Investigation of Glassy and Liquid States of CPs

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1. Background and Research Objectives

Coordination Polymers (CPs) are mostly synthesized as crystalline material with highly ordered metals and ligands arrangments. The recent discovery of CPs as a new glass former system has evoked great interest in investigations of non-crystalline glassy and liquid states of CPs.[1] Additionally, these states exhibit excellent optical and ionic properties towards energy and environmental applications. Structural insights into individual phases and will allow us to design and control the structure of CP glasses, and thus their properties. We synthesized Zinc-phosphate-azolate based melting CPs (ZnPIm (**1**); ZnP2EtIm (**2**) and ZnPBnIm (**3**)). The local structure around Zn center in the Liquid and Glass phase was investigated using variable temperature XAS analysis.

2. Experiments

In a typical procedure, CP powder was mixed with BN and ground well till homogenously mixed. The powder was then pressed to pellets (ϕ = 7 mm, thickness = ~1 mm) and placed in the Quartz cell for transmission using a metal tube. N_2 gas was flown at 100 mL/min and samples were equilibrated for 10 min at each temperature before measurement. The XAS data recorded in ionization/transmission mode.

3. Results and Discussion

Variable temperature XAS analysis was performed to study the changes in the coordination environment around the Zinc center. Figure 1a shows the Zn *K*-edge XANES spectra of Crystalline (RT), Molten Liquid (160 °C) and melt quenched glass (MQ glass; RT) of **1**. The overlapping edge position and comparable white light intensities

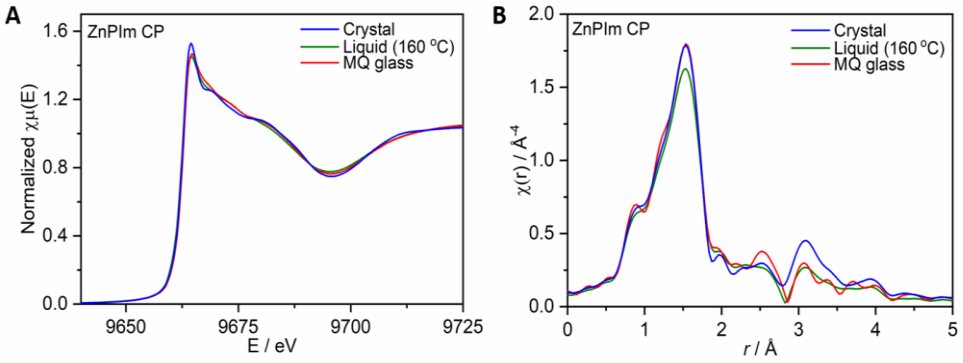

Figure 1: (a) Zn *K*-edge XANES and (b) RDF profiles of , Crystal, Liquid and Glass CP samples

(~1.5) confirm the preservation of Td geometry and 2+ oxidation state in the liquid and glass state of CP. The RDF profiles revealed identical Zn-O radial distances in all phases confirming the overall metal-ligand connectivity is preserved in the liquid state (Fig. 1b). The slight decrease in intensity for liquid RDF is ascribed to disordering at high temperatures (160 °C). The disorder can also be seen from decreased peak intensity of Zn-P distances at ~3Å. Preservation of Zn^{2+} coordination during phase transition was also confirmed for ZnP2EtIm and ZnPBnIm CPs.

4. References

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