Supporting Information

Intrinsic MRI contrast from Amino Acid based Paramagnetic Ionic Liquids

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Characterization

The chemical structure (Table 1) of synthesized PMILs has been analyzed through MS (MicroMass Q-TOF) and ^{1}H NMR (Brüker 500 MH_z) techniques. MS of PMILs were performed in methanol solvent and for ^{1}H NMR PMILs were ultra-diluted in deuterated methanol solvent to avoid inherent magnetization for achieving good spectra. Elemental analysis (Table S1) was carried out with CHNS-15111009 Elementar Vario-Micro tube, Germany; and absolute Fe% composition in PMILs was determined by Perkin Elmer ICP optima 2000 DV ICP-OES (Inductively Coupled Plasma–Optical Emission Spectroscopy) analyser (Table S2). The osmolality of PMILs was measured from WESCOR® Vapro® vapor pressure osmometer (Table 1).

Table S1. Elemental analysis.

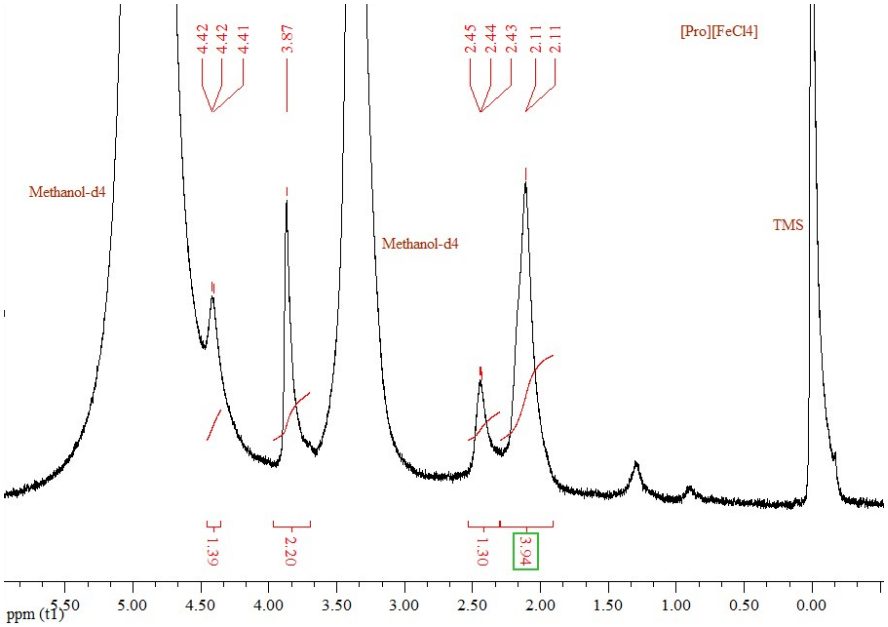
PMILs	C%		N%		H%	
	Cal	Obs	Cal	Obs	Cal	Obs
Pro[$FeCl_4$]	19.14	18.99	4.46	4.12	3.21	3.02
ProC_1[$FeCl_4$]	21.98	22.01	4.27	4.20	3.69	3.81
Glu[$FeCl_4$]	17.34	17.01	4.05	4.21	2.92	2.88
GluC_1[$FeCl_4$]	22.49	22.90	3.75	3.55	3.77	3.78
Ala[$FeCl_4$]	15.92	16.23	4.64	4.52	3.34	3.33
Val[$FeCl_4$]	21.85	22.10	4.25	4.62	4.28	4.12

Table S2. Glass transition temperature, degradation temperature, and Fe % for PMILs (a = observed at present room temperature)

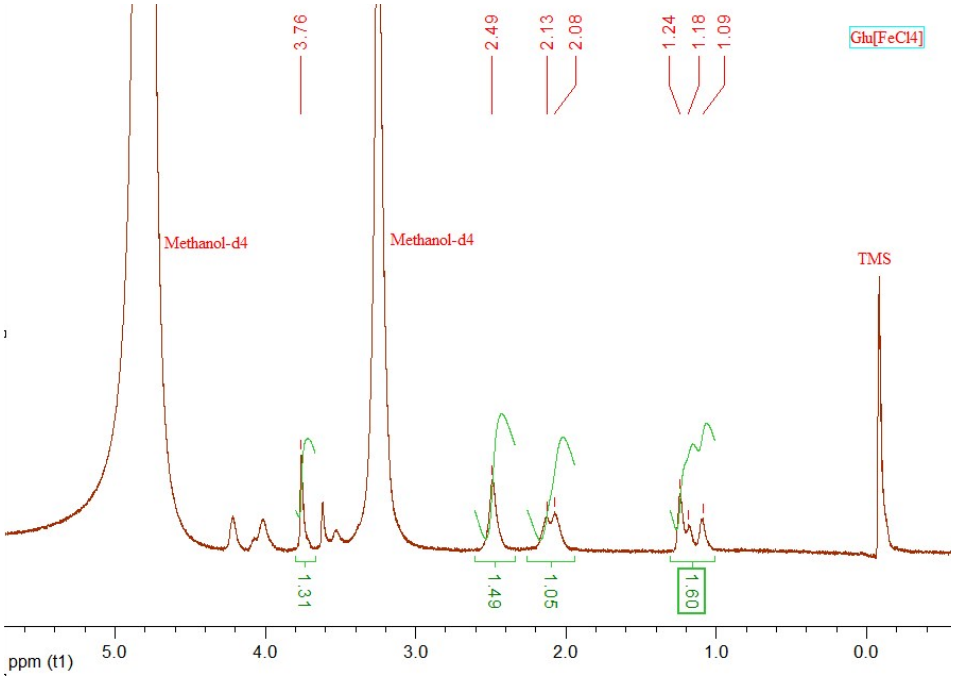
PMILs	T_g (DSC) ^oC	T_d (TGA) ^oC	% Fe (ICP)	State[a]
Pro[$FeCl_4$]	-59	238	14.3	Liquid
ProC_1[$FeCl_4$]	67	236	18.3	Solid
Glu[$FeCl_4$]	-54	233	12.7	Liquid
GluC_1[$FeCl_4$]	-55	240	12.9	Liquid
Ala[$FeCl_4$]	-47	210	19.7	Liquid
Val[$FeCl_4$]	-29	231	17.1	Liquid

NMR spectra of PMILs.

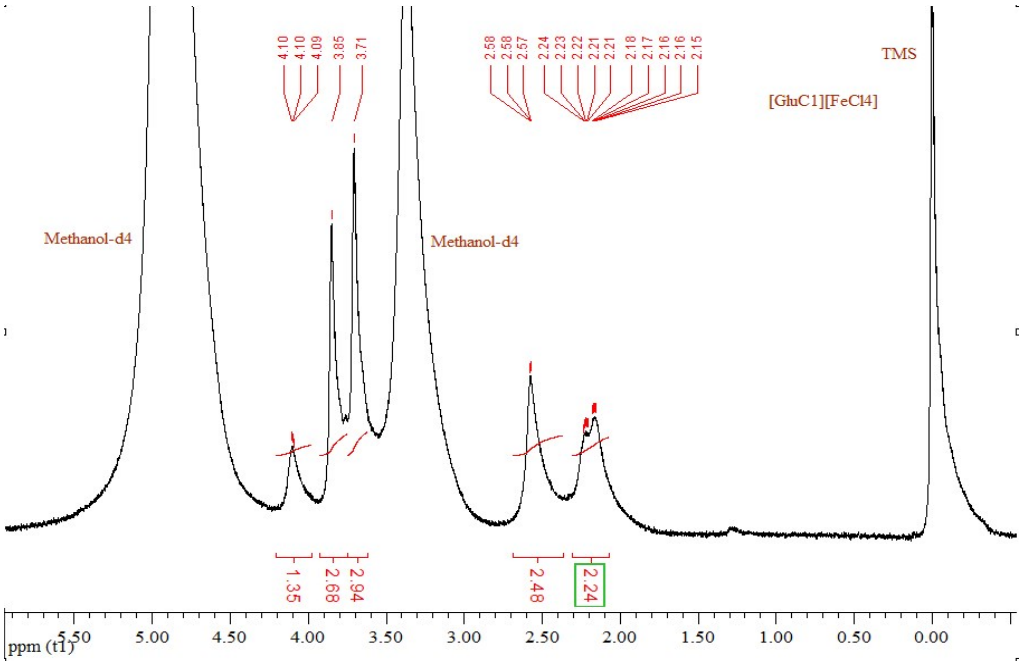
1. ^{1}H NMR of Pro[$FeCl_4$]: Chemical shift (δ) 2.11 (m, 4H), 2.44 (m, 1H), 3.87 (m, 2H), 4.42 (s,1H) LCMS Data: ESI^+ (m/z) 116.2 for $[C_5H_{10}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



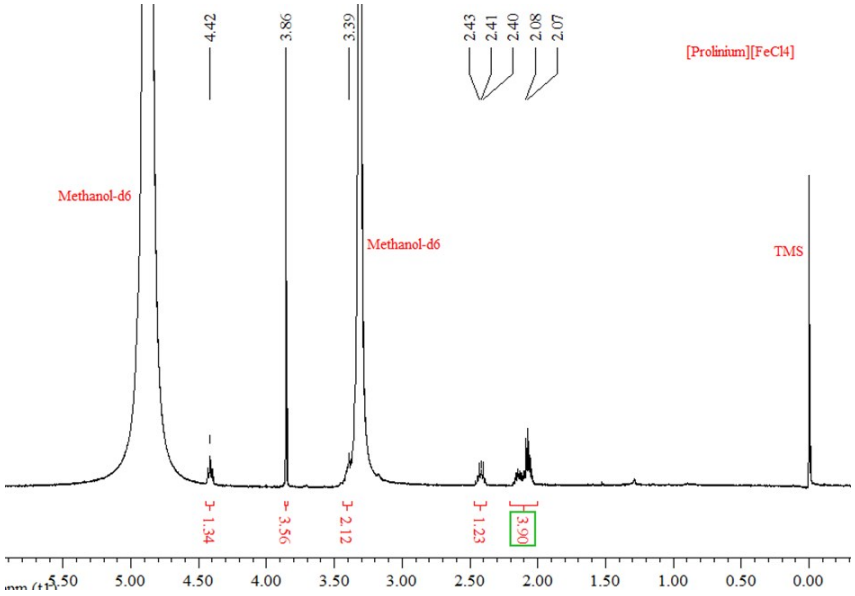
2. ^{1}H NMR of Glu[$FeCl_4$]: Chemical shift (δ, ππμ) 1.18 (t, 2H), 2.13 (d, 2H), 3.76 (t, 1H), LCMS Data: ESI^{+} (m/z) 148.1 for $[C_5H_{10}NO_4]^{+}$, ESI^{-} (m/z) 197.80 for $[FeCl_4]^{-}$



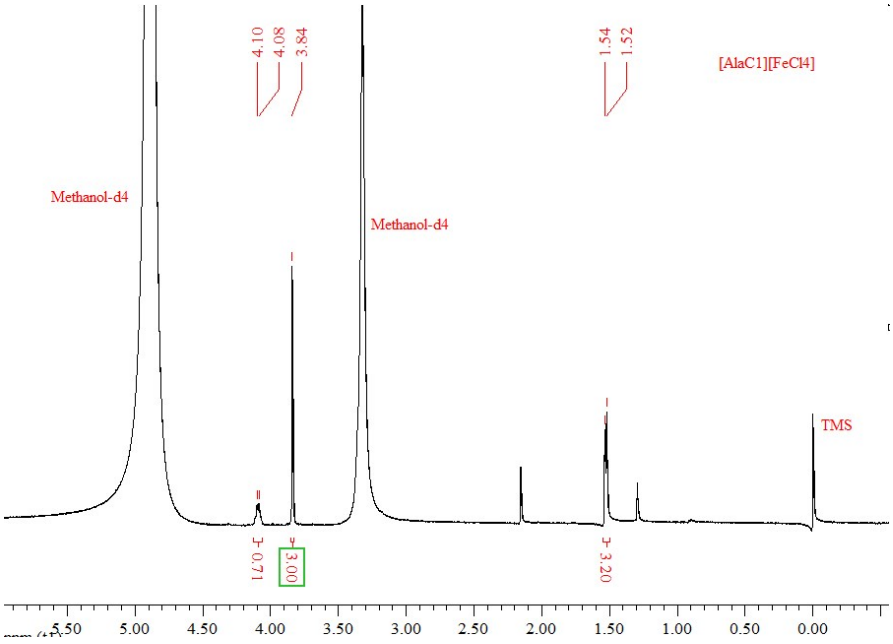
3. ^{1}H NMR of GluC_1[$FeCl_4$]: Chemical shift (δ) 2.2 (m, 2H), 2.58 (m, 2H), 3.7(S, 3H), 3.7(S, 3H), 3.8 (S, 3H), 4.1(m,1H). LCMS Data: ESI^{+} (m/z) 176.1 for $[C_7H_{14}NO_4]^{+}$, ESI^{-} (m/z) 197.80 for $[FeCl_4]^{-}$



4. ^{1}H NMR of ProC_1[$FeCl_4$]: Chemical shift (δ) 2.08 (m,4H), 2.41(m,1H), 3.39 (m, 2H), 3.86 (S, 3H), 4.42 (m,1H). LCMS Data: ESI^+ (m/z) 130.09 for $[C_6H_{12}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



5. ^{1}H NMR of AlaC_1[$FeCl_4$]: Chemical shift (δ) 1.54 (m,3H), 3.84(s,3H), 4.1 (m, 1H). LCMS Data: ESI^+ (m/z) 104.03 for $[C_3H_8NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



6. ^{1}H NMR of $ValC_1[FeCl_4]$ Chemical shift (δ) 1.07 (d,6H), 2.28(m,1H), 3. 85 (s, 3H), 3.92 (m, 1H). LCMS Data: ESI^+ (m/z) 132.1 for $[C_5H_{12}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$

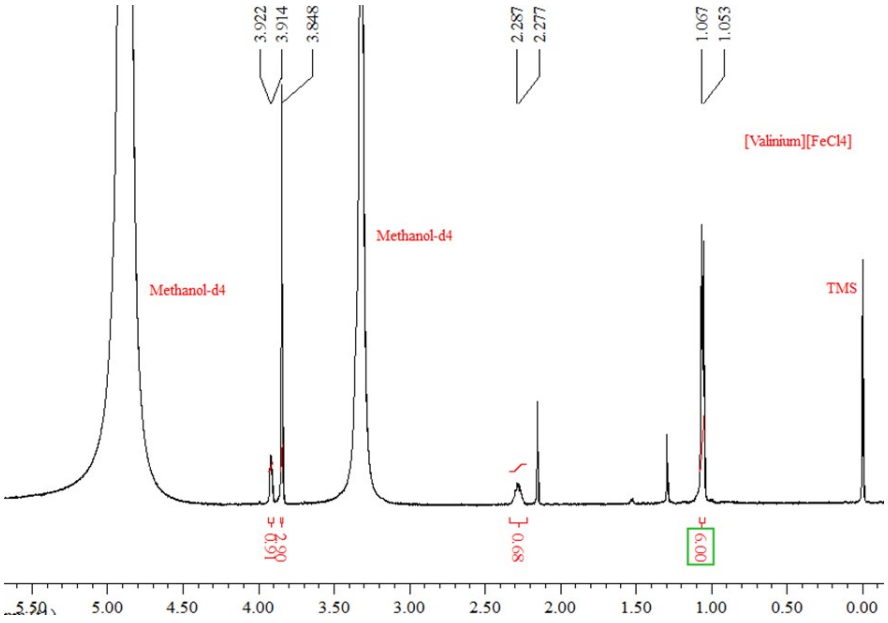


Figure S1. NMR spectra of PMILs.

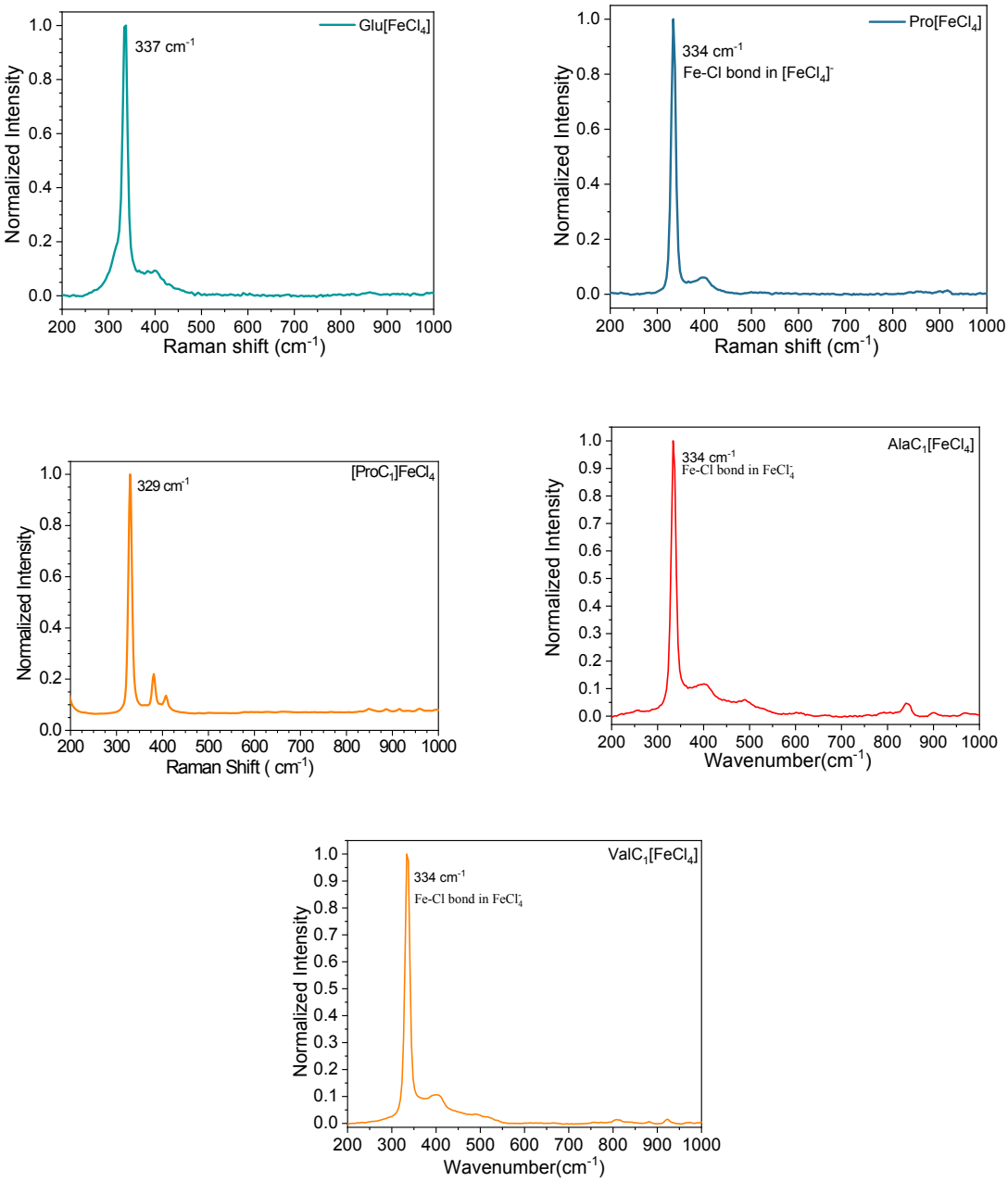


Figure S2. Raman spectra of $[FeCl_4]^-$ anion in various PMILs.

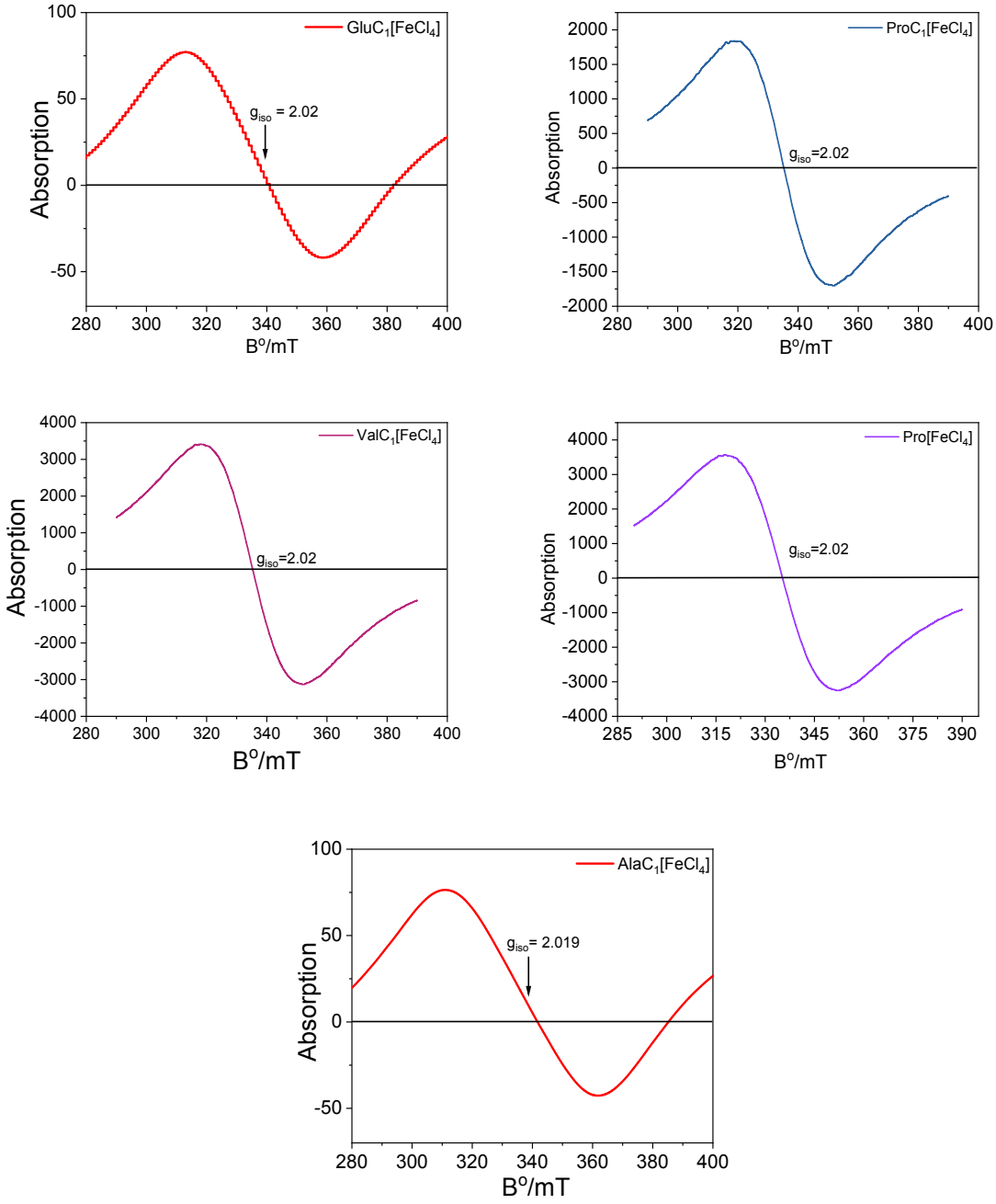
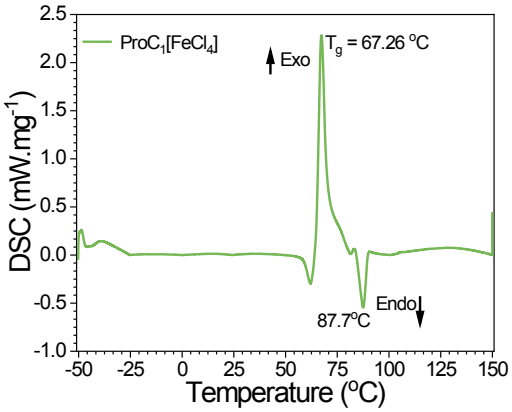
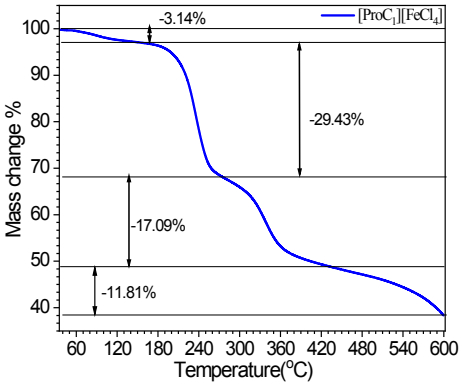
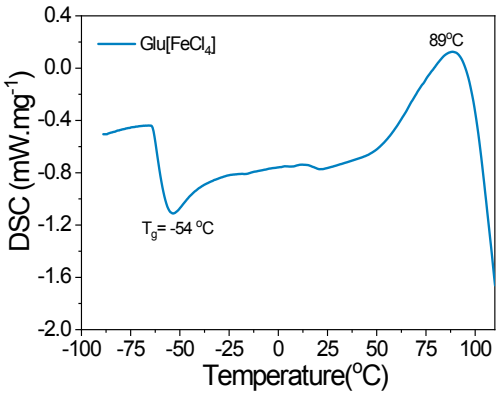
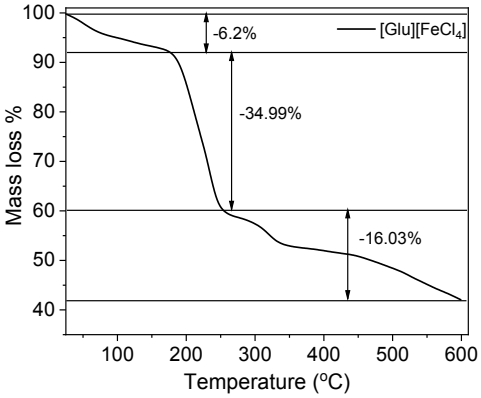


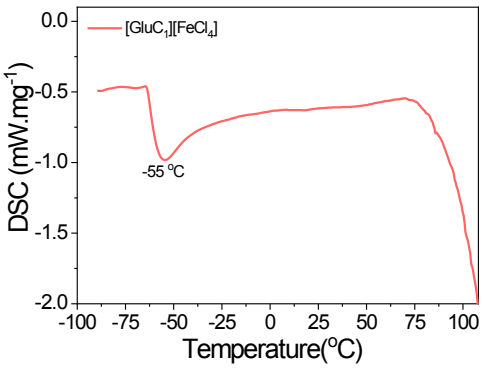
Figure S3. EPR spectra of $[FeCl_4]^-$ anion in various PMILs.

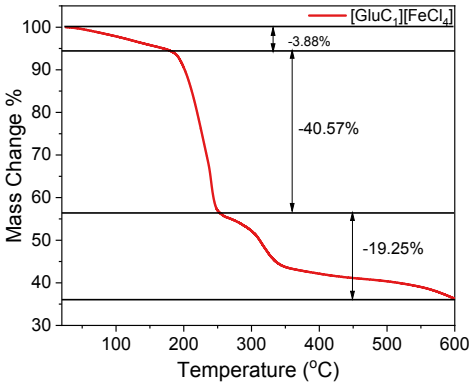

ProC1[FeCl4]
Exo
Tg = 67.26 °C
87.7°C
Endo
DSC (mW.mg-1)
Temperature (°C)

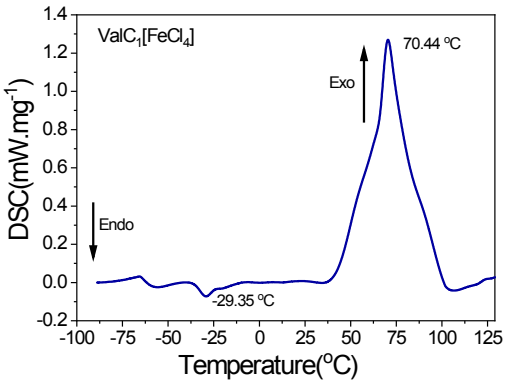

-3.14%
[ProC1][FeCl4]
-29.43%
-17.09%
-11.81%
Mass change %
Temperature(°C)

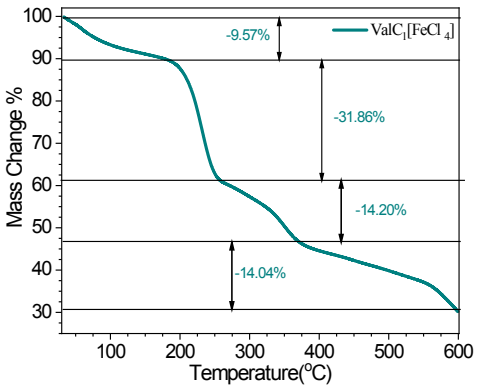

Glu[FeCl4]
89°C
Tg= -54 °C
DSC (mW.mg-1)
Temperature(°C)


-6.2%
[Glu][FeCl4]
-34.99%
-16.03%
Mass loss %
Temperature (°C)


[GluC1][FeCl4]
-55 °C
DSC (mW.mg-1)
Temperature(°C)


[GluC1][FeCl4]
-3.88%
-40.57%
-19.25%
Mass Change %
Temperature (°C)


ValC1[FeCl4]
70.44 °C
Exo
Endo
-29.35 °C
DSC(mW.mg-1)
Temperature(°C)


-9.57%
ValC1[FeCl 4]
-31.86%
-14.20%
-14.04%
Mass Change %
Temperature(°C)

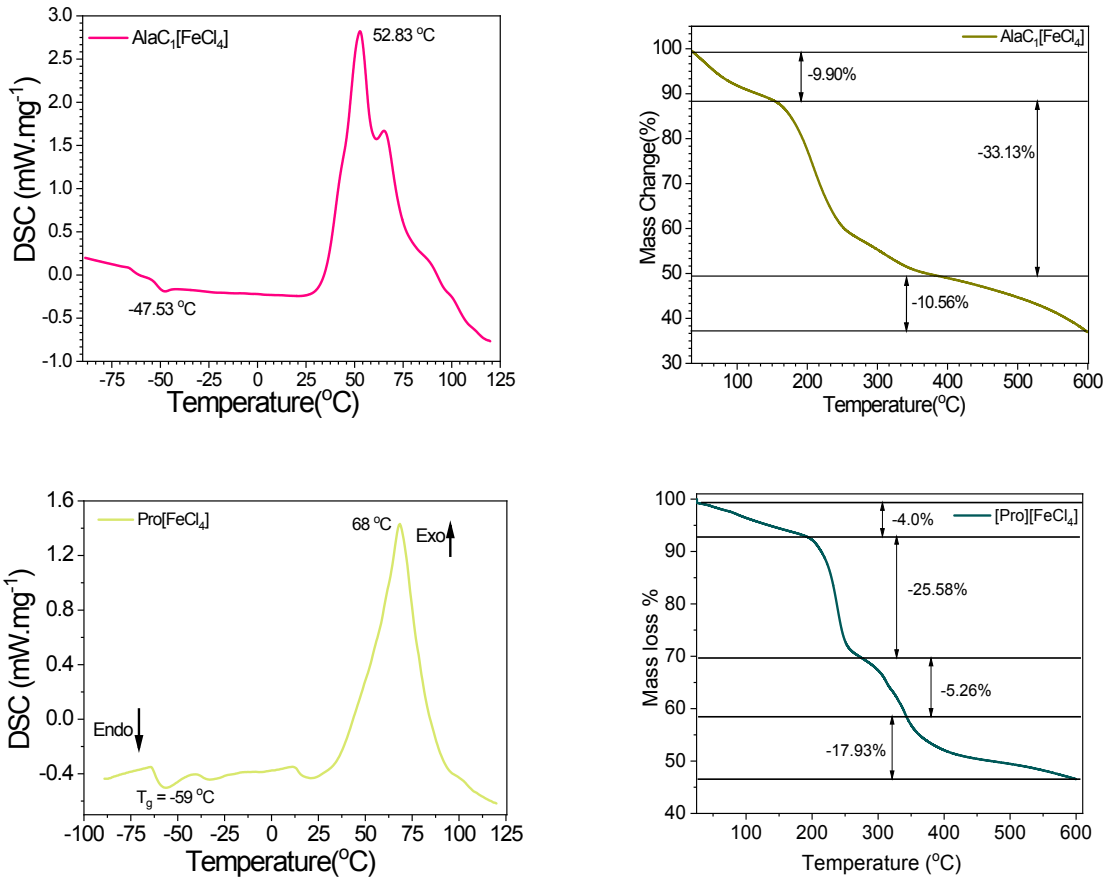


Figure S4. DSC and TGA traces of PMILs.

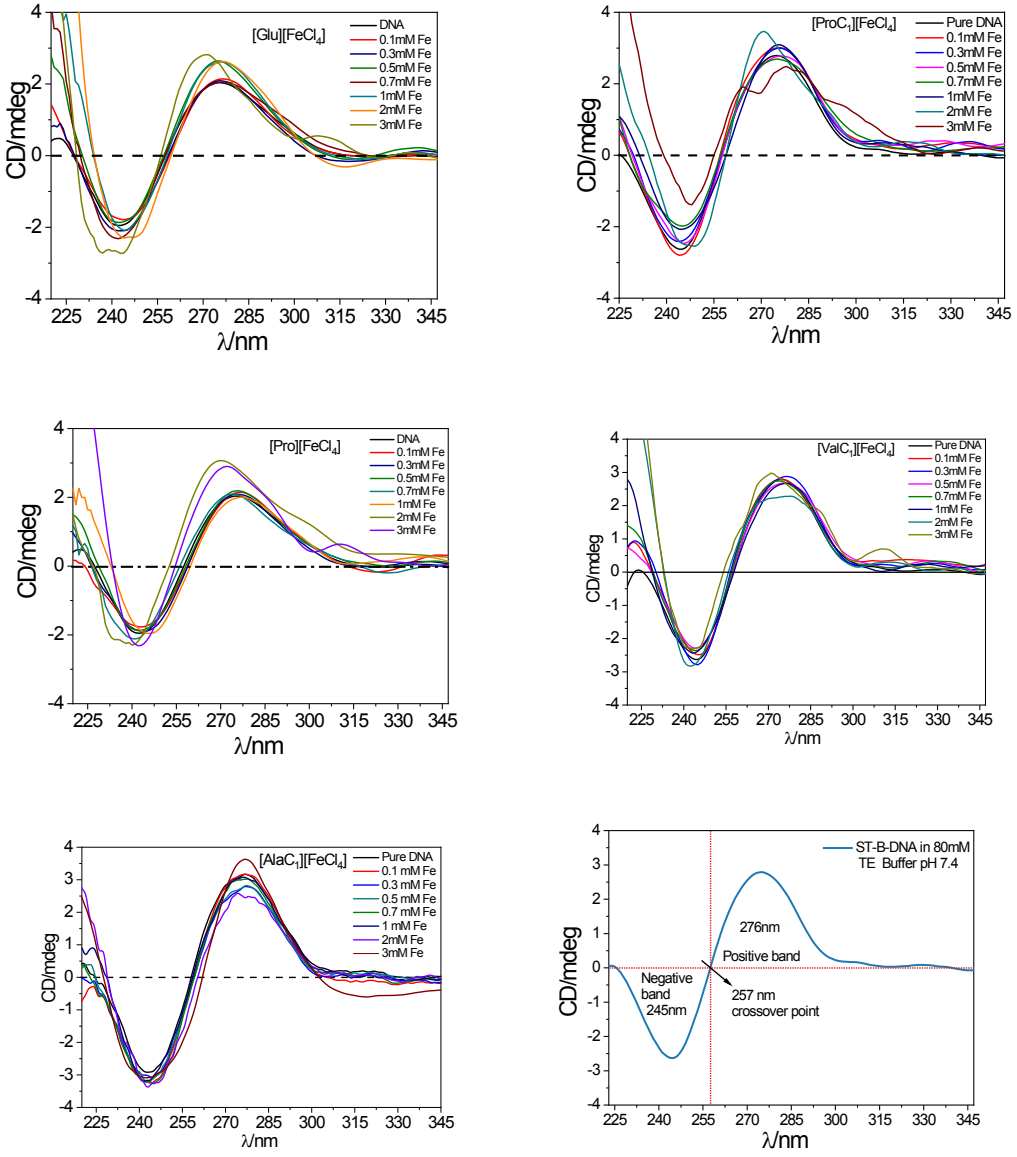
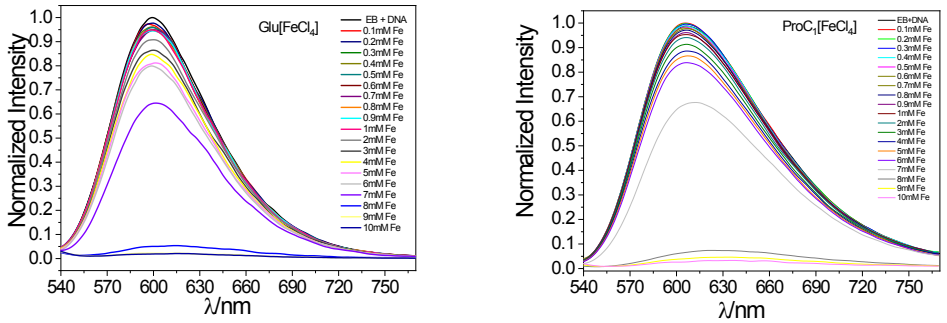


Figure S5. CD spectra of DNA in the presence of PMILs and CD spectrum of pure DNA.



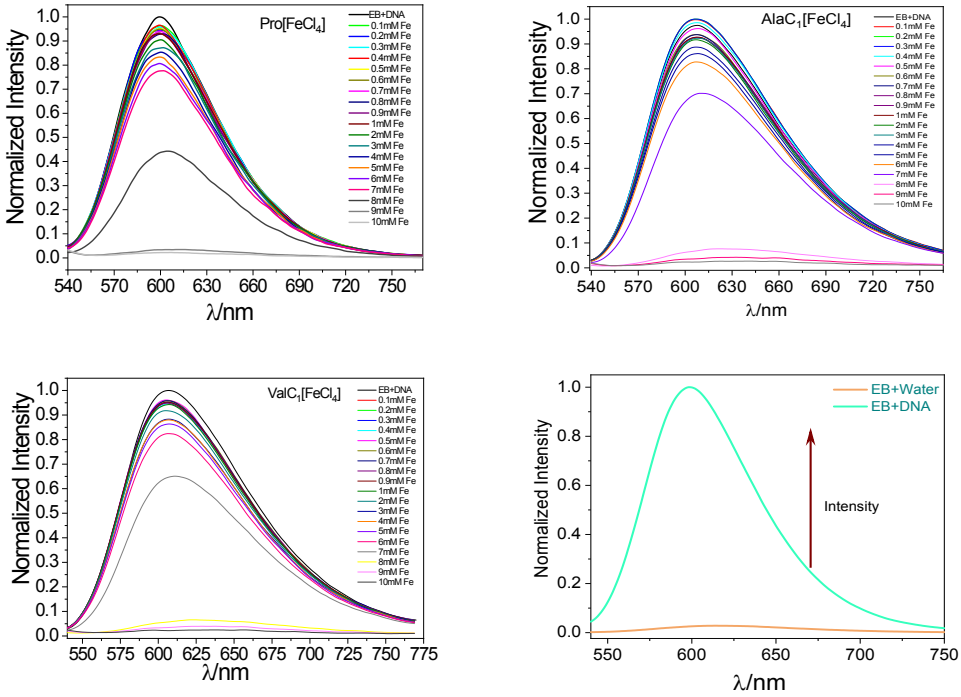


Figure S6. Fluorescence spectra of EB-DNA complex in the presence of PMILs.

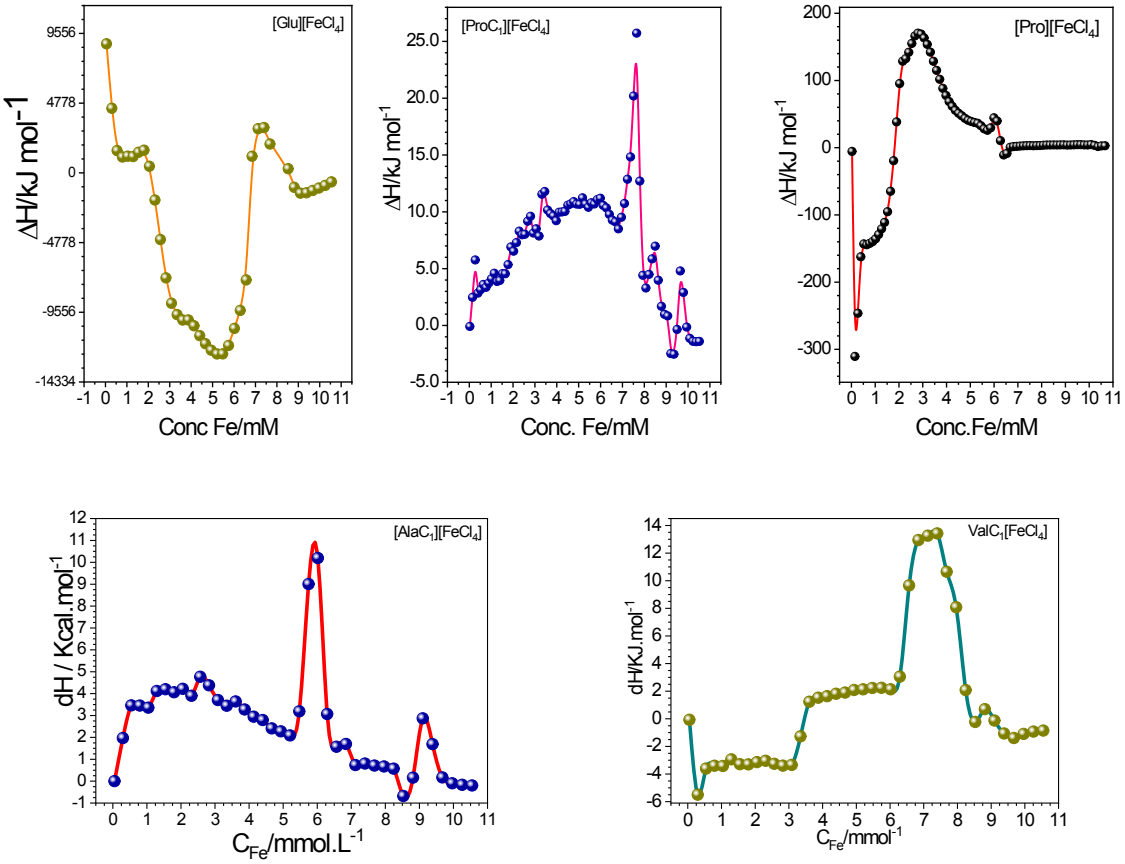


Figure S7. Isothermal binding of PMILs with DNA at various Fe concentration.

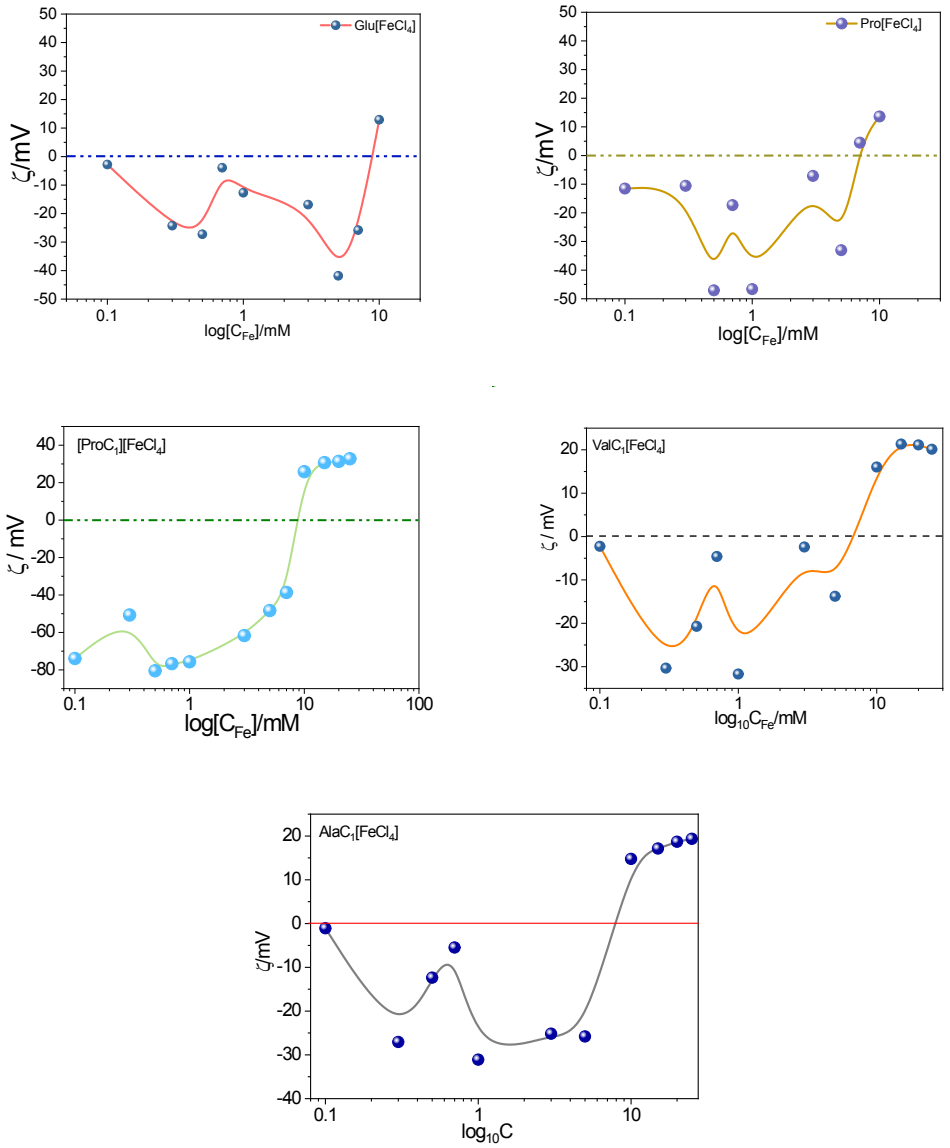


Figure S8. Zeta potential of DNA at various concentration of Fe for different PMILs.

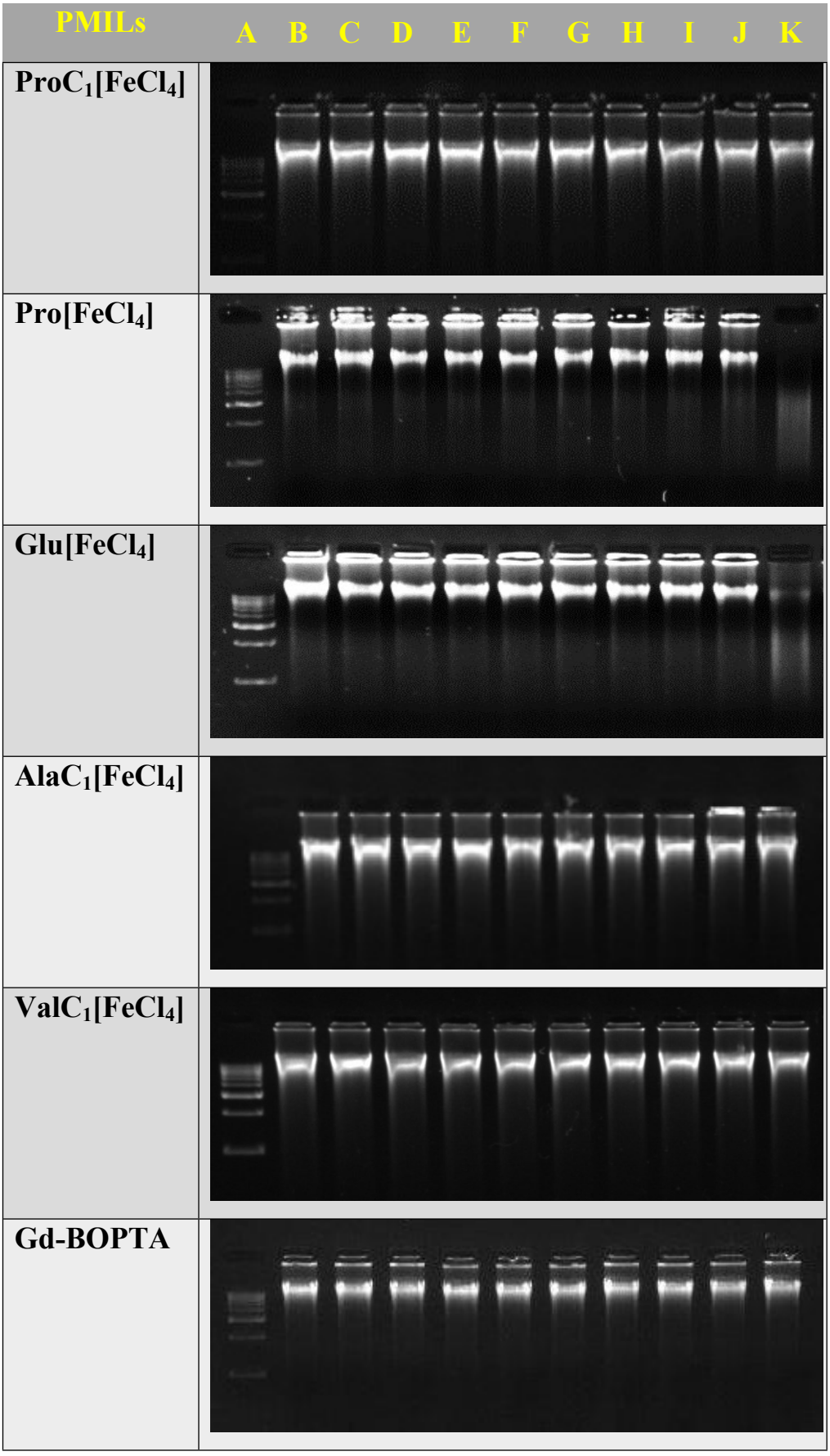


Figure S9. Agarose gel-electrophoresis electrophoresis pattern of DNA in the presence of PMILs and Gd-BOPTA with different metal concentration. (Where, A =

ladder, B= pure DNA, C= 0.1, D= 0.3, E=0.5, F=0.7, G=1.0, H=2.0, I=3.0, J=4.0, K=5.0 mmol.L^{-1})

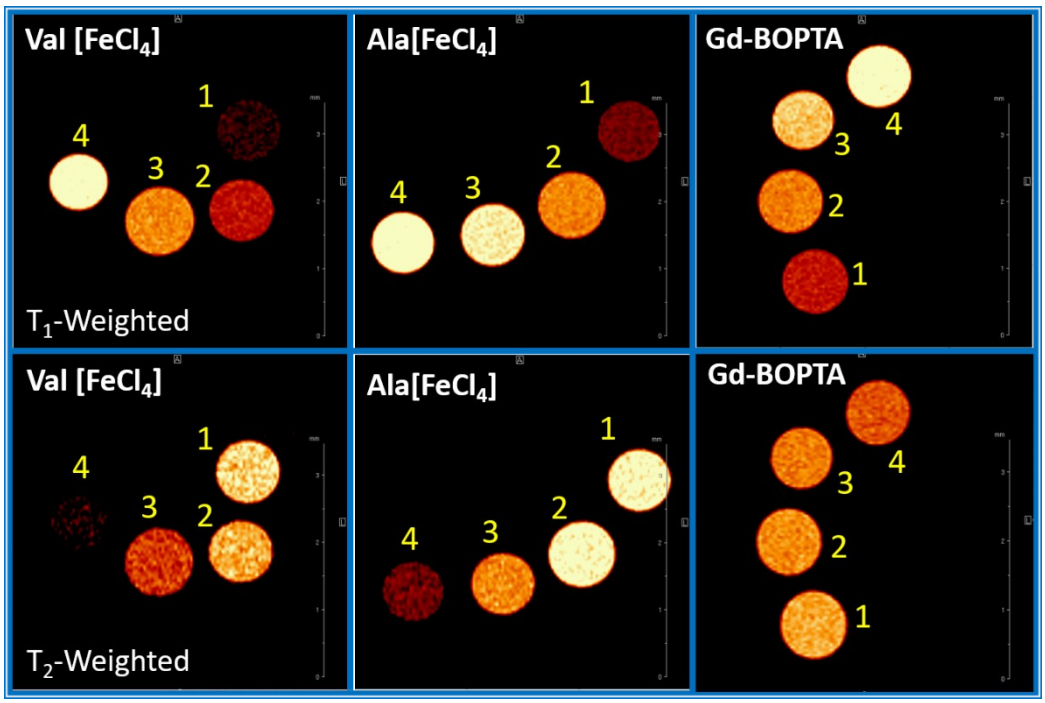


Figure S10. MRI T_1 and T_2 images at various Fe concentration (1 = 0.3, 2 = 0.5, 3 = 0.7 and 4 = 1mM Fe).

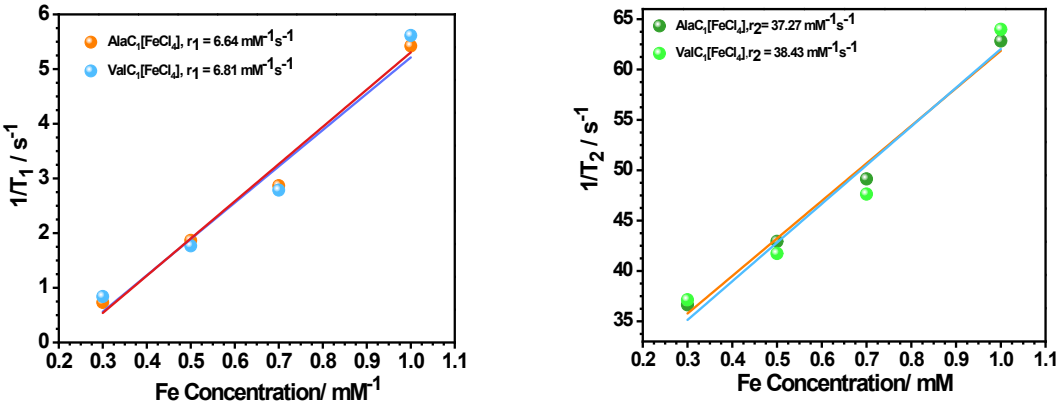


Figure S11. Relaxitivity profile for $AlaC_1[FeCl_4]$ and $ValC_1[FeCl_4]$ PMILs.

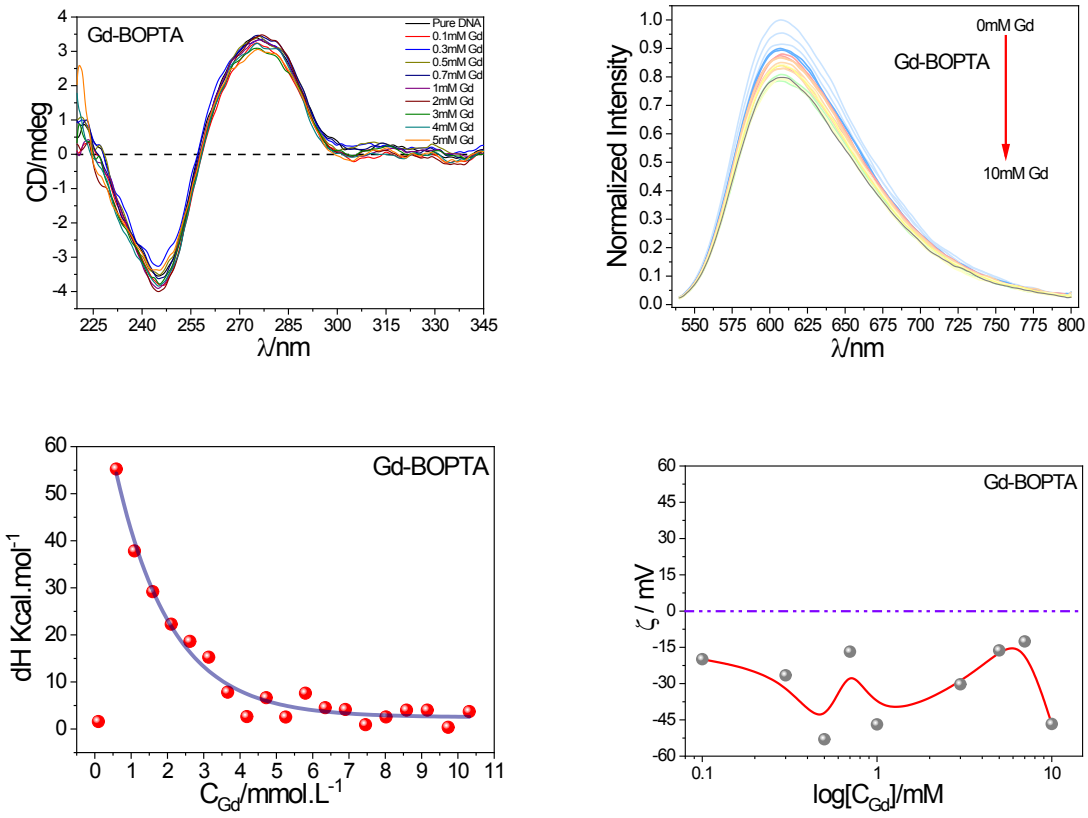
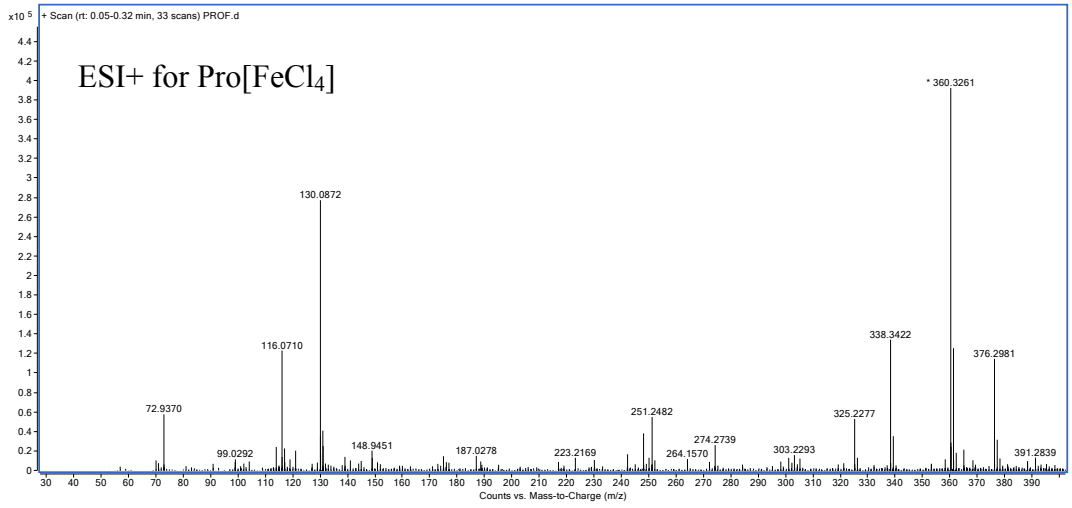
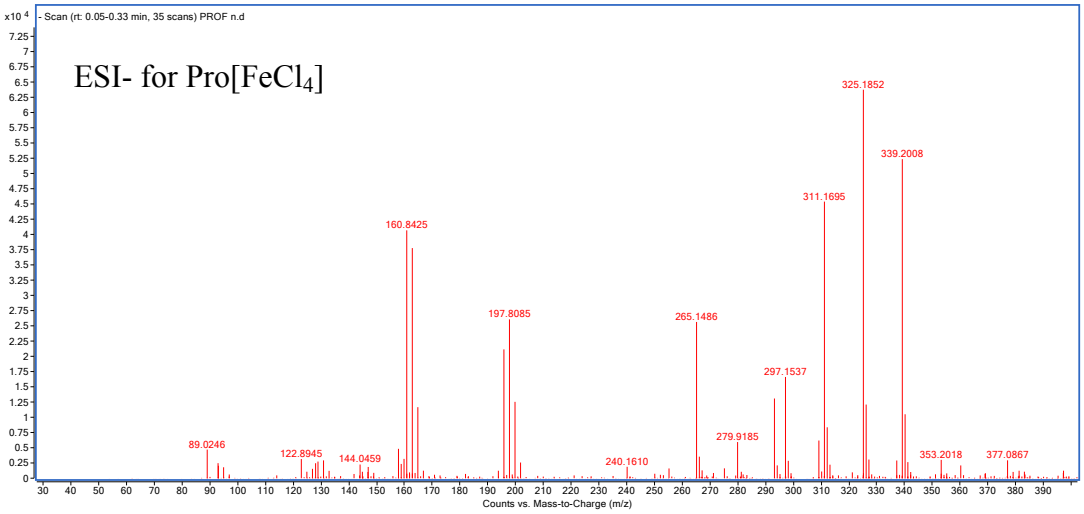


Figure S12. CD, Fluorescence, ITC, and Zeta potential profile of Gd-BOPTA.

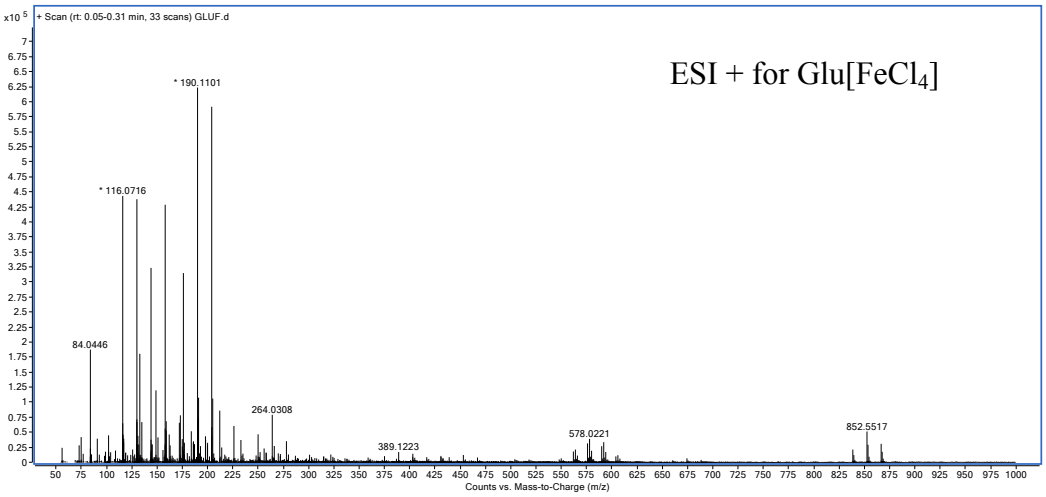
Mass spectra of PMILs

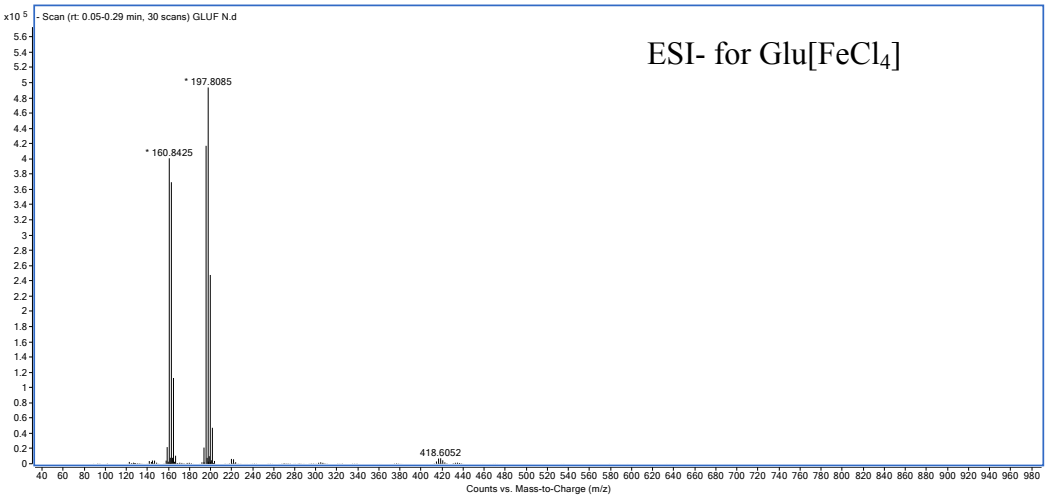
1. LCMS Data of Pro[$FeCl_4$]: ESI^+ (m/z) 116.1 for $[C_5H_{10}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



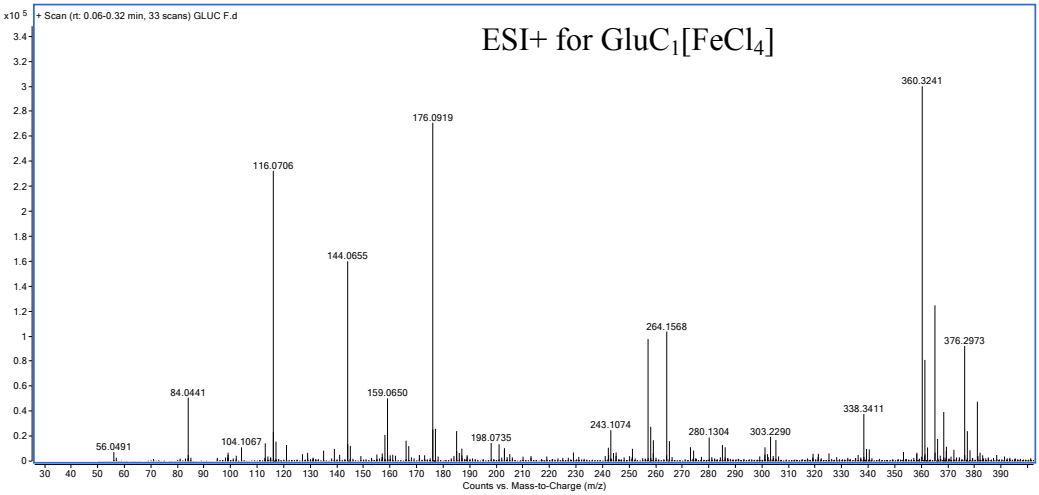


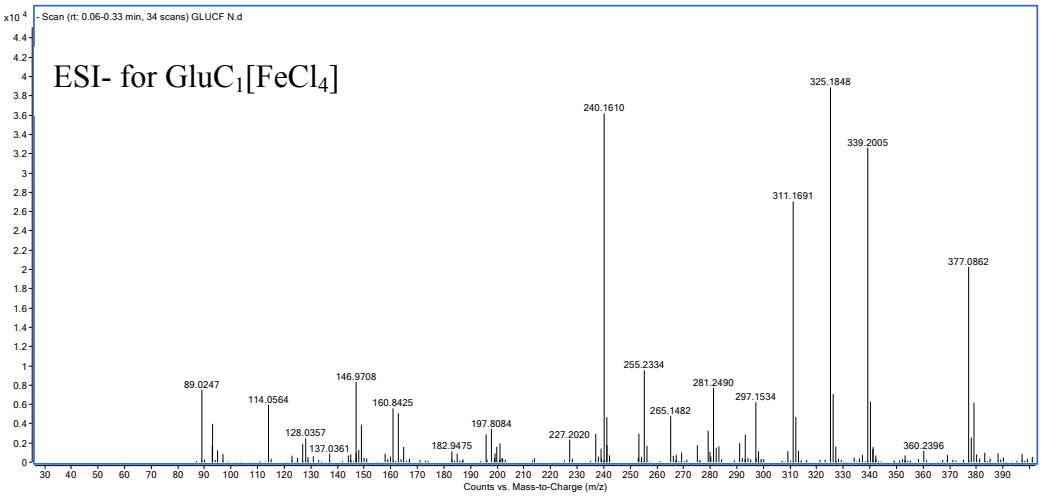
2. LCMS Data of Glu[$FeCl_4$]: ESI^+ (m/z) 148.2 for $[C_5H_{10}NO_4]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



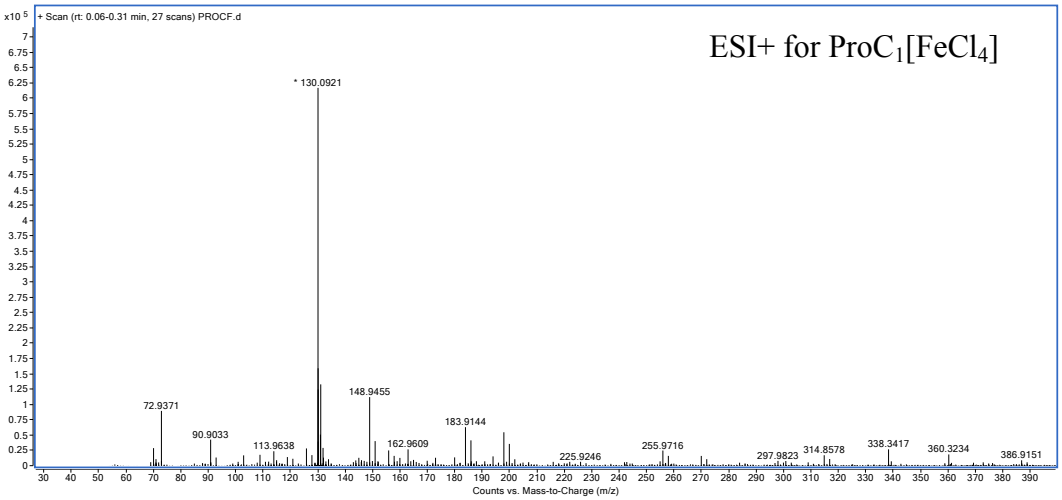


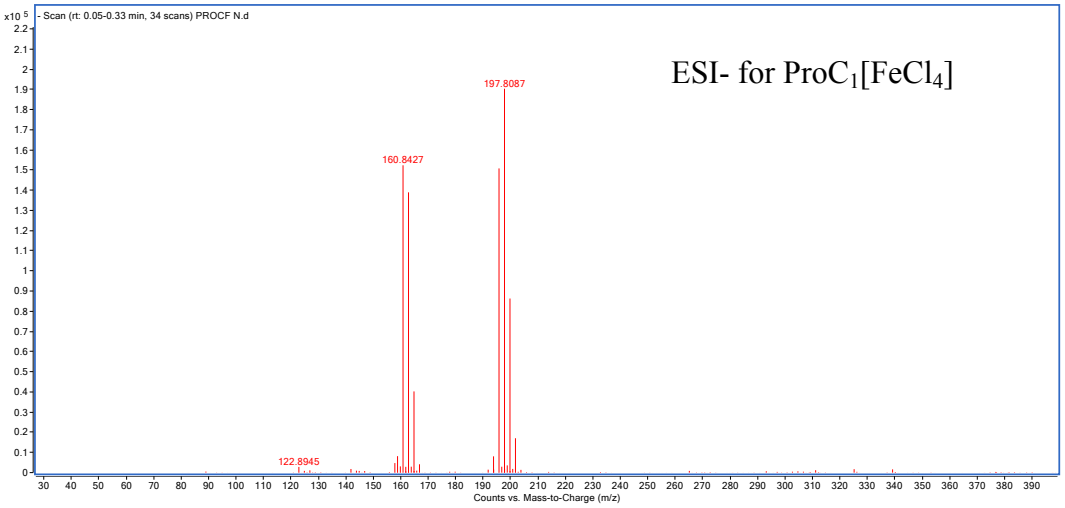
3. LCMS Data of $GluC_1[FeCl_4]$: ESI^+ (m/z) 176.1 for $[C_7H_{14}NO_4]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$



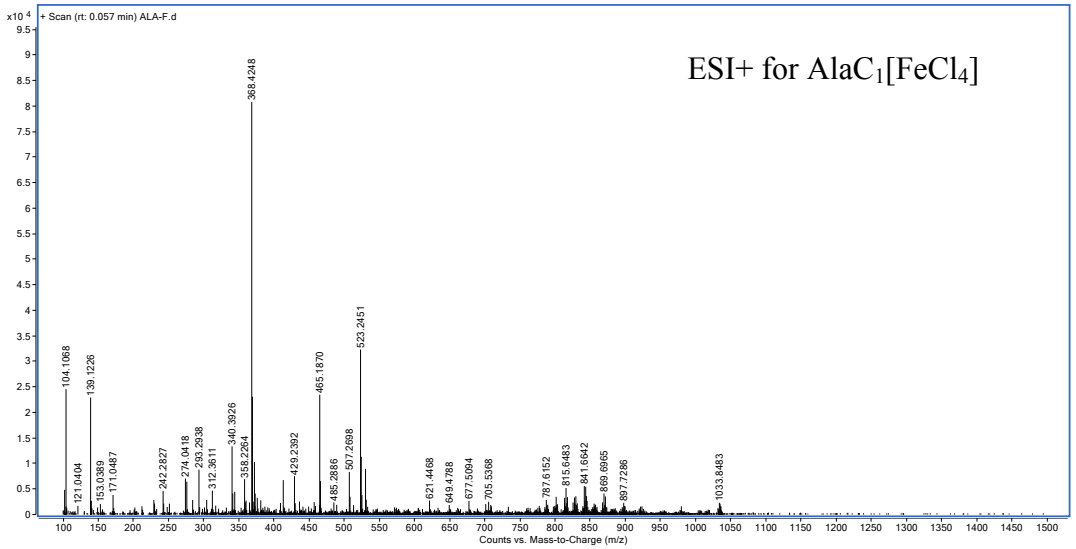


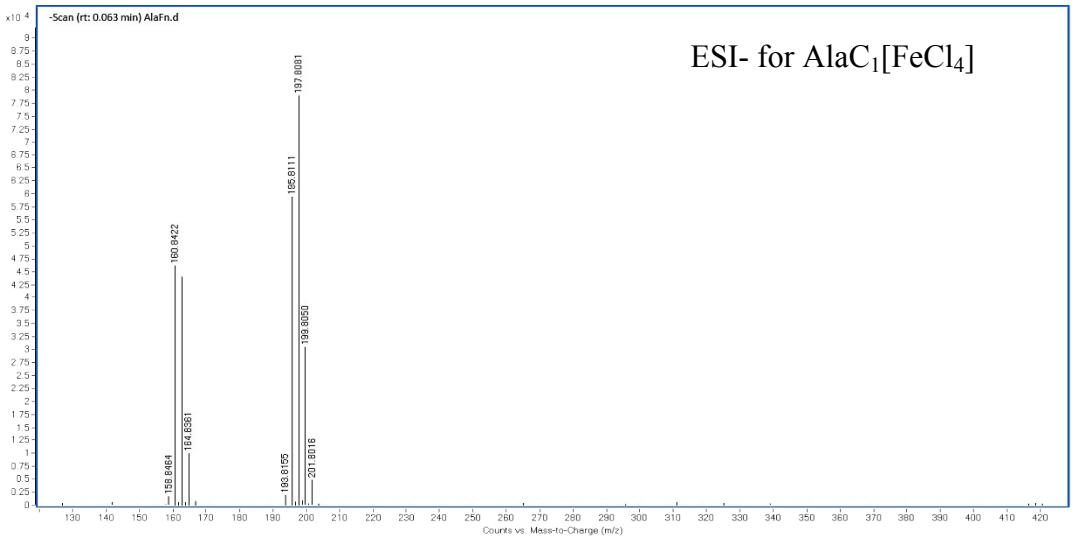
4. LCMS Data of $ProC_1[FeCl_4]$: ESI^+ (m/z) 130.09 for $[C_6H_{12}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$





5. LCMS Data of $AlaC_1[FeCl_4]$: ESI^+ (m/z) 104.03 for $[C_3H_8NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$





6. LCMS Data of $ValC_1[FeCl_4]$: ESI^+ (m/z) 132.1 for $[C_5H_{12}NO_2]^+$, ESI^- (m/z) 197.80 for $[FeCl_4]^-$

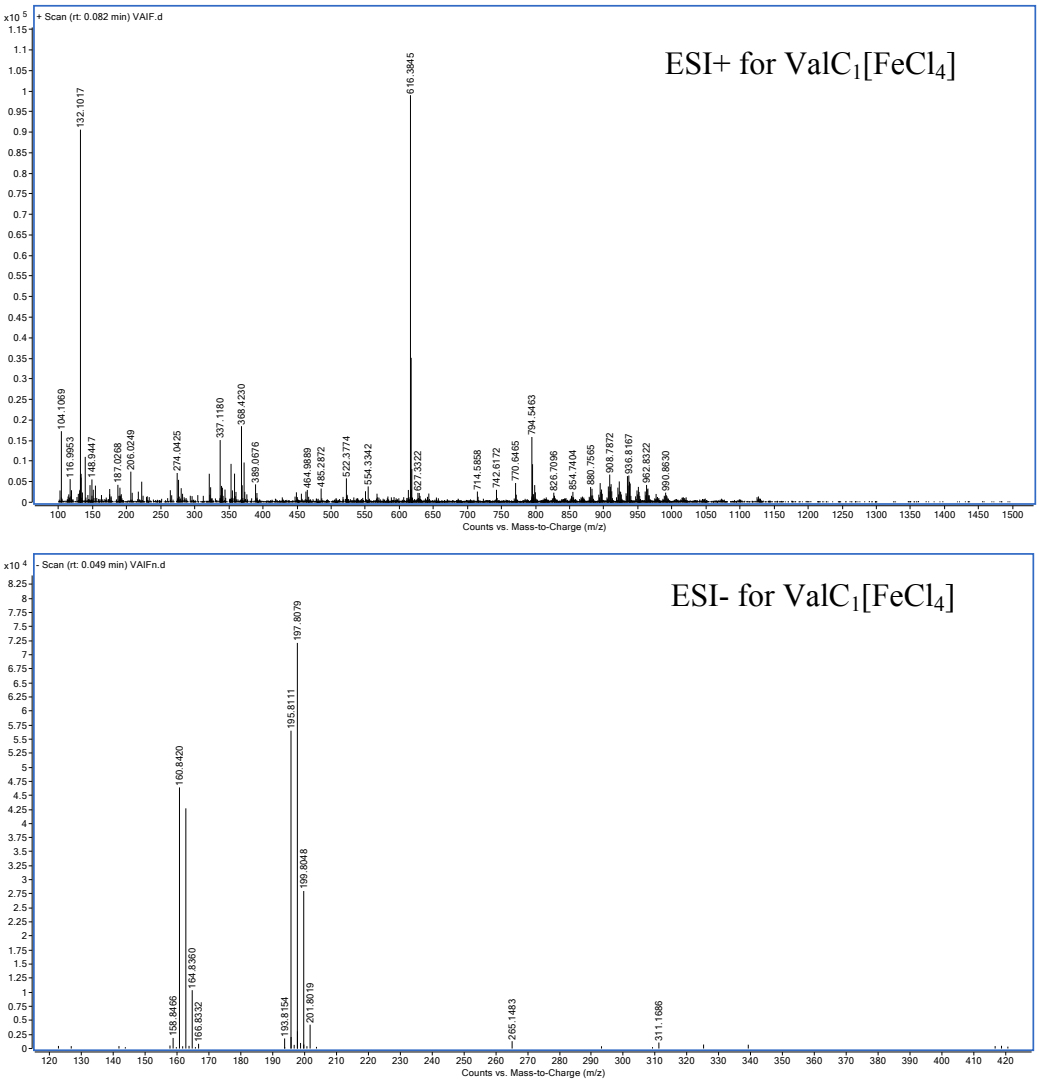


Figure S13. LCMS data of synthesised PMILs ($Pro[FeCl_4]$, $Glu[FeCl_4]$, $GluC_1[FeCl_4]$, $ProC_1[FeCl_4]$, $AlaC_1[FeCl_4]$, and $ValC_1[FeCl_4]$.