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Probing phase transitions of metal-organic frameworks by THz/Far-IR

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Current research on metal–organic frameworks (MOFs) has concentrated predominantly on the properties of ordered crystalline phases. However, there is growing recognition of the importance of the physical properties of MOFs. In particular, the role of disorder, defects, and structural flexibility in installing beneficial physical behaviour is now widely studied. We synthesised four novel crystalline zeolitic imidazolate framework (ZIF) structures using a mixed-ligand approach. The inclusion of both imidazolate and halogenated benzimidazolate-derived linkers leads to glass-forming behaviour by all four structures. Melting temperatures are observed to depend on both electronic and steric effects. In situ THz/far-IR spectroscopic techniques reveal the dynamic structural properties of crystal, glass, and liquid phases of the halogenated ZIFs, linking the melting behaviour of ZIFs to the propensity of the ZnN4 tetrahedra to undergo thermally induced deformation.

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