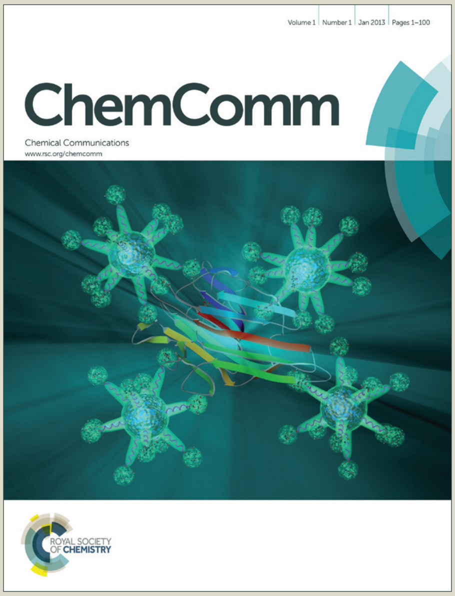
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm RSCPublishing

FEATURE ARTICLE

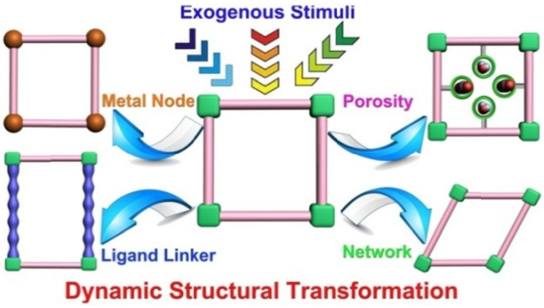
Dynamic structural transformations of coordination supramolecular systems upon exogenous stimuli

Cheng-Peng Li,[a] Jing Chen,[a] Chun-Sen Liu[b] and Miao Du*,[a]

[a] College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, MOE Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. E-mail: dumiao@public.tpt.tj.cn.

[b] Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, P. R. China

Table of Contents Entry



This feature article comments on the dynamic structural transformations of coordination supramolecular systems in the aspects of metal node, organic linker, porosity, and framework, which can be triggered by various exogenous stimuli, such as concentration, temperature, light, mechanical force, and their synergistic effect.

ChemComm RSCPublishing

FEATURE ARTICLE

Dynamic structural transformations of coordination supramolecular systems upon exogenous stimuli

Cite this: DOI: 10.1039/x0xx00000x

Cheng-Peng Li, Jing Chen, Chun-Sen Liu and Miao Du*

Received 00th xxxx xxxx,
Accepted 00th xxxx xxxx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Reaction in the solid state, especially single-crystal-to-single-crystal (SC-SC) transformation, provides an appealing routeway to obtain the target crystalline materials with modified properties via a non-solvent green chemistry approach. This feature article focuses on the up-to-date progress in the context of coordination supramolecular systems (CSSs), especially coordination polymers (CPs) or metal-organic frameworks (MOFs), which show interesting dynamic nature upon various exogenous stimuli, including concentration, temperature, light, mechanical force, as well as their synergic effect. In essence, dynamic CSSs normally possess crucial crystalline-reactive characteristics: i) metal ions or clusters with unstable or metastable electronic configurations and coordination geometries; ii) organic ligands bearing physicochemically active functional groups for post-reactions; iii) polymeric networks of high flexibility for structural bending, rotation, swelling, or shrinking; iv) guest moieties to be freely exchanged or eliminated by varying the environmental conditions. The significant changes in catalytic, sorption, magnetic, or luminescent properties accompanied by the structural transformations will also be discussed, which reveal the proof-of-concept thereof in designing new functional crystalline materials.

Introduction

Reaction, in three states of matter, is the fundamental theme to chemistry and life course.[1] These dynamic processes generally involve the formation and breakage of covalent or noncovalent interactions, by regulating the local binding features of individual ingredients and the overall structural extension/stacking in crystalline state.[2] In the state of solution or gas, molecules are endowed with large freedom to disperse and move, which facilitates the homogenous reactions between the functional groups of reactants. However, reactants in solid phase have more confinement of arrangement and less freedom of movement, owing to the frustrating effect of molecular closing packing. It is felicitously and vividly remarked by Leopold Ruzicka — a crystal is a chemical cemetery. That is, in contrast to liquid and gas states, molecules in the solid state, especially crystalline state, are rigidly and steadily fixed within the lattices to show a nearly lifeless nature.[3] Thus, the reacting functional groups in solid phase generally behave the inert features due to their restricted migration and non-aligning orientation. Nevertheless, chemical reactions in the solid state are not unachievable and a large number of inorganic and organic compounds can feature regioselectively and stereospecifically structural transformations upon exogenous stimuli in the solid state.[4] Early in the 1960s, Schmidt has presented the concept of crystal engineering in domain of solid-state organic photochemistry, in order to erect a bridge between the structure and reactivity of molecules.[5] Since then, chemists have extensively taken advantage of the solid phase reactions to produce the targeted compounds, and obtained a deeper understanding on the nature of such reactions. These excellent breakthroughs have not only made a promise to get the materials that may be impossible to obtain via the reactions in solvent media, but also provided an opportunity to modify their bulk physicochemical properties through the solid-state reactions.

Of significant necessity, it should make no confusion on the definition of the topotactic reaction and single-crystal-to-single-crystal (SC-SC) transformation here. The term of topochemical principle was firstly proposed by Kohlschüetter to describe the inorganic crystal transformation,[6] that is, a reaction in inorganic crystal can occur wherein the crystal lattice of starting reactant (mother crystal) determines the orientation of at least one crystallographic axis of the product crystal (daughter crystal). This phenomenon in inorganic system is described by topotaxy, and such a reaction is a topotactic reaction. With regard to an SC-SC reaction, it is unnecessary to require a perfect lattice consistency on at least one crystallographic axis between the mother and daughter crystals, which however will make an emphasis on the unanimous single-crystallinity with no disintegration.[7] In practice, this term is preferred to be applied in organic or inorganic-organic hybrid systems.

At this stage, coordination supramolecular systems (CSSs), especially coordination polymers (CPs) or metal-organic frameworks (MOFs),[8] are quite appealing, because of their structural aesthetics[9] and remarkable properties for potential applications

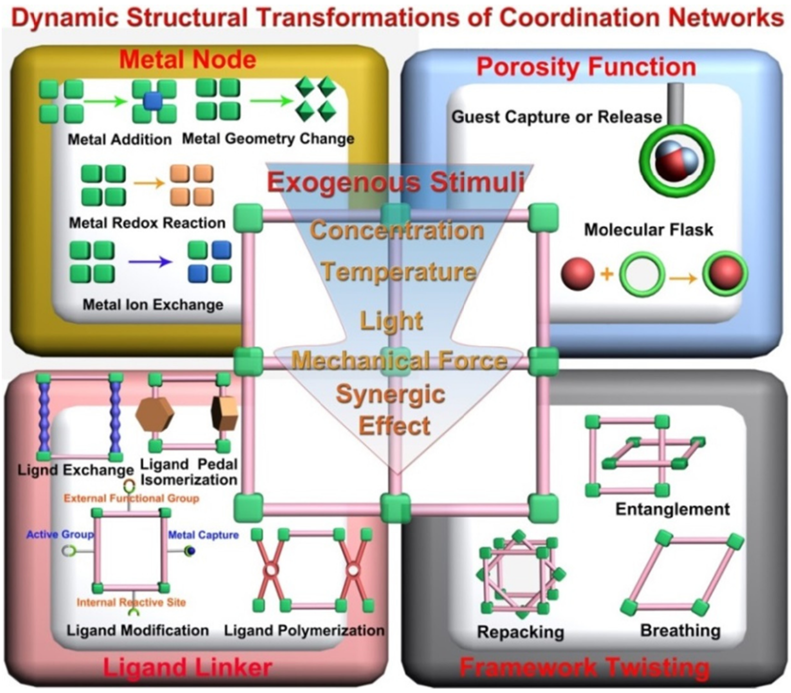


Fig. 1 Schematic diagram for dynamic structural transformations of coordination networks triggered by different exogenous stimuli.

in adsorption, conductivity, chirality, magnetism, catalysis, and optics etc.[10–13] In fact, one of the most interesting characteristics for CSSs is their flexible and dynamic nature, which is properly a result of the synergistic effect of multifunctional organic tectons and predefined metal moieties, normally as the secondary building units (SBUs). Thus, dynamic structural transformation in the solid state, especially SC-SC transformation upon exogenous stimuli, has been well exploited to enhance their diversity and functionality (Fig. 1). Single-crystal X-ray crystallography is the principal method for unequivocally determining the structures before and after the structural transformation. Advances in the instrument capabilities facilitate the rapid collection of data, powerful data processing, accurate structural determination, and controllable testing environment (temperature and pressure etc.), placing a much higher level of proof on the dynamic structural transformations. Although preservation of the single crystalline nature is the prerequisite here, such modern instruments ensure that the size or quality of a single crystal suitable for X-ray diffraction analysis will be of much less strict restriction than before.[14] On the other hand, the results of single crystal diffraction are time/space-averaged and origin/end-emphasized, while the processes of dynamic transformations may considerably deviate from the average and unexpectedly suffer the mutation. Toward this circumstance, in situ X-ray diffraction is to be utilized, so that the trace of molecular motions can be directly and persistently observed to reveal the reaction mechanism on the basis of structural information.[15] Recently, Kawano et al have successfully utilized the ab initio powder X-ray diffraction (PXRD) for structural characterization of the kinetic microcrystals.[16] Kaupp et al have used atomic force microscopy (AFM), grazing incidence X-ray diffraction (GID), and scanning near field optical microscopy (SNOM) to study the solid-state reactions.[17] Additionally, some other techniques such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) have also been applied as the helpful tools to monitor the solid-state structural transformations.

In the past few decades, several excellent reviews have been published, covering the vast area of dynamic behaviors of CSSs. Particularly, two reviews by Vittal in 2007 and 2013 presented the comprehensive accounts on supramolecular structural transformations involving CPs in the solid state.[18] MacGillivray et al described how to achieve the supramolecular control of reactivity in the solid state using molecules and self-assembled MOFs as templates.[19] Recent advances on the reactions of single crystals for inorganic and organometallic compounds and their implications for catalysis were reviewed by Frech[20a] and Kawano and Fujita.[15] Nassimbeni et al[20b] focused on guest exchanges in crystalline-state CSSs, and Zhang et al[21] provided an overview on solvent-induced magnetic changes in SC-SC transformations. Lauher et al[22a] and Garcia-Garibay[22b] emphasized the designed strategy on SC-SC topochemical polymerization. Bharadwaj et al presented an account on the substitution at metal ions of CPs in SC-SC transformations.[23] Ferraro et al summarized the solid-state pressure effect on stereochemically nonrigid structures.[24a] Braga et al reviewed the mechanical forces induced reactions in molecular crystals.[24b] Kawano et al outlined the advancements of ab initio PXRD structural determination on kinetic coordination networks.[16] Notably, the special issue of "single crystal to single crystal transformations" with some informative reviews in *Australian Journal of Chemistry* makes an outstanding contribution on this topic.[7,25,26] However, most of the reviews and examples available in the literatures are limited to focus on the final outcomes of structural transformations, that is, the changes of crystal structures and properties (i.e. color, magnetism, luminescence, chirality, or porosity). In fact, the dynamic behaviors of CSSs invariably originate from different exogenous stimuli and such solid-state reactions can also be considered as stimuli-responsive properties of such crystalline materials.[18b] Clearly, it is of great essence to summarize and classify the various origins of solid-state reactions, and to elucidate the discipline of resultant dynamic structural transformations. Thus, in this article, we will categorize the dynamic structural transformations of CSSs by exogenous stimuli, and primarily discuss the changes on the building units (metal node and ligand linker) as well as porosity function and framework twisting in this course.

Some structural characteristics can be found for CSSs which possess the potential capability of crystalline reactivity: i) metal ions or clusters with unstable or metastable electronic configurations and coordination geometries; ii) organic ligands bearing physicochemically active groups for post-reactions; iii) polymeric networks of high flexible nature for structural bending, rotation, swelling, or shrinking; iv) lattice guests to be freely removed or exchanged. In this context, the delicate selection of stimulation will play a critical role to effectively induce the dynamic structural transformations for specific coordination systems. Herein, we will comment on dynamic structural transformations of CSSs upon diverse exogenous stimuli, including concentration, heat (temperature), light, mechanical force, as well as their synergic influence. Notably, most of the examples presented in this work will be subject to drastic structural changes, normally with the formation and breakage of covalent or noncovalent interactions.

Dynamic structural transformations induced by Concentration

Solid-state structural transformation can be induced by the concentration environment of a certain component inside or outside the material, mainly involving guest (solvent, gas, anion, or free molecule) sorption or exchange, post-synthetic exchange (PSE), and post-synthetic modification (PSM). Of great significance, such dynamic processes are usually accompanied by changes in both crystal structures and properties.

Guest adsorption or exchange. Molecular cages can selectively capture guests in solution via specific host-guest interactions and molecular recognitions.[2a,27] While in the solid state, particularly in the crystalline state, this is often invalid due to the close packing nature of crystal. Fujita et al successfully combined the molecular cages into crystalline CPs to transfer the richness of solution-state host-guest chemistry into solid state.[28] An interesting example was illustrated in $[Co_3(SCN)_6(tpt)_4]_n$ coordination network (**1**), where tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine, which behaves as a crystalline molecular sponge engineered on the molecular level for guest recognition similar to those found in solution. This network is constructed from the infinite arrays of octahedral $Co_6(tpt)_4$ cages arranged in a metal vertex-sharing fashion, defining the void spaces with alternating cuboctahedral $Co_{12}(tpt)_8$ and $Co_{12}(tpt)_{24}$ cages (Fig. 2). When soaked in a saturated toluene solution of tetrathiafulvalene (ttf), the cages could be activated to adsorb four ttf molecules, and the crystal system flexibly changes from cubic to tetragonal. However, the encapsulation of Ph_2NH into the crystalline cages will not change the cubic framework. Moreover, the nanoscale voids can adsorb up to an impressive 35 wt% of C_{60} or C_{70} by soaking the crystals in a toluene solution of fullerene. Remarkably, a preferential adsorption of C_{70} over C_{60} is also observed when the crystals are immersed in a mixed solution of C_{60}/C_{70} fullerenes.

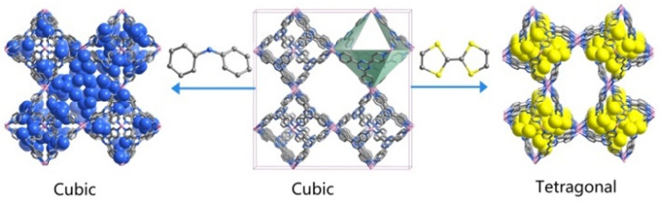


Fig. 2 Structural transformations of **1** upon the inclusion of tetrathiafulvalene or Ph_2NH.[28]

As one of the most interesting characters of CPs, the breathing phenomenon is often observed, when a framework presents multiple stable states to fabricate the flexible pores with diverse shapes and sizes for guest sorption.[29] Upon inclusion of different guests, such crystalline materials can show specific framework flexibility in the solid state. Zhang et al studied the flexibility of a series of isoreticular $[M_3(\mu_3\text{-OH})(L)_3]_n$ frameworks[30a] with the (3,9)-connected **xmz** topological network,[31] which are constructed by 3-connected, tripodal pyridyl-dicarboxylate ligands and 9-connected, tricapped trigonal-prismatic $M_3(\mu_3\text{-OH})(O_2CR)_6(py)_3$ clusters (Fig. 3). Powder and single-crystal X-ray diffraction analyses indicate that $[Ni_3(\mu_3\text{-OH})(cpby)_3]_n$ (**2**, cpby = 2,6-di-*p*-carboxyphenyl-4,4'-bipyridine) can drastically swell 70–105% in volume and 75–121% in length upon accommodation of different solvents, including pyridine, 1,4-dioxane, DMF, DMA, EtOH, MeOH, and water. The thermal expansion coefficient of **2·DMF** is extremely large up to 437 × 10^{-6} K^{-1} upon inclusion of DMF at 295 K. The distinct breathing effects of the

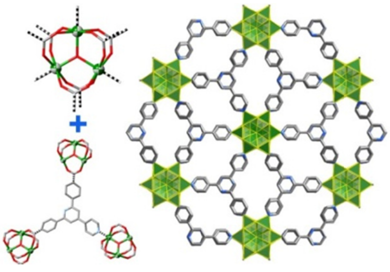


Fig. 3 Perspective view of the (3,9)-connected **xmz** framework.[30a]

frameworks are mainly due to the organic ligand of cpby with a suitable backbone. Lee, Lah, and Vittal et al reported a soft CP, $\{[Zn(pnmi)](solvent)\}_n$ (**3**, pnmi = N-(4-pyridyl)-1,4,5,8-naphathalenetetracarboxymonoimide) with the **rtl** topology based on paddle-wheel $Zn(O_2CR)_4(py)_2$ SBUs.[30b] The 1D rhombic channels can show the flexible breathing effect to exchange the solvents in SC-SC fashion, with the SBUs remaining intact. Upon exchange with DMF, EtOH, ethylene glycol, triethylene glycol, or allyl alcohol, the reduction in unit cell volume and the void volume will be up to 16% and 33.1%, respectively.

To serve as the outstanding chemosensors, CSSs can exhibit guest-responsive structural transformations (even in trace concentration) and the changes of physical properties (color, magnetism, and electric resistance) facilitate the sensitive and selective detection of gas- or vapor-phase analytes for application in chemical threat alert, medical diagnostics, thermal battery, and environmental monitoring.[32] Yaghi et al proposed three criteria for high performing porous materials in water sorption, including condensation pressure of water in the pores, the uptake capacity, and recyclability and water stability of the materials.[33] A comparison of water sorption properties of 23 porous materials reveals that their performances can be well-defined by intermolecular interactions between the adsorbed water molecules.

Blue block crystals of $\{[Co_{1.5}(tipb)(SO_4)(tp)_{0.5}](DMF)_{1.75}\}_n$ (**4·DMF**, tipb = 1,3,5-tris(*p*-imidazolphenyl)benzene, tp = terephthalate), synthesized by Bu et al, exhibit the self-penetrating network with 1D ultramicropores for the inclusion of DMF (Fig. 4).[34] When these crystals are exposed to air, they gradually turn to red in the SC-SC transformation, affording a 2-fold interpenetrating network of $\{[Co_{1.5}(tipb)(SO_4)(H_2O)_{3.6}](tp)_{0.5}(solvent)\}_n$ (**4·H₂O**). During this transformation, water ligands displace tp^{2-} ligands and the coordination geometries of Co(II) change from tetrahedral to octahedral, which induce an obvious color change from blue to red. Notably, the framework changes from neutral to cationic, and the tp^{2-} anions are randomly distributed in the channels to maintain a charge balance. Similar structural transformation can also be stimulated by NH_3. Of great significance, **4·DMF** can effectively encapsulate DMF molecules and release them in the presence of water vapor (in humidistat) or water (by immersion) in SC-SC transformation, revealing the gate effect for controllable guest trapping and release. Such gate effect for selective adsorption of solvents is usually found in the dynamic CPs with hemiopen channels.[35] Zeng and Kurmoo et al reported a 4-fold interpenetrating pseudodiamond coordination network $\{[Co(pybz)_2](DMF)_2\}_n$ (**5·DMF**, pybz = 4-(4-pyridyl)benzoate), which can be transformed upon exchanges with MeOH, EtOH, benzene, or cyclohexane in different concentrations, showing a vapochromism SC-SC process.[36] The vapochromism phenomenon can be ascribed to the modification of coordination geometry, from a very strained octahedron with two chelating carboxylate groups to a more relaxed octahedron with unidentate carboxylate and water ligands, which results in a change in ligand-field energies of the *d* orbital of Co(II) ion. Notably, besides the chemical sensors of CSSs to humidity,[37] some excellent prototypes for such CSSs sensors to alcohols,[38a,38b] formaldehyde,[38c] nitroaromatic compounds,[38d] oxygen,[38e] chromophores[38f] and so on, were also documented.

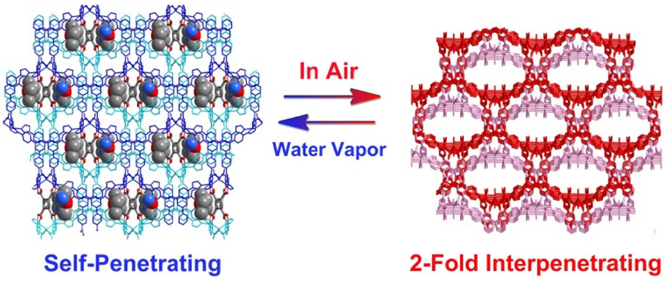


Fig. 4 Reversible SC-SC transformations between the self-penetrating and 2-fold interpenetrating frameworks.[34]

Anion exchange. When neutral organic ligands are used for the assemblies of CSSs, the cationic host frameworks will normally be formed and correspondingly, the anions must be involved to balance the charge.[39] The interactions between the host frameworks and anions, such as coordinative bond, H-bonding interaction, and electrostatic force, may provide good opportunities for anion chemosensors based on anion-exchanged approaches. Bu et al reported a 4-fold interpenetrating coordination framework $\{[Cu(pytpy)](NO_3)(CH_3OH)\}_n$ (**6·NO₃**, pytpy = 2,4,6-tris (4-pyridyl)pyridine), which can serve as a naked-eye colorimetric sensor for different anions such as F^-, Cl^-, Br^-, I^-, N_3^-, SCN^-, and CO_3^{2-}.[40a] Ghosh et al prepared a dynamic luminescent cationic porous framework, which has the order of affinity to guest anions ($SCN^- > N_3^- > N(CN)_2^- > ClO_4^-$) owing to their various sizes, shapes, geometries, coordination tendencies to metal ions, as well as the distinct π···π interactions and H-bonding abilities with the host network.[40b] We synthesized two isostructural 3D CPs $\{[M(L^{242})_2](ClO_4)_2\}_n$ (**7·ClO₄**, M^{II} = Cd^{II} or Zn^{II}, L^{242} = 4-(4-pyridyl)-3,5-bis(2-pyridyl)-1,2,4-triazole), which have 2-fold interpenetrating **lvt** networks and exhibit the exclusive and irreversible anion-exchange behavior toward acetate (Fig. 5) with a structural change.[40c] Also, other anion chemosensors and selective anion-exchanged materials of CSSs were reported.[40d-40h]

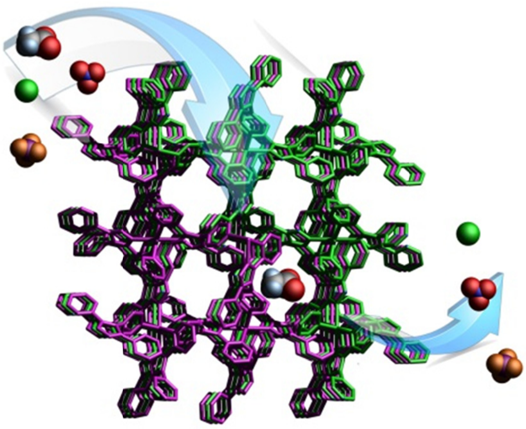


Fig. 5 A cationic porous CP with the exclusive anion-exchange for OAc^- over Cl^-, BF_4^-, and NO_3^- anions.[40c]

The hazard-free treatment on waste water with metal pollutants, normally in their oxo-/hydroxo- anionic forms, including AsO_4^{3-}, TcO_4^-, SeO_3^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, ReO_4^-, and MnO_4^-, is a worldwide problem that is listed as priorities by the U.S. Environmental Protection Agency.[41] Many efforts have been devoted in designing materials with good selectivity and efficiency to this end. In this point, organic polymer-based bifunctional anion-exchange resins show limited applications due to their poor thermal and chemical stability.[42] Recently, a series of inorganic anion-exchanged materials, layered double hydroxides (LDHs), were prepared by Albrecht-Schmitt and Oliver et al, which can rapidly capture the target oxoanions with high exchange capacity.[43] Cheng[44a] and Wang[44b] et al prepared two 3D porous cationic MOFs, with fast exchange, high capacity, and good selectivity for the capture and separation of CrO_4^{2-} and $Cr_2O_7^{2-}$, even in SC-SC transformations, which can be ascribed to the stronger interactions between the oxoanions and cationic frameworks. Recently, we obtained a 3D cationic framework with 1D porous channels, i.e. $\{[Ag(L^{243})](CHCl_3)(ClO_4)\}_n$ (**8·ClO₄**, L^{243} = 3-(2-pyridyl)-4-(4-pyridyl)-5-(3-pyridyl)-1,2,4-triazole), showing the remarkable dual features in SC-SC transformations induced by exchanging the included ClO_4^- anions with different toxic oxo-metal anions (Fig. 6).[45] On the one hand, **8·ClO₄** possesses the rigid nature to be partially exchanged with MnO_4^- in water solution, affording a new product $\{[Ag(L^{243})](ClO_4)_x(MnO_4)_{1-x}\}_n$ (**8·ClO₄·MnO₄**), along with a clear color change from colorless to purple. On the other hand, **8·ClO₄** shows the flexible nature to capture CrO_4^{2-} anions, in which the CrO_4^{2-} anions are dynamically transformed into $Cr_2O_7^{2-}$ anions. Also, the pores shrink in the *c* axis to facilitate the formation of coordination interactions between Ag(I) centers and $Cr_2O_7^{2-}$ anions, resulting in a square pyramid coordination geometry of Ag(I) ion in the yellow crystal of $\{[Ag(L^{243})](Cr_2O_7)_{1/2}\}_n$ (**8·Cr₂O₇**). In water solution, forms of Cr(VI) existence can be well regulated by pH condition, that is, CrO_4^{2-} and $Cr_2O_7^{2-}$ are predominant in a basic environment and in pH 2–6, respectively.[46] This is the first example of MOF molecular flask for catalyzing such an inorganic reaction. Some crystalline materials reported by Hou,[47a] Zeng,[47b] and Pan and Su[47c] et al can act as the hosts for trapping various iodine species, which is also a prominent problem in water pollution.

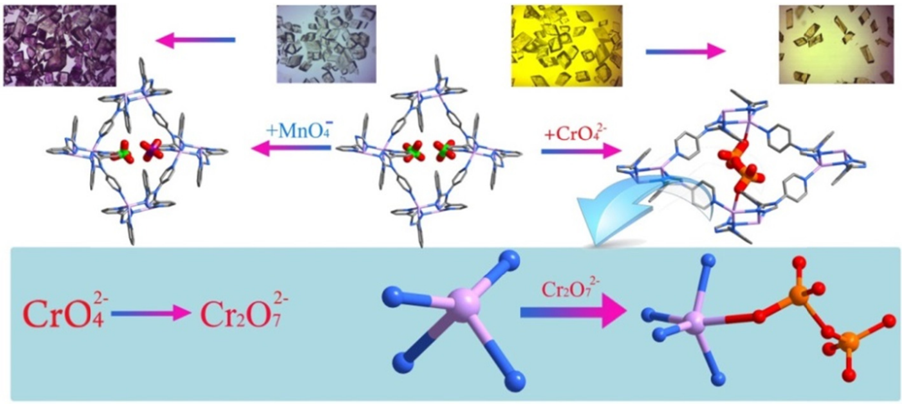


Fig. 6 A 3D cationic framework showing the dual behaviors in SC-SC transformations induced by anion-exchange.[45]

A 3D MOF $\{[Ag(L^{424})(H_2O)](NO_3)\}_n$ (**9·NO₃**, L^{424} = 3,5-bis(4-pyridyl)-4-(2-pyridyl)-1,2,4-triazole) with 1D channels along the *c* axis for the inclusion of NO_3^- also shows the dual dynamic SC-SC transformations induced by anion-exchange stimuli.[48] In this structure, the tetrahedral Ag(I) ion is surrounded by three N atoms and one water ligand, and the overall network shows a 3-fold interpenetrating **lvt** pattern. When exchanged by NO_2^-, the product $\{[Ag(L^{424})(NO_2)](H_2O)_{1.5}\}_n$ (**9·NO₂**) also takes a 3-fold interpenetrating framework, but with the breakage of Ag–O_{water} bonds and the formation of Ag–$O_{nitrite}$ interactions. However, by immersing in CF_3COO^- solution, the coordination environment of Ag(I) in **9·NO₃** is completed by CF_3COO^- instead of water to afford **9·CF₃COO**, accompanied by a change of the interpenetrating pattern from 3-fold to 2-fold during this SC-SC process (Fig. 7). Zhang et al reported a series of nanoporous networks constructed by a polycatenated isoreticular 1D ribbon of rings, and their pore sizes or shapes can be systematically adjusted by the anion-exchange processes, which allow the dynamic trans formations between the interpenetrating net structures in different dimensions.[49] These materials can also be post-synthetically modified by SC-SC [2+2] photopolymerization, to reinforce the porous frameworks through the covalent locking effect and also, affect their adsorption properties.

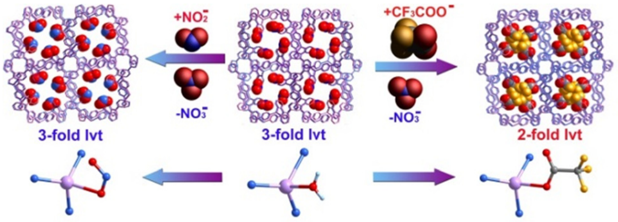


Fig. 7 A 3D cationic framework showing the dual dynamic behaviors of SC-SC transformations upon different anion-exchange processes.[48]

Post-synthetic exchange (PSE). CSSs are normally assembled in one-pot solvothermal synthesis, where structural regulation is realized by the delicate choice of metal ions, organic linkers, or synthetic routes. Recently, the sophisticated synthetic strategies were developed to achieve multifunctional hybrid materials via stepwise reactions of CSSs.[50] These PSE strategies involve the metathesis of organic linkers as well as metal ions in the SBUs (Fig. 8), which are normally observed in solvent-mediated solid-solid reactions and solid-liquid conditions.

As for metathesis of organic linkers, solvent-assisted linker exchange (SALE) provides a promising approach that involves exposing parent crystalline materials to a concentrated solution of accessional organic linkers in a specific solvent. As a result, the daughter materials possess the same frameworks as the parent ones but with distinct organic linkers coming from the solution. In the early 1990s, Robson et al proposed the SALE concept,[51a] and Kitagawa[51b] and Chen[51c] et al successfully obtained the 3D targeted networks by linking the 2D paddle-wheel layers by bipyridyl pillars. Then, Zhou et al extended this strategy into molecular metal-organic polyhedra (MMOP).[51d] Also, Choe,[51e] Cohen,[51f] and Hupp[51g] et al implemented SALE for chemically inert MOFs, which currently arises an intense interest in exploitation of PSE.

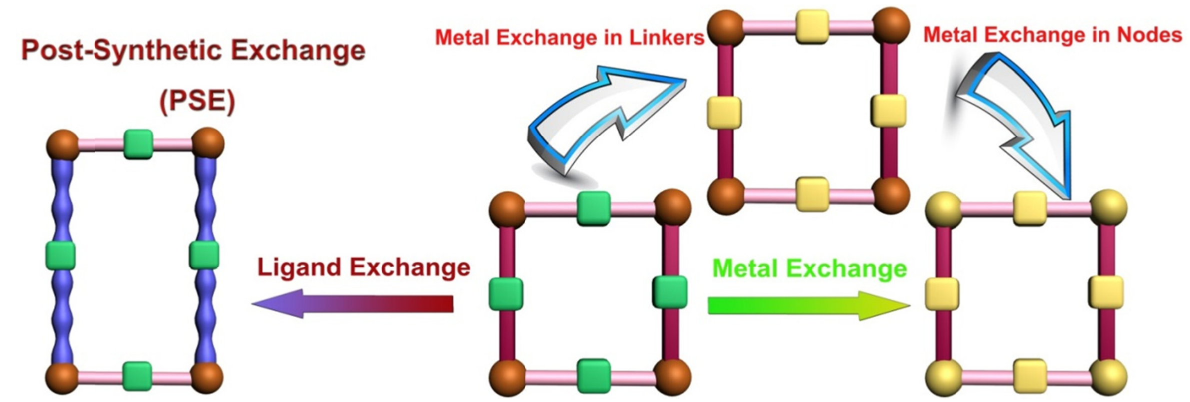


Fig. 8 Schematic view of the PSE strategy.

In 2012, Hupp et al reported the first example of SALE for zeolitic imidazolate frameworks (ZIFs).[51g] Immersing the crystal sample of $[Cd(eim)]_n$ (**10·CdIF-4**, eim = 2-ethylimidazolate) into solutions containing the excess 2-nitroimidazole (nim) and 2-methylimidazole (mim), respectively, will give two daughters ZIFs, $[Cd(nim)]_n$ (**10·CdIF-9**) and $[Cd(mim)]_n$ (**10·SALEM-1**) of RHO zeolitic topology in an SC-SC SALE process. It is noteworthy that **10·SALEM-1** cannot be directly prepared from the organic ligands and metal ions. Further, the dpea linker (dpea = *meso*-1,2-di(4-pyridyl)-1,2-ethanediol) with a length of ca. 9 Å in **SALEM-5** can be readily replaced by the 11-Å pillar of 4,4'-(2,3,5,6-tetramethyl-1,4-phenylene)dipyridine, 14-Å pillar of 2, 6-di(pyridin-4-yl)naphthalene, and 17-Å pillar of 4,4'-((2,3,5,6-tetramethyl-1,4-phenylene)bis(ethyne-2,1-diyl))dipyridine at the reasonable rates to form **SALEM-6**, **SALEM-7**, and **SALEM-8**, respectively (Fig. 9).[52a] Of further significance, such a strategy can also be feasible in controlling over the net catenation in pillared paddle-wheel MOFs. That is, SALE-generated MOFs show the noncatenated structure, while the *de novo* synthesized analogues have the 2-fold interpenetrating patterns.[52b] Lah et al reported the SALE reactions of $[Ni(Hbtc)(bpy)]_n$ (**11a**, H_3btc = 1,3,5-benzenetricarboxylic acid, bpy = 4,4'-bipyridine) by 1,4-diazabicyclo[2.2.2]octane linker (dabco) to afford two daughter materials with the formulae $[Ni(Hbtc)(dabco)]_n$ (**11b**) and $[Ni_2(Hbtc)_2(bpy)_{0.6}(dabco)_{1.4}]_n$ (**11c**).[53] In these transformations, the entropically favorable product **11b** with completely exchanged dabco and the enthalpically favorable species **11c** with partially exchanged bpy/dabco in the alternating layers, can be obtained by controlling the concentration of dabco. Rosi et al utilized the SALE strategy to prepare a series of isoreticular **bio-MOF-100** crystals with progressively longer dicarboxylate linkers.[54] Correspondingly, the products show the progressively larger mesoporous cavities, with pore sizes ranging from 2.1 to 2.9 nm and surface areas ranging from 2704 to 4410 m^2/g.

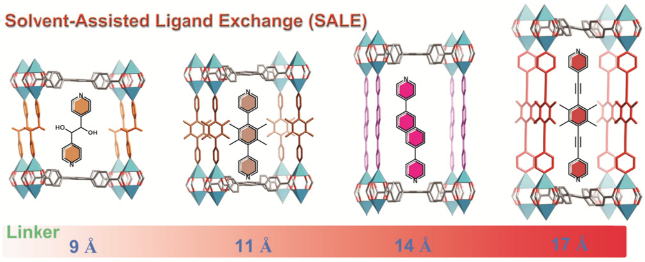


Fig. 9 Insertions of progressively longer ligand pillars into the pillared paddle-wheel structures of MOFs through SALE strategy.[52a]

Metathesis of metal centers in CSSs was initially investigated by Long, Hou, and Zaworotko et al, revealing the feasibility of partial metal exchange through SC-SC transformation.[55] Kim et al reported the first example SC-SC transformation involving complete and reversible exchange of metal ions (Cd^{2+} and Pb^{2+}) in MOFs.[56] Some excellent work on this scope of research was reviewed by Hupp and Farha in 2013.[57] Notably, Zaworotko et al synthesized a unique porphyrin-encapsulating MOF material $\{[Cd_4(bpt)_4[Cd(porph)(solvent)](solvent)\}_n$ (**12·Cd·Cd-porph**, bpt = biphenyl-3,4',5-tricarboxylate), which can be stepwisely transformed into **12·Cu·Cd-porph** and **12·Cu·Cu-porph** upon transmetalation reaction in the SC-SC mode (Fig. 10).[58] During this transformation, the binuclear $[Cd_2(COO)_6]^{2-}$ unit will suffer a transformation into the tetranuclear $[Cu_4X_2(COO)_6(solvent)_2]$ (X = anion) unit, resulting in a 20% unit cell expansion, higher surface area, and larger pore size in the **12·Cu·Cu-porph** material. Moreover, Cohen et al developed the general tandem strategy for exchange of metal ions and organic linkers consecutively in MOFs, which will also be helpful to the research on probing the chemical dynamics of MOFs.[58]

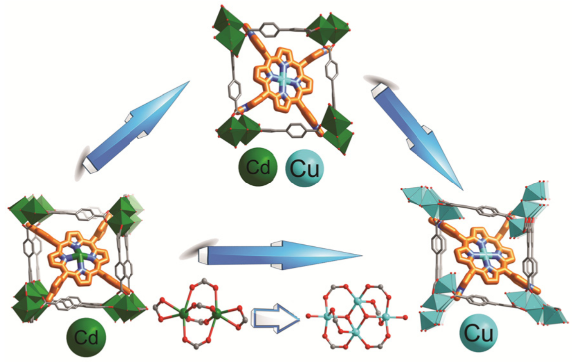


Fig. 10 The stepwise transformation of porphyrin-encapsulating MOF upon transmetalation reaction as well as the structural changes of SBUs.[58]

Post-synthetic modification (PSM). PSM refers to the chemical modification of organic linker or metal node in coordination network, which can be considered as a facile approach to obtain much sought-after extended frameworks (Fig. 11). Modification on organic struts is to recover the internal reactive functionality, introduce external functional groups, or capture additional metal ions with unreacted group, which usually cannot be achieved in *de novo* MOF synthesis. It should be noted that the excellent work on PSM till 2012 has been reviewed by Cohen,[59] and thus herein we only concern some uncovered examples.

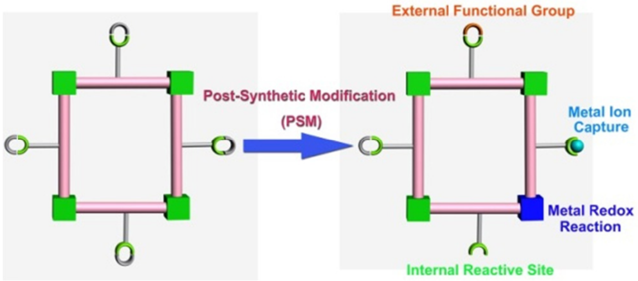


Fig. 11 Scheme view of different types of PSM.

Hupp et al reported an noninterpenetrating MOF, with 4,4'-(2,5-divinyl-1,4-phenylene)bis(3-vinylpyridine) as organic strut, to which the Ru-based olefin metathesis catalyst can function to produce a PSM-transformed MOF with the polycyclic aromatic hydrocarbon pillars (Fig. 12).[60a] Such a PSM reaction can occur in the solid state and the final product cannot be isolated from the solution reaction. Rosi et al successfully introduced various active groups into the pore walls of azide-functionalized MOF, to promote the straightforward coupling of biomolecules to the pore walls.[60b] Cui et al utilized the PSM strategy, replacing one proton of the dihydroxyl group in enantiopure 2,2'-dihydroxy-1,1'-biphenyl pillars by Li^+ ions, to synthesize a highly efficient and recyclable heterogeneous catalyst for asymmetric cyanation of aldehydes with up to >99% ee.[60c]

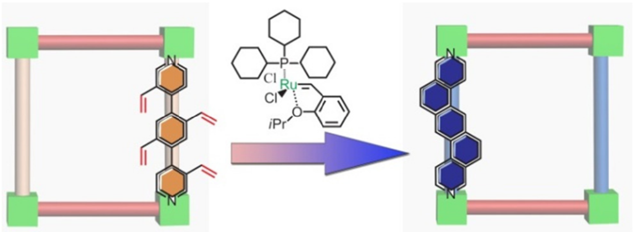


Fig. 12 PSM reaction catalyzed by Ru-based olefin metathesis catalyst.[60a]

Dalgarno and Thallapally et al reported an anionic framework $\{[Mn_3(tcom)_2]\cdot[NH_2(CH_3)_2]_2\cdot(solvent)\}_n$ (**13·Mn**, H_4tcom = tetrakis[4-(carboxyphenyl)oxamethyl]methane acid), which is transformed into a neutral heterobimetallic coordination system $\{[MnCo_3(tcom)_2(H_2O)_2](solvent)\}_n$ (**13·Mn·Co**).[61a] In this SC-SC transformation, one terminal octahedral Mn^{2+} ion becomes tetrahedral geometry and then is replaced with the inserted Co^{2+} ion with octahedral sphere, which is accompanied by cooperative bond breakage and formation. Of further interest is that this material has highly selective capture of divalent transition metals (Co^{2+} and Ni^{2+}) over alkali metals (Li^+ and Na^+). A similar SC-SC transformation of PSM was also demonstrated by Tao et al, where a post-synthetic uptake of free $\{Co_3O\}$ metal clusters with $Co_3O(CO_2)_6$ SBUs results in larger $Co_3O(CO_2)_6$ SBUs.[61b] Also, Hardie et al reported a rare example for framework PSM involving direct site-specific Cu^+ uptake, proceeding in the SC-SC transformation.[61c]

Dynamic structural transformations induced by temperature

Activation of MOFs by heating is one of the most familiar ways to obtain evacuated porous samples. However, dynamic SC-SC transformation may occur in this process triggered by temperature change, involving the bond breakage/formation and lattice motion, such as shrinkage/expansion, distortion, and sliding.[62]

Sun et al reported the thermally induced head-to-tail dimerization for a mononuclear compound $[Cu(NH_3)_3(pmsb)](solvent)$ (**14a**, pmsb = 2,2'-(1,2-phenylenebis(methylene))bis(sulfanediyl)dibenzoic acid), which can be dimerized to form a binuclear complex $[Cu_2(NH_3)_6(pmsb)_2](solvent)$ (**14b**) via thermal SC-SC transformation.[63a] This course also involves the formation of a new Cu–O_{pmsb} bond between the mononuclear motifs, changing the coordination sphere from square-planar to square-pyramidal and the crystal color from blue to green. This intra-framework [2+2] dimerization is different from that of the solid-state photo-chemical [2+2] cycloadditions of organic molecules. Further, this transformation can also be realized by ball milling method through the SC-polycrystal mechanical reaction. Ovcharenko et al reported a reversible topotactic SC-SC reaction of polymerization-depolymerization via repeated cooling-heating cycles.[63b] In this transformation, variation of the temperatures (295 vs 225 K) causes considerable mutual displacement of adjacent molecules, and thus the trinuclear structure and 1D polymeric chain isomer can reversibly transform with the coordination geometry of Cu(II) changing from square-pyramidal to octahedral. Such a structural conversion is also accompanied by magnetic anomaly caused by the modulation between the odd electron of Cu^{2+} and nitroxide, resulting in a reversible transition from antiferromagnetic to ferromagnetic coupling. Mesbh et al reported a two-step dehydration of $[Ni_3(OH)_2(tp)_2(H_2O)_4]_n$ (**15·4H₂O**) upon heating, leading to sequential removal of coordination water to produce $[Ni_3(OH)_2(tp)_2(H_2O)_2]_n$ (**15·2H₂O**) at 433 K and $[Ni_2(OH)_2(tp)]_n$ (**15**) at 483 K.[63c] Such reversible structural transformations will affect the magnetic behavior of each phase, from antiferromagnetic, to canted antiferromagnetic, and then to ferromagnetic.

Barbour et al studied a 2-fold interpenetrating pillared-layer MOF $[Zn_2(ndc)_2(bpy)]_n$ (**16·2-fold**, ndc = naphthalenedicarboxylate), which can convert to its triply interpenetrating analogue **16·3-fold** upon desolvation by heating.[64a] With the aid of single crystal diffraction and computational method, the mechanism of this SC-SC course was postulated as that, during the conversion, the metal-carboxylate layers slide laterally with their connectivity unchanged, while the bpy pillars undergo Zn–N bond cleavage and reformation. $\{[Cu(ina)_2(H_2O)][Cu(ina)_2(bpy)](H_2O)_2\}_n$ (**17·2H₂O**, ina = isonicotinate), reported by Kumar et al, shows two different 2D layers, one of which includes open metal sites (OMSs) and functional organic sites (FOSs) (Fig. 13).[64b] Upon removal of water guests by heating, **17·2H₂O** undergoes an SC-SC reaction to produce $\{[Cu(ina)_2(H_2O)][Cu(ina)_2(bpy)]\}_n$ (**17**), with the gliding of the two layers and expansion of the effective void and space. Remarkably, due to the presence of both OMSs and free FOSs, this material can be viewed as a multifunctional platform to act as both Lewis acid catalyst and small molecule sensor for CO_2 and CH_3OH, as well as Lewis base catalyst and cation sensor for Ag^+ ion. Additionally, it shows strong second-harmonic generation/nonlinear optical activity, due to its non-centrosymmetry with large polarity along the *b* axis. Hou and Batten et al reported a (3,18)-connected MOF $[Co(cpn)(H_2O)_2]_n$ (**18**, cpn = 5-(3'-carboxylphenyl)nicotinate), which comprises a relative smaller hydrophilic channel constructed by convergent saddle-shaped cycloclusters $[Co_6(COO)_6(H_2O)_{12}]^{6+}$ and cpn^{2-}.[64c] The inert channel can only be opened upon refluxing in hydrated DMF solvent at 160 ºC, to afford a new hydrated framework $\{[Co(cpn)(H_2O)_2](H_2O)\}_n$ (**18·H₂O**) via an SC-SC process with the crystal color changing from pink to dark-purple.

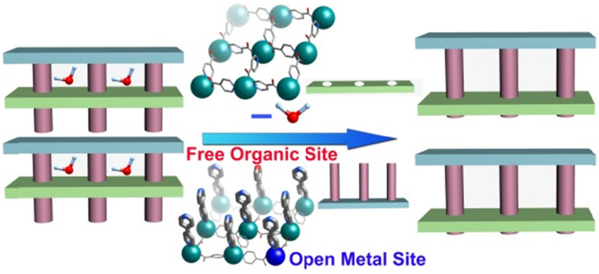


Fig. 13 Scheme view of SC-SC transformation showing the gliding behavior of the two layers and expansion of the effective void and space.[64b]

Dynamic structural transformations induced by light

Photochemical [2+2] cycloaddition reactions are earliest in the history of solid-state reaction chemistry.[5] The pioneer work and outstanding outcomes have already been reviewed.[18,19,22a] Thus, here we only refer to some interesting examples in the last two years, especially light-induced SC-SC transformations.

Lee and Vittal et al reported an SC-SC photo-polymerization by [2+2] cycloaddition for a 2-fold interpenetrating framework $[Zn_2(bpeb)(tp)(HCOO)_2]_n$ (**19a**, bpeb = 1,4-bis[2-(4'-pyridyl)-ethenyl]benzene) (Fig. 14).[65] **19a** is photoreactive owing to the fact that the infinitely slip-stacked conjugated C=C bonds of the bpeb ligands constitute a plane. Photo-dimerization of the C=C bond pairs in the solid state is triggered by UV light, to afford a new MOF $\{[Zn_2(poly\text{-}bppcb)(tp)(HCOO)_2](H_2O)\}_n$ (**19b**, bppcb = 1,3-(4,4'-bipyridyl)-2,4-phenylene-cyclobutane). For this SC-SC dimerization, the relative orientations of bpeb ligands facilitate a close packing of the C=C bonds, and an organic polymer based on cyclobutane rings of poly-bppcb is formed. This SC-SC photo-polymerization leads to a structural transformation of the entangled **cds** network to a nonentangled ***jjv2*** framework.

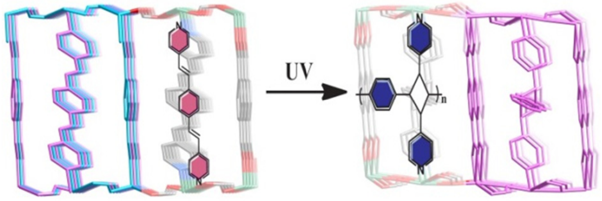


Fig. 14 Scheme view of SC-SC photo-polymerization by [2+2] cycloaddition with a structural change from 2-fold interpenetrating to noninterpenetrating pattens.[65]

Yang and Naumov et al reported the first example of a regioselective SC-SC transformation via [2+2] photo-dimerization in the pores of CP $\{[Mn(bpeb)(pda)](bpeb)\}_n$ (**20**, H_2pda = 1,3-phenylenediacrylic acid).[66] **20** reveals a molecular reactor comprising a 2D porous CP with three photoreactive sites: the bpeb guest and the bpeb or pda ligand (Fig. 15). Upon irradiation by UV light, three types of photoreactions, including the photopolymerization of bpeb guests, the photodimerization of bpeb ligands, and the photoisomerization of pda ligands, will be strongly coupled together stereochemically. The (quasi)-equilibria for

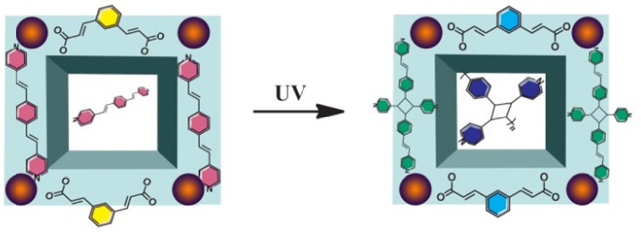


Fig. 15 Scheme view of a 2D porous CP as molecular reactor, showing three types of photoreactive reactions: polymerization, dimerization, and pedal-like isomerization.[66]

the three reactions (polymerization, dimerization, and pedal-like isomerization) can be considered as the natural consequence of intricate and intrinsic structural feedback of this dynamic CP.

Dynamic structural transformations induced by mechanical force

The correlation on mechanical control of solid-state structures and phase changes in molecular crystals has remained relatively unexplored. In fact, researches on anisotropic bulk forces, such as shearing and ball-milling or grinding, stimulated structural changes of the molecular crystals have been proved to be feasible, even leading to SC-SC trasnformations.[67] However, anisotropic forces at the bulk scale normally break the integrity of a single crystal. Significantly, Ito et al reported the first example of mechanical triggered SC-SC transformation (Fig. 16).[68] The compound phenyl(phenyl isocyanide)gold(I) ($\mathbf{21{\cdot}I_b}$, $\mathbf{I_b}$ = polymorph I in blue color), as the kinetic polymorph, can be rapidly isolated and crystallized from hexane/dichloromethane, showing the blue photoluminescence under UV irradiation. In this case, each molecule forms a herringbone-like pattern with a head-to-tail arrangement of the phenyl ligands on the Au(I) centers, and these discrete mononuclear motifs can be well isolated with the Au···Au distance longer than 4.65 Å, indicating the absence of aurophilic interactions. Fascinatingly, when a small pit was first produced by pricking the fixed sample with a needle, the phase transformation gradually spreads over the entire crystal after 9 hours, and a new thermodynamically favored polymorph $\mathbf{21{\cdot}II_y}$ ($\mathbf{II_y}$ = polymorph II in yellow color) is obtained with the crystal color changing from blue to yellow. Single-crystal X-ray analysis indicates that the molecules of $\mathbf{21{\cdot}II_y}$ take a nearly flat conformation, showing a head-to-tail arrangement with the Au···Au distance of 3.177 Å (i.e. the presence of aurophilic interactions). Notably, this mechanical force-triggered SC-SC transformation resembles dominoes and proceeds through self-replication. And then, Ito et al further introduced the methyl substituent into the basic structure of **21** to afford a green emissive metastable polymorph of phenyl(3,5-dimethylphenyl isocyanide)gold(I) ($\mathbf{22{\cdot}I_g}$, $\mathbf{I_g}$ = polymorph I in green color).[69] Remarkably, changes for the profile of crystal structure and emission energy in SC-SC transformation for **22** are opposite to those observed for **21**. Notably, the crystals of $\mathbf{22{\cdot}I_g}$, with intermolecular aurophilic interactions (Au···Au: 3.112–3.274 Å) will undergo a picking-triggered SC-SC transformation to afford the blue-shifted, weakly blue emissive phase $\mathbf{22{\cdot}II_b}$ without aurophilic interactions. This abnormity can be attributed to the formation of multiple C–H···π interactions involving the added methyl groups of **22**, which induce the emergence of the thermodynamically stable phase $\mathbf{22{\cdot}II_b}$.

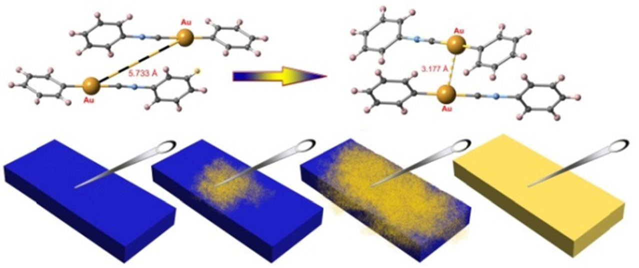


Fig. 16 Scheme view of dominoes reaction through self-replication of SC-SC transformation triggered by mechanical force.[68]

Recently, Tao et al reported a new polymorph for co-crystal 7,7,8,8-tetracyanoquinodimethane-p-bis(8-hydroxyquinolinato) copper(II), which can show an oriented SC-SC phase transition upon mechanical stimulation (i.e. pricked with a metal needle). This structural conversion is accompanied by almost doubling its length and halving its thickness in a macroscopic viewpoint, which can be attributed to the prominent changes of molecular stacking, with the dihedral angles between the molecular layers decreasing from 55.6º to 27.7º, and the *a*-axis lengths increasing from 8.035 Å to 14.098 Å, respectively.[70]

Dynamic structural transformations induced by synergic stimuli

In some SC-SC transformations, it is necessary to consider multiple stimuli that may play a synergic role in triggering different solid-state reactions. On the one hand, a transformation requires more than one external stimulus to provide appropriate energy, facilitating the reactions and maintaining the integrity of single-crystallinity. On the other hand, a given compound can be activated by different stimuli to suffer dual SC-SC transformations, and even multi-steps reversible transformations.

Multiple stimuli in one SC-SC transformation. Su and Lan et al reported an unprecedented SC-SC reaction controlled by both temperature and time in the presence or absence of solvent. The transformation from a 3D noninterpenetrating MOF $\{[(Zn_4O)_2(tcom)_3](solvent)\}_n$ (**23a**) to a 3D chiral self-penetrating MOF $\{[(Zn_4O)_2(tcom)_3(H_2O)](solvent)\}_n$ (**23b**), which can be viewed as the kinetic and dynamic products, respectively, will suffer an intermediate state.[71] During this transformation, the solvents in **23a** move faster in channels upon heating with a partial breakage of the coordination bonds, and different $Zn_4O(CO_2)_6$ SBUs move closer to each other and are dimerized by water molecules to form $[Zn_4O(CO_2)_6](H_2O)$ SBUs in **23b** in a certain time (Fig. 17). Of further interest, **23a** displays selective CO_2 uptake over N_2 and more excellent gas sorption ability than **23b**, while **23b** has an efficient capability in reversible adsorption of iodine.

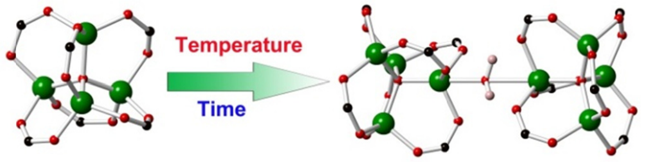


Fig. 17 SC-SC transformation doubly triggered by temperature and time.[71]

Multiple stimuli in dual SC-SC transformations. A 3D MOF $\{[Cu(iba)_2](H_2O)_2\}_n$ (**24·2H$_2$O**, iba = 4-(1H-imidazol-1-yl)benzoate), reported by Du et al, shows a 3-fold interpenetrating **lvt** framework with the inclusion of lattice water cubes.[72] Induced by different stimuli, temperature and time, this crystalline material shows distinct dual SC-SC transformations upon removing the lattice water clusters (Fig. 18). As a result, the polymorphic isomers of 3D porous framework for **24** and 2D polymeric **kgm** layer for $[Cu(iba)_2]$ (**24b**) can be isolated during the kinetic and thermodynamic dehydrated courses, respectively.

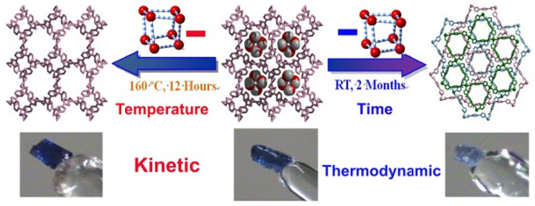


Fig. 18 Dual kinetic and thermodynamic SC-SC transformations upon removing lattice water clusters, triggered by temperature and time.[72]

Interestingly, by simply replacing the iba ligand with 4-(1H-1,2,4-triazol-1-yl)benzoate (tba) in the above case, a distinct 3D MOF $\{[Cu(tba)_2](DMF)\}_n$ (**25·DMF**) with the 4-fold interpenetrating **dia** framework, can be obtained.[73] The desolvated product **25** shows exclusive CO_2 adsorption selectivity over CH_4, H_2, O_2, Ar, and N_2 gases. Further, $[Cu(tba)_2]_n$ (**25**) can suffer divergent kinetic and thermodynamic SC-SC hydration processes, by immersing the crystal in water for minutes or exposing the crystal to air for several weeks, to produce its isostructural hydrate $\{[Cu(tba)_2](H_2O)\}_n$ (**25·H$_2$O**) and $[Cu(tba)_2(H_2O)_4]$ (**25b**) as a mononuclear complex. Such completely different SC-SC transformations of **25** first reveal the duality and sensitivity of MOF materials toward water.

Ghosh et al reported a 3D biporous soft MOF $\{[Cd_{1.5}(btb)(H_2O)](THF)_2\}_n$ (**26a**, H_3btb = 4,4',4''-(benzene-1,3,5-triyltrimethylene)tribenzoic acid), which shows the dual SC-SC transformations to regulate the chemical blocking and unblocking of active pores along with guest-dependent framework contraction and expansion (Fig. 19).[74] **26a** comprises two types of channels both filled with THF guests, in which one contains coordinated water molecules protruding into the internal voids and the other is lined with the hydrophobic surfaces of aromatic rings and an ether-linking moiety. This material shows two-way modulation of the framework porosity via dual SC-SC transformations. The lattice THF in the former pores can be easily replaced with acetone to form $\{[Cd_{1.5}(btb)(H_2O)](CH_3COCH_3)_2\}_n$ (**26b**) and then upon heating, the coordinative water ligands and lattice acetone are both removed to give active pores. While left in room temperature, the coordinated water molecules are partially replaced with THF to afford $\{[Cd_3(btb)_2(H_2O)(THF)](THF)\}_n$ (**26c**) and then upon heating, it exhibits a completed replacement of water ligands by THF to block the active pores. The dynamic activity of this porous material, as demonstrated by dual SC-SC transformations upon multiple stimuli, can also be supported by their distinct sorption capacities for carbon dioxide.

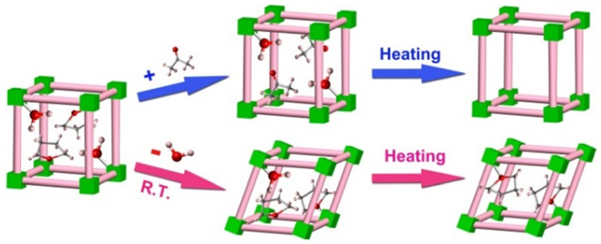


Fig. 19 Schematic view showing dual SC-SC transformations to regulate the chemical blocking and unblocking of active pores.[74]

Multiple stimuli in reversible SC-SC transformations. Lee, Zaworotko, and Vittal et al reported an outstanding example to manipulate the polymerization and depolymerization of organic polymer ligands in CP via reversible SC-SC transformations.[75a] Yellow crystals of $\{[Zn(bpeb)(tp)](solvent)\}_n$ (**27a**), which has a 6-fold interpenetrating **dia** framework, can be irradiated under xenon lamp at wavelength of 365 nm for 2 hours to afford pale yellow crystals of $\{[Zn(poly\text{-}bppcb)(tp)](solvent)\}_n$ (**27b**) with a new (4,4)-connected ***jjv1*** net (Fig. 20). The significant structural change is mainly due to the light-triggered [2+2] cycloaddition reaction, which can unite the six interpenetrating **dia** nets into a single ***jjv1*** net. Further, heating the crystals of **27b** to 250 ºC for 3 hours in a hot-air oven will result in the crystals of **27a**. This is the first example involving the reversible formation and cleavage of cyclobutane rings in a CP through SC-SC transformation. Also, Kawano and Vittal et al reported another example for reversible SC-SC transformations of cyclobutane formation or cleavage, with regard to the photoreactive ligand *trans*-4,4'-stilbenedicarboxylic acid.[75b] Jenkins et al reported the interesting gate effect of the 1D metal-organic nanotubes in 2D coordination frameworks.[75c] In such an SC-SC transformation triggered by moisture or heating, the phenyl groups as the tube walls can rotate between two positions to regulate the switch on/off of the pores.

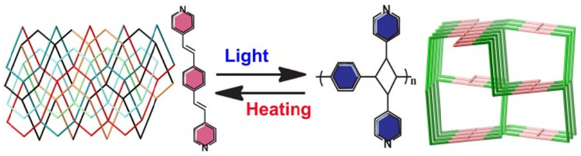


Fig. 20 Reversible SC-SC transformations from the 6-fold interpenetrating **dia** framework to single ***jjv1*** net triggered by light and heating.[75a]

Tao et al reported a unique square $Fe^{II}_4[N(CN)_2]_4$ compound, which can show the two-step complete spin transition via guest desorption/resorption-induced SC-SC transformation stimulated by thermal and optical irradiation.[76a] Tong and Bousseksou et al found the quasi-reversible transformation between the two-step spin crossover and half spin crossover complexes, under moisture and heating conditions.[76b] Costa and Aromí et al reported a reversible SC-SC cycle for $[Fe(bpp)(bmpp)](ClO_4)_2(C_3H_6O)_{3/2}$ (**28a**, bpp = 2,6-bis(pyrazol-3-yl)pyridine, H_2bmpp = 2,6-bis(5-(2-methoxy-phenyl)pyrazol-3-yl)pyridine), $[Fe(bpp)(bmpp)](ClO_4)_2(CH_3COCH_3)$ (**28b**), and $[Fe(bpp)(bmpp)](ClO_4)_2(CH_3OH)_{5/4}(H_2O)_{1/2}$ (**28c**), via adsorption, desorption, and exchange of small molecules (Fig. 21).[76c] Upon heating, **28a** transformed into **28b** by loss of partial acetone guests, switching from low-spin state (LS) to high-spin state (HS). Interestingly, such an SC-SC transformation can be reversed by incorporating the acetone vapor. Moreover, two-step SC-SC transformations from **28b** to **28c**, and then to **28a** can also be achieved by providing saturated methanol and acetone, with a magnetic state switching from HS to LS. As a result, a reversible conversion cycle is formed. Similar cycling SC-SC transformation triggered by moisture and heating was also observed in the work by Ma and Cheng et al, which features an unusual and controllable metal ion movement in the voids of CP.[76d]

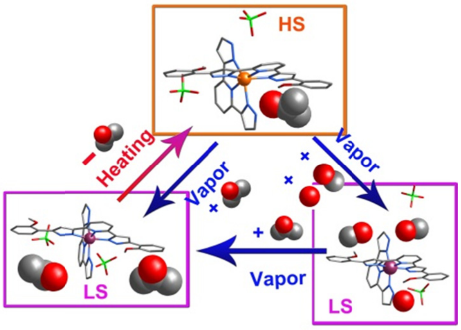


Fig. 21 SC-SC conversion cycle induced by heating or vapor.[76c]

Multiple stimuli in tandem structural transformations. The CSSs may possess the rigid or flexible nature at the low or high temperature, respectively, and provide the possibility of tandem behaviors in SC-SC transformation.[77] For example, Brammer et al reported a multiple SC-SC transformation, that is, the nonporous CP discards the lattice solvent by mild heating with the 1D polymeric structure intact and by further heating, a 2D CP with the crosslinking of organic ligands will be formed.[78a] Also, another tandem SC-SC transformation upon desorption/adsorption of water spirals and coordinated water by heating to 323 or 400 K, was reported by Zang, Song, and Mak et al, which provides the first example of switchable ferroelectric and optical behaviors.[78b]

Zeng and Kurmoo et al reported an unusual tandem PSM of a MOF $\{[Zn_3(hbmc)_2(OH)_2](H_2O)_6\}_n$ (**29·H₂O**, H_2hbmc = 2-(1-hydroxyethyl)-1*H*-benzo[d]imidazole-5-carboxylic acid) using thermal elimination and subsequent bromination (Fig. 22).[79] In particular, **29·H₂O** suffers an SC-SC transformation to form the guest-free framework **29** upon heating to 120 ºC. The hydroxyethyl tag group (–$CHOHCH_3$) is free in the channel of **29** which can be modified upon further heating to 250 ºC to give the vinyl group (–$CH{=}CH_2$), though crystallinity is lost after this process. Such a PSM method affords an unprecedented simple molecule 2-vinyl-1*H*-benzo[d]imidazole-5-carboxylic acid, which cannot be prepared via traditional organic synthesis. Further, the vinyl group can tandemly undergo an addition reaction with bromine. Notably, the two consecutive PSMs of elimination and bromination are realized on the tag group within the highly crystalline solid, which will have drastic effect on adsorption and luminescence properties of the material.

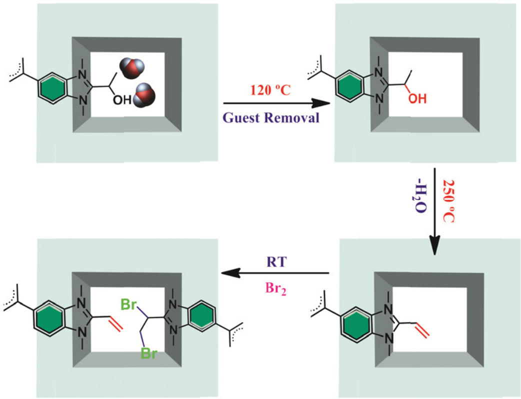


Fig. 22 Schematic view of the tandem PSM for **29**.[79]

Conclusions and perspectives

In this article, dynamic structural transformations of coordination supramolecular systems triggered by different exogenous stimuli have been illustrated. With regard to the object of study, some crystalline reactive characteristics, including metal nodes with adjustable electronic configurations or coordination geometries, ligand linkers with active functional groups, frameworks with flexibility for twisting, and special voids for guest capture or reaction, are of the necessity. More importantly, the delicate selection of the pivotal factors, such as concentration, temperature, light, mechanical force, as well as their synergic influence, will be key to achieve the proposed structural transformation. On one hand, upon exogenous stimuli, the metal nodes will undergo the change of coordination geometries, insertion of additional metal nodes, redox reaction, or exchange of metal nodes. On the other hand, organic linkers can also suffer appropriate transformations, such as ligand exchange, ligand pedal isomerization, ligand modification, or ligand polymerization. As a result, the host frameworks will show diverse functionality as guest adsorbents or molecular reactors, and network flexibility in breathing phenomenon, entanglement, and repacking arrangement.

Benefiting from the advantages of single-crystal X-ray diffraction and other analysis techniques, there is an obscure borderline between single-crystallinity and poly-crystallinity. Thus, a solid-state reaction may be remarkably monitored as a whole story from alpha to omega. More fascinatingly, some coordination supramolecular systems, which may only be obtained from dynamic structural transformations, will have peculiar physicochemical properties in adsorption, magnetism, luminescent, and catalysis, revealing proof-of-concept for applications in the rational design of new functional crystalline materials.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Nos. 21031002, 91122005, and 21101116), Program for Innovative Research Team in University of Tianjin (No. TD12-5038), and Plan for Scientific Innovation Talent of Henan Province for financial support.

Notes and references

[a] *College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, MOE Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China. E-mail: dumiao@public.tpt.tj.cn.*
[b] *Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, P. R. China*

1 (*a*) V. V. Boldyrev, *Reactivity of Solids: Past, Present and Future*, Blackwell Science, Cambridge, 1996; (*b*) G. R. Desiraju, *Organic Solid State Chemistry*, Elsevier, Amsterdam, 1987.

2. (*a*) J. M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, Germany, 1995; (*b*) G. Burns, *Solid State Physics*, Academic Press, New York, 1985.

3. J. D. Dunitz, V. Schomaker and K. N. Trueblood, *J. Phys. Chem.*, 1988, **92**, 856–867.

4. (*a*) F. K. Lotgering, *J. Inorg. Nucl. Chem.*, 1959, **9**, 113–123; (*b*) H. Morawetz, S. Z. Jakabhazy, J. B. Lando and J. Shafer, *Proc. Natl. Acad. Sci.*, 1963, **49**, 789–793.

5. G. M. Schmidt, *J. Pure Appl. Chem.*, 1971, **27**, 647–678.

6. (*a*) V. Kohlschüetter, *Z. Anorg. Allg. Chem.*, 1918, **105**, 1–25; (*b*) G. Kaupp, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 131–138.

7. L. J. Barbour, *Aust. J. Chem.*, 2006, **59**, 595–596.

8. S. R. Batten, N. R. Champness, X. M. Chen, J. Garvia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *CrystEngComm*, 2012, **14**, 3001–3004.

9. (*a*) M. O'Keeffe, *Chem. Soc. Rev.*, 2009, **38**, 1215–1217; (*b*) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **239**, 424–428; (*c*) D. M. Proserpio, *Nat. Chem.*, 2010, **2**, 435–436; (*d*) M. Du, C. P. Li, C. S. Liu and S. M. Fang, *Coord. Chem. Rev.*, 2013, **257**, 1282–1305.

10 (*a*) S. H. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710–716; (*b*) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402–8403; (*c*) D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa and J. Groll, *Nat. Chem.*, 2010, **2**, 410–416; (*d*) Y. Kobayashi, B. Jacobs, M. D. Allendorf and J. R. Long, *Chem. Mater.*, 2010, **22**, 4120–4122; (*e*) M. H. Zeng, Q. X. Wang, Y. X. Tan, S. Hu, H. X. Zhao, L. S. Long and M. Kurmoo, *J. Am. Chem. Soc.*, 2010, **132**, 2561–2563; (*f*) R. E. Morris and X. Bu, *Nat. Chem.*, 2010, **2**, 353–361.

11 (*a*) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191–214; (*b*) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330–1352; (*c*) M. Du and X. H. Bu, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 539–554.

12 (*a*) J. L. Liu, Y. C. Chen, Y. Z. Zheng, W. Q. Lin, L. Ungur, W. Wernsdorfer, L. F. Chibotaru and M. L. Tong, *Chem. Sci.*, 2013, **4**, 3310–3316; (*b*) L. Cao, J. Tao, Q. Gao, T. Liu, Z. C. Xia and D. F. Li, *Chem. Commun.*, 2014, **50**, 1665–1667; (*c*) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459; (*d*) A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284–1293.

13 (*a*) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353–1379; (*b*) D. Maspoch, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770–818; (*c*) O. Sato, J. Tao and Y.-Z. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152–2187.

14 I. Halasz, *Cryst. Growth Des.*, 2010, **10**, 2817–2823.

15 M. Kawano and M. Fujita, *Coord. Chem. Rev.*, 2007, **251**, 2592–2605.

16 J. Martí-Rujas and M. Kawano, *Acc. Chem. Res.*, 2013, **46**, 493–505.

17 G. Kaupp, *Top. Curr. Chem.*, 2005, **254**, 95–183.

18 (*a*) J. J. Vittal, *Coord. Chem. Rev.*, 2007, **251**, 1781–1795; (*b*) G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755–1775.

19 L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, T. D. Hamilton, D.-K. Bučar, Q. Chu, D. B. Varshney and I. G. Georgiev, *Acc. Chem. Res.*, 2008, **41**, 280–291.

20 (*a*) C. M. Frech, *ChemCatChem*, 2010, **2**, 1387–1389; (*b*) L. R. Nassimbeni and H. Su, *CrystEngComm*, 2013, **15**, 7396–7401.

21 Z.-M. Hao and X.-M. Zhang, *Dalton Trans.*, 2011, **40**, 2092–2098.

22 (*a*) J. W. Lauher, F. W. Fowler and N. S. Goroff, *Acc. Chem. Res.*, 2008, **41**, 1215–1229; (*b*) M. A. Garcia-Garibay, *Angew. Chem., Int. Ed.*, 2007, **46**, 8945–8947.

23 S. Neogi, S. Sen and P. K. Bharadwaj, *CrystEngComm*, 2013, **15**, 9239–9248.

24 (*a*) J. R. Ferraro and G. J. Long, *Acc. Chem. Res.*, 1975, **8**, 171–179; (*b*) D. Braga and F. Grepioni, *Angew. Chem., Int. Ed.*, 2004, **43**, 4002–4011.

25 G. J. Halder and C. J. Kepert, *Aust. J. Chem.*, 2006, **59**, 597–604.

26 M. P. Suh and Y. E. Cheon, *Aust. J. Chem.*, 2006, **59**, 605–612.

27 Q. W. Li, W. Y. Zhang, O. S. Miljanic, C. H. Sue, Y. L. Zhao, L. H. Liu, C. B. Knobler, J. F. Stoddart and O. M. Yaghi, *Science*, 2009, **325**, 855–859.

28 Y. Inokuma, T. Arai and M. Fujita, *Nat. Chem.*, 2010, **2**, 780–783.

29 C. R. Murdock, B. C. Hughes, Z. Lu and D. M. Jenkins, *Coord. Chem. Rev.*, 2014, **258**, 119–136.

30 (*a*) Y. S. Wei, K. J. Chen, P. Q. Liao, B. Y. Zhu, R. B. Lin, H. L. Zhou, B. Y. Wang, W. Xue, J. P. Zhang and X. M. Chen, *Chem. Sci.*, 2013, **4**, 1539–1546; (*b*) R. Medishetty, D. Jung, X. Song, D. Kim, S. S. Lee, M. S. Lah and J. J. Vittal, *Inorg. Chem.*, 2013, **52**, 2951–2957.

31 For the three-letter net symbols, see: M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782–1789 and the associated website http://rcsr.anu.edu.au/.

32 (*a*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125; (*b*) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126–1162.

33 H. Furukawa, F. Gandara, Y. B. Zhang, J. C. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369–4381.

34 Q. Chen, Z. Chang, W. C. Song, H. Song, H. B. Song, T. L. Hu and X. H. Bu, *Angew. Chem., Int. Ed.*, 2013, **52**, 11550–11553.

35 C. P. Li, J. M. Wu and M. Du, *Chem.-Eur. J.*, 2012, **18**, 12437–12445.

36 M. H. Zeng, Y. X. Tan, Y. P. He, Z. Yin, Q. Chen and M. Kurmoo, *Inorg. Chem.*, 2013, **52**, 2353–2360.

37 (*a*) M. Du, C. P. Li, J. M. Wu, J. H. Guo and G. C. Wang, *Chem. Commun.*, 2011, **47**, 8088–8090; (*b*) Z. Su, M. Chen, T.-A. Okamura, M.-S. Chen, S.-S. Chen and W.-Y. Sun, *Inorg. Chem.*, 2011, **50**, 985–991.

38 (*a*) A. D. Naik, K. Robeyns, C. F. Meunier, A. F. Leonard, A. Rotaru, B. Tinant, Y. Filinchuk, B. L. Su and Y. Garcia, *Inorg. Chem.*, 2014, **53**, 1263–1265; (*b*) J. Y. Ge, J. C. Wang, J. Y. Cheng, P. Wang, J. P. Ma, Q. K. Liu and Y. B. Dong, *Chem. Commun.*, 2014, **50**, 4434–4437; (*c*) Y. Yu, X.-M. Zhang, J.-P. Ma, Q.-K. Liu, P. Wang and Y.-B. Dong, *Chem. Commun.*, 2014, **50**, 1444–1446; (*d*) T. K. Kim, J. H. Lee, D. Moon and H. R. Moon, *Inorg. Chem.*, 2013, **52**, 589–595; (*e*) R. B. Lin, F. Li, S. Y. Liu, X. L. Qi, J. P. Zhang and X. M. Chen, *Angew. Chem., Int. Ed.*, 2013, **52**, 13429–13433; (*f*) Y.-Q. Lan, H.-L. Jiang, S.-L. Li and Q. Xu, *Inorg. Chem.*, 2012, **51**, 7484–7491.

39 R. Custelcean and B. A. Moyer, *Eur. J. Inorg. Chem.*, 2007, 1321–1340.

40 (*a*) Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang and X.-H. Bu, *Chem. Sci.*, 2013, **4**, 3678–3682; (*b*) B. Manna, A. K. Chaudhari, B. Joarder, A. Karmakar and S. K. Ghosh, *Angew. Chem., Int. Ed.*, 2013, **52**, 998–1002; (*c*) C. P. Li, J. Guo and M. Du, *Inorg. Chem. Commun.*, 2013, **38**, 70–73; (*d*) Q. Y. Yang, K. Li, J. A. Luo, M. Pan and C. Y. Su, *Chem. Commun.*, 2011, **47**, 4234–4236; (*e*) J. P. Ma, Y. Yu and Y. B. Dong, *Chem. Commun.*, 2012, **48**, 2946–2948; (*f*) J. Chen, C. P. Li, J. Shang and M. Du, *Inorg. Chem. Commun.*, 2012, **15**, 172–175; (*g*) M. Du, X. J. Zhao, J. H. Guo and S. R. Batten, *Chem. Commun.*, 2005, 4836–4838; (*h*) T. K. Maji, R. Matsuda and S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142–148.

41 (*a*) *US Department of Health and Human Services*, Toxicological Profile for Chromium, Public Health Service Agency for Toxic Substances and Diseases Registry, Washington, DC, 1991; (*b*) L. H. Keith and W. A. Teillard, *Environ. Sci. Technol.*, 1979, **13**, 416–423; (*c*) S. R. J. Oliver, *Chem. Soc. Rev.*, 2009, **38**, 1868–1881.

42 (*a*) B. H. Gu, G. M. Brown, P. V. Bonnesen, L. Y. Liang, B. A. Moyer, R. Ober and S. D. Alexandratos, *Environ. Sci. Technol.*, 2000, **34**, 1075–1080; (*b*) P. V. Bonnesen, G. M. Brown, S. D. Alexandratos, L. B. Bavoux, D. J. Presley, V. Patel, R. Ober and B. A. Moyer, *Environ. Sci. Technol.*, 2000, **34**, 3761–3766.

43 (*a*) P. Yu, S. A. Wang, E. V. Alekseev, W. Depmeier, D. T. Hobbs, T. E. Albrecht-Schmitt, B. L. Phillips and W. H. Casey, *Angew. Chem., Int. Ed.*, 2010, **49**, 5975–5977; (*b*) S. A. Wang, E. V. Alekseev, D. W. Juan, W. H. Casey, B. L. Phillips, W. Depmeier and T. E. Albrecht-Schmitt, *Angew. Chem., Int. Ed.*, 2010, **49**, 1057–1060; (*c*) S. A. Wang, P. Yu, B. A. Purse, M. J. Orta, J. Diwu, W. H. Casey, B. L. Phillips, E. V. Alekseev, W. Depmeier, D. T. Hobbs and T. E. Albrecht-Schmitt, *Adv. Funct. Mater.*, 2012, **22**, 2241–2250; (*d*) H. H. Fei, C. S. Han, J. C. Robins and S. R. J. Oliver, *Chem. Mater.*, 2013, **25**, 647–652; (*e*) H. H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202–7209; (*f*) H. H. Fei, M. R. Bresler and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2011, **133**, 11110–11113.

44 (*a*) P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231–8233; (*b*) X. X. Li, H. Y. Xu, F. Z. Kong and R. H. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 13769–13773.

45 C. P. Li, B. L. Liu, W. Guo, and M. Du, unpublished work.

46 M. Owlad, M. K. Aroua and W. M. A. W. Daud, *Bioresour. Technol.*, 2010, **101**, 5098–5103.

47 (*a*) J. H. Fu, H. J. Li, Y. J. Mu, H. W. Hou and Y. T. Fan, *Chem. Commun.*, 2011, **47**, 5271–5273; (*b*) M. H. Zeng, Z. Yin, Y. X. Tan, W. X. Zhang, Y. P. He and M. Kurmoo, *J. Am. Chem. Soc.*, 2014, **136**, 4680–4688; (*c*) L. Fu, Y. Liu, M. Pan, X. J. Kuang, C. Yan, K. Li, S. C. Wei and C. Y. Su, *J. Mater. Chem. A*, 2013, **1**, 8575–8580.

48 C. P. Li, W. Guo and M. Du, unpublished work.

49 J. K. Sun, B. Tan, L. X. Cai, R. P. Chen, J. Zhang and J. Zhang, *Chem.-Eur. J.*, 2014, **20**, 2488–2495.

50 (*a*) Z. Q. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315–1329; (*b*) K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519; (*c*) K. Oisaki, Q. W. Li, H. Furukawa, A. U. Czaja and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 9262–9264; (*d*) Y. Q. Lan, S. L. Li, H. L. Jiang and Q. Xu, *Chem.-Eur. J.*, 2012, **18**, 8076–8083; (*e*) M. J. Zaworotko, *Nat. Chem.*, 2009, **1**, 267–268; (*f*) J. R. Li and H. C. Zhou, *Nat. Chem.*, 2010, **2**, 893–898; (*g*) Z. Huang, P. S. White and M. Brookhart, *Nature*, 2010, **465**, 598–601.

51 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546–1554; (*b*) R. Kitaura, F. Iwahori, R. Matsuda, S. Kitagawa, Y. Kubota, M. Takata and T. C. Kobayashi, *Inorg. Chem.*, 2004, **43**, 6522–6524; (*c*) Z. X. Chen, S. C. Xiang, D. Y. Zhao and B. L. Chen, *Cryst. Growth Des.*, 2009, **9**, 5293–5296; (*d*) J. R. Li, D. J. Timmons and H. C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368–6369; (*e*) B. J. Burnett, P. M. Barron, C. Hu and W. Choe, *J. Am. Chem. Soc.*, 2011, **133**, 9984–9987; (*f*) M. Kim, J. F. Cahill, Y. X. Su, K. A. Prather and S. M. Cohen, *Chem. Sci.*, 2012, **3**, 126–130; (*g*) O. Karagiaridi, W. Bury, A. A. Sarjeant, C. L. Stern, O. K. Farha and J. T. Hupp, *Chem. Sci.*, 2012, **3**, 3256–3260.

52 (*a*) O. Karagiaridi, W. Bury, E. Tylianakis, A. A. Sarjeant, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2013, **25**, 3499–3503; (*b*) W. Bury, D. Fairen-Jimenez, M. B. Lalonde, R. Q. Snurr, O. K. Farha and J. T. Hupp, *Chem. Mater.*, 2013, **25**, 739–744.

53 S. Jeong, D. Kim, X. Song, M. Choi, N. Park and M. S. Lah, *Chem. Mater.*, 2013, **25**, 1047–1054.

54 T. Li, M. T. Kozlowski, E. A. Doud, M. N. Blakely and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 11688–11691.

55 (*a*) M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172–11176; (*b*) L. W. Mi, H. W. Hou, Z. Y. Song, H. Y. Han, H. Xu, Y. T. Fan and S. W. Ng, *Cryst. Growth Des.*, 2007, **7**, 2553–2561; (*c*) A. J. Cairns, J. A. Perman, L. Wojtas, V. C. Kravtsov, M. H. Alkordi, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2008, **130**, 1560–1561.

56 S. Das, H. Kim and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814–3815.

57 M. Lalonde, W. Bury, O. Karagiaridi, Z. Brown, J. T. Hupp and O. K. Farha, *J. Mater. Chem. A*, 2013, **1**, 5453–5468.

58 (*a*) M. Kim, J. F. Cahill, H. H. Fei, K. A. Prather and S. M. Cohen, *J. Am. Chem. Soc.*, 2012, **134**, 18082–18088; (*b*) H. H. Fei, J. F. Cahill, K. A. Prather and S. M. Cohen, *Inorg. Chem.*, 2013, **52**, 4011–4016.

59 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970–1000.

60 (*a*) N. A. Vermeulen, O. Karagiaridi, A. A. Sarjeant, C. L. Stern, J. T. Hupp, O. K. Farha and J. F. Stoddart, *J. Am. Chem. Soc.*, 2013, **135**, 14916–14919; (*b*) C. Liu, T. Li and N. L. Rosi, *J. Am. Chem. Soc.*, 2012, **134**, 18886–18888; (*c*) K. Mo, Y. H. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746–1749.

61 (*a*) J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno and P. K. Thallapally, *J. Am. Chem. Soc.*, 2012, **134**, 9581–9584; (*b*) J. Li, P. Huang, X. R. Wu, J. Tao, R. B. Huang and L. S. Zheng, *Chem. Sci.*, 2013, **4**, 3232–3238; (*c*) T. Jacobs, R. Clowes, A. I. Cooper and M. J. Hardie, *Angew. Chem., Int. Ed.*, 2012, **51**, 5192–5195.

62 (*a*) M. C. Bernini, F. Gándara, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla, E. V. Brusau, G. E. Narda and M. A. Monge, *Chem.-Eur. J.*, 2009, **15**, 4896–4905; (*b*) X. F. Wang, Y. Wang, Y. B. Zhang, W. Xue, J. P. Zhang and X. M. Chen, *Chem. Commun.*, 2012, **48**, 133–135; (*c*) H. L. Zhou, R. B. Lin, C. T. He, Y. B. Zhang, N. D. Feng, Q. Wang, F. Deng, J. P. Zhang and X. M. Chen, *Nat. Commun.*, 2013, **4**, 2534.

63 (*a*) J. Sun, F. N. Dai, W. B. Yuan, W. H. Bi, X. L. Zhao, W. M. Sun and D. F. Sun, *Angew. Chem., Int. Ed.*, 2011, **50**, 7061–7064; (*b*) V. I. Ovcharenko, S. V. Fokin, E. T. Kostina, G. V. Romanenko, A. S. Bogomyakov and E. V. Tretyakov, *Inorg. Chem.*, 2012, **51**, 12188–12194; (*c*) A. Mesbah, P. Rabu, R. Sibille, S. Lebègue, T. Mazet, B. Malaman and M. François, *Inorg. Chem.*, 2014, **53**, 872–881.

64 (*a*) H. Aggarwal, P. M. Bhatt, C. X. Bezuidenhout and L. J. Barbour, *J. Am. Chem. Soc.*, 2014, **136**, 3776–3779; (*b*) R. Saha, B. Joarder, A. S. Roy, S. M. Islam and S. Kumar, *Chem.-Eur. J.*, 2013, **19**, 16607–16614; (*c*) Y. Han, H. Xu, Y. Y. Liu, H. J. Li, H. W. Hou, Y. T. Fan and S. R. Batten, *Chem.-Eur. J.*, 2012, **18**, 13954–13958.

65 I. H. Park, A. Chanthapally, H. H. Lee, H. S. Quah, S. S. Lee and J. J. Vittal, *Chem. Commun.*, 2014, **50**, 3665–3667.

66 S. Y. Yang, X. L. Deng, R. F. Jin, P. Naumov, M. K. Panda, R. B. Huang, L. S. Zheng and B. K. Teo, *J. Am. Chem. Soc.*, 2014, **136**, 558–561.

67 (*a*) Y. Sagara and T. Kato, *Angew. Chem., Int. Ed.*, 2011, **50**, 9128–9132; (*b*) Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605–610; (*c*) A. L. Balch, *Angew. Chem., Int. Ed.*, 2009, **48**, 2641–2644.

68 H. Ito, M. Muromoto, S. Kurenuma, S. Ishizaka, N. Kitamura, H. Sato and T. Seki, *Nat. Commun.*, 2013, **4**, 2009.

69 T. Seki, K. Sakurada and H. Ito, *Angew. Chem., Int. Ed.*, 2013, **52**, 12828–12832.

70 G. F. Liu, J. Liu, Y. Liu and X. T. Tao, *J. Am. Chem. Soc.*, 2014, **136**, 590–593.

71 P. Shen, W. W. He, D. Y. Du, H. L. Jiang, S. L. Li, Z. L. Lang, Z. M. Su, Q. Fu and Y. Q. Lan, *Chem. Sci.*, 2014, **5**, 1368–1374.

72 X. D. Chen, X. H. Zhao, M. Chen and M. Du, *Chem.-Eur. J.*, 2009, **15**, 12974–12977.

73 M. Du, C. P. Li, M. Chen, Z. W. Ge, X. Wang, L. Wang and C. S. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 10906–10909.

74 A. K. Chaudhari, S. S. Nagarkar, B. Joarder, S. Mukherjee and S. K. Ghosh, *Inorg. Chem.*, 2013, **52**, 12784–12789.

75 (*a*) I. H. Park, A. Chanthapally, Z. J. Zhang, S. S. Lee, M. J. Zaworotko and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2014, **53**, 414–419; (*b*) G. K. Kole, T. Kojima, M. Kawano and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2014, **53**, 2143–2146; (*c*) C. R. Murdock, N. W. McNutt, D. J. Keffer and D. M. Jenkins, *J. Am. Chem. Soc.*, 2014, **136**, 671–678.

76 (*a*) R. J. Wei, Q. Huo, J. Tao, R. B. Huang and L. S. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 8940–8943; (*b*) X. Bao, H. J. Shepherd, L. Salmon, G. Molnár, M. L. Tong and A. Bousseksou, *Angew. Chem., Int. Ed.*, 2013, **52**, 1198–1202; (*c*) J. S. Costa, S. Rodriguez-Jiménez, G. A. Craig, B. Barth, C. M. Beavers, S. J. Teat and G. Aromí, *J. Am. Chem. Soc.*, 2014, **136**, 3869–3874; (*d*) Z. Niu, J. G. Ma, W. Shi and P. Cheng, *Chem. Commun.*, 2014, **50**, 1839–1841.

77 (*a*) G. C. Lv, P. Wang, Q. Liu, J. Fan, K. Chen and W. Y. Sun, *Chem. Commun.*, 2012, **48**, 10249–10251; (*b*) E. Q. Procopio, T. Fukushima, E. Barea, J. A. R. Navarro, S. Horike and S. Kitagawa, *Chem.-Eur. J.*, 2012, **18**, 13117–13125; (*c*) T. Zheng, J. M. Clemente-Juan, J. Ma, L. Dong, S. S. Bao, J. Huang, E. Coronado and L. M. Zheng, *Chem.-Eur. J.*, 2013, **19**, 16394–16402.

78 (*a*) I. J. Vitórica-Yrezábal, G. M. Espallargas, J. Soleimannejad, A. J. Florence, A. J. Fletcher and L. Brammer, *Chem. Sci.*, 2013, **4**, 696–708; (*b*) X. Y. Dong, B. Li, B. B. Ma, S. J. Li, M. M. Dong, Y. Y. Zhu, S. Q. Zang, Y. Song, H. W. Hou and T. C. W. Mak, *J. Am. Chem. Soc.*, 2013, **135**, 10214–10217.

79 F. Sun, Z. Yin, Q. Q. Wang, D. Sun, M. H. Zeng and M. Kurmoo, *Angew. Chem., Int. Ed.*, 2013, **52**, 4538–4543.

Photographs and Brief Biographies

Cheng-Peng Li was born in 1981, in Linfen, Shanxi Province, China. He received his BS in 2003 and MS in 2006 from Tianjin Normal University, and his PhD in 2009 from Tianjin University. Currently, he is an associate professor at Tianjin Normal University and focuses on coordination supramolecular systems and their properties, especially dynamic structural transformations.

Jing Chen was born in 1986, China. She obtained her BS in 2008 and MS in 2011 from Tianjin Normal University under the supervision of Prof. Miao Du. Then, she joined the faculty at Tianjin Normal University and her current research focuses on crystal engineering of coordination polymers.

Chun-Sen Liu was born in Zhengzhou, China. He obtained his BS in 1997 from Tianjin Normal University, and his PhD in 2007 from Nankai University under the supervision of Prof. Xian-He Bu. And then, he joined the faculty at Zhengzhou University of Light Industry, where he is now a Professor of Chemistry. His recent research interest focuses on metal-organic frameworks (MOFs) for potential applications.

Miao Du was born in Kaifeng, Henan Province, China (1976). He received his BS from Nankai University (1998), and subsequently his doctorate there (2003) under the supervision of Prof. Xian-He Bu. Then, he joined the faculty at Tianjin Normal University and now is a Professor of Chemistry. He has worked with Prof. Thomas C. W. Mak at the Chinese University of Hong Kong and Dr Qiang Xu at the Institute of Advanced Industrial Science and Technology of Japan (JSPS fellow). His current research lies in coordination chemistry and crystal engineering.