Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Neutral N-donor Ligand Based Flexible Metal-Organic Frameworks

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This short review gives a focus discussion on MOFs made of neutral N-donor ligands which show structural flexibility under various exogenous stimuli. Chemical stimuli such as anion, free guests, coordinated guests and physical stimuli (light,heat etc.) render structural flexibility in such MOFs. Single-crystal-to-single-crystal (SCSC) transformation studies have found immense attentions for understanding of such flexible MOF materials. Such a dynamic structural behavior with proper host-guest interactions find very interesting functions such as chemical separation, sensing and magnetic properties etc.

1. Introduction

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have emerged as a rapidly evolving class of porous materials and commanded significant research attention in domain of material and solid-state chemistry over the last couple of decades.[1] These porous crystalline solids are fabricated from bi- or multi-dentate organic linkers and held by metal-ion nodes in a periodic manner. The coordination bonded self-assembled polymers are endowed with well-ordered porosity by virtue of regularized arrangement of the building units in the infinite network. On account of the potential applications in the domain of storage, separation, sensing, ionic conduction, MOFs have been sought after in recent years.[2-5]

The key distinction of MOFs over congener porous materials is the class of 3rd generation MOFs or soft porous crystals which pertain to the enzymatic flexibility in such materials. Several studies over the last decade have demonstrated the advantage of examining molecular motions in crystalline polymeric solids.[6-8] The relatively easy access to characterize nano-scale rearrangements unambiguously renders a remarkable additional advantage to these systems. Owing to the assigned softness, MOFs have been able to function as guest-responsive host matrices without compromising on the polymeric character.[9-12]

In pursuit of synthesizing pre-designed architectures in general and dynamic MOFs in particular, several donor groups have been investigated over the years. Among them, carboxylate and neutral N-heterocycle terminal ligands have been prominently preferred, with the former type dominating literature reports. Neutral N-donor linkers afford formation of the coordination bond leaving the maintenance of ionic equilibrium to the components of metal-salts used in the synthesis. This provides a simplistic route for the preparation of cationic frameworks, in case where the counter-anion is left uncoordinated to the metal centre.[13-19] Broadly, dynamic MOFs have relied on the flexibility possessed by the ligand and/or metal-ion with the reorganization primarily driven by desorption/resorption of neutral guest molecules, while N-donor ligands based MOFs provide the additional aspect of enforcing an ionic stimuli (anion).

N-donor based ligands have been previously perceived only as pillars to increase the dimensionality in carboxylate ligand linked frameworks.[20-21] Recent years have witnessed the importance of such donor ligands in the domain of dynamic MOFs both in terms of understanding structural dynamism and probing structure-property correlation. This review focuses on the consolidation of flexibility aspect in MOFs and efficacy of N-donor ligands with representative examples concerning the structural aspects and the subsequent properties induced by the reorganization of the frameworks.

2. Scope of the review

The main focus of this particular review is to give a till date report of flexible MOFs made of neutral N-donor ligands. A flexible MOF can be perturbed by various external stimuli (both chemical and physical) (Scheme 1).

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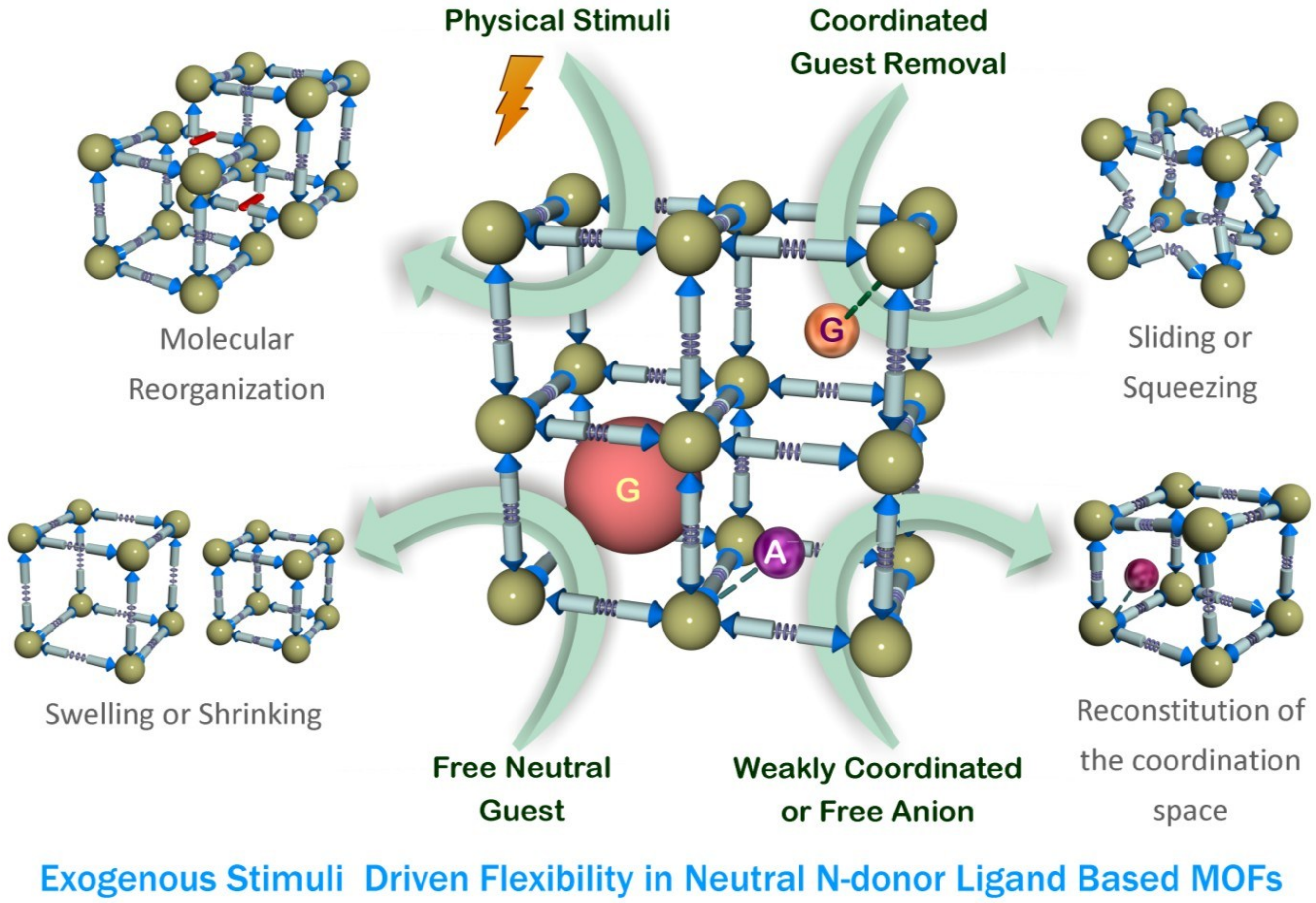

Scheme 1 Various exogenous stimuli (chemical and physical) that render flexibility in Neutral N-donor ligand based MOFs.

Such aspects to render flexibility in N-donor ligand based MOFs are discussed in detail in this article. In addition to this, different kinds of structure-property correlations have also been considered in comprehensive manner. It is worth noting that the neutral N-donor ligands are widely used classical ligands that can form MOFs upon binding to metal ions. In spite of availability of few reviews on flexible MOF systems, the current concern topic lacks such report in the literature. Several papers and reviews covered in this article might attract readers for further investigations in such flexible MOF systems towards various functions.

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3. Synthesis routes to construct flexible frameworks

Generally, the uncontrolled polymeric self-assembly in MOFs makes it a challenging task to pre-design flexible systems. In principle, neutral N-donor ligand based MOFs are relatively well-suited for imparting dynamism owing to the moderate strength of the primary bond involved. The free solvent molecules occluded during synthesis play the role of principal trigger to modulate the overall structure in MOFs. In particular, use of low-boiling solvents facilitates structural dynamism because of feasible

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escaping tendencies of such solvents from the frameworks upon keeping those MOF crystals away from mother liquor. Although anticipating coordination of guest molecules to metal sites is not possible, usage of coordinating solvents and/or moderately interacting anions may afford a greater possibility to furnish easily dissociable mono-dentate coordinated guests. The mandatory presence of the mono/multi-dentate anions, on some occasions uncoordinated to the metal centre, within N-donor ligand based MOFs offers the desirable stimulus of exogenous anions to study solid-state structural transformations.[22] In comparison physical stimuli driven investigations, light irradiated transformations in particular, have been found to be simpler in terms of design principles. With further work, the ambiguity in the understanding synthesis strategies of such systems can be significantly elapsed.

4. Structural Dynamism of N-donor ligand based MOFs

Neutral N-donor ligand based MOFs are generally observed to bear guests which remain free or weakly coordinated to the metal centres. Variations of such guests inside the framework can cause alteration in framework structures due to the presence of relatively weaker coordinate bonds (M-N). Apart from such guest induced framework flexibility, dynamism can also be imparted via the perturbation of extra-framework anions.[23] Moreover, inserting proper ligand functionality enhances the chance for molecular reorganization upon shining light (physical stimuli) on such frameworks. Single crystal to single crystal structural transformation method is one of the best direct and key technique for understanding such molecular level chemical changes in such dynamic frameworks. Various exogenous stimuli (both chemical and physical) that induce structural dynamism will be encountered in detail in the subsequent sections.

4.1 Flexibility driven by chemical stimuli

On account of various exogenous stimuli (chemical) flexible MOFs undergoes structural alteration. Such structural variations often have been well validated by SCSC studies. Chemical stimuli (viz. counter anion, free guests, coordinated guests and gaseous guests) have found profound role in rendering flexibility in such MOFs.[24] In the following sections we categorize different types of chemical stimuli that cause flexibility in such MOF systems.

4.1.1 Anion induced framework flexibility

MOFs made of neutral N-donor ligands and metal ions posses counter anions in their framework lattice to make up the charge of the metal centers. Such counter anions present in the framework structure remain free in the voids or are weakly coordinated to metal ions and are found to interact with the cationic framework via various kinds of non-covalent interactions. Now depending upon how strong those interactions are, replacement of such anions by incursive anions can be possible. It has been observed that such anion replacement process often makes a change in the structure of original MOF system and thereby creating flexibility in MOFs.[25-27]

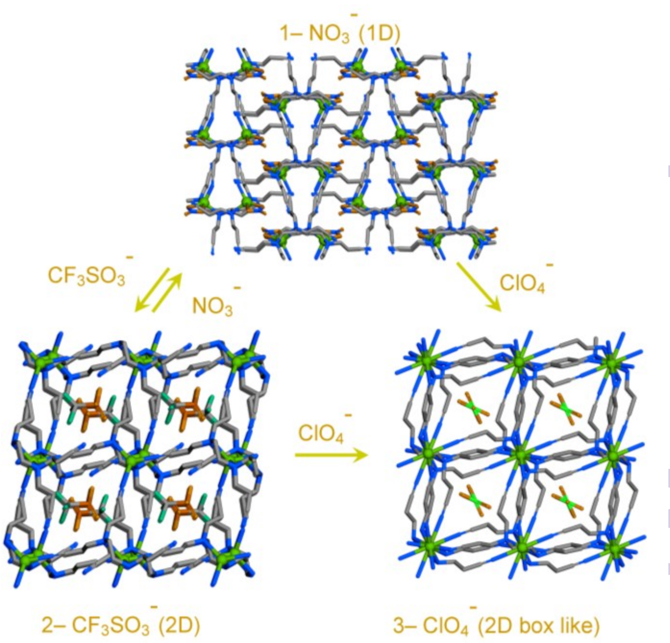

Fig.1 Anion dependent structural transformation in cationic polynitrile based network.

Yaghi et.al described long back structural transformation via reversible anion exchange.

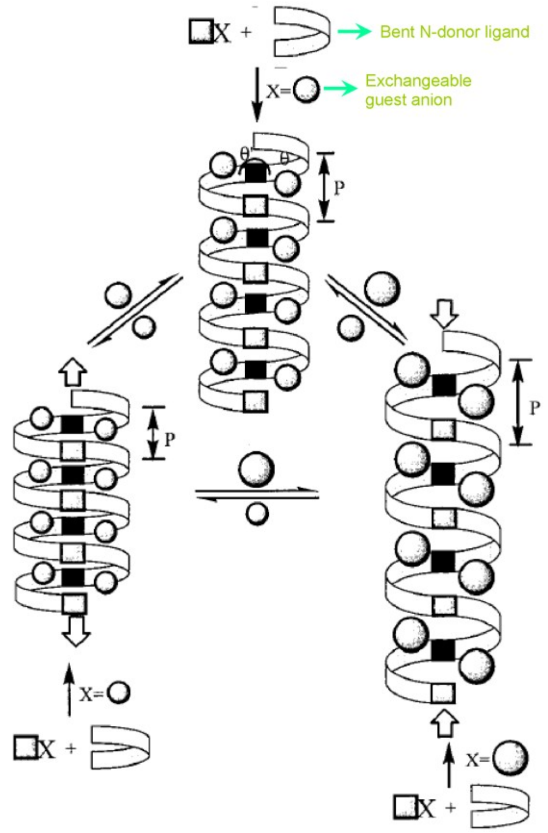

Fig.2 Helical pitch tuning by anion exchange in a cationic solid. Reproduced with permission from Ref. 30, Copyright (2000) American Chemical Society.

For example, $[Ag(4,4'\text{-bpy})(NO_3)]_n$ transforms to a exchanged solid upon addition of excess amount of KPF_6.[28] On addition of excess KNO_3 onto the exchanged solid original network is restored. Suh et.al showed anion dependent structural transformation in a cationic polynitrile based network.[29] During the course of this anion exchange 1D [Ag (edtpn)(NO_3)]$_n$ (edtpn- ethylenediaminetetrapropionitrile) transforms to 2D layer structure [Ag(edtpn)(CF_3SO_3)]$_n$, 2D box like network [Ag(edtpn)(ClO_4)]$_n$ in reversible and irreversible manner respectively. [Ag(edtpn)(ClO_4)]$_n$ can also be obtained from [Ag(edtpn)(CF_3SO_3)]$_n$ in irreversible manner(Fig. 1). Helical pitch of cationic infinite solids can be tuned by variation of extra framework anions. Jung et.al explained a cationic CP {[Ag(Py_2O)].X}$_n$ (X=NO_3^-, BF_4^- , ClO_4^- and PF_6^-) (Py_2O - 3,3'-oxybispyridine)as a smart helical spring [30] as this can stretch reversibly owing to the counter anion exchange which can be correlated to the volume of anion(Fig.2). Anion induced framework engineering has been shown in a 2D-interpenetrated cationic coordination polymer based on Cu(II) and 4,4'-bpy by S.Kitagawa et al.[31] The exchange of anion in an interpenetrated framework leads to increase in the pore size of the overall framework.[32] Replacement of free $N(CN)_2^-$ in the framework {[Ni(bpe)$_2$($N(CN)_2$)]($N(CN)_2$)}$_n$ (bpe- 1,2-bis(4-pyridyl)ethane) by smaller N_3^- causes mutual dislocations of the interpenetrating nets for enlargement in the effective porous area in the framework(Fig.3). Such enhancement in the porous area in the framework affects the gas uptake property of the material. N_3^- exchanged solid with larger porous aperture shows more uptake of gas than the original framework. Our group came up with a dynamic luminescent cationic framework [{Zn (L^1)(MeOH)$_2$}.(NO_3)$_2$.xG]$_n$ (L^1- 4,4'-(ethane-1,2-diyl)bis(N-(pyridin-2-ylmethylene)aniline which showed interesting anion dependent structural dynamism depending on the size, shape and coordinating tendencies of various anions (NO_3^-, N_3^-, SCN^-, ClO_4^- and $N(CN)_2^-$).[33] Du et.al showed acetate anion driven structural change in two isostructural 3D cationic frameworks {[M(L^2)$_2$] (ClO_4)$_2$}$_n$ (M= Co(II) or Zn(II)) (L^2- 4-(4-pyridyl)-3,5-bis(2-pyridyl)-1,2,4-Triazole).[34] Dong et.al reported spherical halide anions (Cl^- and Br^-) dependent structural changes in a Cd(II) based cationic framework Cd(L^3)$_2$(NO_3)$_2$.2THF(L^3-3,5-bis(3-pyridyl-3-(3′ -methylphenyl)-1,3,4-oxadiazole).[35]

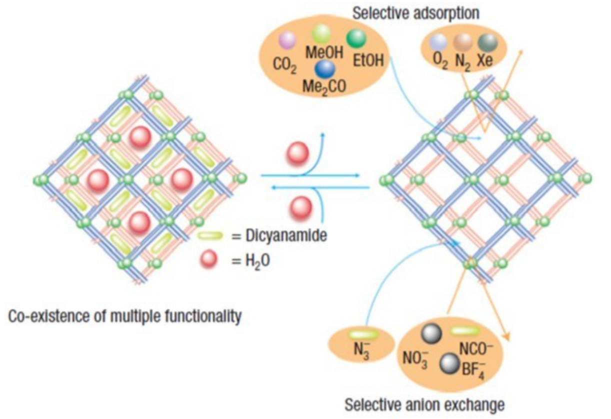

Fig.3 Schematic illustration of mutual sliding of nets induced by anion exchange in a cationic MOF. Reprinted with permission from Ref. 32, Copyright (2007) Macmillan Publishers Ltd.

In an early work, our group came up with two MOF-based supramolecular isomers [{Cd(L^4)$_2$(ClO_4)$_2$}·toluene·MeOH]$_n$ and [{Cd_2(L^4)$_4$(ClO_4)$_4$}·3(mesitylene)]$_n$ (L^4- 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) which show anion induced structural changes for incoming strongly coordinating N_3^- and SCN^- anions owing to the replacement of weakly coordinated ClO_4^- anions in the original frameworks.[36] Anion driven structural transformation has also been exploited for visual colorimetric detection of anions.

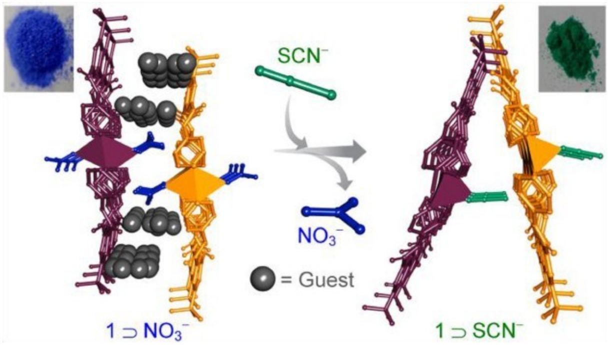

Fig.4 Visual colorimetric anion sensing in a dynamic cationic MOF. Reproduced with permission from Ref. 37, Copyright (2015) Wiley-VCH.

For example, a 1D amide functionalized Cu(II) based framework [{CuL^5_2(NO_3)$_2$}·o-Xylene·DMF]$_n$ changes its structure to 2D framework [{CuL^5(SCN)$_2$}·xG]$_n$ (L^5- 5-tert-butyl-N1,N3-di(pyridin-4-yl)isophthalamide) upon treating with SCN^- accompanying a naked eye color change from blue to green(Fig.4).[37]

4.1.2 By alteration of free guests

MOFs composed of such neutral N-donor ligands often are found to have free guests inside the framework. Those free guests are bound to the network by weak molecular interactions and thereby enhance the chances for the variations of such guests inside the framework. Alteration of such guests within the framework leads to structural changes of the system. Owing to this structural flexibility, 3rd generation MOFs posses bistable or multistable states and show enhanced host-guest interactions over rigid MOFs.[38]

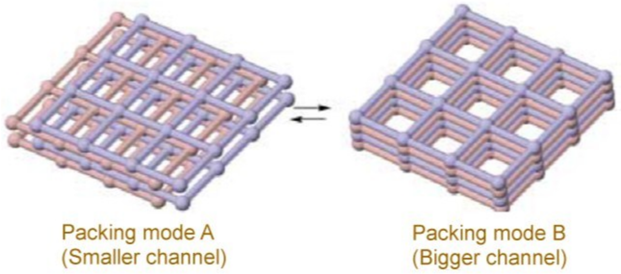

Fig. 5 Guest induced sliding of 2D layers in reversible way. Reproduced with permission from Ref. 40, Copyright (2002) Wiley-VCH.

Cianni and co-workers showed sponge like behavior in a Cu(II) based framework [Cu_5(bpp)$_8$(SO_4)$_4$(EtOH)(H_2O)$_5$](SO_4).EtOH.25.5H_2O. (bpp- 1,3-bis(4-pyridyl)propane) The compound exhibits guest dependent reversible structural transformation towards desolvation and resolvation.[39] S.Kitagawa et.al reported a 3D framework $\{[Cu(AF_6)(4,4'\text{-bpy})_2].xH_2O\}_n$ that changes to a 2D interpenetrating network $\{[Cu(4,4'\text{-bpy})_2(H_2O)_2].AF_6\}_n$(A= Si, Ge and Ti) in aqueous environment.[31] Guest driven sliding of 2D layers in a MOF has been demonstrated by Fujita and co-workers.[40] Upon guest exchange the 2D framework $[Ni(L^6)_2(NO_3)_2.4(o\text{-xylene})]_n$ transformed to $[\{Ni(L^6)_2(NO_3)_2.1.7(\text{mesitylene})\}_n]$ (L^6 - 2,4,6-tris(4-pyridyl)triazine)with a significant increase in the channel dimension(Fig.5).

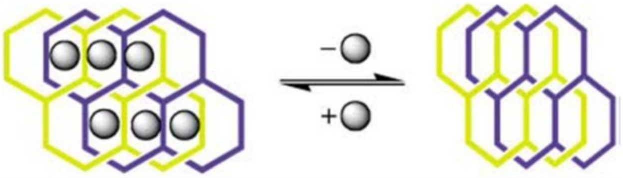

Fig. 6 Schematic representation of guest dependent shrinking or swelling in a dynamic MOF. Reproduced with permission from Ref. 42, Copyright (2002) Wiley-VCH.

In continuation, Fujita et.al also exhibited a dynamic MOF which remarkably shrinks or swells upon desorption or adsorption of guest molecule.[41] When the crystals of the framework $[\{(ZnI_2)_3(L^6)_2.6C_6H_5NO_2\}_n]$ were kept at open atmosphere for one day, they changed to new phase with a remarkable compression of the network without losing their single crystalline nature. Interestingly, upon immersing the crystals of new phase into nitrobenzene, parent crystals are restored (Fig.6). Reversible Crystal to amorphous structural transformation has been examined in a amide functionalized 3D MOF by S.Kitagawa et.al. The 3D framework $\{[Co(NCS)_2(4\text{-peia})_2].4Me_2CO\}_n$ (4-peia- N-(2-pyridin-4-yl-ethyl)-isonicotinamide) transformed to a amorphous state upon complete removal of guest acetone molecules and get back to the original state when the amorphous phase is being exposed to acetone vapour.[42] Guest dependent structural flexibility has also been shown in a cage based coordination network.[43] For example $[Co_3(SCN)_6(TPT)_4]_n$ transformed to $[Co_3(SCN)_6(TPT)_4.(TTF)]_n$ (TPT-2,4,6-tris(4-pyridyl)triazine) while taking up guests (tetrathiafulvalen)with a change crystal system cubic tetragonal (Fig.7).

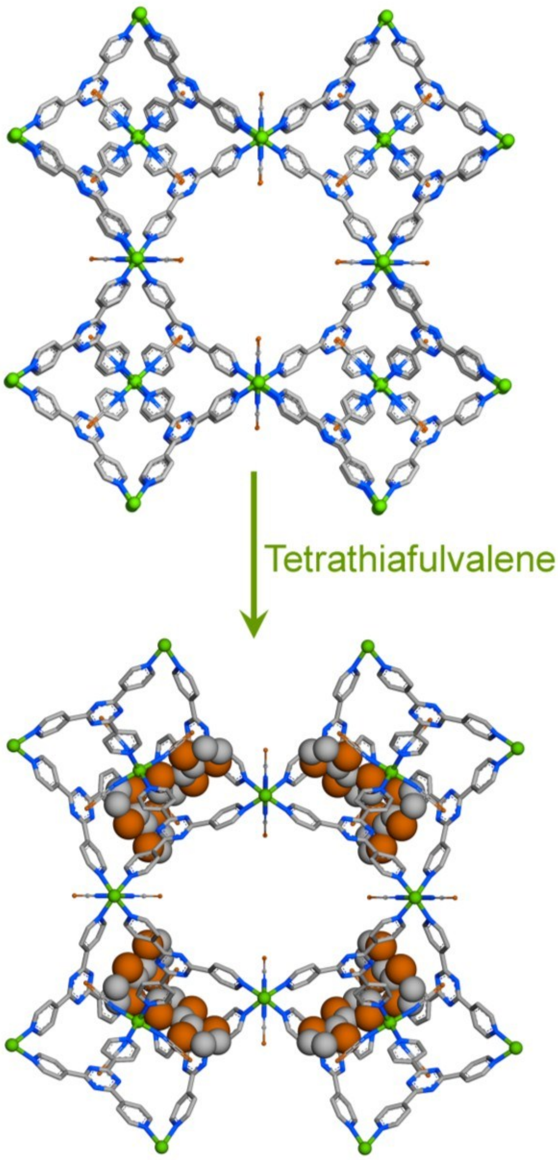

Fig. 7 TTF mediated structural changes in a networked molecular cage.

Recently, Sumby and co-workers demonstrated guest induced crystal to crystal expansion and contraction in a Ag(I) based 3D MOF $\{[Ag(dpzm)]ClO_4.1.1\ (DMSO).0.9(ETOAC)\}_n$ (dpzm-Di-2-pyrazinylmethane)(1 As-made).[44]

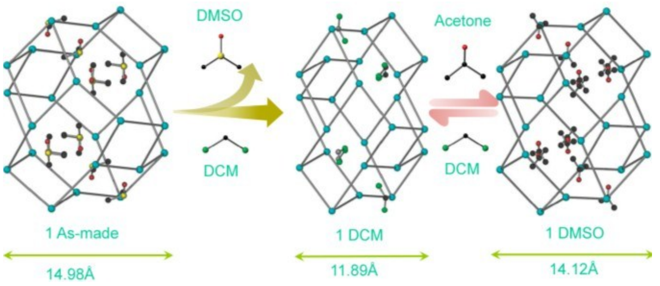

Fig. 8 Guest mediated crystal expansion and contraction in a cationic MOF. Reproduced from Ref. 44, Copyright (2012) The Royal Society of Chemistry.

Upon guest exchange with dichloromethane (DCM), 1 As-made changed to 1 DCM in crystal to crystal manner accompanied by a dramatic contraction of 3.09Å along *c* axis. But 1 DCM expanded to 1 Acetone in a reversible fashion while soaking in acetone for few days (Fig.8). In continuation, the authors reported a similar series of MOFs which exhibited similar breathing transformations upon guest exchange.[45] In a very recent report our group showed a 3D interpenetrated cationic MOF $[\{Zn(L^7)_2\}(NO_3)_2{\cdot}xG]_n$ (L^7-[(E)-N′ -[1-(pyridin-4-yl)ethyidene]hydrazine carbohydrazide)which upon dynamic structural transformation transformed to a 2D MOF(Fig.9).[46]

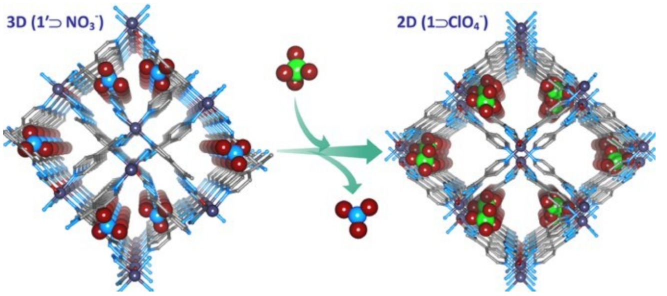

Fig. 9 Anion induced structural transformation from 3D framework to 2D sheets. Reproduced with permission from Ref. 46, Copyright (2014) American Chemical Society.

In continuation, guest driven inherent dynamic behaviour of a Cd(II) based cationic MOF has been exhibited by us .[47] Upon air-drying , the as-made MOF $[\{Cd(L^4)_3.(ClO_4)_2\}.xG]_n$ transforms to a 2D MOF $[\{Cd(L^4)_2(OH_2)_2(ClO4)_2\}.THF)]_n$ via the loss of a coordinated ligand molecule(Fig.10).

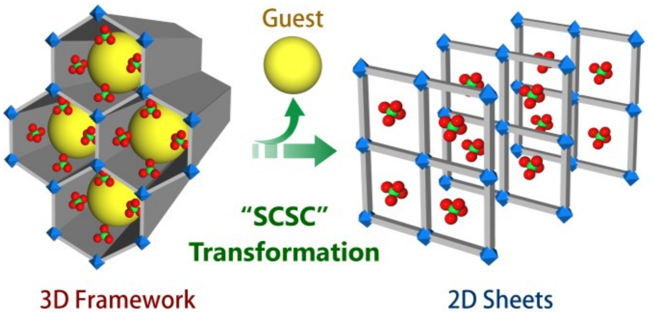

Fig. 10 SCSC transformation from a 3D porous framework to 2D non porous sheets. Reproduced from Ref. 47, Copyright (2015) The Royal Society of Chemistry.

4.1.3 Flexibility driven by variation of coordinated guests

A facile route to achieve perturbation in the coordination sphere of metal nodes can be through substitution of coordinated neutral molecules. By virtue of mono-denticity of such coordinated molecules, they can easily be substituted or the framework can reorganize itself to make up for the presence of open metal sites. In certain cases the regulation over flexibility by coordinated guests has been associated with change in certain physical properties.[48-49] Some of the key results in recent years have been presented below.

Rosseinsky et al. demonstrated the flexibility of a MOF by regulating the coordinated neutral guest via thermal stimuli.[50] The authors synthesized a neutral compound $[Co_2(bipy)_3(SO_4)_2(H_2O)_2](bipy)(CH_3OH)$, (bipy - 4,4'-bipyridyl) bearing an uncoordinated ligand and a solvent molecule. Upon heating the coordinated water molecules were replaced by the uncoordinated species in the parent compound. This change was accompanied by alteration in the structure of the compound to give a new phase. The reversibility of this experiment and the hypothesis was validated by controlled cooling in the presence and absence of atmospheric moisture (Fig.11).

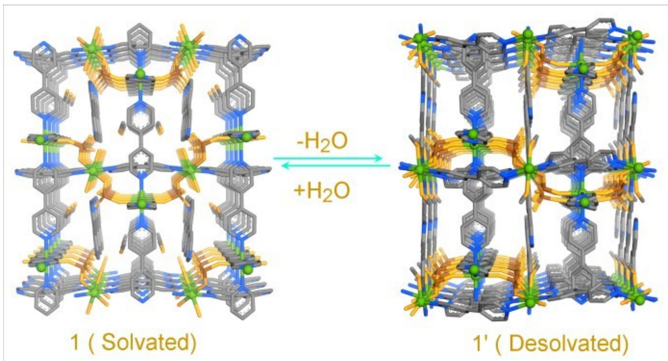

Fig. 11 Rearrangement of coordination environment by loss of bounded water.

In a similar report, Morsali and co-workers exhibited drastic structural changes of a coordination polymer by removal of coordinated solvent upon heating.[51] A one-dimensional (1D) coordination polymer $[Pb_2(8\text{-}Quin)_2(NO_3)_2(MeOH)]$, (8-Quin - 8-hydroxyquinoline) was synthesized which converted to a 2D structure $[Pb(8\text{-}Quin)\text{-}(NO_3)]$ when the compound was heated at 165-170 °C. The Pb-O bond with methanol was replaced by a Pb-O bond from the nitrate anion. This transition was also accompanied with a visual change in the colour of the crystal.

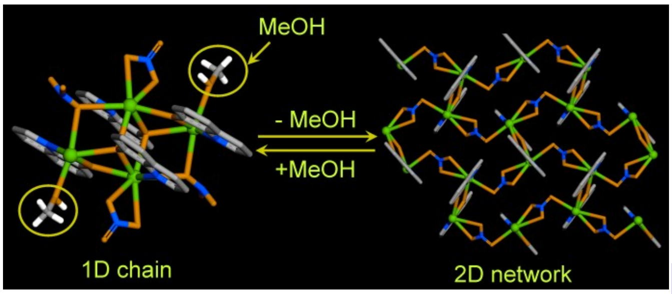

Fig. 12 Increasing in framework dimensionality via loss of coordinated MeOH.

The resolution of the compound to its parent phase was achieved when this was dipped in methanol and the authors observed such multiple reversible transformations (Fig.12). Su et al. extended this concept through fabrication of a Cd(II) based MOF $[(Cd(ImBNN)_2(CF_3SO_3)_2).guest]_n$, (ImBNN - 2,5-bis[4'-(imidazol-1-yl)phenyl]-3,4-diaza-2,4-hexadiene) bearing weakly coordinated triflate anions and free toluene molecules.[52] Upon removal of the toluene molecules by heating, the metal-anion bond is weakened. When the compound was cooled under atmospheric conditions, one water molecule replaced the triflate anion leading to slight structural changes.

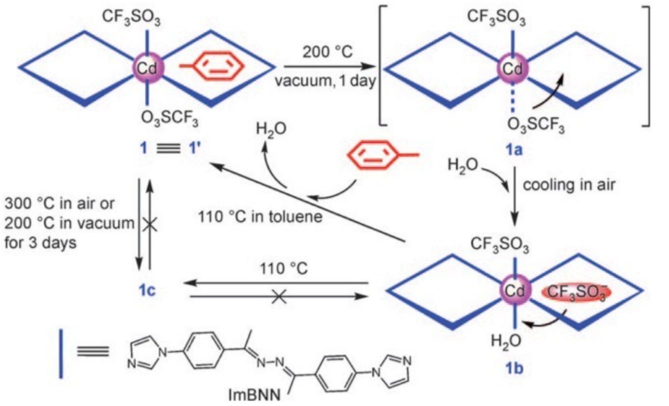

Fig. 13 Schematic illustration of structural transformation upon loss and gain of coordinated guests. Reproduced with permission from Ref. 52, Copyright (2009) Wiley-VCH.

The original phase of the compound was restored by heating the water coordinated phase in toluene at 110 °C. Toluene molecules occupied the free space of the MOF and both the anions were coordinated to the metal centre. This report yields an example of neutral guest molecules competing with charged anions for metal-coordination leading to structural changes (Fig.13).

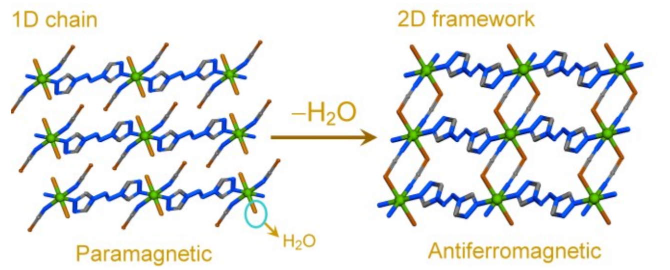

Fig. 14 SCSC transformation upon dehydration accompanied by changes in magnetic properties.

Chen and co-workers observed the structural changes to accompany promising magnetic regulation in a MOF based material.[53] The authors synthesized a Co(II) centred 1D coordination polymer $[Co(SCN)_2(bta)(H_2O)_2]$, (bta - 1,2-di(4H-1,2,4-triazol-4-yl)diazene) comprising of water molecules in the coordination sphere of the metal ion. Upon desolvation at 100 °C the authors observed structural changes along with increase in dimensionality of the packing. Interestingly, magnetic variation was noticed during this transition from simple paramagnetic behaviour of the parent compound to antiferromagnetic nature of the desolvated phase (Fig.14). As discussed in the previous section, we have reported a MOF exhibiting anion and guest dependent structural changes.[33] The as-synthesized compound on air-drying underwent noticeable structural modifications, via SCSC characterization, and accompanied with change in coordination environment of the metal centre. The coordinated methanol molecules were replaced by water from atmospheric moisture.

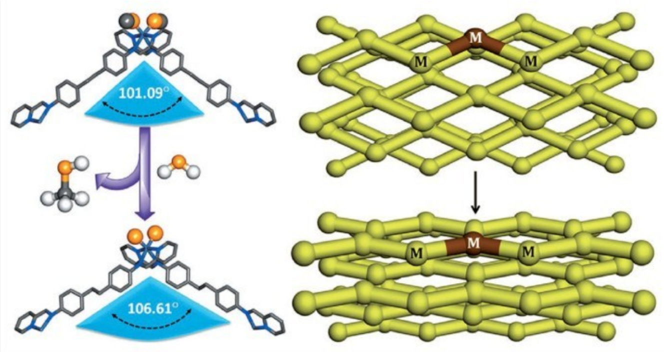

Fig. 15 Guest triggered dynamic structural transformation in a flexible cationic MOF. Reproduced with permission from Ref. 33, Copyright (2013) Wiley-VCH.

The affinity of the framework towards several hydrophilic adsorbates was further studied, which yielded size selective uptake (Fig.15).

4.1.4 Flexibility driven by gas adsorption

Another route to encounter flexibility is the structural changes effected by the interaction of gas molecules with the framework components under pressure.[54-55] Since the precise understanding of gate-opening phenomenon in MOFs, few N-donor ligand based MOFs have been found to follow such behaviour. Some of the important recent examples have been discussed herewith.

In an early work Kaneko studied the adsorption behaviour for a Cu(II) MOF $[Cu(bpy)(BF_4)_2(H_2O)_2.(bpy)]_n$, (bpy - 4,4,'-bipyridine).[56] An alike response to different gases like N_2, Ar, CO_2 was observed in which the relatively non-porous packed compound was able to adsorb significant amount of these gases after respective gate-pressures. The authors attribute the breach of hydrogen-bond assisted packing of the compound (owing to the presence of BF_4^- anions) by the respective gate-pressures of the adsorbed gases (Fig.16).

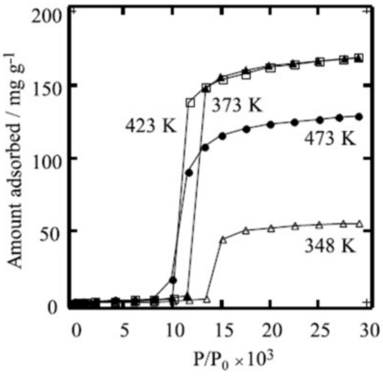

Fig. 16 Gate opening behaviour for CO_2 adsorption in a Cu(II) MOF. Reprinted with permission from Ref. 56, Copyright (2001) Elsevier.

Kondo et al. reported a dual flexible MOF system which underwent structural alterations upon guest removal and later upon adsorption of gas molecules.[57] The authors synthesized a 3D MOF {[Cu(bpy)$(BF_4)_2(H_2O)_2$].(bpy)}, (bpy - 4,4'-bipyridine) which underwent a dimensionality reduction to form a 2D framework having formula [Cu$(BF_4)_2$$(bpy)_2$](Fig.17).

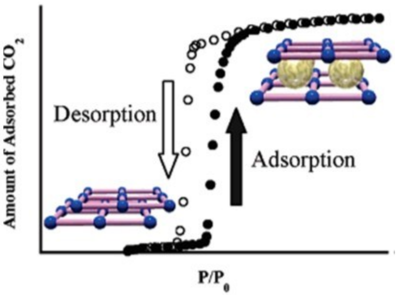

Fig. 17 Schematic representation of clathrate formation during CO_2 adsorption. Reproduced with permission from Ref. 57, Copyright (2006) American Chemical Society.

Upon studying CO_2 adsorption for the 2D compound, a notable change in the interactions between two 2D sheets was found to happen, which was ascribed to the clathrate formation between the gaseous molecules and the framework in the adsorbed state.

In a continuation, Kanoh et al. demonstrated the flexibility of dynamic frameworks upon inclusion of gaseous molecules by constructing a Cu(II) based 2D MOF [Cu$(bpy)_2$$(OTf)_2$].2EtOH.$H_2O$, (bpy - 4,4'-bipyridine).[58] An isostructural MOF with methanol occluded guests has also been reported in this work to study the effect of free guest molecules. Upon desolvation the parent compound was subjected to low temperature N_2 adsorption, wherein the authors observed the typical gate-opening behaviour at P/P_0 = 0.16-0.22. PXRD measurements at the first step of gate-opening evidenced the structural changes corresponding to the expansion of the 2D layers in the compound (Fig.18).

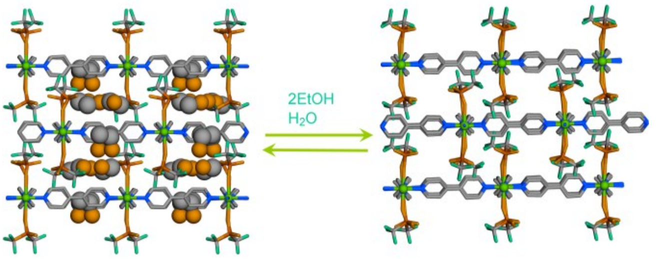

Fig. 18 Guest induced reversible structural transformation in a flexible MOF.

Kanoh and co-workers expanded the above work by fabricating a series of MOFs having the same composition viz. [Cu$(bpy)_2$$(OTf)_2$]$_n$, (bpy - 4,4'-bipyridine) in different solvent combinations.[59] In the 2D architectures the authors observed stepwise adsorption for gases like N_2, CO_2, Ar, CH_4. This behaviour was not observed for the 3D compounds wherein a Type-I adsorption profile was seen in all cases and the uptake follows molecular sieving effect. The layered 2D structures have been ascribed undergo sliding to accommodate the respective adsorbents(Fig.19).

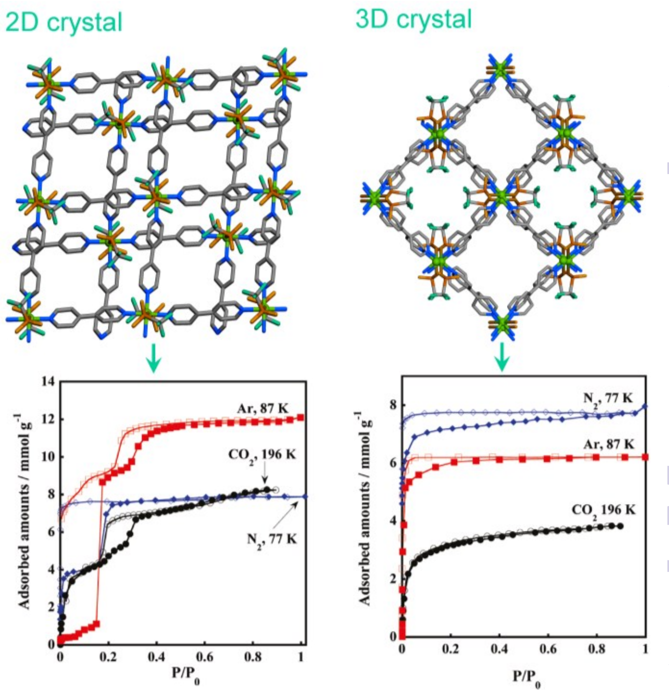

Fig. 19 Differential adsorption behaviours in two MOFs having the same composition. Reproduced with permission from Ref. 59, Copyright (2011) American Chemical Society.

In a similar work, Maeda et al. synthesized a Cu(II) based 1D coordination polymer viz. Cu$(bpp)_2$$(BF_4)_2$, (bpp - 1,3-bis(4-pyridyl)propane) which underwent structural changes upon desolvation.[60] Low temperature N_2 adsorption was performed on the guest-free phase, which did not show any uptake. When CO_2 adsorption was performed on the same phase under moderate conditions, the compound exhibited gate-opening adsorption profile.

4.2 Flexibility arising from physical stimuli

MOFs are known to be responsive to physical stimuli owing to the dual advantages bestowed by the metal ions and organic ligands. Among them, light irradiated structural changes have commanded significant attention among other physical stimuli. Vittal et al. have pioneered the domain of cycloaddition reaction based structural changes in olefin-bearing ligands.[61] Owing to the lack of chemical stability in neutral N-donor ligand based MOFs, solid-state reactions are more favoured for investigation of structural subtleties. The prominent reports among such class of studies are discussed below.

In an early study on this aspect, Vittal et al. reported anisotropic movements within a CP structure.[62] The authors synthesized a CP [Ag(μ-bpe)(H_2O)](CF_3CO_2).CH_3CN, (bpe - 4,4'-bipyridylethylene) which upon desolvation was subjected to photo-irradiation. The resultant compound was found to bear the desired cyclobutane rings, as suggested by NMR studies. Although the crystallographic evidence could not be provided for the desolvated structure, the authors crystallized an alike compound bearing coordinated anions [{(μ-O_2CCF_3)Ag}$_2$(μ-bpe)$_2$].H_2O supporting their claim of the formation of a ladder-like CP. The authors hypothesize the reorganization of the compound after desolvation to align the ethylene groups suitable for cycloaddition reaction.

Carrying this knowledge, Vittal and co-workers used photochemical cycloaddition reaction to evidence the formation of the intermediate upon dehydration of a 1D coordination polymer $[Cd(bpe)(CH_3COO)_2(H_2O)]_n$, (bpe - 4,4'-bipyridylehtylene).[63] The synthesized compound upon dehydration was subjected to UV irradiation to achieve 100% formation of the cyclobutane ring. As against this result, only 33% conversion was noted when the parent compound was irradiated. Thus among the two possible intermediates, the authors could conclusively infer the formation of the 1D ladder-like structure formation upon dehydration.

In continuation, the same group synthesized a triple-stranded ladder CP $[Pb_3(bpe)_3(O_2CCF_3)_4(O_2CCH_3)_2]$, (bpe - *trans*-1,2-bis(4-pyridyl)ethene) which underwent solid state cycloaddition reaction.[64] A two-step progress of the reaction was observed which was ascribed to anisotropic movements among the adjacent strands of the CP. In the first step ~67% photodimerization was noted corresponding to the reaction between a pair of bpe ligand of the triple-stranded structure. The second step involves the remaining 33% reaction with cooperative movements in the polymeric structure to align the unreacted olefin for completing the dimerization(Fig.20).

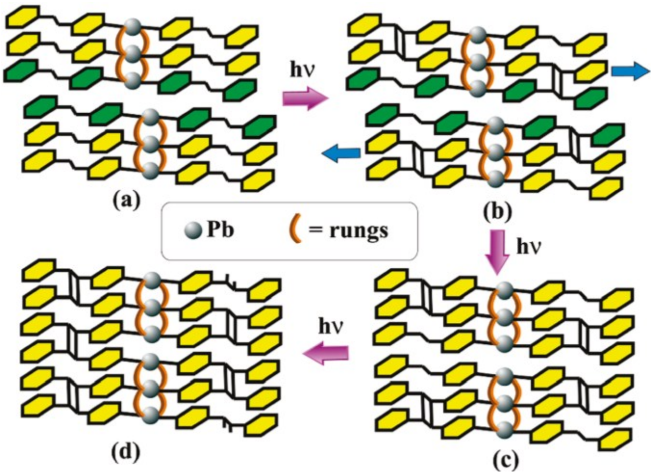

Fig. 20 Schematic representation of two step photo induced dimerization. Reproduced with permission from Ref. 64, Copyright (2010) American Chemical Society.

In a parallel manner, the authors have reported development of CPs using the photoactive monomers. By employing a Zn(II) salt and mono-dentate N-donor ligand, a monomer $[ZnBr_2(4spy)_2]$, (spy - *trans*-2-fluoro-4'-styrylpyridine) was synthesized.[65] Upon irradiation, a dimer was obtained which could be reversibly brought back to the monomer by heating. When the dimer was irradiated for a longer duration a 1D CP was synthesized, the reaction of which was not found to be reversible. The authors further observed drastic photoluminescence change along-with the photopolymerization (Fig.21). More recently, the authors undertook a comprehensive study of understanding the photo-activeness of monomeric systems bearing photo-active olefinic groups .[66]

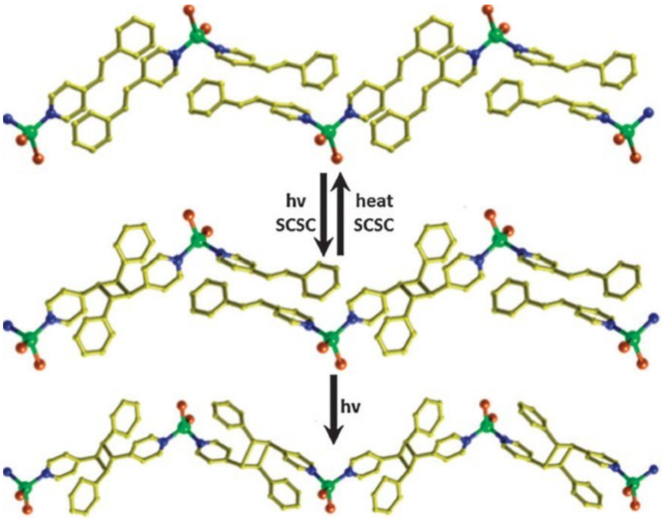

Fig. 21 Photo induced cycloaddition reaction in the formation of 1D CP. Reproduced from Ref. 65, Copyright (2013) The Royal Society of Chemistry.

A series of Ag(I) centred compounds were synthesized by varying the ligand and anion. All the compounds were found to undergo photo-induced cycloaddition reactions, which provided conclusive evidence for the effect of the shape, nature, size of the counter-anions on the photo-activity of the compound.

5. Flexibility driven physical and chemical properties

The flexibility endowed by dynamic MOF systems permits investigation of these materials for controlled regulation of certain physical or chemical properties and/or finding suitability for prospective real-time applications.[67-68] Few important results in this regard have been discussed below.

In an early report, Kepert et al. found a flexible Fe(II) centred MOF to exhibit guest-dependent spin-crossover (SCO) properties.[69] The authors synthesized a MOF $Fe_2(azpy)(NCS)_4{\cdot}(EtOH)$, (azpy - *trans*-4,4'-azopyridine) wherein a weak interaction between O-H···S was found to prevail. Temperature dependent magnetic susceptibility was recorded followed by desolvation. In the guest-free form, the slightly bent thiocyanate ions were found to be aligned in a linear fashion giving rise to structural changes.

Upon measurement of magnetic susceptibility for this phase of the compound, a significant change in the crossover onset temperature was observed. To corroborate with the proposed mechanism, the desolvated phase was dipped separately in EtOH, MeOH & PrOH to obtain resolvated guest included compounds. These phases were found to show similar susceptibility patterns (Fig.22). In continuation and carrying from the knowledge of the previous work, the authors synthesized a Fe(II) MOF $[Fe(NCS)_2(bpbd)_2]{\cdot}\{acetone\}$, (bpbd - 2,3-bis(4'-pyridyl)-2,3-butanediol) comprising of free hydroxylbearing groups in the ligand.[70] The O-H···S interactions as previously noted was found to persist in the interpenetrated packing of the compound, rendering inflexibility to the compound and keeping out any host-guest non-covalent interaction.

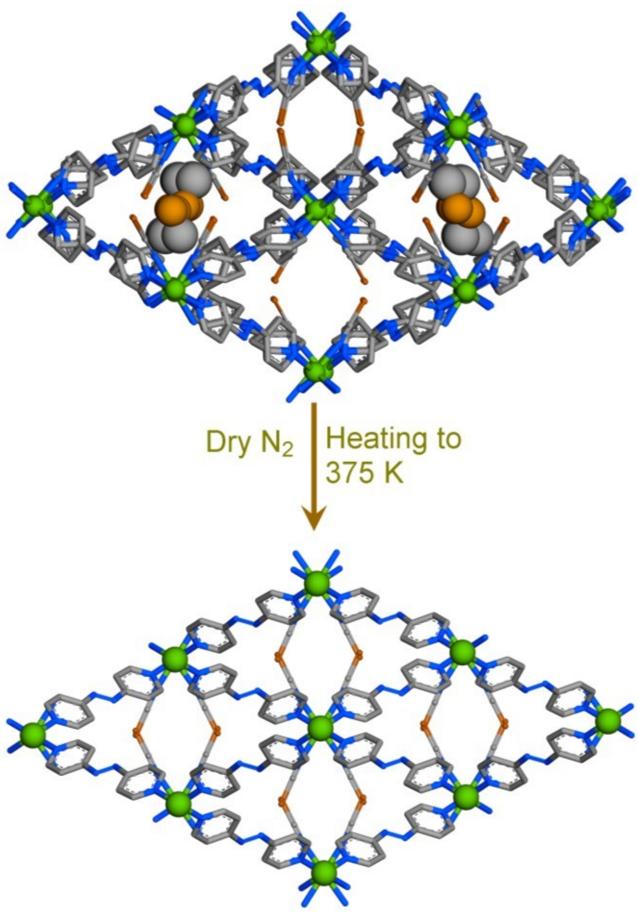

Fig. 22 Guest dependent spin crossover behaviour in dynamic MOF.

Temperature dependent subtle structural changes were observed for the compound. Temperature dependent magnetic susceptibility measurements were carried for as-synthesized phase and the desolvated phase which displayed almost alike tendency, reaffirming the hypothesis of employing a free hydroxyl-based ligand (Fig.23).

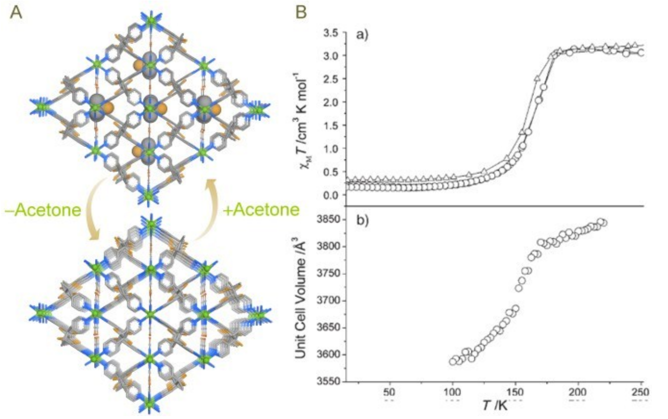

Fig. 23 (A) Guest induced reversible structural changes (B) without affecting the magnetic behaviour of host framework. Reproduced with permission from Ref.70, Copyright (2007) Wiley-VCH.

Investigating further, Kepert and co-workers have reported few studies in this regard including SC-SC transformations of Fe(II) SCO frameworks,[71] mechanistic understanding of multi-step SCO transitions [72] and structural modulations by guest-dependent SCO behaviour of seemingly iso-structural MOFs.[73]

In a distinct domain of investigation, Kitagawa et al. demonstrated the usage of dynamic nature of a two-fold interpenetrated 3D MOF $\{[Ni(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$, (bpe - 1,2-bis(4-pyridyl)ethane) for controlled gas adsorption.[32] The compound bears two kinds of porous channels occupied by the solvent (water) and anions separately. Upon desolvation, a noticeable change in colour was observed which was restored upon resolvation. The dehydrated framework bestows dual function to the compound wherein N_3^- anions are exchanged selectively with $N(CN)_2^-$ ions in competition with NCO^-, NO_3^-, BF_4^-. The anion-exchanged phase in-turn renders an additional feature of significantly enhanced gas adsorption by enlarging the window of the larger pore and squeezed smaller pore, by virtue of linear shape of the exchanged anion.

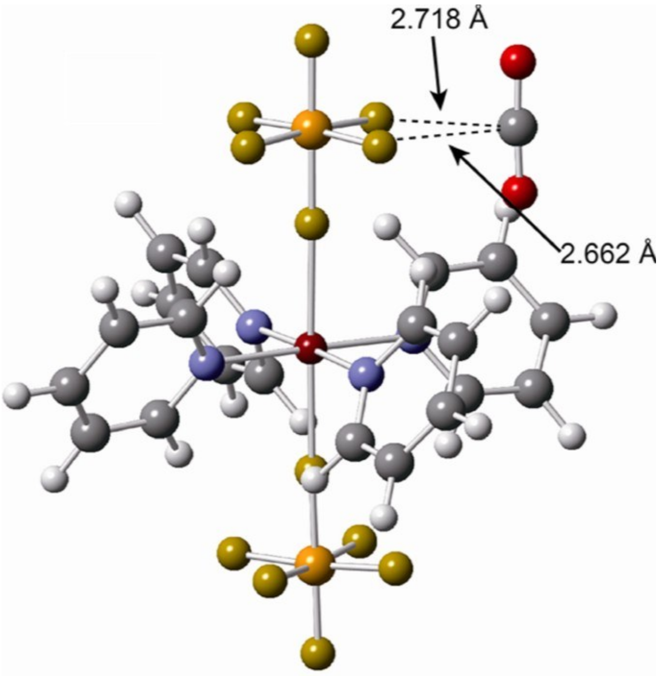

Fig. 24 Optimized structure of $[Cu(PF6)_2(pyridine)4]$ with CO_2 obtained by DFT. Reproduced with permission from Ref. 74, Copyright (2013) American Chemical Society.

In a parallel work, Nakamura et al. have reported selective CO_2 adsorption by a 2D PCP.[74] The authors synthesized a Cu(II) centred MOF $\{[Cu(PF_6)(4,4'\text{-}bpy)_2(MeOH)]\cdot PF_6\cdot 3MeOH\}_n$, (4,4'-bpy - 4,4'-bipyridine) which upon desolvation underwent change in structure to $[Cu(PF_6)_2(4,4'\text{-}bpy)_2]_n$ wherein the uncoordinated PF_6^- ions replaced the coordinated MeOH molecules in the parent compound. Upon checking the adsorption behaviour towards various gases like CO_2, N_2, O_2 and Ar, a strong preference and high uptake for CO_2 at both low and high temperatures was observed. Theoretical calculations revealed the affinity of the fluorine ions towards CO_2 as the primary driving force for the high uptake and low energy regeneration (Fig.24). CO_2 separation based on a similar adsorption mechanism has also been studied by Zaworotko et al. using a SiF_6^{2-} bridged N-donor ligand based MOFs.[75]

Apart from these properties, such dynamic MOFs have found utility as luminescent probes for a few important neutral and ionic analytes. Li and co-workers have reported a comprehensive study of structure-property correlation in a flexible MOF $[Cu(CN)_3L^{8}\cdot(H_2O)(CH_3CH_2OH)]_n$, ($L^8$ - 2,6-bis((3,5-dimethyl-1H-pyrazol-4-yl)methyl)pyridine) acting as a naked-eye solvent-vapour sensor.[76] The compound has an interpenetrated structure which leaves room for pre-organziation towards the guest according to its nature and size. Upon desolvation a change in PXRD was found which was restored upon resolvation. Additionally this process was visible under UV irradiation with a notable difference of emitted light frequency.

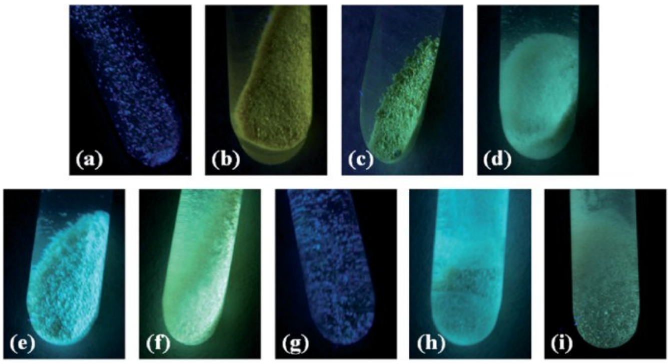

Fig. 25 Naked eye fluorescence changes in a guest responsive dynamic MOF upon immersion in several VOC solvents a) parent compound, b) acetonitrile, c) methanol, d) ethanol, e) tetrahydrofuran, f) benzene, g) cyclohexane, h) cyclohexane (longer time), i) dichloromethane. Reproduced from Ref.76, Copyright (2013) The Royal Society of Chemistry.

A drastic change in the luminescence of the desolvated compound was observed when it was immersed in several solvents like acetonitrile, methanol, ethanol, tetrahydrofuran, benzene, cyclohexane, cyclohexene and dichloromethane. To gain molecular insights into these photophysical observations, the authors synthesized a few compounds having the included guest molecules. Further to understand the real-time applicability of the compound, solid-state fluorescence studies towards acetonitrile vapours were investigated. Along with the response towards different concentration of acetonitrile vapours, the change in fluorescence for solvent mixtures too was examined (Fig.25).

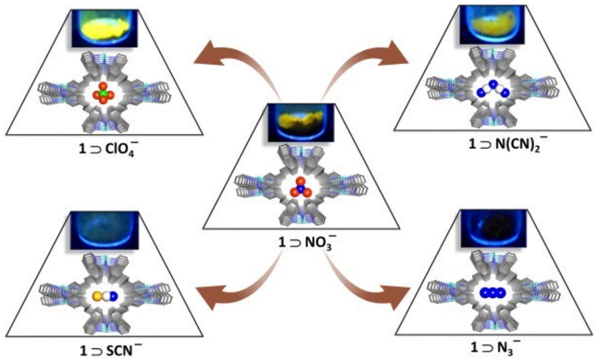

Fig. 26 Anion responsive tunable luminescent behaviour in a dynamic cationic MOF.

As discussed partly in the earlier sections [33], we have reported a dynamic, luminescent PCP exhibiting guest & anion dependent flexibility. The ligand used is a π-conjugated molecule which bestows ligand based fluorescence to the compound. The parent compound was found to exhibit high solid-state emission primarily due to intraligand charge transfer. Upon anion-exchange the fluorescence intensities & positions were perturbed owing to plausible changes in the interactions of the anions with the framework (Fig.26). Such a visible, non-sophisticated tool to monitor anion-exchange/capture process may find important applications in material/biological regimes.

6. Conclusions and future prospects

In this review, we systematically illustrate an update in the field of flexible MOFs composed of neutral N-donor ligands. A range of exogenous stimuli which trigger structural flexibility / softness to such MOF systems have been covered. Especially, various chemical stimuli such as framework anions, free guests, coordinated guests and gaseous guests along with physical stimuli (light) have drawn attention in creating flexibility in these kinds of MOF systems. Flexibility driven various functions in these materials (e.g. separation of gases, sensing of small molecules, magnetic properties etc.) which include proper host-guest interactions have been thoroughly examined. For better understanding of such a flexible MOF system, it is very important to gain structural insights of all the phases. But, to get a single crystal structure after each dynamic process is quite difficult. Hence, utilization of SCXRD, PXRD, other modern structure determining tools and theoretical methods,[77] neutral N-donor ligand based MOFs might show new functions owing to its structural flexibility towards the development of new functional materials for various potential applications.

Acknowledgements

‡ B.M. and A.V.D have contributed equally to this article.

B.M. is thankful to CSIR for research fellowship, while IISER Pune is acknowledged for the same from B.M., A.V.D.; DST (Project No.GAP/DST/CHE-12-0083) and DST-FIST (SR/FST/CSII-023/2012) are acknowledged for generous financial support.

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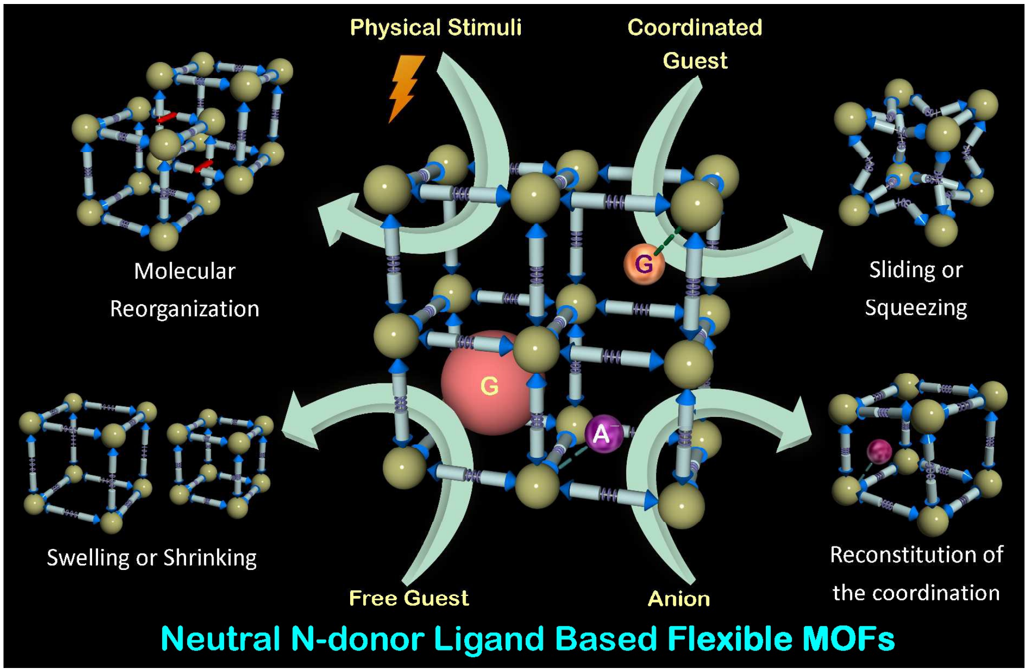
Graphical Abstract



This short review focuses on the flexibility aspect in MOFs based on neutral N-donor ligands with representative examples concerning the structural aspects and the subsequent properties induced by the reorganization of the frameworks.