Liquid–Liquid Transition in Coordination Polymer Melt Studied by Dynamic Mechanical Analysis

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Melting and glassy coordination polymers (CPs) have been attracting attention as novel functional materials due to their optical properties, moldability, and mechanical durability.[1] The network and coordination structures in the melt states were analyzed in detail for some melting CP systems.[2] However, mechanical properties or dynamics of the melt are still remaining to be elucidated, and a comprehensive understanding of transition behavior in CPs did not progress. The melting and glass transition behaviors of CPs have been discussed assuming a single melt phase.

We studied the properties of supercooled melt states of $Cu(TFSI)_2(bip)_2$ (**1**, $TFSI^-$ = Bis(trifluoromethanesulfonyl)imide, bip = 1,3-Bis(1*H*-imidazol-1-yl)propane, Fig. a). Dynamic mechanical analysis (DMA) observed a reversible rheological transition depending on temperature, and suggested a liquid–liquid transition (Fig. b). The application of mechanical stimuli in DMA formed a different melt state with the same components. Two melt states underwent a glass transition at different temperatures. X-ray scattering analysis revealed their structural dissimilarities and different crystallization behavior. The variety of nanometer-scale network structures in melt states explains these differences.

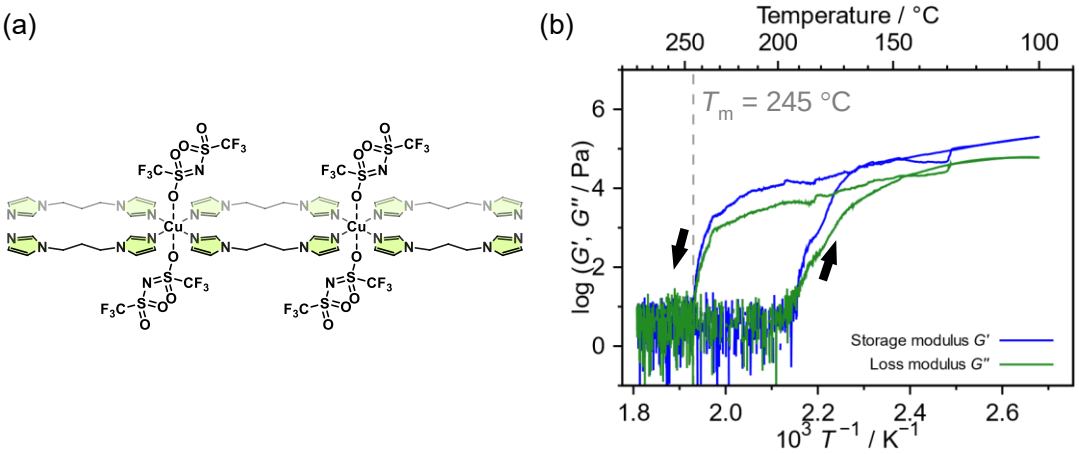

Fig. (a) Schematic representation of crystal structure of **1** (b) Temperature-ramp DMA profile of **1** melt. The dashed line represents the melting temperature of **1** crystal.

1) S. Horike, *et al.*, *Chem. Rev.* **2022**, *122*, 4163.
2) T. D. Bennett, F.-X. Coudert, *et al.*, *Nat. Mater.* **2017**, *16*, 1149.