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Symmetric Imidazolium-Based Paramagnetic Ionic Liquids

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Overview



- Synthesis, characterization, and physical properties of bis(alkyl)imidazolium bromotrichloroferrates for use as potential infusing liquids in high-temperature SLIPS
- Despite symmetric cation, compounds are room temperature ILs, some with melting points below -90°C



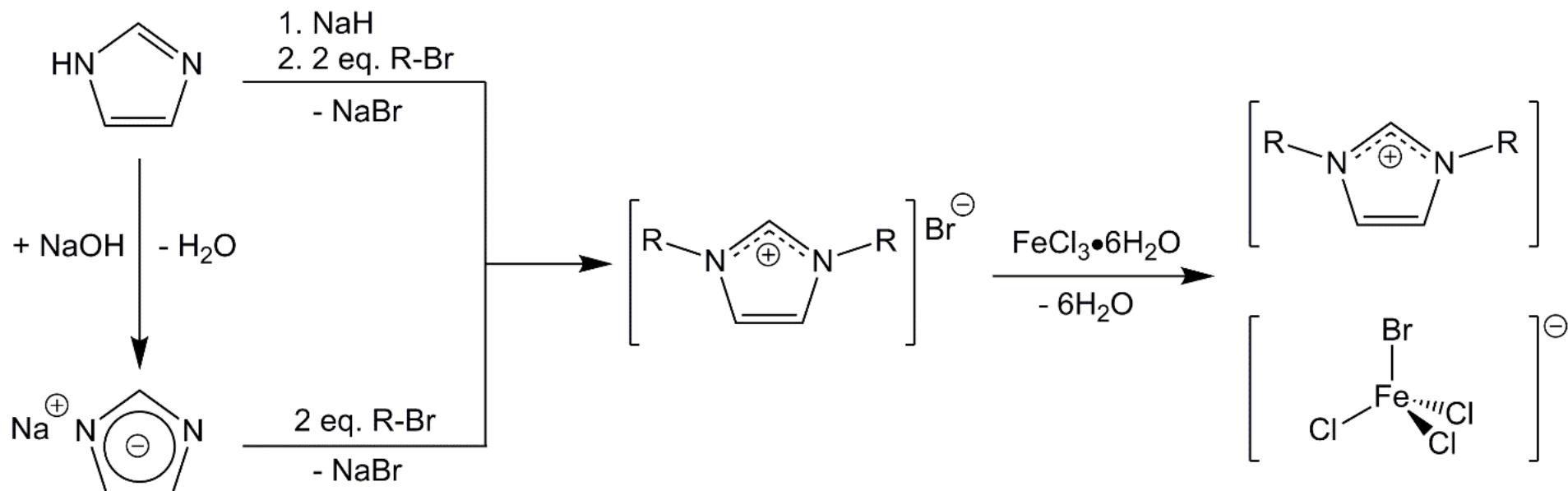
Motivation



- SLIPS at high temperatures
- ILs: stable at high temperatures but high surface tension
- Alkyl chains to reduce surface tension
- Paramagnetic anion to decrease melting point and to be able to apply external force



Synthesis



- Utilized easier route to produce [R₂Im]Br
- [Im(C_n)₂][FeCl₃Br] prepared neat

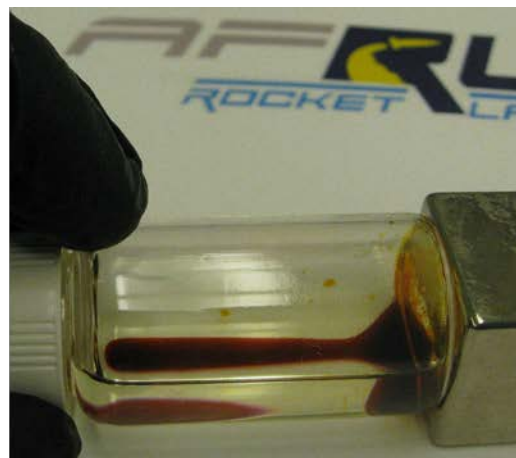
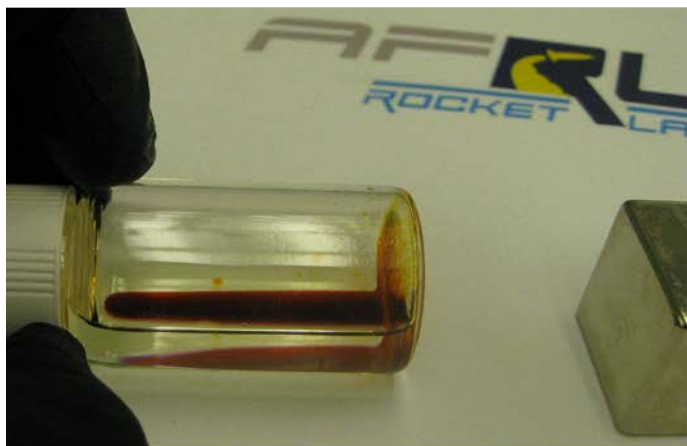


Thermal and Magnetic Properties



Compound	Melting Point (°C) ^a	Thermal Stability (°C) ^b	χ_{mol} ($\text{m}^3 \text{mol}^{-1} \times 10^{-7}$)	μ_{eff} (μ_{B})
$[\text{Im}(\text{C}_2)_2][\text{FeCl}_3\text{Br}]$	-0.1	361	1.77	5.73
$[\text{Im}(\text{C}_4)_2][\text{FeCl}_3\text{Br}]$	<-90	341	1.76	5.71
$[\text{Im}(\text{C}_6)_2][\text{FeCl}_3\text{Br}]$	<-90	342	1.76	5.69
$[\text{Im}(\text{C}_8)_2][\text{FeCl}_3\text{Br}]$	<-90	326	1.73	5.65
$[\text{Im}(\text{C}_{10})_2][\text{FeCl}_3\text{Br}]$	4.6	337	1.75	5.69
$[\text{Im}(\text{C}_{12})_2][\text{FeCl}_3\text{Br}]$	25.1	324	1.79	5.75

- a) Melting point determined via DSC endotherm.
b) TGA temperature at which 5 wt% loss of compound is observed.



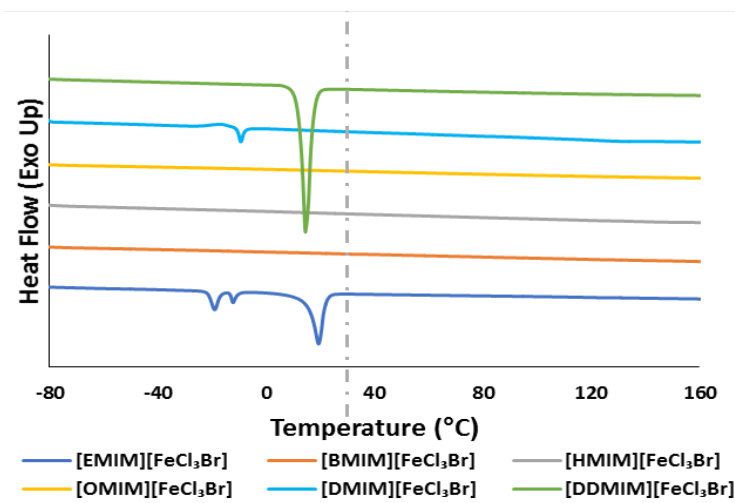
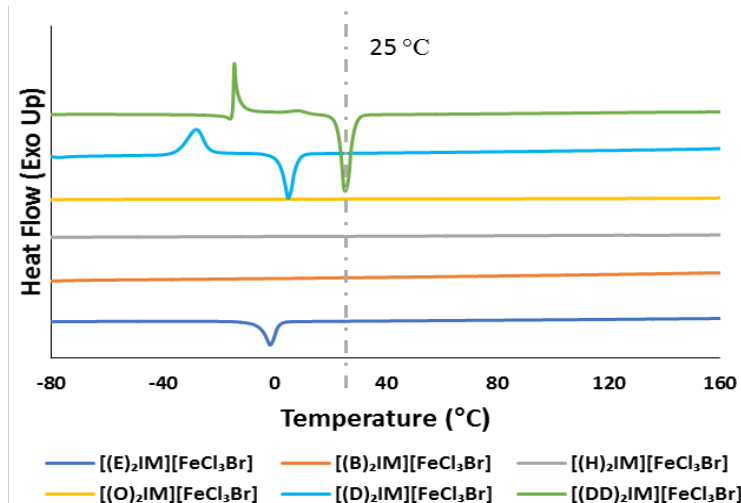


Cation Symmetry & DSC



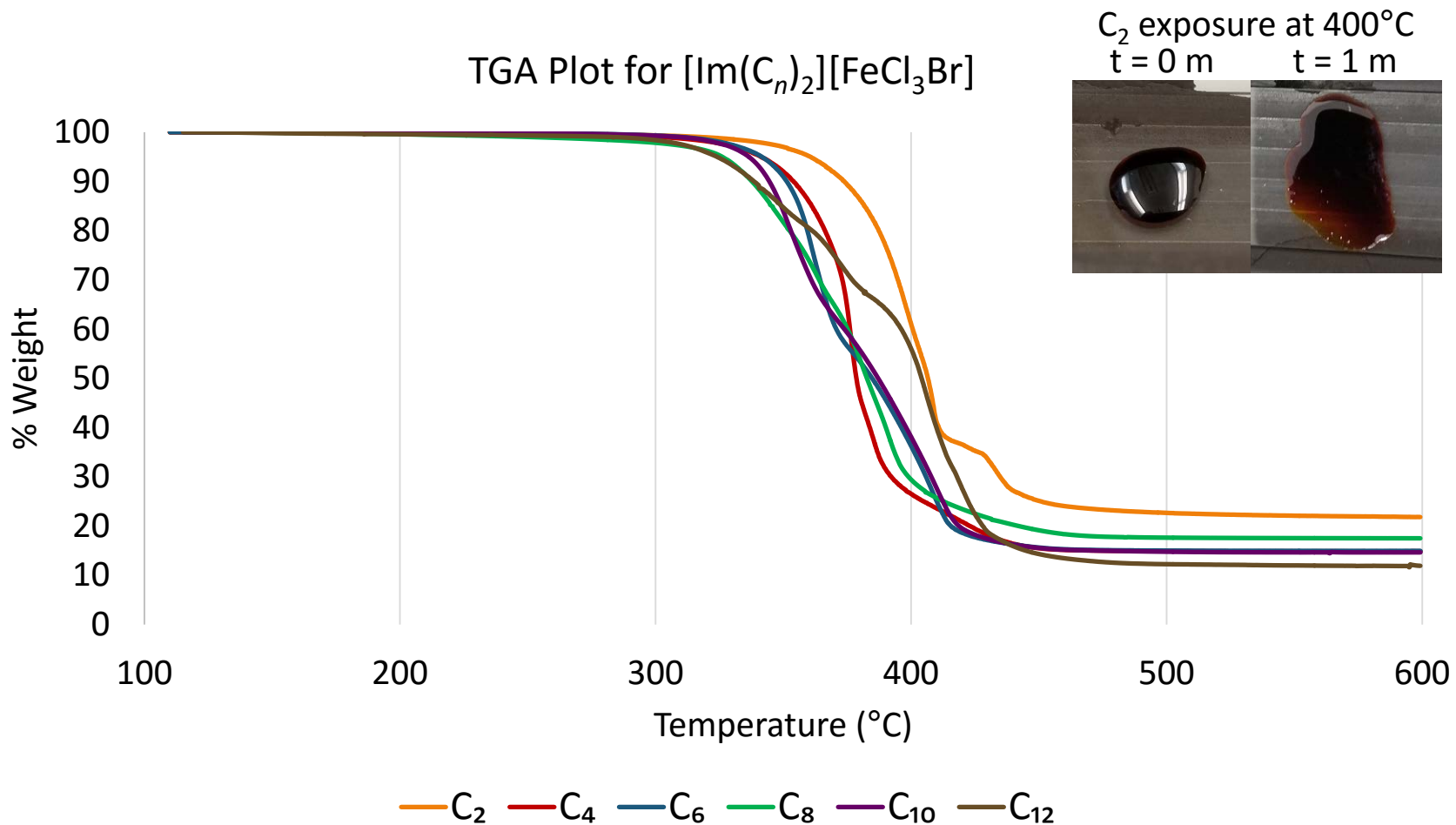
N	$[\text{Im}(\text{C}_n)_2][\text{FeCl}_3\text{Br}]$	$[\text{ImC}_n\text{C}_1][\text{FeCl}_3\text{Br}]$
2	-0.1	19.4
4	<-90	<-90
6	<-90	<-90
8	<-90	<-90
10	4.6	-9.4
12	25.1	14.5

All values are °C. Melting points determined via DSC endotherm.



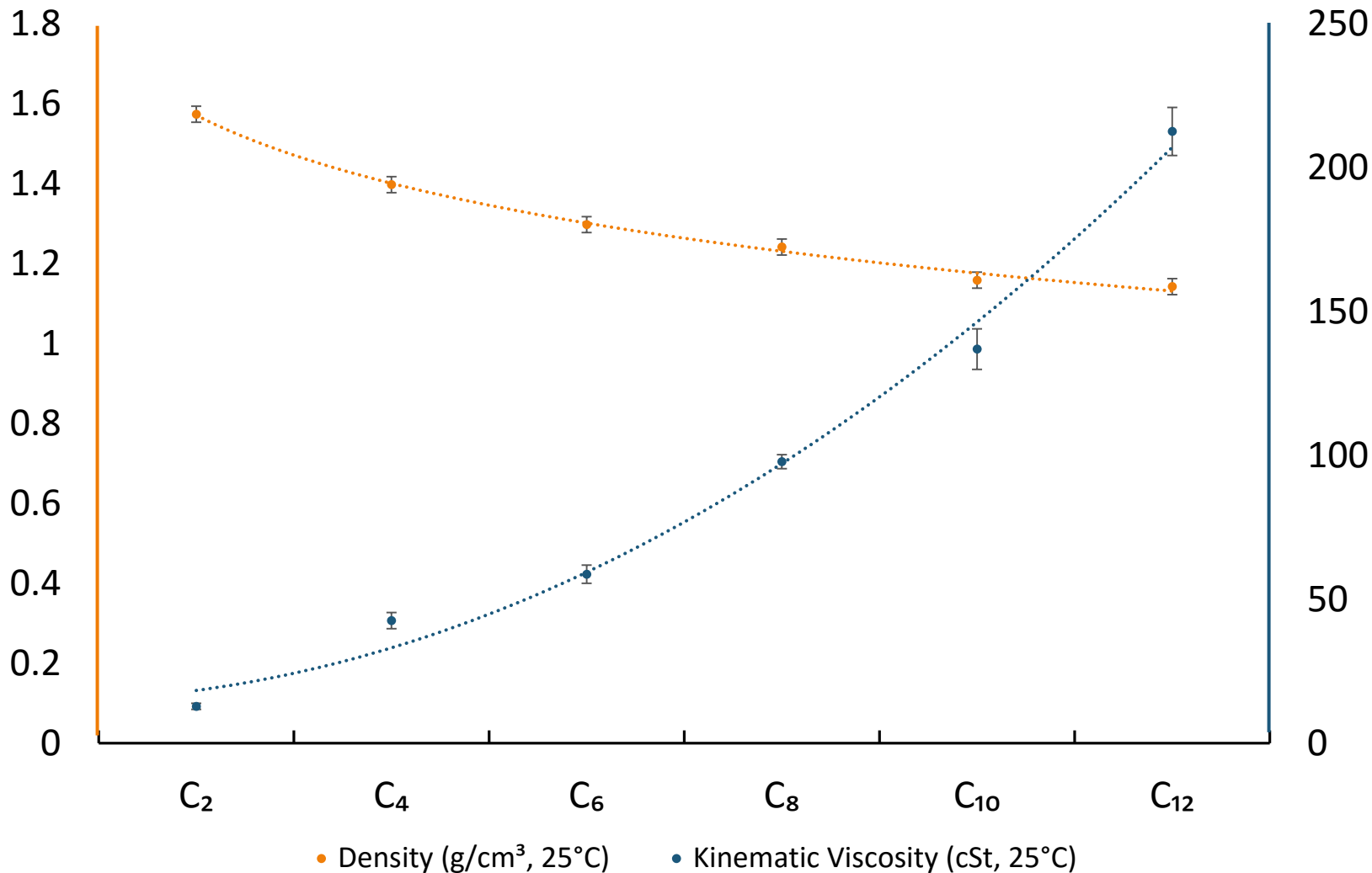


Thermal Stability



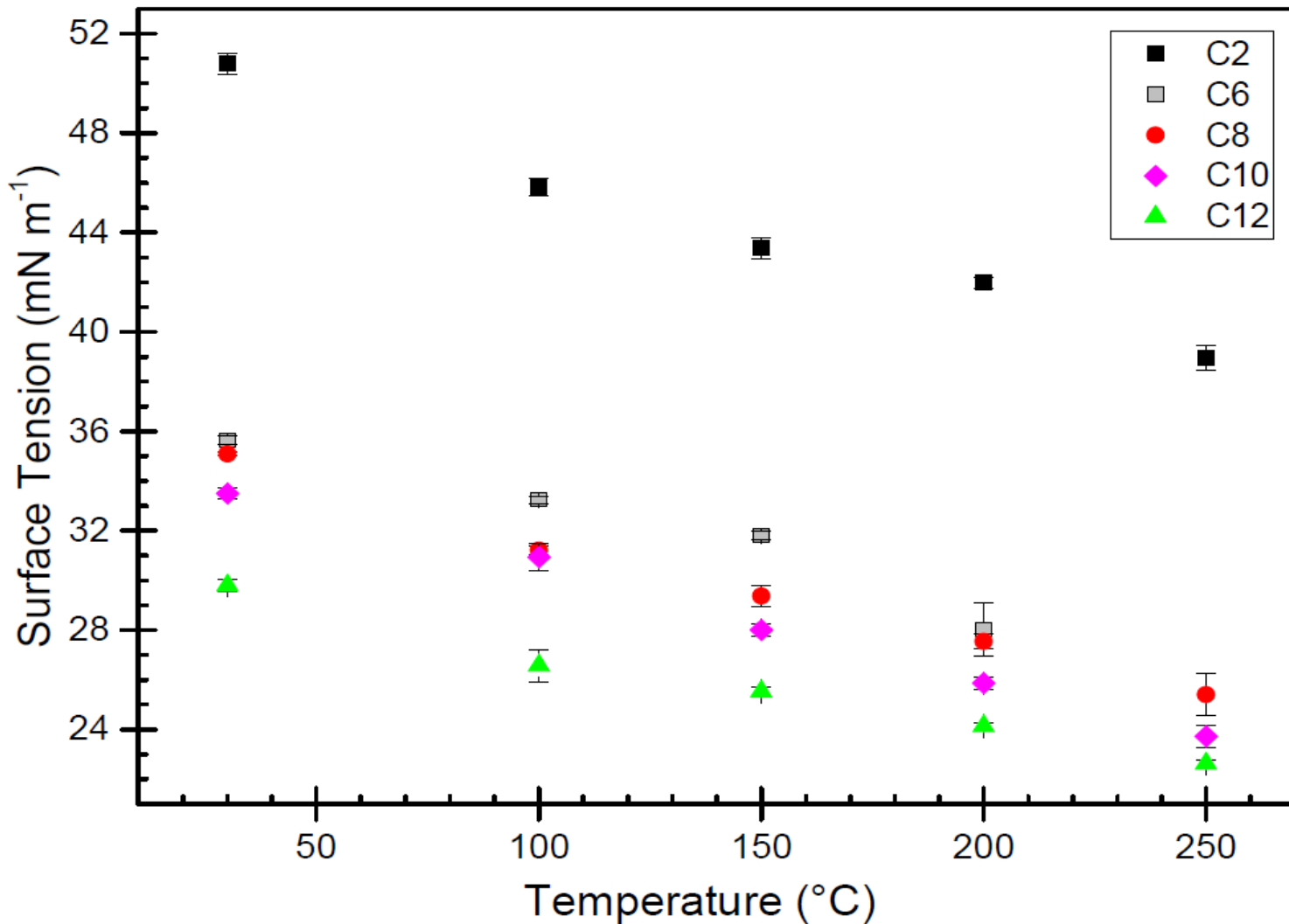


Physical Properties



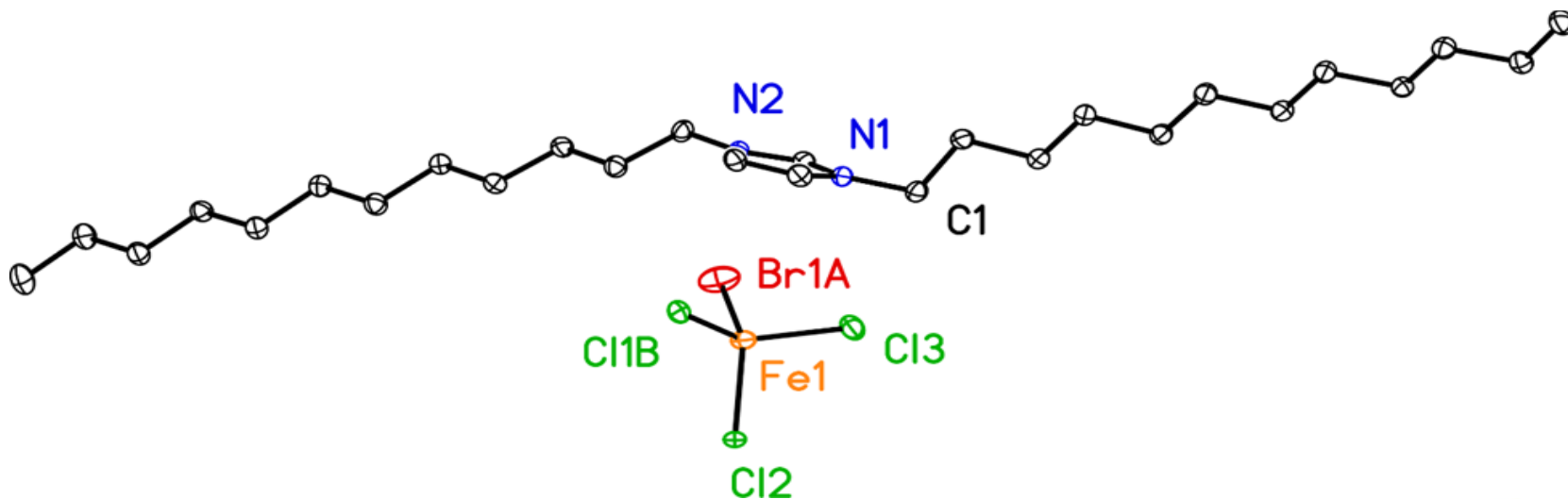
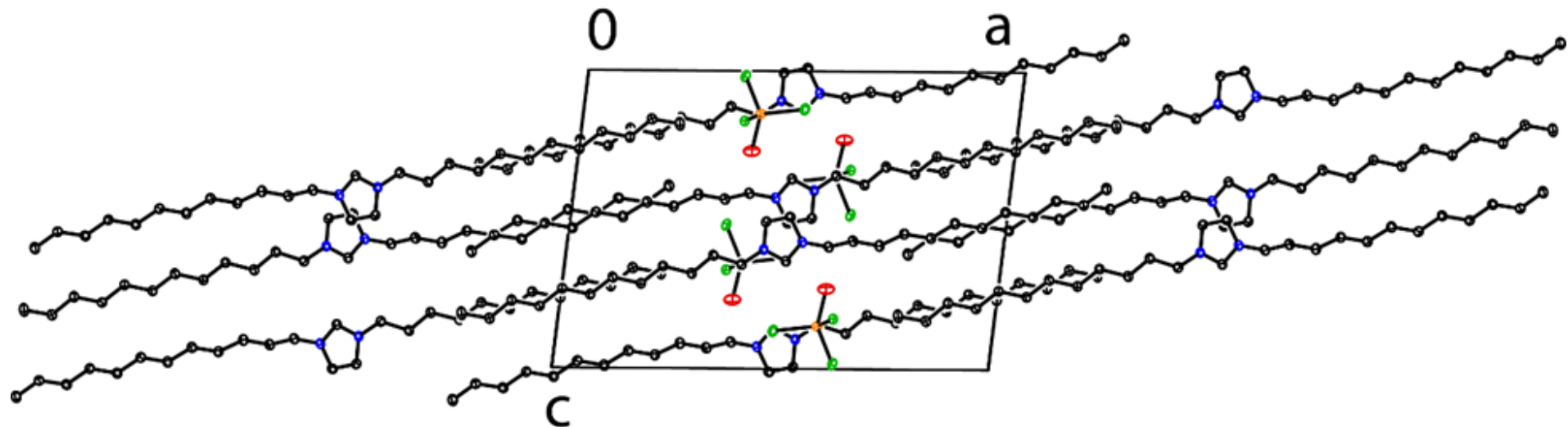


Surface Tension





[Im(C₁₂)₂][FeCl₃Br] Crystal Structure





Summary



- Although $[\text{Im}(\text{C}_N)_2][\text{FeCl}_3\text{Br}]$ ILs have symmetric cations which generally lead to more crystalline behavior, there is no significant difference in the melting points of these and $[\text{ImC}_N\text{C}_1][\text{FeCl}_3\text{Br}]$ ILs.
- Other properties of $[\text{Im}(\text{C}_N)_2][\text{FeCl}_3\text{Br}]$ for $N=2,4,6,8,10,12$ match expectations based on properties of the non-symmetric counterparts.



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Questions

