Crystalline solids towards enzymatic behaviour

Flexibility is the essence of many naturally developed self-assembled systems which drives several key biological processes. This attribute is reflected precisely in the specific function of an enzyme. An enzyme does have flexible pocket which helps to reorient its structure during the binding with a specific substrate. Thus taking advantage of such structural flexibility, nature performs such an important job in daily life. It would be very exciting if such macroscopic flexible behaviours are brought down to the molecular scale mimicking enzymatic nature, especially with regard to controlling molecular motions in pursuit of designing & fabrication of flexible artificial receptors.

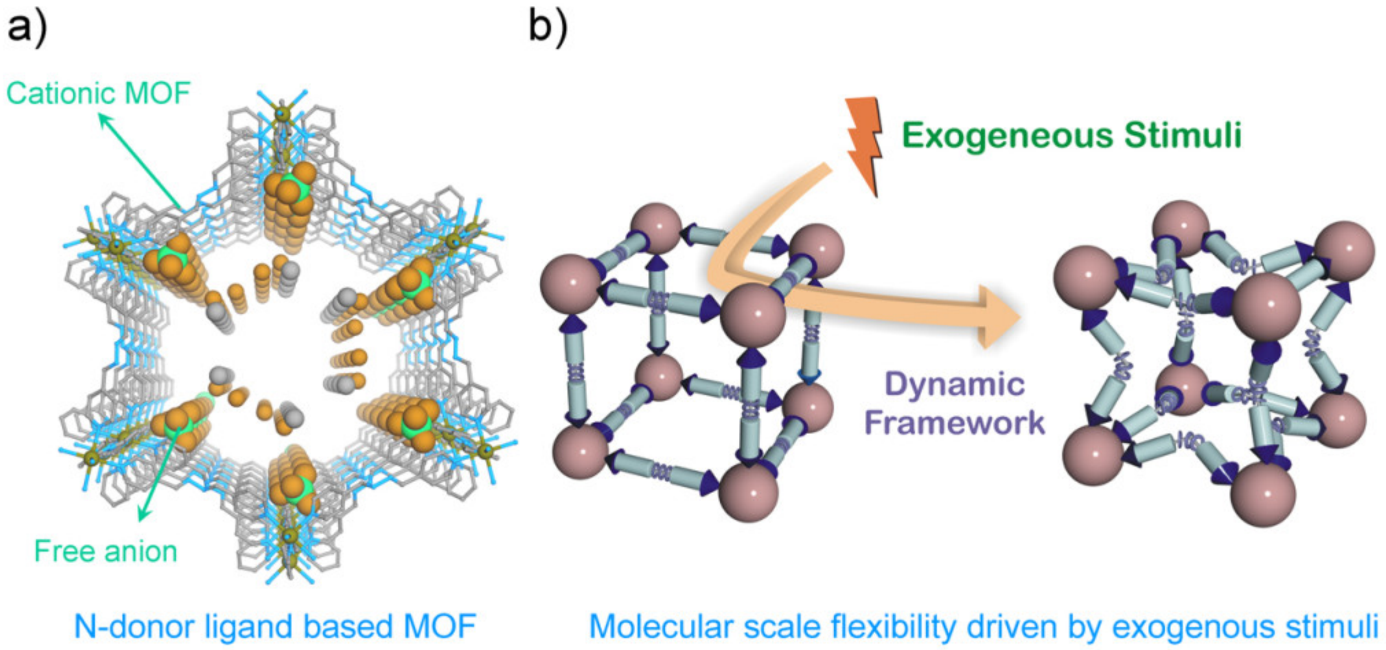

Fig 1: a) N-donor ligand based cationic MOF showing free anions in the lattice; b) schematic illustration of structural alteration in N-donor ligand based MOF via various exogenous stimuli.

In this regard crystalline molecular systems have been sought after for investigating such features owing to the feasible accessory of unambiguous characterization of molecular scale rearrangements. Among synthetic molecular systems, the class of metal-organic frameworks (MOFs)/porous coordination polymers (PCPs) have commanded significant research attention for imparting enzymatic softness at the molecular level. MOFs/PCPs are self-assembled; higher dimensional, polymeric networks based on strong coordination bonds which possess tuneable porous channels. On account of various metal ion coordination numbers or geometries and ample choice of organic linkers in terms of denticity, coordinating angles, coordinating moieties; MOFs have the significant advantage of designable architecture over other polymeric materials. In this context, soft porous MOFs are found to be key materials which respond to a number of exogenous stimuli. Several donor groups have been trialled for the synthesis of MOFs, among which carboxylate based ligands and neutral N-donor based linkers have been favoured, with the former type dominating literature reports. N-donor based MOFs are more suited for the development of dynamic systems because of the relatively weaker strength of the primary bond involved in the formation of the networked structure. Thus far, N-donor ligands have been commonly perceived only as linkers to increase the dimensionality of carboxylate linked MOFs, but progress in recent years has exuded greater promise for the examination of such systems as flexible porous compounds. Neutral N-donor ligand systems involve the anionic part of the metal salt used during synthesis of MOFs for the maintenance of ionic equilibrium; which in certain cases leads to the formation of cationic MOFs having uncoordinated, easily substitutable anions in the voids (Fig 1a). Thus employing N-donor based ligands afford the feasibility of ionic stimuli for inducing flexibility in addition to dynamic behaviour rendered by other kinds of perturbations (e.g. chemical stimuli, light, temperature, magnetic field etc.) (Fig 1b). In this highlight we have outlined the state-of-the-art progress of neutral N-donor ligand based MOFs functioning as dynamic systems, in terms of design principles, synthetic guidelines and structure-property correlations by in-depth discussion of representative examples. The greater understanding of host-guest interactions in such flexible systems has presented potential applications for gas/solvent separation, sensing, magnetic/electrical properties etc. Thus further investigation of such systems might indeed actuate the realization of the targeted artificial flexible systems which respond to specifically to an external stimulus, without compromising its structural integrity.

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Publication

Neutral N-donor ligand based flexible metal-organic frameworks.
Manna B, Desai AV, Ghosh SK
Dalton Trans. 2015 Oct 28