

## Thermal stability of Glass forming Metal-Organic Framework: Role of metal-ligand bonding

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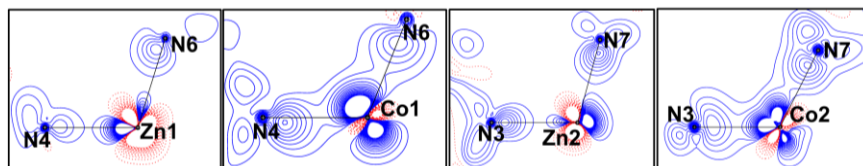
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Melt-quenched glasses from metal-organic frameworks (MOF) represents a new class of hybrid functional materials, which have generated a lot of attention amongst the material science community due to their novel short-range structures and potential applications such as gas-mixture separations, ion conductivity, etc [1]. To improve the thermal stability window of the liquid phase of MOFs, substantial efforts are directed to lower the melting temperature of the crystalline MOF state [2, 3]. However, in this context, the relationship between chemical bonding and melting/decomposition of MOFs is still unexplored.

In this work, we compare the electron density distribution of two isostructural Zeolitic Imidazole Framework (ZIF) molecules-meltable Zn-ZIF-zni with Co-ZIF-zni that undergoes thermolysis, using high-resolution synchrotron single-crystal X-ray diffraction data measured at 25 K. Several ZIFs such as ZIF-4, ZIF-1, ZIF-3, ZIF-zeg, ZIF-nog undergo thermal amorphization and recrystallization to ZIF-zni prior to melting/decomposition [4]. Charge density analysis along with derived topological parameters based on Bader's QTAIM theory [5] shows that Zn-N bonds are primarily closed shell ionic in nature and weaker in strength. On the other hand, Co-N bonds are dominated by polar covalent interactions with significant electron density accumulation in bonding region and distinct  $\pi$ -backbonding features (Fig. 1).

*In situ* temperature dependent Raman spectroscopy (300 K-773 K) revealed a greater degree of bond weakening in the imidazolate ligands of Co-ZIF-zni during heating. In addition, variable temperature crystallography (25 K-400 K) confirmed that Zn-ZIF-zni are less prone to framework distortion in comparison to a more rigid framework in Co-ZIF-zni. To further validate the role of metal-ligand bonds on thermal behavior of these ZIF compounds, for the first time we prepared a set of eight novel solid solutions-Co<sub>x</sub>Zn<sub>1-x</sub>-ZIF-zni where mole fraction (x) of Co ranges from 0.4 to as low as 0.003. Using differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA), we observed that a presence of very low quantity (~4%) of doped Co in Zn-ZIF-zni lattice results in thermal decomposition of the crystal framework. We identified this phenomenon as 'butterfly effect' of Co-N bonds on thermal stability of these solid solution MOFs.



**Figure 1.** 2D deformation maps along N-M-N plane plotted at a contour level of  $\pm 0.1 \text{ e}\text{\AA}^{-3}$ . Blue represents charge concentration, and red represents charge depletion regions

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