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An invited talk

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### Glass formation mechanism of metal-organic frameworks

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Metal-organic frameworks (MOFs) are microporous inorganic-organic hybrid materials that have been applied in many fields such as gas absorption, catalysis and sensing. In particular, a subset of MOFs called zeolitic imidazolate frameworks (ZIFs) has exhibited a great potential to be used in many areas owing to their tailorable zeolitic structure. Recently, it has been discovered that certain types of ZIFs can melt prior to decomposition, and hence, can be vitrified upon quenching.<sup>1-3</sup> However, the mechanism of glass formation of MOFs is a challenging problem to be understood. In this work, we attempt to clarify this problem by characterizing a good MOF glass former, namely, ZIF-62 (Zn(Im)<sub>1.75</sub>(bIm)<sub>0.25</sub>). We have found that the ZIF-62 glass is extremely stable against crystallization during heat-treatment. Furthermore, we have observed a pronounced increase of both the glass transition temperature  $(T_g)$  and the melting temperature  $(T_m)$  of ZIF-62 with increasing the bIm/Im ratio. The  $T_g/T_m$  ratio of ZIF-62 is higher than that of any other glass forming systems measured so far, and remains unchanged with the Im/bIm ratio. The viscosity of ZIF-62 at  $T_{\rm m}$ is higher than that of most of the investigated organic and inorganic of glass-forming systems, and but comparable to the fully polymerized strong systems like SiO<sub>2</sub>. By combining these dynamic data with structure analysis, we infer that a balance between the steric hindrance and the degree of the translational motion of structure units is the origin of the high glass forming ability of ZIF-62. The degree of this balance could be the key factor determining whether a MOF can be melted and vitrified.

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