

**Phosphonium Chloromercurate Room Temperature Ionic Liquids of Variable Composition**

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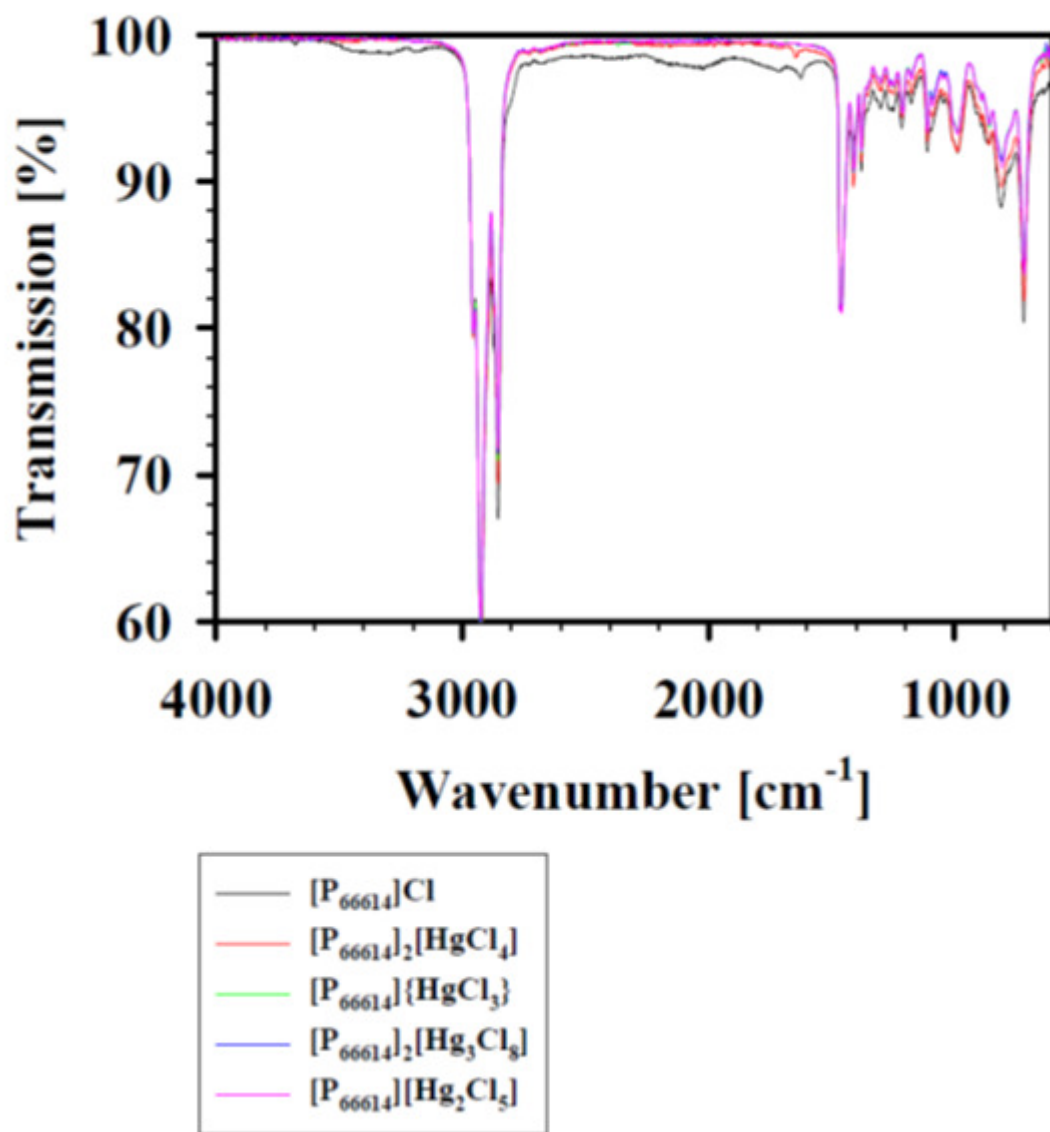


Figure S1: IR spectra of the compounds (2), (4), (5), (6) and  $[\text{P}_{66614}]\text{Cl}$ .

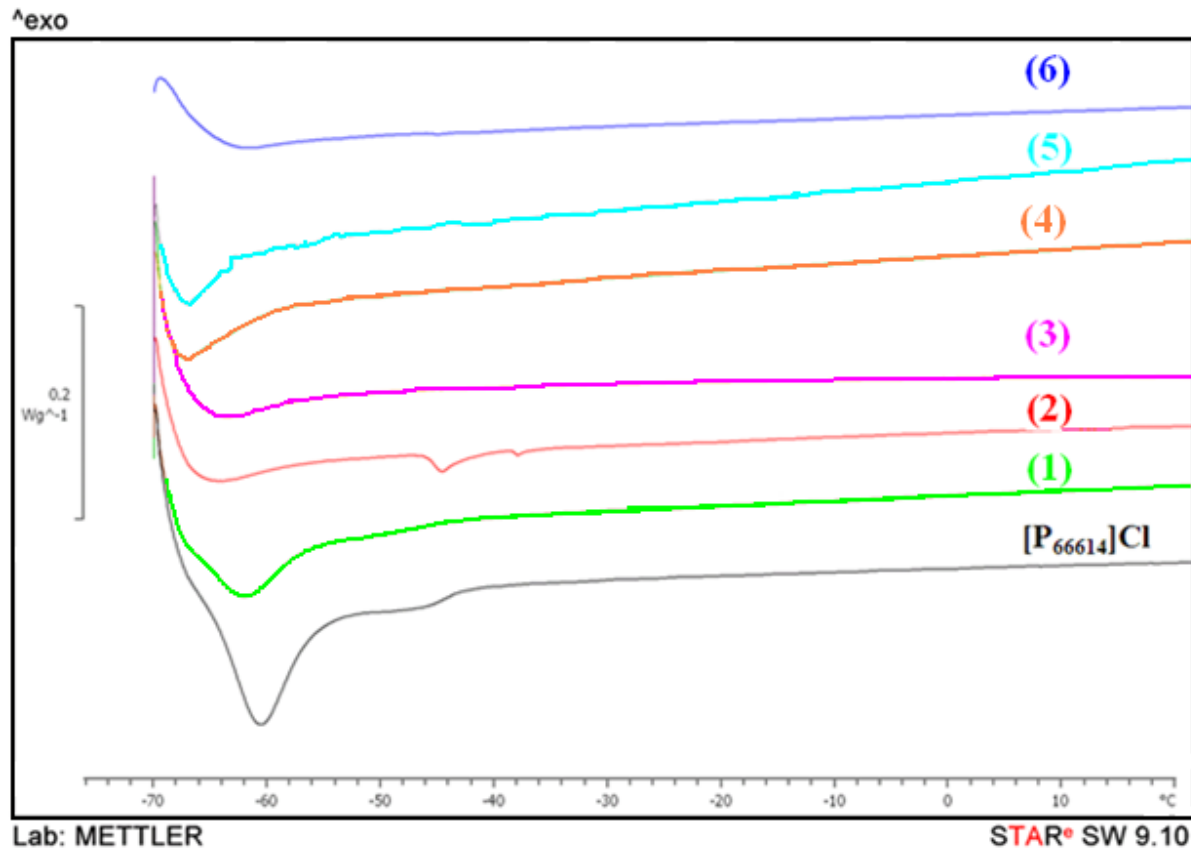


Figure S2: DSC traces of compounds (1)-(6) and  $[P_{66614}]Cl$ .

The features of the parent IL diminish with increasing amount of  $HgCl_2$ , such as the glass transition at  $-45\text{ }^{\circ}C$  and the peak at  $-60\text{ }^{\circ}C$ , what could be a kind of solidification, although most likely no real crystallization. The composition with 0.5 molar equivalents of  $HgCl_2$  (formally  $[P_{66614}]_2[HgCl_4]$  with discrete  $[HgCl_4]^{2-}$  - anions) shows two small transitions that disappear again when the amount of Hg is increased further. As soon as the regiment of polymeric anionic species has been reached, no significant changes are observable anymore. The IL with the highest loading appears to show an exothermic event at  $-70\text{ }^{\circ}C$ ; however, as this was the lowest temperature achievable during the measurement, it cannot be said with certainty that a crystallization occurred; an artifact is also not impossible.

The heating/cooling rate was ( $5\text{ }^{\circ}C/min$ ).

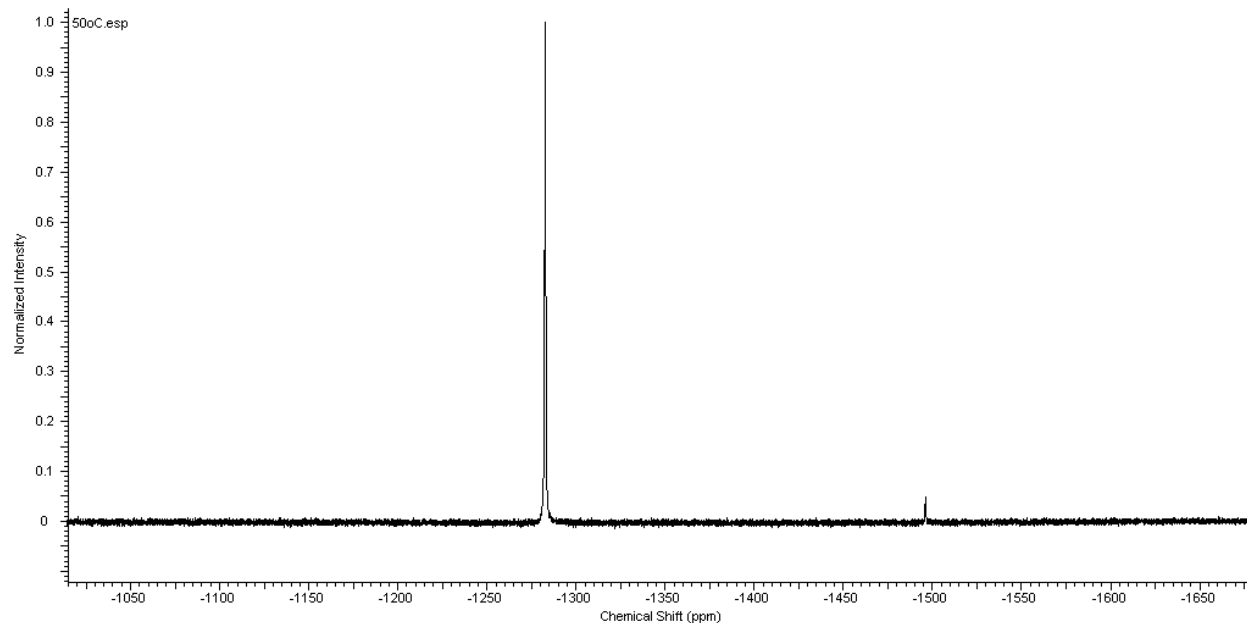


Figure S3:  $^{199}\text{Hg}$  NMR of **(4)** at 50 °C.

Heating compound **(4)** to 50 °C results in a well defined and narrow signal in the  $^{199}\text{Hg}$  NMR spectrum what contrasts to the compounds signal at room temperature. Instead of polynuclear species, monomeric  $[\text{HgCl}_3]^-$  or dimeric  $[\text{Hg}_2\text{Cl}_6]^{2-}$  might be the dominant species at this temperature. The observed high field shift of the peak compared to the room temperature signal is attributed to the decreased viscosity at 50 °C.

## ELECTRONIC SUPPLEMENTARY INFORMATION



Picture S4: left: control experiment ( $\text{H}_2\text{O}$  +  $[\text{P}_{66614}]\text{Cl}$ ); right:  $[\text{P}_{66614}]\text{Cl}$  contacted with 0.18 M  $\text{HgCl}_2$  forming a denser phase than the parent IL or water.