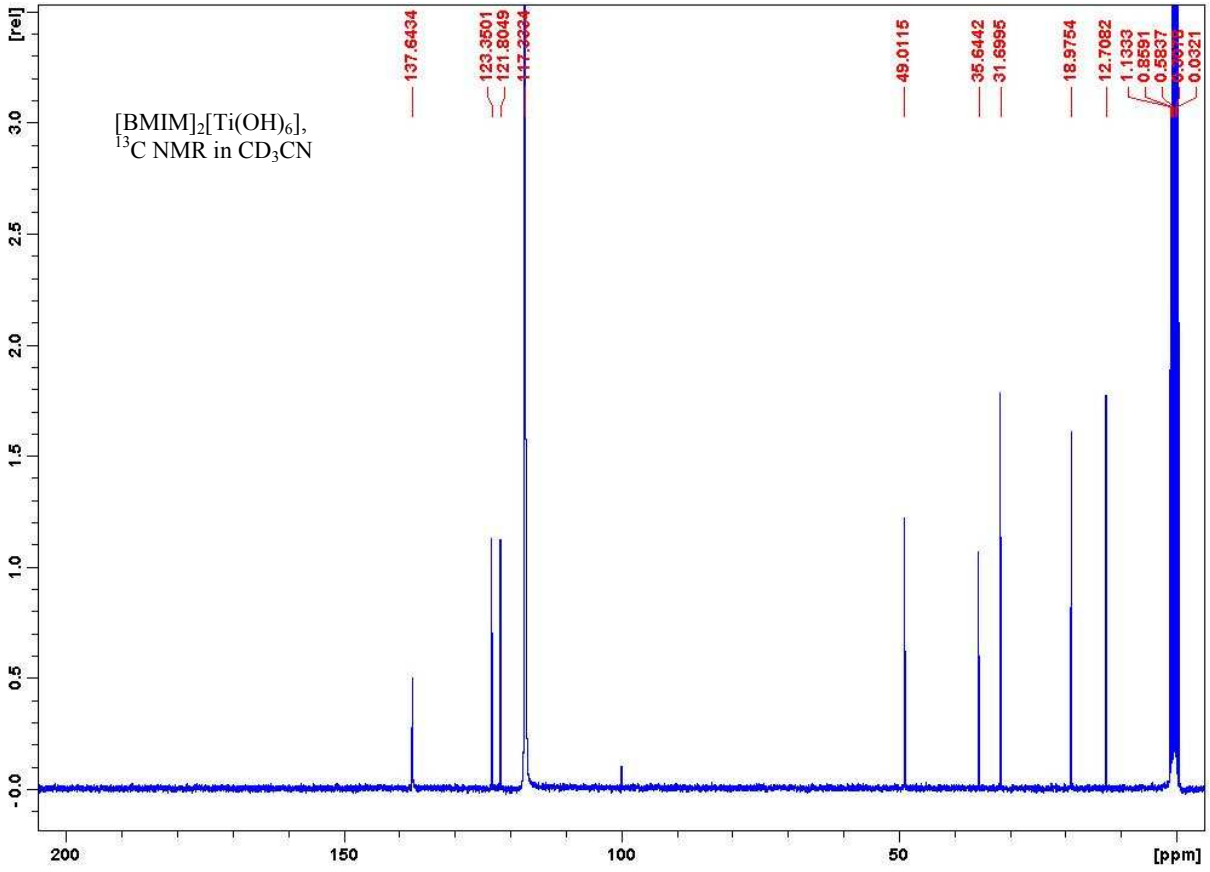

[BMIM][BF4], 19F NMR
in D2O
-150.3638
-150.4111
[rel]
[ppm]

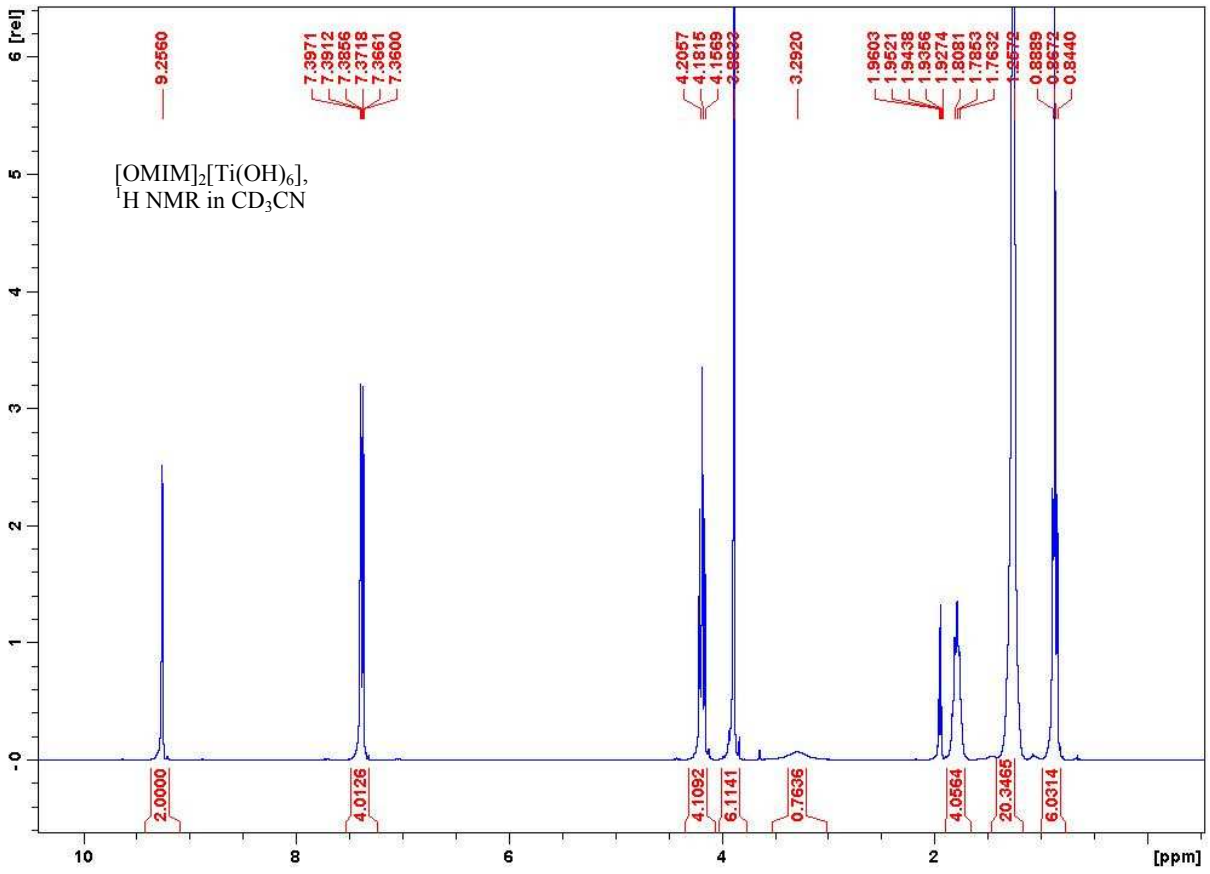

[BMIM][BF4]: Ti(OiPr)4 =
2: 1, 1H NMR in CD3CN
8.9713
7.3800
7.3747
4.1872
4.1629
4.1388
3.8610
3.8372
1.9605
1.9523
1.9441
1.9359
1.9277
1.8306
1.8055
1.7984
1.7871
1.7811
1.7737
1.7622
1.7560
1.7313
1.3249
1.2996
1.2741
1.2494
1.2255
0.9266
0.9023
0.8776
[rel]
[ppm]

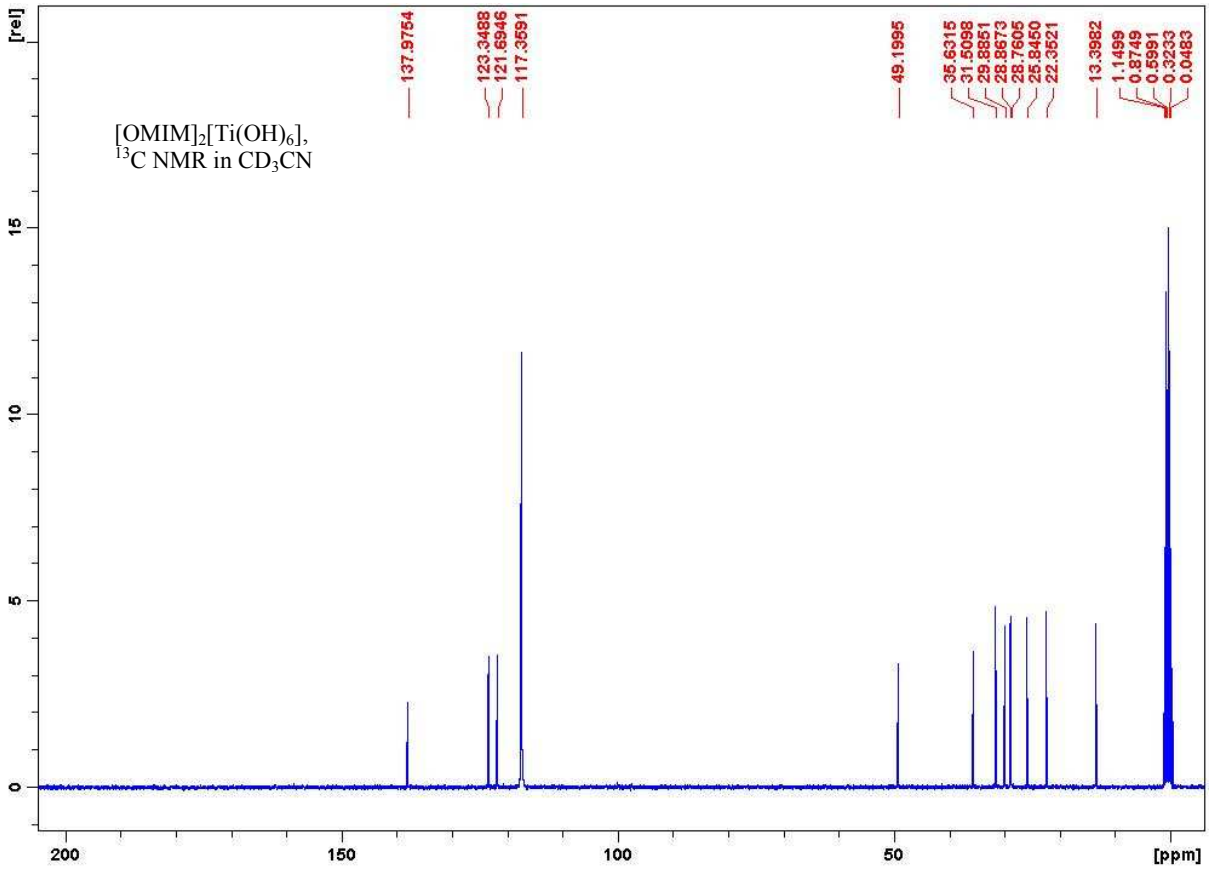

[BMIM][BF4]: Ti(OiPr)4 =
2: 1, 13C NMR in CD3CN
137.2073
123.4645
121.9210
117.3760
49.0378
35.6738
31.6848
18.9661
12.7072
1.1269
0.8518
0.5762
0.3004
0.0252
[rel]
[ppm]

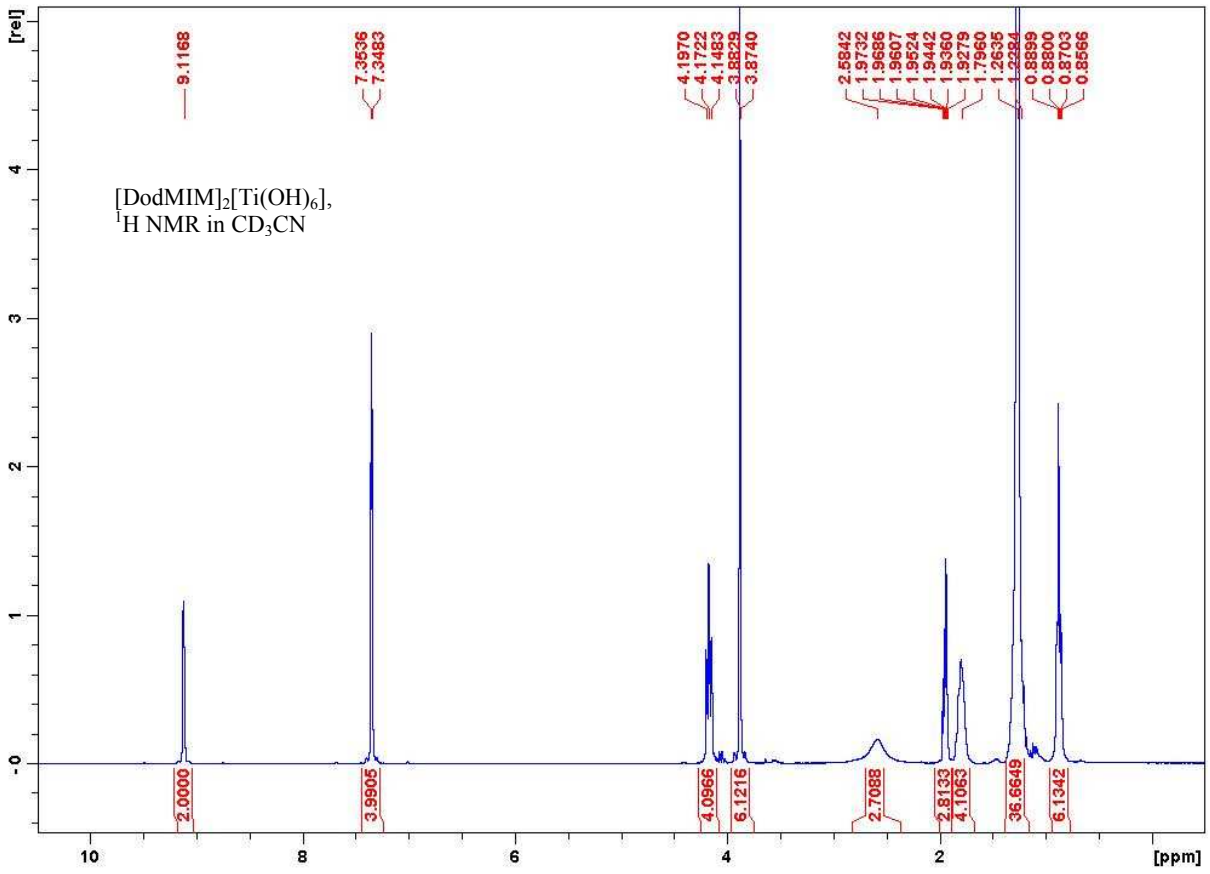

[BMIM][BF4]: Ti(OiPr)4 =
2: 1, 19F NMR in D2O
-129.7198
-143.6450
-143.6931
-143.7450
-143.7933
-150.4322
-150.4446
[rel]
[ppm]

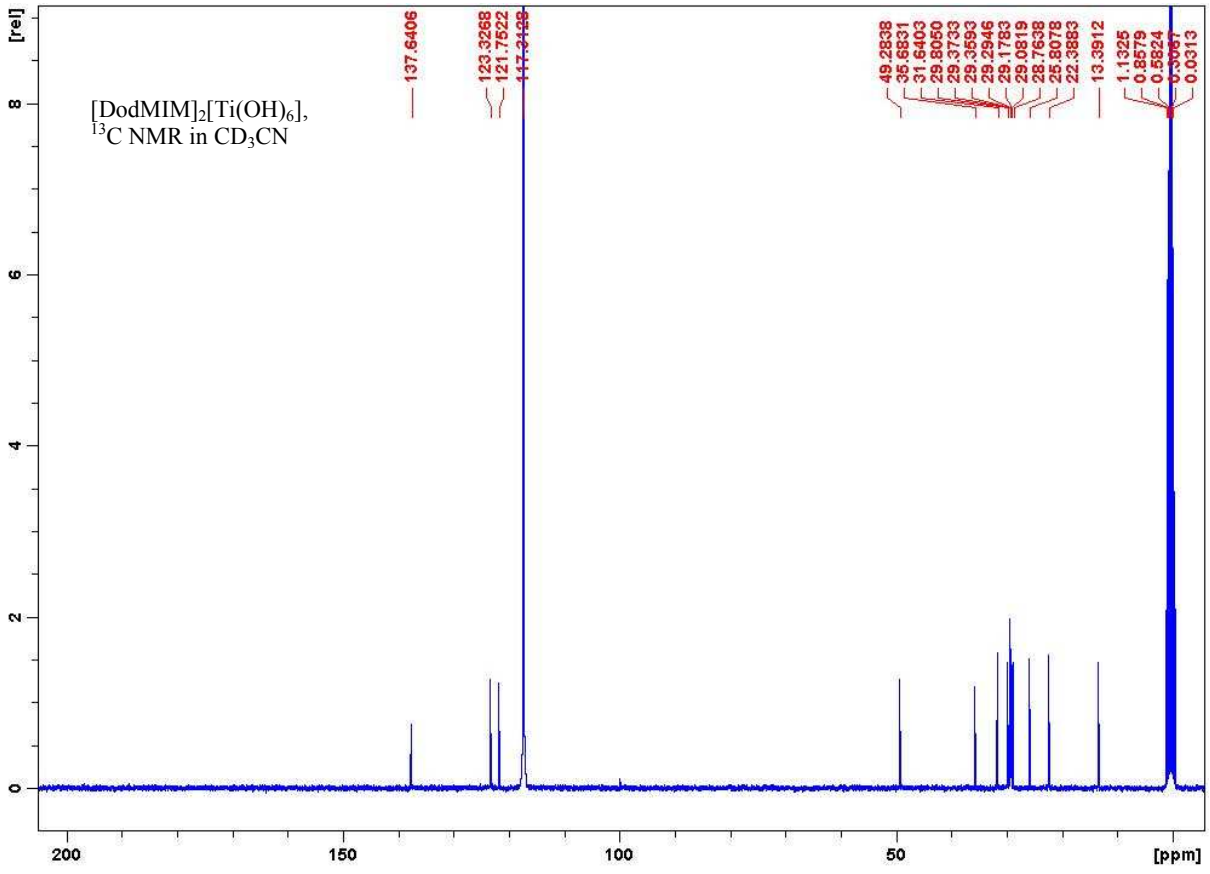

[BMIM]2[Ti(OH)6],
1H NMR in CD3CN
[rel]
[ppm]
9.1832
7.3631
7.3580
4.2054
4.1813
4.1570
3.8742
2.4488
1.9602
1.9520
1.9438
1.9355
1.9273
1.8148
1.7957
1.7903
1.7826
1.7658
1.3342
1.3093
1.2836
1.2587
0.9368
0.9124
0.8878
2.0000
3.9271
4.0713
6.0591
1.9992
4.0679
4.0377
6.0068

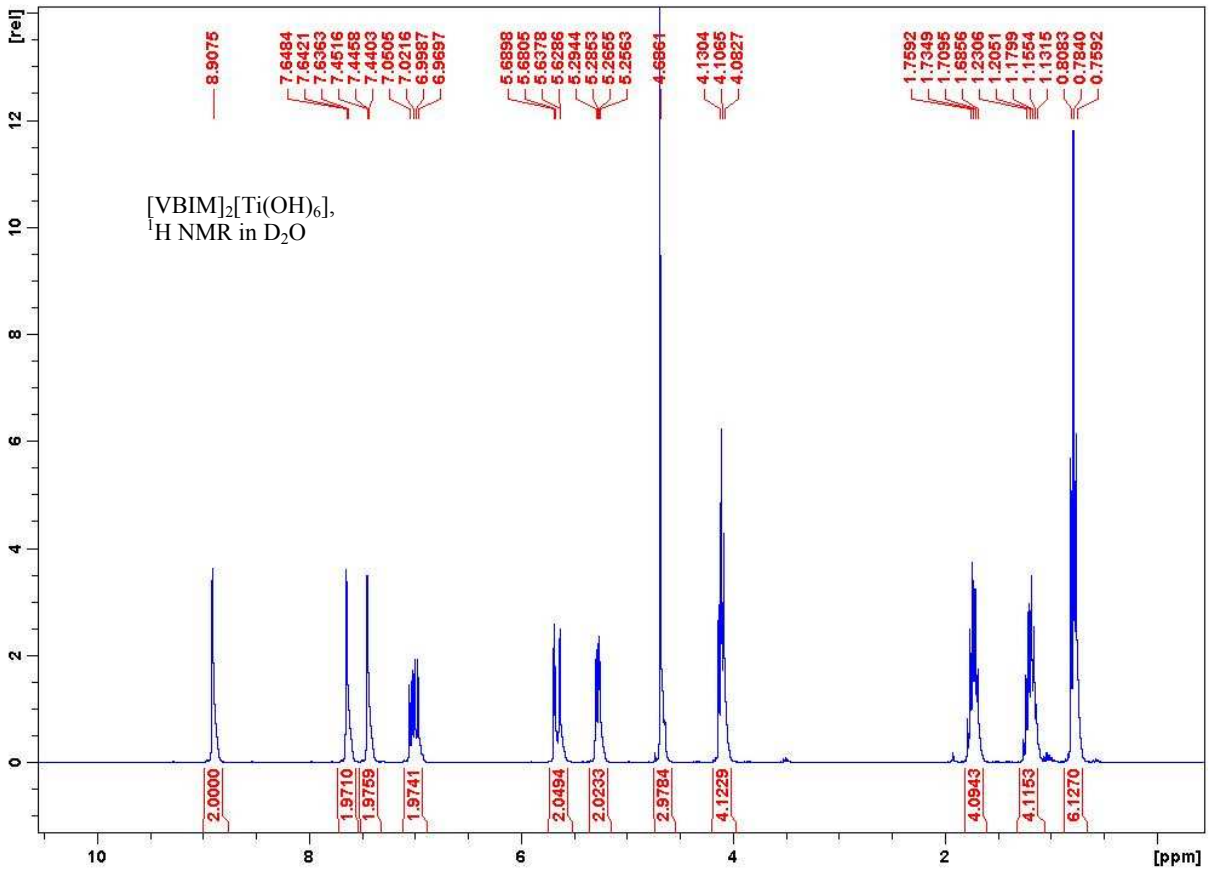

[BMIM]2[Ti(OH)6],
13C NMR in CD3CN
[rel]
[ppm]
137.6434
123.3501
121.8049
117.3334
49.0115
35.6442
31.6995
18.9754
12.7082
1.1333
0.8591
0.5837
0.0321

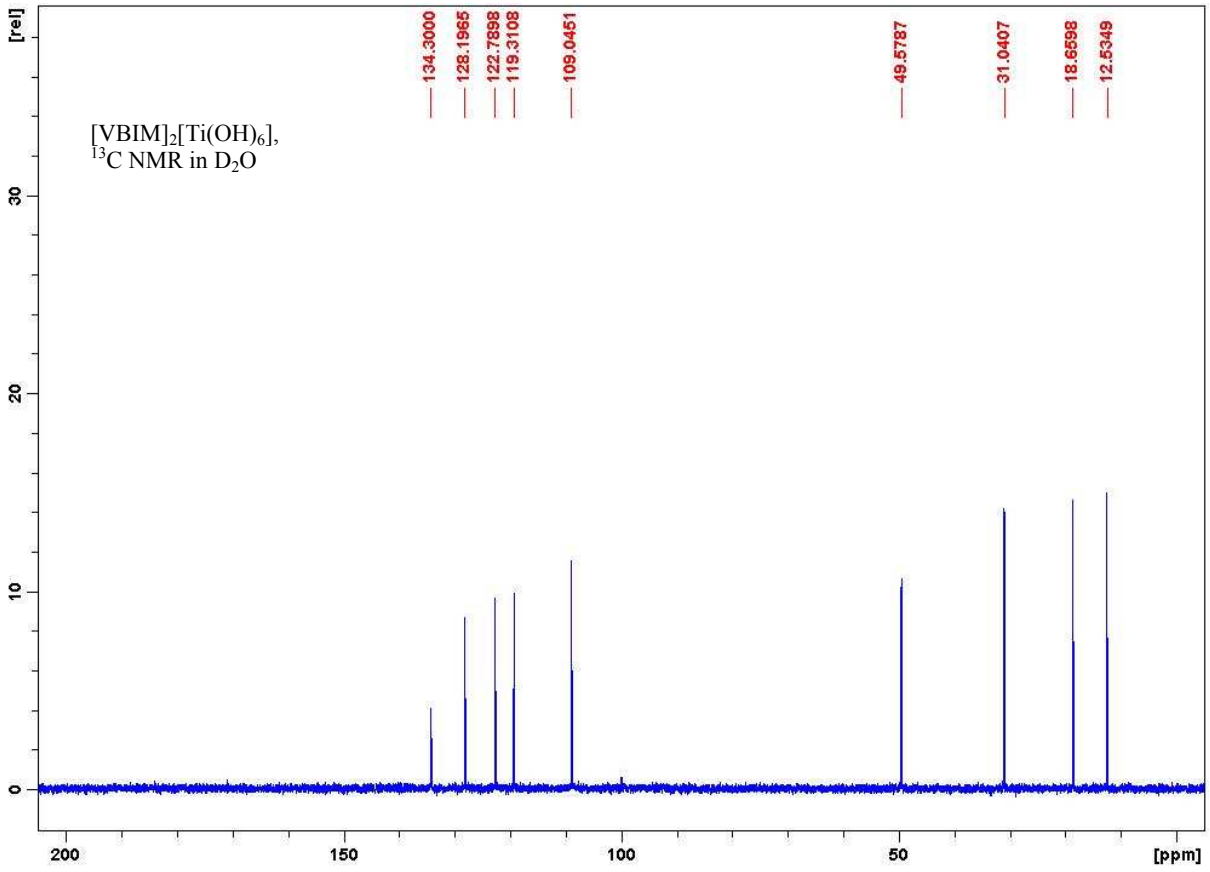

[OMIM]2[Ti(OH)6],
1H NMR in CD3CN
9.2560
7.3971
7.3912
7.3856
7.3718
7.3661
7.3600
4.2057
4.1815
4.1569
3.8833
3.2920
1.9603
1.9521
1.9438
1.9356
1.9274
1.8081
1.7853
1.7632
1.5572
0.8889
0.8672
0.8440
2.0000
4.0126
4.1092
6.1141
0.7636
4.0564
20.3465
6.0314
[rel]
[ppm]

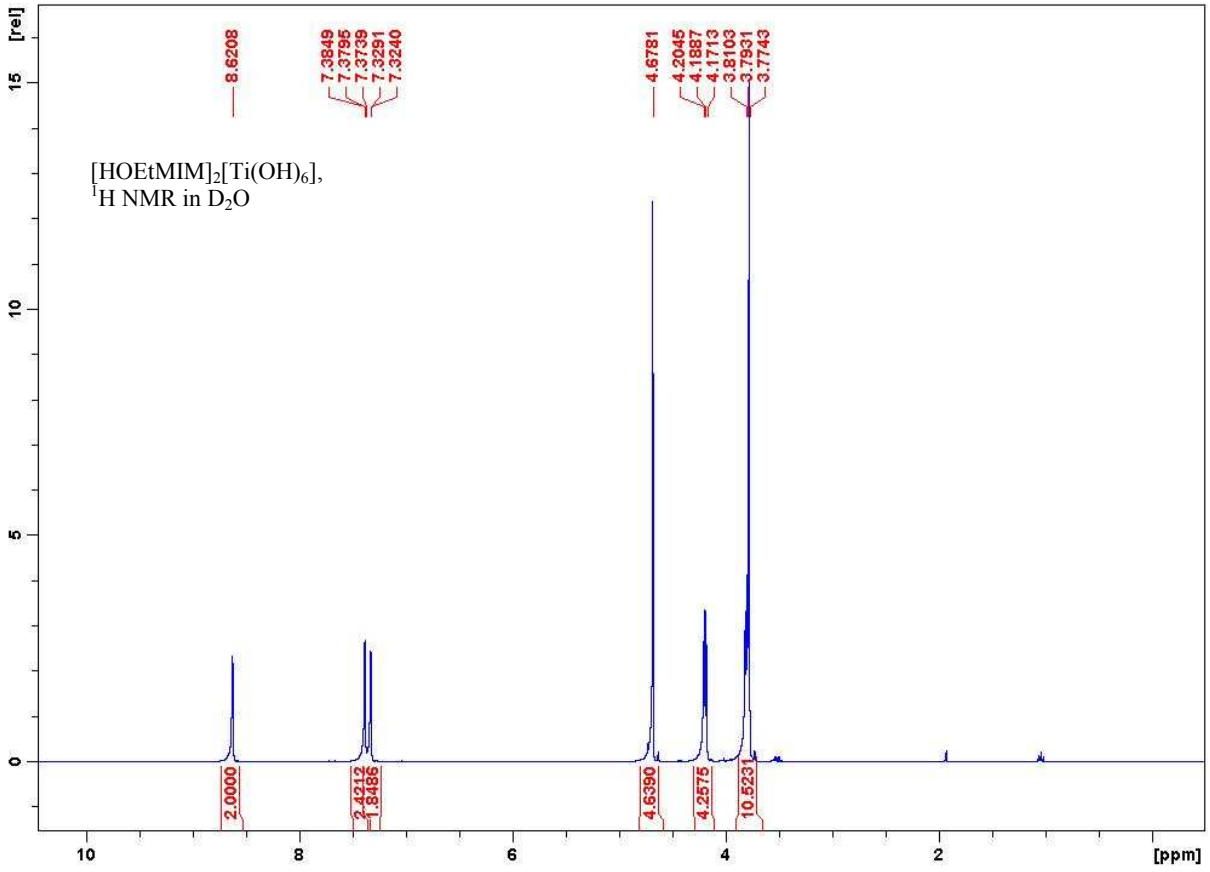

[OMIM]2[Ti(OH)6],
13C NMR in CD3CN
137.9754
123.3488
121.6946
117.3591
49.1995
35.6315
31.5098
29.8851
28.8673
28.7605
25.8450
22.3521
13.3982
1.1499
0.8749
0.5991
0.3233
0.0483
[rel]
[ppm]

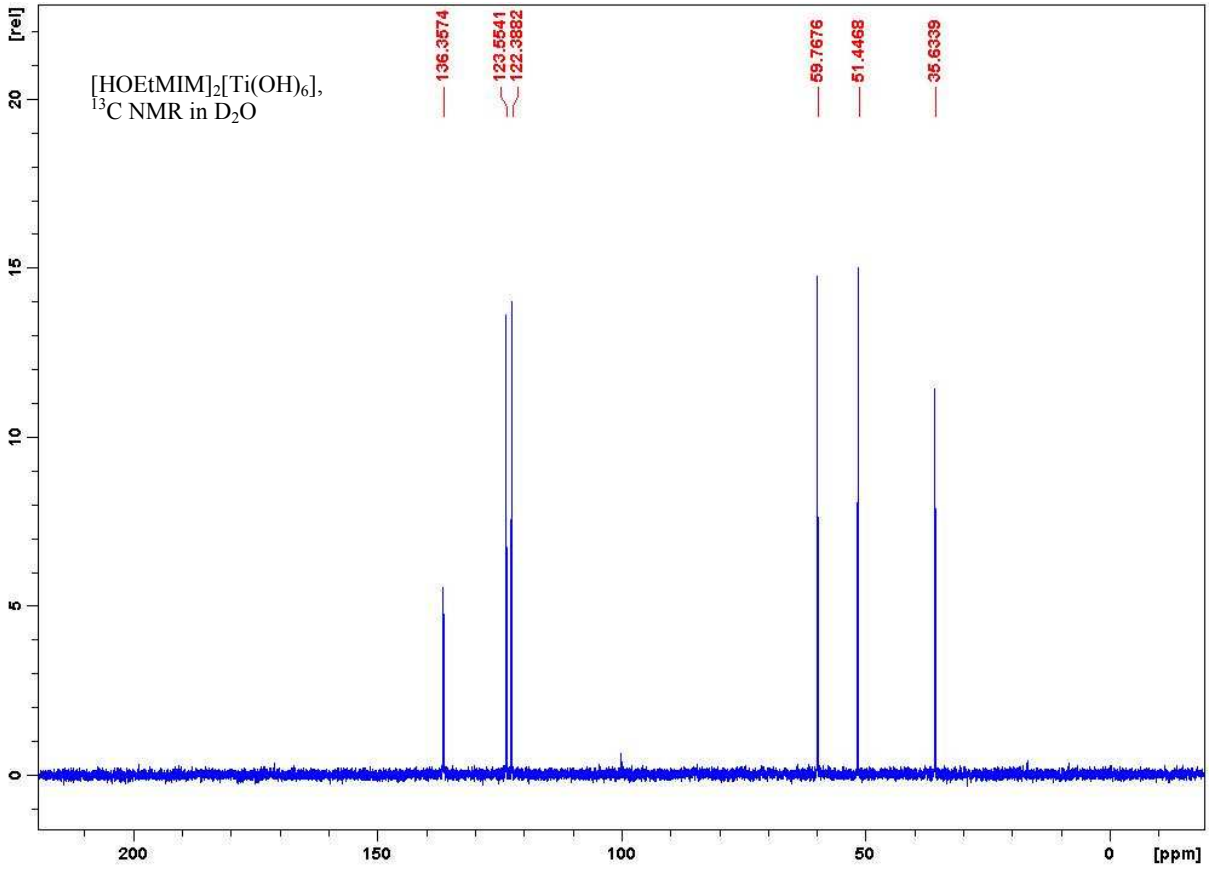

[DodMIM]2[Ti(OH)6],
1H NMR in CD3CN
9.1168
7.3536
7.3483
4.1970
4.1722
4.1483
3.8829
3.8740
2.5842
1.9732
1.9686
1.9607
1.9524
1.9442
1.9360
1.9279
1.7960
1.2635
0.8899
0.8800
0.8703
0.8566
2.0000
3.9905
4.0966
6.1216
2.7088
2.8133
4.1063
36.6649
6.1342
[rel]
[ppm]

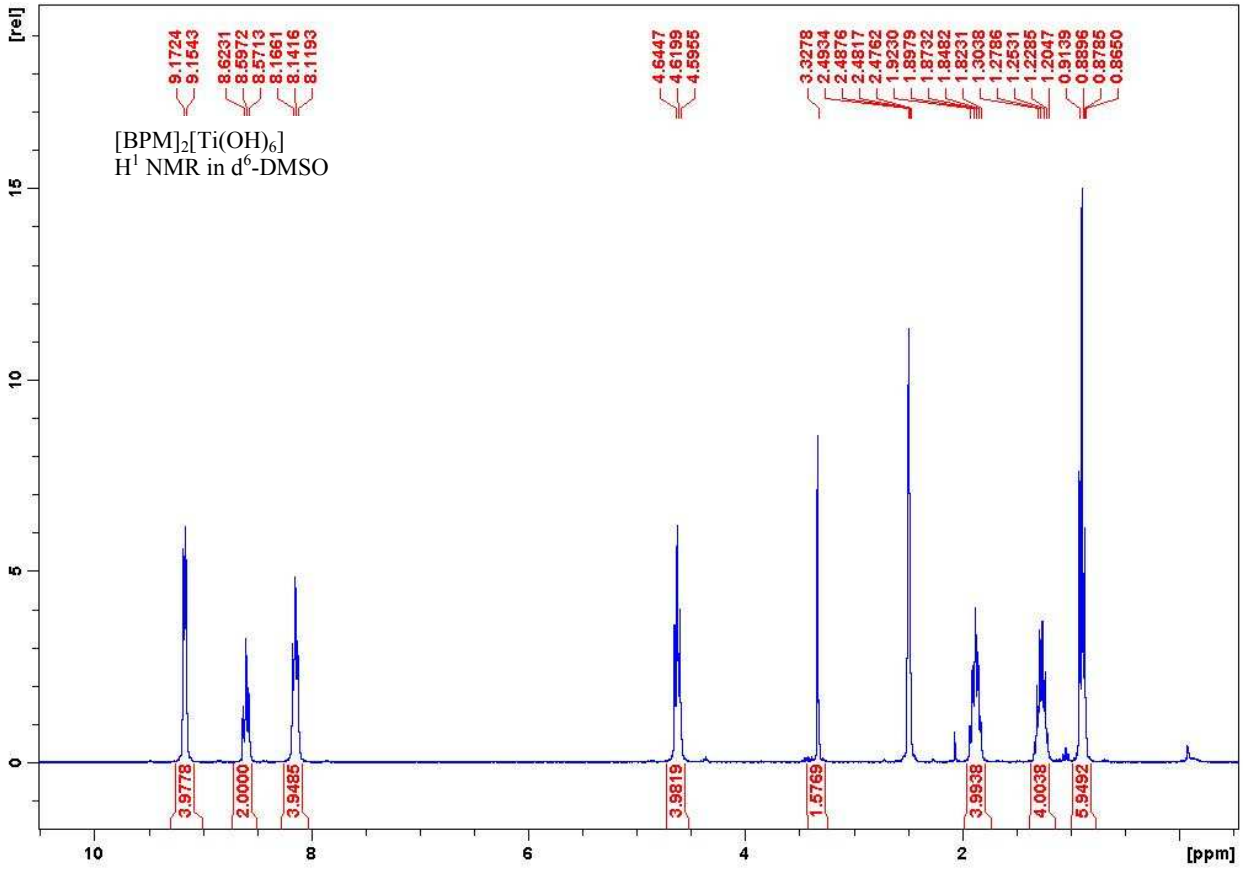

[DodMIM]2[Ti(OH)6],
13C NMR in CD3CN
137.6406
123.3268
121.7522
49.2838
35.6831
31.6403
29.8060
29.3733
29.3593
29.2946
29.1783
29.0819
28.7638
25.8078
22.3883
13.3912
1.1325
0.8579
0.5824
0.0313
[rel]
[ppm]

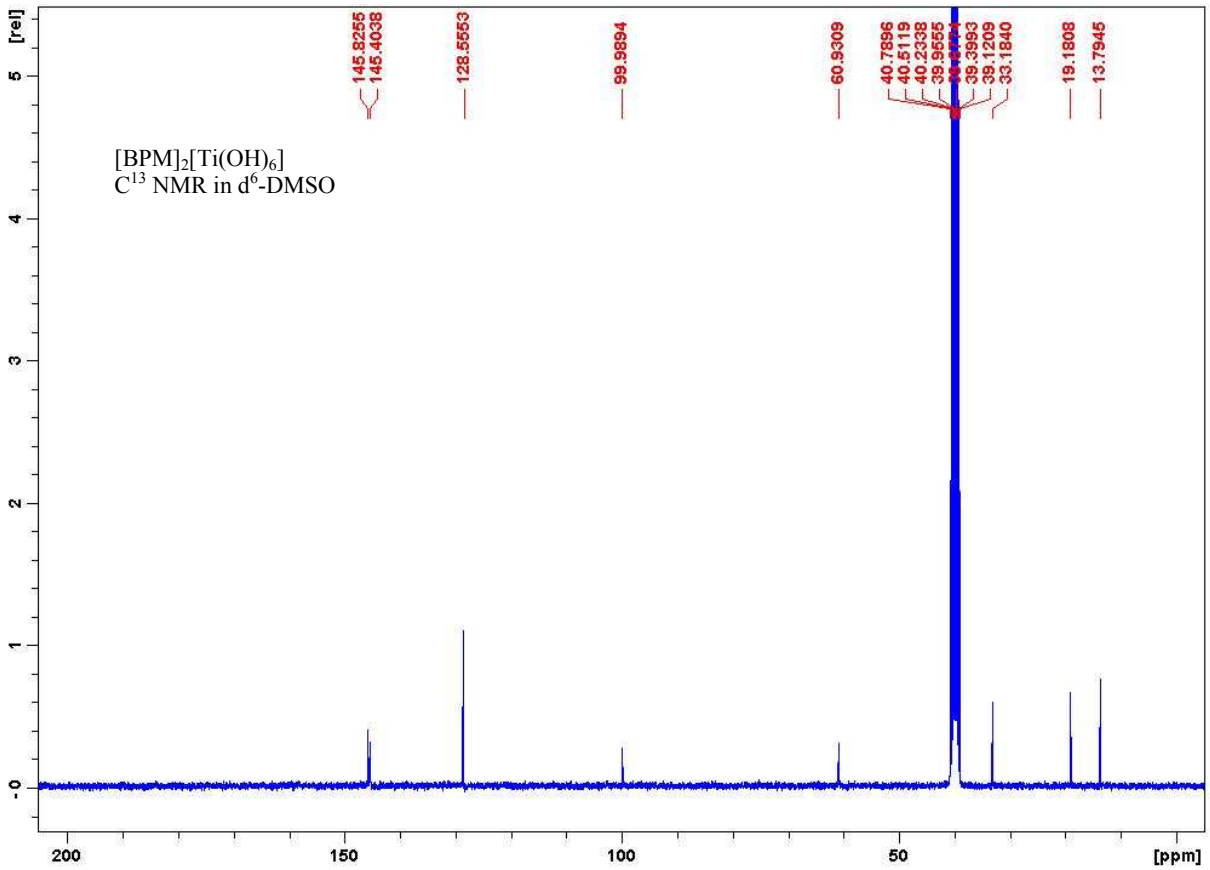

[rel]
8.9075
7.6484
7.6421
7.6363
7.4516
7.4458
7.4403
7.0505
7.0216
6.9987
6.9697
5.6898
5.6805
5.6378
5.6286
5.2944
5.2853
5.2655
5.2563
4.6861
4.1304
4.1065
4.0827
1.7592
1.7349
1.7095
1.6856
1.2306
1.2051
1.1799
1.1554
1.1315
0.8083
0.7840
0.7592
2.0000
1.9710
1.9759
1.9741
2.0494
2.0233
2.9784
4.1229
4.0943
4.1153
6.1270
[VBIM]2[Ti(OH)6],
1H NMR in D2O
[ppm]

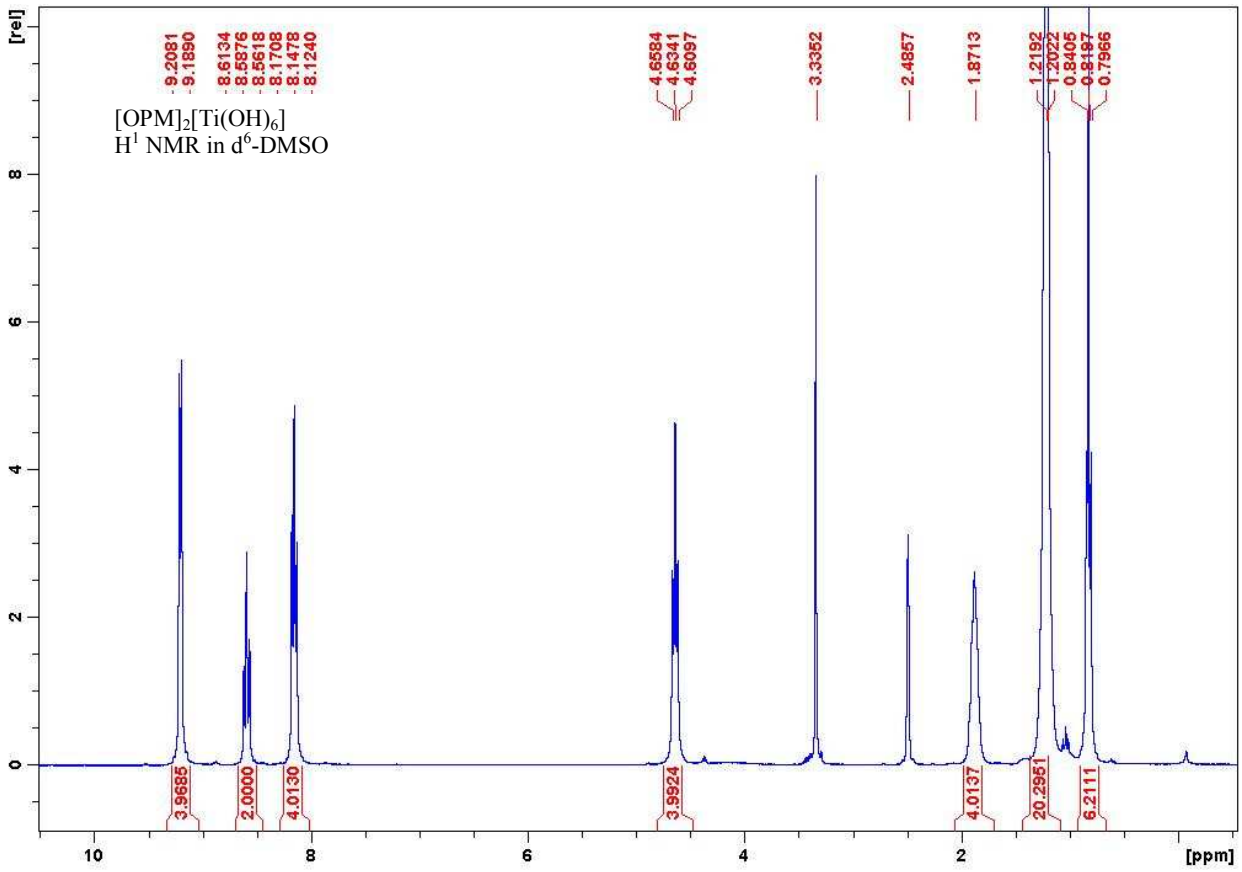

[rel]
134.3000
128.1965
122.7898
119.3108
109.0451
49.5787
31.0407
18.6598
12.5349
[VBIM]2[Ti(OH)6],
13C NMR in D2O
[ppm]

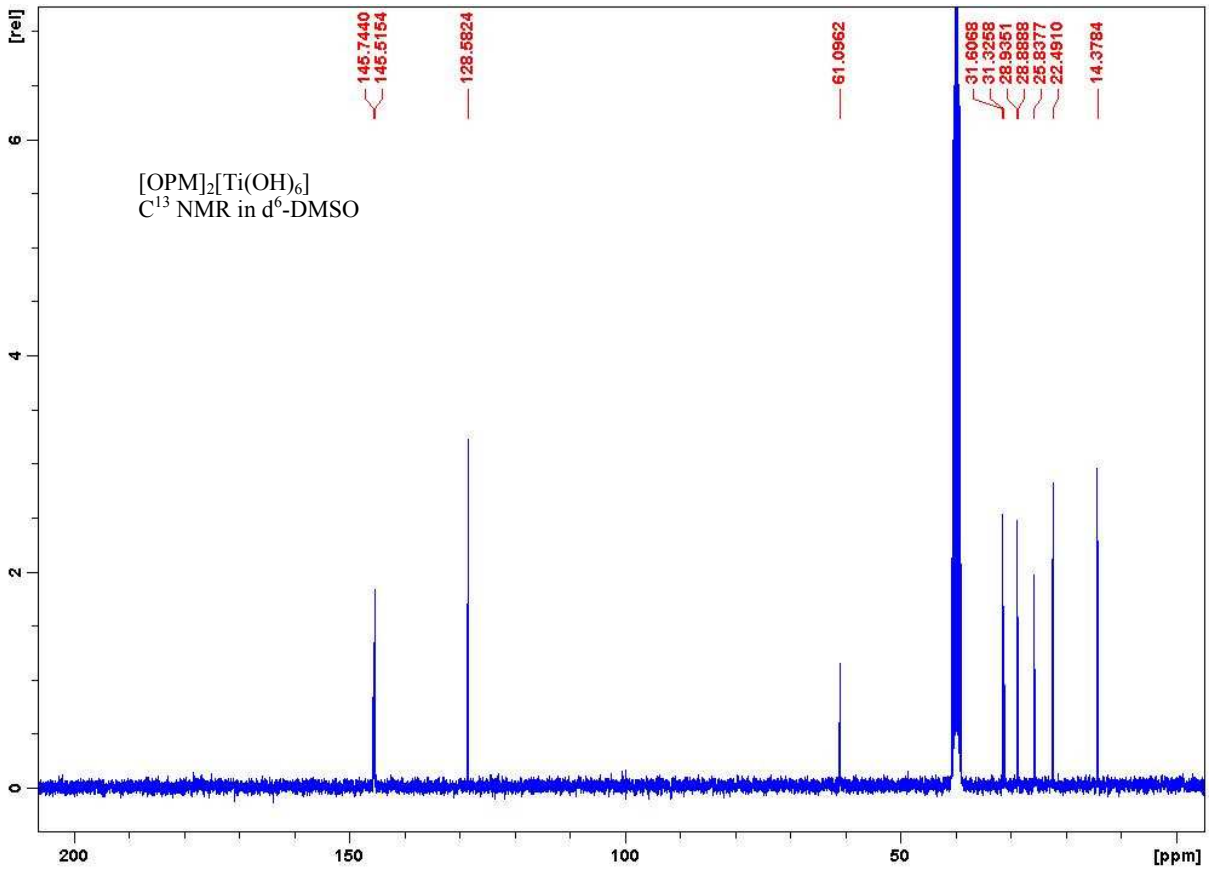

[rel]
8.6208
7.3849
7.3795
7.3739
7.3291
7.3240
4.6781
4.2045
4.1887
4.1713
3.8103
3.7931
3.7743
[HOEtMIM]2[Ti(OH)6],
1H NMR in D2O
2.0000
2.4212
1.8486
4.6390
4.2575
10.5231
[ppm]

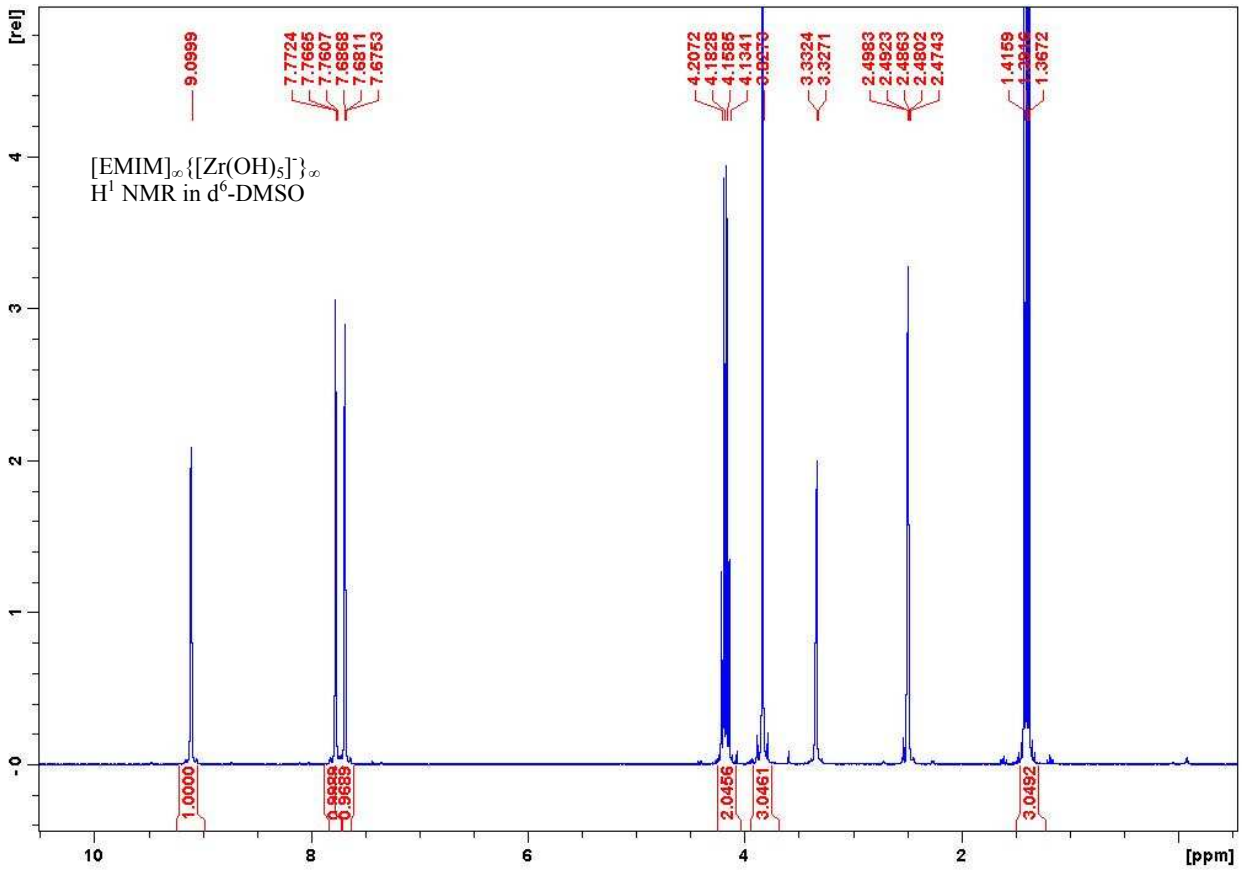

[rel]
136.3574
123.5541
122.3882
59.7676
51.4468
35.6339
[HOEtMIM]2[Ti(OH)6],
13C NMR in D2O
[ppm]

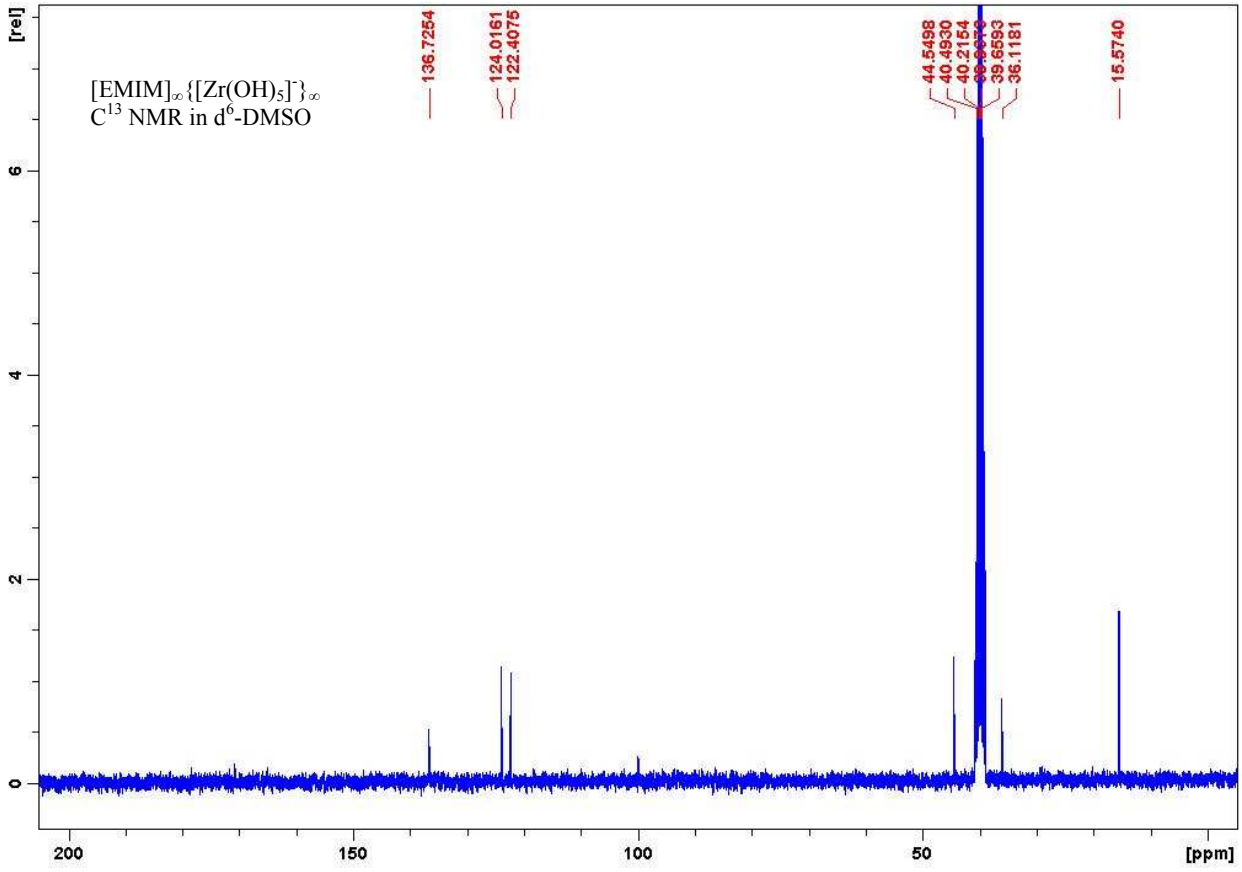

[rel]
9.1724
9.1643
8.6231
8.5972
8.5713
8.1661
8.1416
8.1193
4.6447
4.6199
4.5955
3.3278
2.4934
2.4876
2.4817
2.4762
1.9230
1.8979
1.8732
1.8482
1.8231
1.3038
1.2786
1.2531
1.2285
1.2047
0.9139
0.8896
0.8785
0.8650
[BPM]2[Ti(OH)6]
H1 NMR in d6-DMSO
3.9778
2.0000
3.9485
3.9819
1.5769
3.9938
4.0038
5.9492
[ppm]

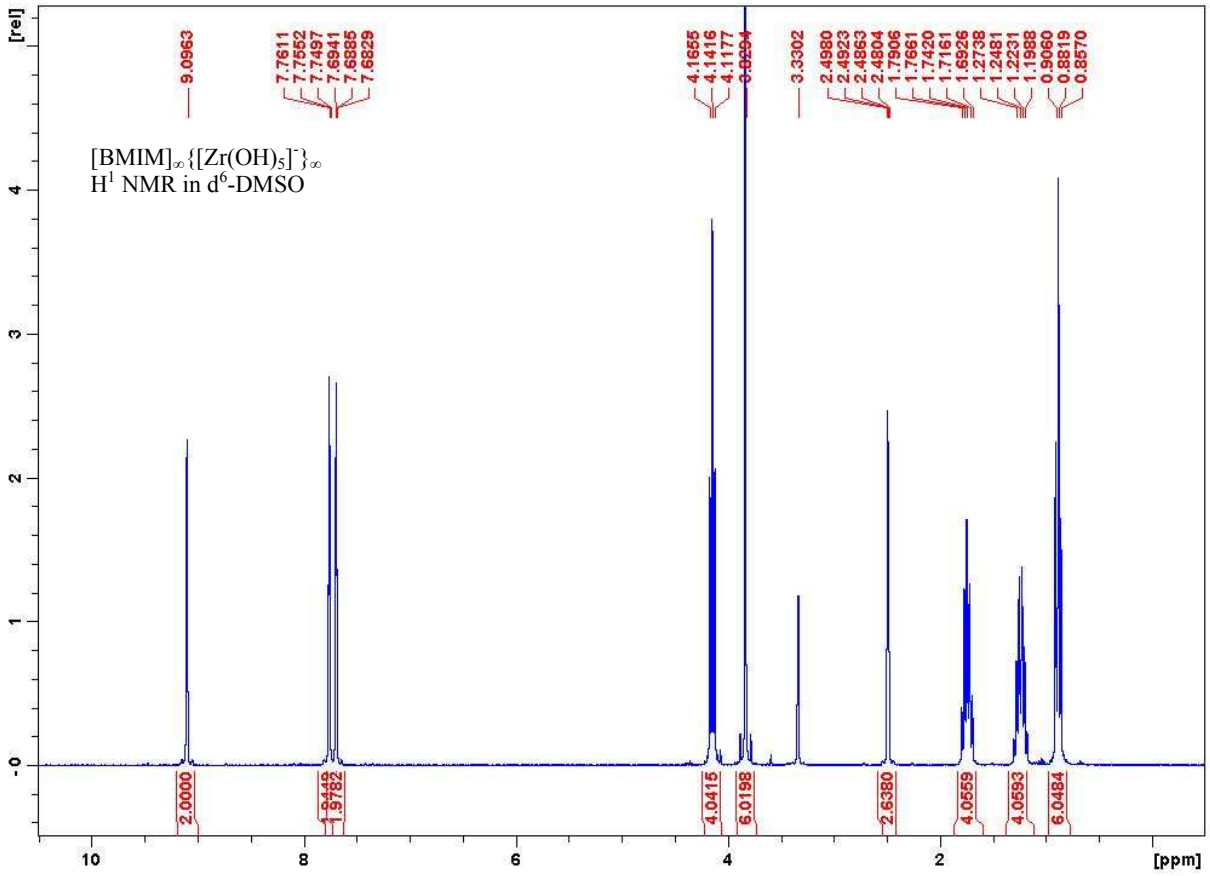

[rel]
145.8255
145.4038
128.5553
99.9894
60.9309
40.7896
40.5119
40.2338
39.9555
39.3993
39.1209
33.1840
19.1808
13.7945
[BPM]2[Ti(OH)6]
C13 NMR in d6-DMSO
[ppm]


[rel]
9.2081
9.1890
8.6134
8.5876
8.5618
8.1708
8.1478
8.1240
4.6584
4.6341
4.6097
3.3352
2.4857
1.8713
1.2192
1.2022
0.8405
0.8187
0.7966
[OPM]2[Ti(OH)6]
H1 NMR in d6-DMSO
3.9685
2.0000
4.0130
3.9924
4.0137
20.2951
6.2111
[ppm]


[rel]
145.7440
145.5154
128.5824
61.0962
31.6068
31.3258
28.9351
28.8888
25.8377
22.4910
14.3784
[OPM]2[Ti(OH)6]
C13 NMR in d6-DMSO
[ppm]


[rel]
9.0999
7.7724
7.7665
7.7607
7.6868
7.6811
7.6753
4.2072
4.1828
4.1585
4.1341
3.3324
3.3271
2.4983
2.4923
2.4863
2.4802
2.4743
1.4159
1.3672
[EMIM]∞{[Zr(OH)5]-}∞
H1 NMR in d6-DMSO
1.0000
0.9889
2.0456
3.0461
3.0492
10
8
6
4
2
[ppm]


[rel]
136.7254
124.0161
122.4075
44.5498
40.4930
40.2154
39.6553
36.1181
15.5740
[EMIM]∞{[Zr(OH)5]-}∞
C13 NMR in d6-DMSO
200
150
100
50
[ppm]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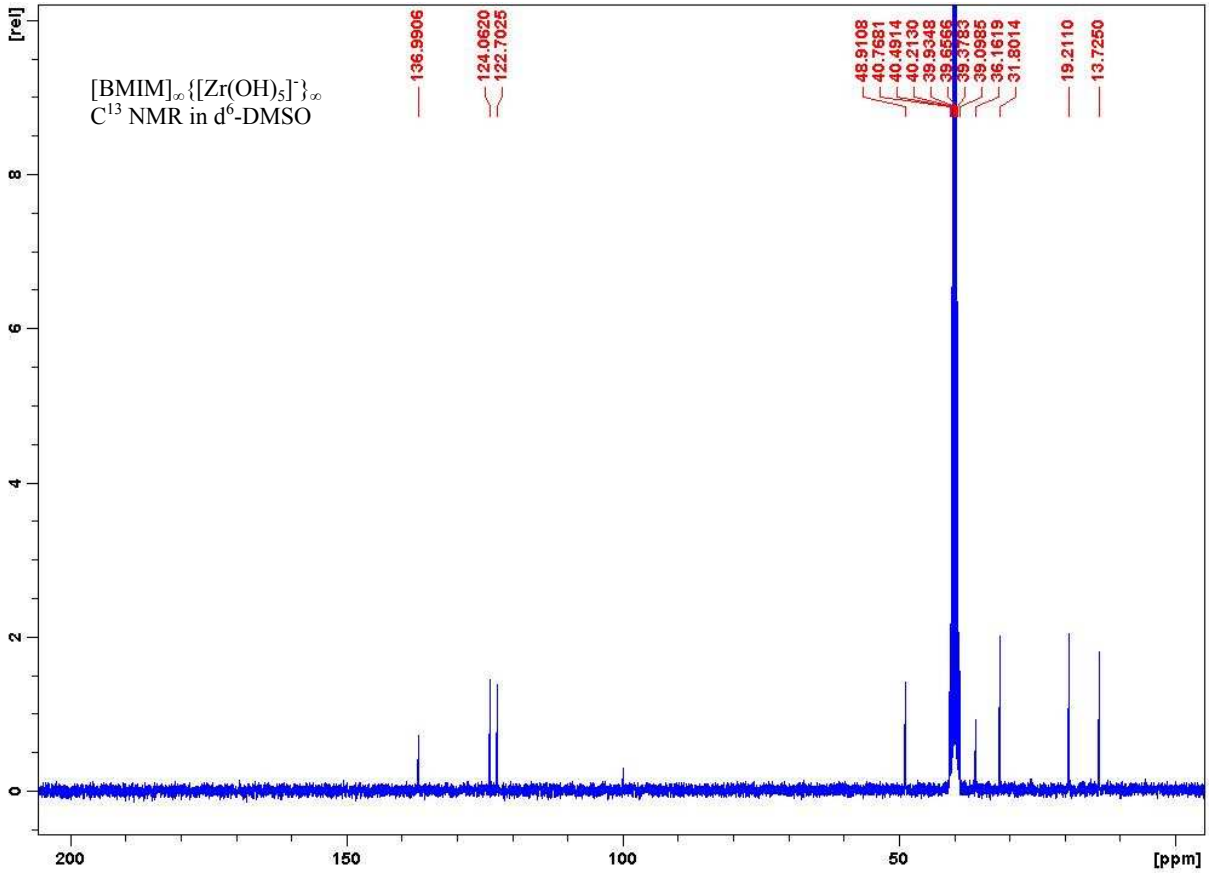
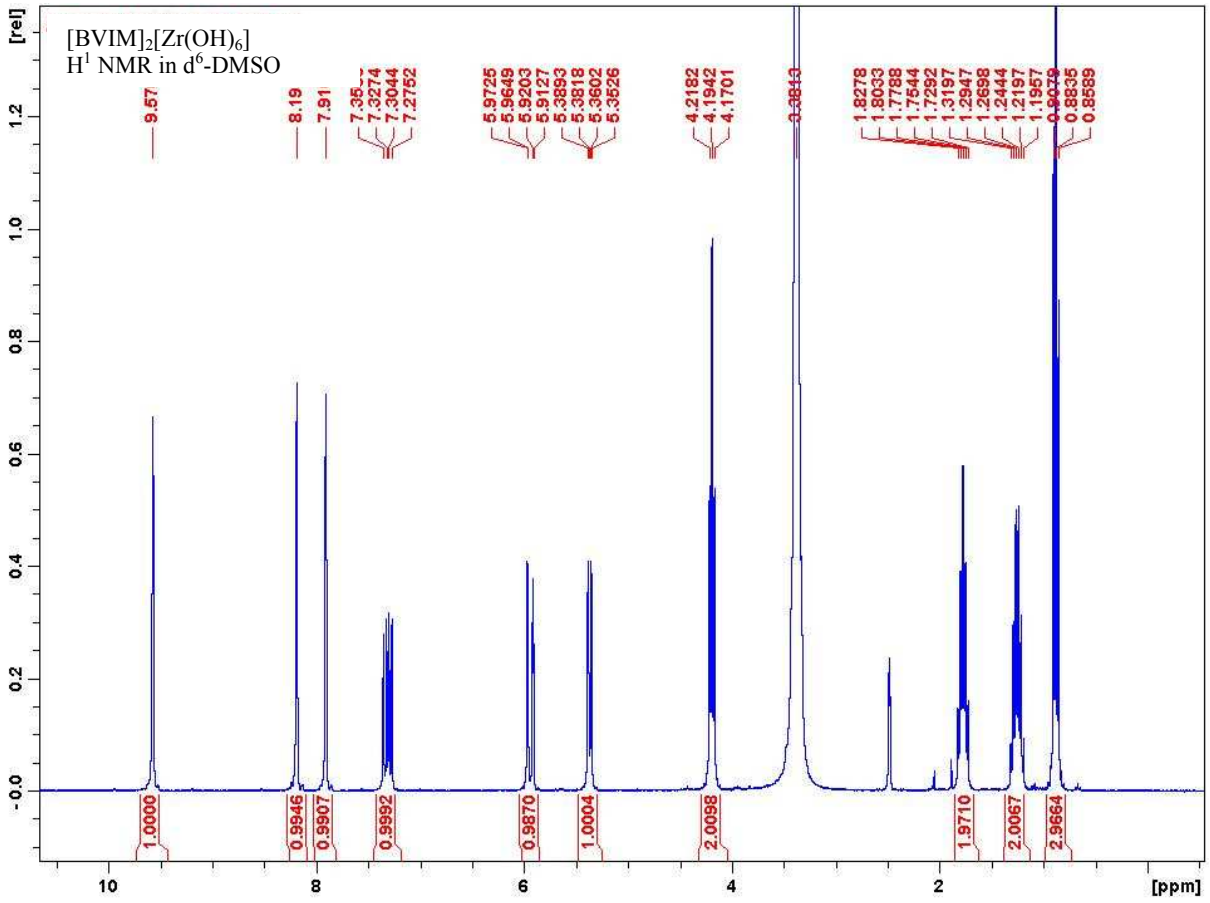
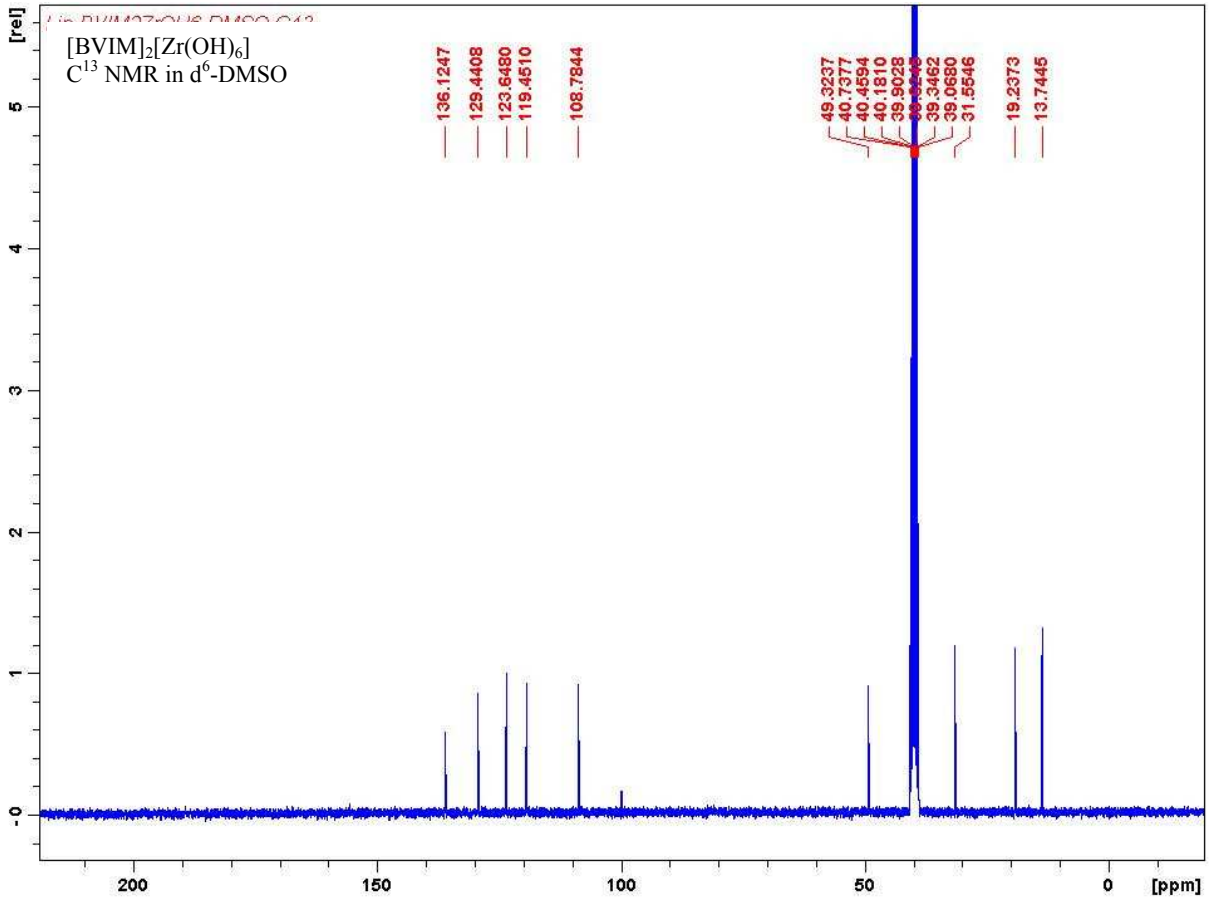
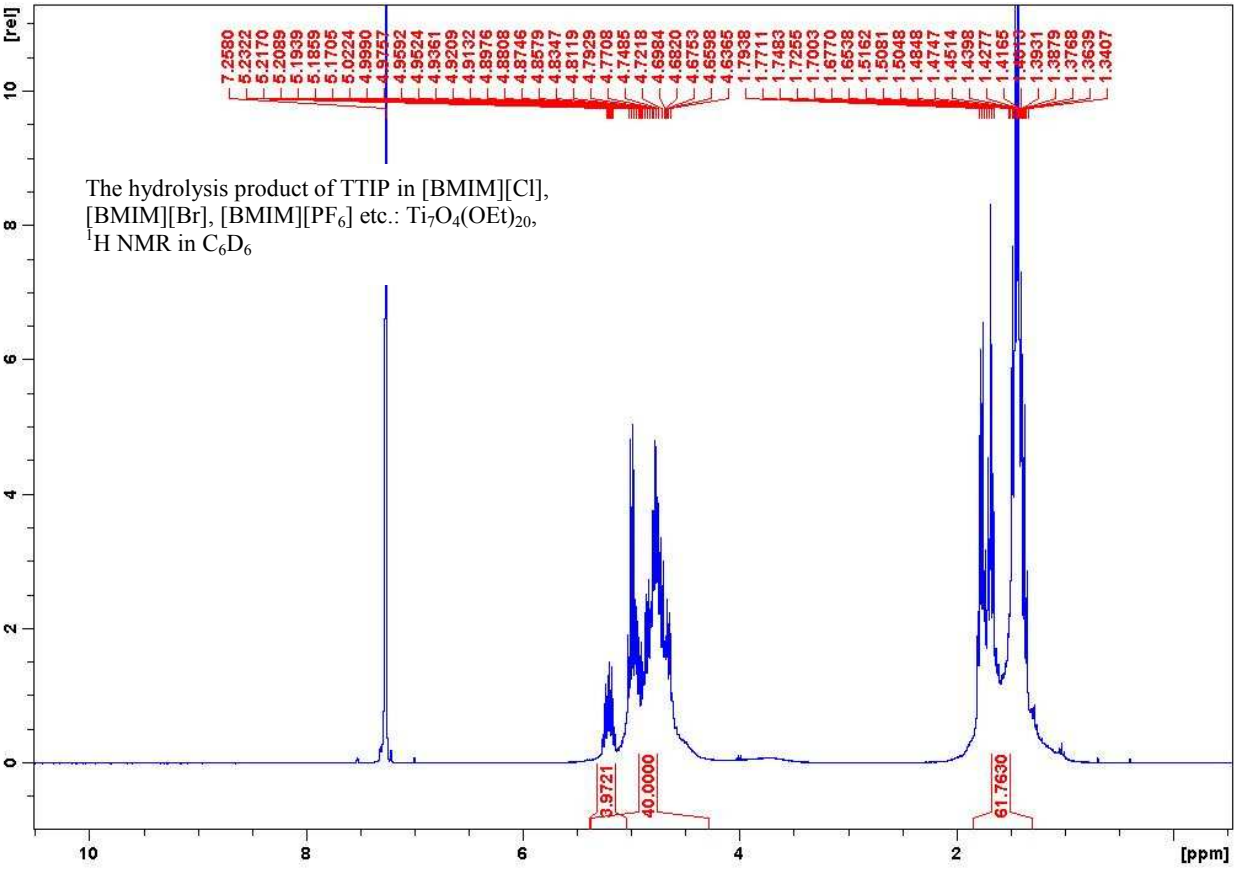
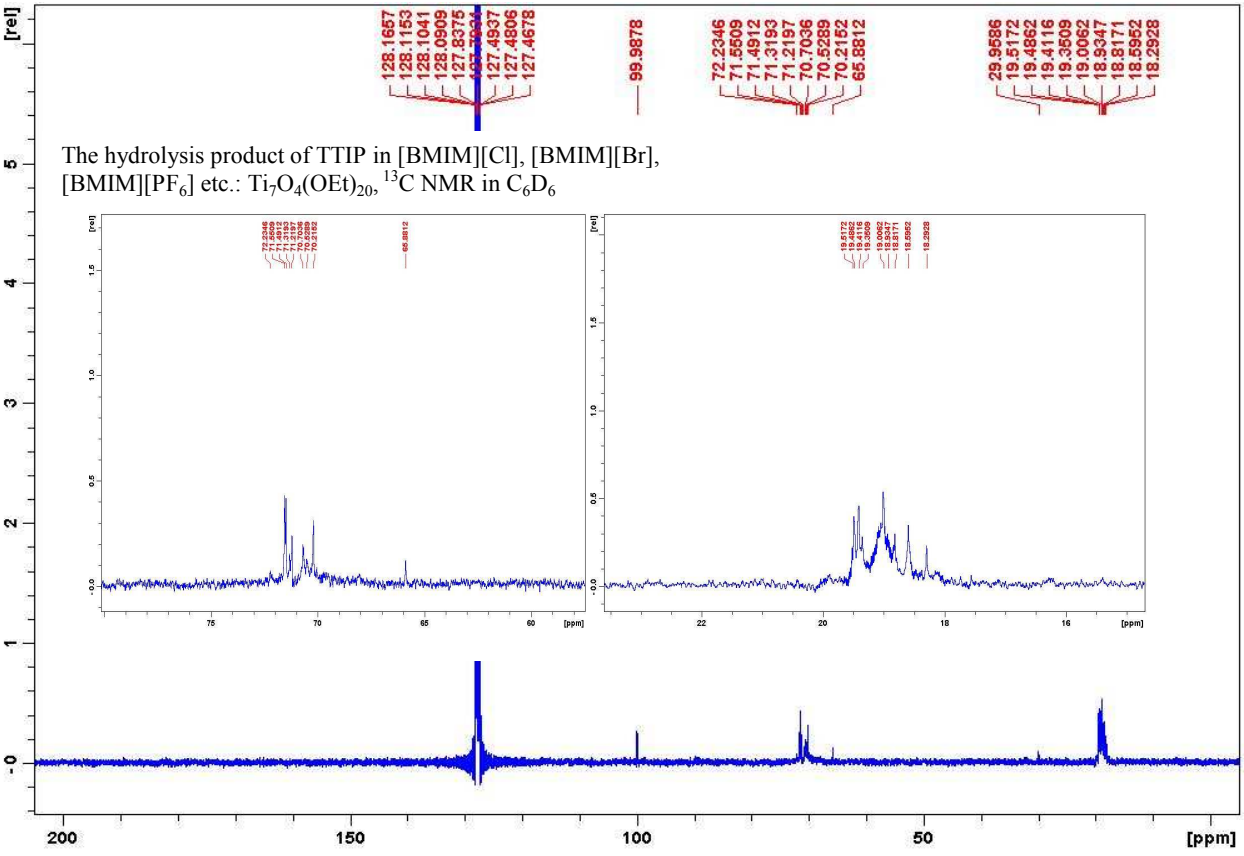
9.0963
7.7611
7.7552
7.7497
7.6941
7.6885
7.6829
4.1655
4.1416
4.1177
3.3302
2.4980
2.4923
2.4863
2.4804
1.7906
1.7661
1.7420
1.7161
1.6926
1.2738
1.2481
1.2231
1.1988
0.9060
0.8819
0.8570
[BMIM]∞{[Zr(OH)5]-}∞
H1 NMR in d6-DMSO
2.0000
1.9449
1.9782
4.0415
6.0198
2.6380
4.0559
4.0593
6.0484
[ppm]


[rel]
136.9906
124.0620
122.7025
48.9108
40.7681
40.4914
40.2130
39.9348
39.6565
39.3783
39.0985
36.1619
31.8014
19.2110
13.7250
[BMIM]∞{[Zr(OH)5]-}∞
C13 NMR in d6-DMSO
[ppm]


[BVIM]2[Zr(OH)6]
H1 NMR in d6-DMSO
[rel]
[ppm]
9.57
8.19
7.91
7.35
7.3274
7.3044
7.2752
5.9725
5.9649
5.9203
5.9127
5.3893
5.3818
5.3602
5.3526
4.2182
4.1942
4.1701
0.3813
1.8278
1.8033
1.7788
1.7544
1.7292
1.3197
1.2947
1.2698
1.2444
1.2197
1.1957
0.8839
0.8635
0.8589
1.0000
0.9946
0.9907
0.9992
0.9870
1.0004
2.0098
1.9710
2.0067
2.9664


[BVIM]2[Zr(OH)6]
C13 NMR in d6-DMSO
[rel]
[ppm]
136.1247
129.4408
123.6480
119.4510
108.7844
49.3237
40.7377
40.4594
40.1810
39.9028
39.3462
39.0680
31.5546
19.2373
13.7445


The hydrolysis product of TTIP in [BMIM][Cl], [BMIM][Br], [BMIM][PF6] etc.: Ti7O4(OEt)20, 1H NMR in C6D6
[rel]
[ppm]
3.9721
40.0000
61.7630


The hydrolysis product of TTIP in [BMIM][Cl], [BMIM][Br], [BMIM][PF6] etc.: Ti7O4(OEt)20, 13C NMR in C6D6
[rel]
[ppm]