

Soft porous crystals

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The field of host-guest complexation is intensely attractive from diverse perspectives, including materials science, chemistry and biology. The uptake and encapsulation of guest species by host frameworks are being investigated for a wide variety of purposes, including separation and storage using zeolites, and recognition and sensing by enzymes in solution. Here we focus on the concept of the cooperative integration of 'softness' and 'regularity'. Recent developments on porous coordination polymers (or metal-organic frameworks) have provided the inherent properties that combine these features. Such soft porous crystals exhibit dynamic frameworks that are able to respond to external stimuli such as light, electric fields or the presence of particular species, but they are also crystalline and can change their channels reversibly while retaining high regularity. We discuss the relationship between the structures and properties of these materials in view of their practical applications.

It is generally well recognized that host compounds exist both in liquid and in solid phases. Zeolites and aluminophosphates are representatives of porous crystalline materials used for molecular sieving, heterogeneous catalysis and storage. Their rigid regular porous structures have significant roles in sorting the size and shape of guest species. In contrast, one of the typical host compounds working in liquid media is an enzyme in which protein molecules provide a porous environment for specific interactions with substrates. The structural reformation of their channels and cavities enhances selective recognition and capture of substrates. In other words, structural flexibility is key for a unique and efficient function.

The flexible structure could be compared to a human hand because it can recognize forms and shapes and has a multifunctional character. Both rigid porous crystalline solids and enzymes in liquid phase have intrinsic advantages: crystallinity allows an efficient collection of guests because of the large number of the same porous units, whereas flexibility produces a highly selective capture of guests. When one designs a new class of functional host materials based on state-of-the-art host-guest systems, could one extrapolate from a solid material possessing integrated attributes of both crystallinity and flexibility (or dynamism)? Such bimodality of a host framework would provide not only rigid zeolitic properties, but also enzyme-like specificity, producing intelligent host materials that are responsive to guests under the appropriate conditions. In particular, in the crystalline phase, softness hardly exists because the solid is a form in which components are closely and regularly packed, making the overall structure rigid and condensed, therefore the atomic and molecular freedom of motion that is required for softness are prohibited.

To integrate these features in a single-entity host material, we have focused on porous coordination polymers (PCPs) — or metal-organic frameworks (MOFs) — which consist of metal ions and organic linkers¹⁻¹⁶. Although other molecular crystals of organic compounds^{17,18}, discrete metal complexes¹⁹, lamellar zirconium phosphates^{20,21}, and a few zeolites²² might also be suitable, porous coordination polymers are among the most appropriate materials for combining regularity and softness (Fig. 1a). They can provide high crystallinity and diverse structural topologies with porous architectures. Moreover, the attractive forces used to assemble components are also versatile, ranging from van der Waals interactions

to coordination bonds. Control of these interactions could provide soft materials that have a porous scaffold^{23,24}. Herein, to clarify the nature and the potential of porous coordination polymers, we describe them as a new category of materials, 'soft porous crystals'. We define the necessary conditions for the formation of soft porous crystals, introduce their structural features and properties, and discuss their potential applications and prospects in materials science.

What is a soft porous crystal?

In 1998, porous coordination polymers were classified into three categories — first, second and third generations (Fig. 1b) — predicting the presence and importance of soft porous crystals². The first-generation materials have frameworks whose porosity collapses irreversibly after the removal of the guests — that is, there is no permanent porosity. The second generation has stable and robust frameworks, which maintain the original porous structures before and after guest sorption. The second-generation compounds can be used as an adsorbent and are regarded as analogous to zeolites. For the third-generation compounds, we emphasize flexible or dynamic porous frameworks, which reversibly respond to external stimuli, not only chemical but also physical. Thanks to the recent discoveries of new crystal structures of porous coordination polymers, we are able to perform on-demand synthesis of functional pores by tuning size, shape and chemical properties, and in the past couple of years, the third-generation compounds — soft porous crystals — have emerged.

Soft porous crystals are defined as porous solids that possess both a highly ordered network and structural transformability. They are bistable or multistable crystalline materials with long-range structural ordering, a reversible transformability between states, and permanent porosity. The term permanent porosity means that at least one crystal phase possesses space that can be occupied by guest molecules, so that the framework exhibits reproducible guest adsorption.

In soft porous crystals, two types of transformation are possible. In most cases transformations occur while retaining the crystalline state (crystal-to-crystal), but sometimes perfect crystallinity is lost during the transformation (from crystal to another form with imperfect crystallinity). Imperfect crystallinity does not mean that the form is amorphous, but that the long-range order of the framework is lost, without the polymer network collapsing.

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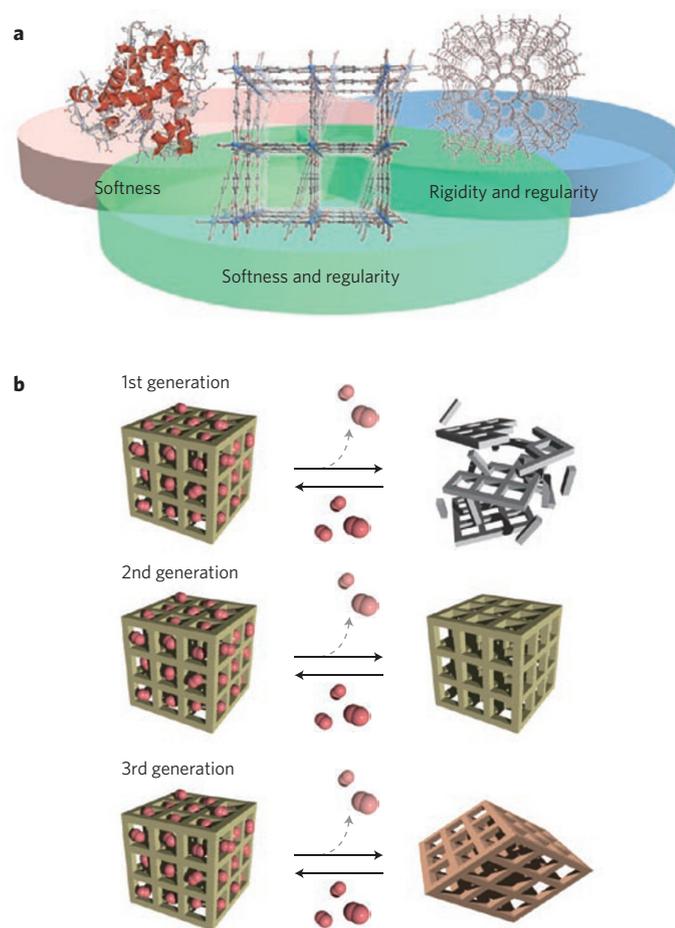


Figure 1 | Soft porous crystal as a new class of adsorptive solid materials.

a, Three classes of host materials categorized according to attributes of softness, hardness (rigidity) and regularity. Materials at the left and right sides have softness and hardness, respectively. Materials at the centre possess both attributes with regularity. The overlapping zone of the two stages indicates materials belonging to either of the ends. **b**, Classification of porous coordination polymers into three categories. The first-generation materials collapse on guest removal. The second-generation materials have robust and rigid frameworks, and retain their crystallinity when the guests are not present in the pores. The third-generation materials are transformable accompanied by structural transformation. A combination of metal ion and organic ligand gives freedom to both structural and physical properties (such as spin, charge or photonic) and the various softness factors represents a synergistic effect in the porous structure. This effect can also be observed when the specific guests access the channels.

It is noteworthy that the softness of the porous framework is not just a structural transformation but accompanies other physical properties such as electron transfer and spin transition. The structural degree of freedom is related to the mutual displacement of frameworks such as layers and cubic grids and the flexibility of the framework itself. This often evokes the electronic degree of freedom leading to spin crossover, magnetic ordering, electron/charge transport or dielectric properties, while retaining the soft porous characteristics.

Properties based on motif displacement

Storage and separation of a target gas are typical functions of porous materials, and the performance of these tasks is evaluated by the amount released under suitable conditions. For the development of a relevant adsorbent, there is a need to control the sorption isotherms, but because of the dynamic guest accommodation behaviour, adsorption isotherms of soft porous crystals sometimes

cannot be classified according to the conventional IUPAC classification²⁵. For instance, a 'gate type' sorption profile shows no uptake at low concentration of the guest molecules, and an abrupt increase in adsorption after a threshold concentration. This so-called gate-opening pressure is a representative characteristic of a soft porous crystal. The behaviour is associated with a structural transformation from a non-porous to a porous phase, and the gate-opening pressure is sensitive to the property of gas to be adsorbed.

One way to create this kind of compound is to have a loose assembly of rigid coordination networks. Coordination frameworks with stiff linkers tend to be robust, giving no softness. However, they can be interdigitated or interpenetrated — where several independent, identical networks are entangled, either in an extricable manner (without breaking internal connections), in interdigitated frameworks, or inextricably (that is, disentanglement can only be achieved by breaking bonds), in interpenetrated frameworks²⁶. The constituent networks can then undergo a dislocation of their mutual positions, resulting in an increase in the effective pore size, and a higher accommodation of adsorbate than without guests.

The two-dimensional (2D) sheet system has been studied as a good motif for this type of sorption property²⁷. $[\text{Cu}_2(\text{dhbc})_2(\text{bpy})]_n$ (see Glossary for definition of abbreviations) consists of 2D sheets, but has an interdigitation of π - π stacking interactions between the benzene rings of dhbc, which act as pillars between adjacent sheets²⁸ (Fig. 2a). The π - π stacking provides moderate interaction for stabilization of the structure, and the sliding motion of π - π stacking forms an open structure when a guest is adsorbed. This structural transformation is accompanied by shrinking of the layer distance with release of adsorbed gases. The compound shows a characteristic hysteretic adsorption isotherm of CO_2 vapour and various supercritical gases, CH_4 , O_2 and N_2 at room temperature. An important point of the sorption is that the gate-opening pressures for these gases are obviously different; CO_2 is adsorbed at low pressure (0.4 bar), whereas CH_4 , O_2 and N_2 start to be adsorbed at 8.1, 35 and 50 bar, respectively (Fig. 2b). Recent thermodynamic considerations indicate a difference of about 5 kJ mol⁻¹ in free energy with respect to the mutual framework arrangement between the open and closed forms of this compound²⁹. A subtle balance and competition of the interaction of guest-framework and framework-framework can be the key for selective sorption of gases. In recent works it has been demonstrated that the interdigitation of frameworks (or motifs) can be designed in a variety of ways. In particular, the combination of a dicarboxylate ligand and a linear bipyridyl ligand with a transition metal systematically constructs an interdigitated structure^{30,31}, and is effective for the separation of gases with high selectivity.

The interpenetration system is another useful assortment of motifs to induce softness into a porous framework. Interpenetrated grid frameworks can form open and closed phases by interdigitation using a simple glide motion without any bond cleavage or distortion. A square-grid-based 3D framework with double interpenetration is obtained in $[\text{Zn}_2(\text{bdc})_2(\text{bpy})]_n$ (MOF-508) (Fig. 2c; ref. 32). A guest-free structure (closed phase) has no porosity because double interpenetration of networks occupies the space, and as guests are incorporated into the solid, micropores are generated and eventually a porous framework with pore diameter of $4 \times 4 \text{ \AA}^2$ is formed. This dynamic framework with the bimodal pore system can separate linear and branched isomers of pentane and hexane molecules. When the crystalline powder was placed in a gas chromatographic (GC) column, it was found, for example, that 2-methylpentane runs through the column faster than its linear isomer *n*-hexane, and the other isomer, 2,2-dimethylbutane, elutes even faster (Fig. 2d). The separation capability of GC is a result of its differential interaction with the alkane isomers; unlike branched alkanes, linear alkanes have suitable shapes for the 1D pore and so they can easily transform the framework from closed-phase to open-phase, and be preferentially accommodated.

The bimodality of the interpenetration framework enables us to control the size of the micropores. $\{[\text{Ni}(\text{bpe})_2(\text{N}(\text{CN})_2)](\text{N}(\text{CN})_2)\}_n$ is also an interpenetrating 3D-grid-type framework linking with bpe and the $\text{N}(\text{CN})_2^{2-}$ anion³³. The compound initially contains the coordination-free anion $\text{N}(\text{CN})_2^{2-}$ in the small apertures, which is exchangeable for the smaller N_3^- anion. The exchange of $\text{N}(\text{CN})_2^{2-}$ for N_3^- leads to a dislocation of the positions of the interpenetrating framework, resulting in an increase in the effective porous area in the channels. This alteration of pore size directly affects the gas uptake. The framework containing N_3^- anions can adsorb a larger amount of gas than the original one containing $\text{N}(\text{CN})_2^{2-}$ anions. Such anion insertion can promote a sliding motion of the interpenetration network, and consequently we can tune the pore size to within 0.1 nm.

As in the interdigitating systems mentioned above, some interpenetration systems also show hysteretic sorption using a gate-opening process; they are a good subject of research and new insights about the sorption phenomena of soft porous crystals have been provided by theoretical approaches^{34–36}. The gate-opening-type hysteretic adsorptions are well accounted for by grand canonical Monte Carlo simulations and free energy analysis with a model of a mutually interpenetrating structure of two frameworks, each resembling a jungle gym (JG) with the cubic lattice structure of a benzene-type force field³⁷. In the phenomenon of this system, the antagonism between guest–guest, guest–surface (where the surface is a JG), and JG–JG interactions have vital roles. At the ‘central configuration’, the base point of the free energy, guest molecules cannot be accommodated, as if the gate were ‘closed’. In a low-pressure regime, the free energy increases on the approach of two JGs because of the steric repulsion between the rods of the JG. With increasing pressure, the guest molecules get adsorbed in the framework, resulting in reduction in the free energy of the contact configuration that has the space available for adsorption, and the appearance of a local minimum (Fig. 3a). The calculations demonstrate that the stabilization provided by the guest adsorption drives the structural transition, overcoming the energy cost in creating the adsorption space because of the movement of the host framework; the calculation reproduces the hysteretic profile of adsorption (Fig. 3b).

Various types of interpenetration systems have been designed and synthesized^{26,38–40}. Although these systems may cause loss in porosity, they have the advantage of creating flexibility in the porous structure, and they should be of considerable value in the field of soft porous crystals. Networks can often acquire multiple interpenetrations by the introduction of a long, linear ligand with a square-grid metal cluster like that of Zn_4O and the paddle-wheel Cu_2 dimer. That is, we can enlarge the pore diameter in the open phase or functionalize the pore surface for efficient selectivity of larger target molecules.

Properties arising from the framework's flexibility

Another strategy for making a soft porous crystal is the incorporation of a component with flexibility into the porous framework and thus creating softness throughout the network. For coordination polymers, metal- or ligand-based components that can show reversible rotation, bending and breaking are important for the expansion or shrinkage of porous frameworks. Coordination and hydrogen bonding are useful resources because their bond energies are typically between 10 and 200 kJ mol^{-1} , clearly lower than the covalent or ionic bond whose energies are typically between 200 and 1,000 kJ mol^{-1} (ref. 41). $[\text{Cr}(\text{OH})(\text{bdc})]_n$ (MIL-53(Cr)), is one of the compounds showing pore expansion and contraction triggered by local reorientation of the coordination bond (Fig. 4a). In this compound, as water guest molecules are accommodated the pores actually shrink as the $\text{Cr}-\text{O}(\text{OH})-\text{Cr}$ angle changes from 128° to 124° and the cross-section of the diamond-shaped pore changes from $16.8 \times 13.0 \text{ \AA}^2$ to $19.7 \times 7.9 \text{ \AA}^2$, with a hydrogen bond between the pore wall and

guest⁴². Even for this structural change, there is a small difference in free energy of about 2.5 kJ mol^{-1} between the large and small pore phases, and this low-transition-energy large breathing motion can be used to generate novel or advanced pore functions. As shown in Fig. 4b, the partially hydrated phase of MIL-53 does not show any adsorption uptake for CH_4 even at 20 bar at room temperature, however, it starts to adsorb CO_2 at 10 bar and forms an open phase, resulting from the formation of hydrogen bonds between CO_2 and the host framework⁴³. There have been some attempts to use this breathing property for practical applications⁴⁴. MIL-53(Fe) shows unusually long times for the delivery of the anti-inflammatory drug, Ibuprofen⁴⁵. The flexible swelling framework, which fits with the geometric and energetic characteristics of the drug and therefore enhances the confinement effects, is key to this phenomenon. This type of sorption property would be made useful for a slow-release system for drug-delivery applications by using biocompatible elements. Understanding the kinetic adsorption/desorption process of the dynamic porous system of soft porous crystals is important, and leads to the next step of porous functions.

In conventional porous materials, a multistep adsorption profile comes from the distribution of various porous structures in a robust static framework (type VI isotherm)²⁵. Soft porous crystals show another type of multistep adsorption based on structural transformations that occur in response to guest concentration. $[\text{Co}(1,4\text{-benzenedipyrazolate})]_n$ with guest molecules has square-grid 1D pores with dimensions $10 \times 10 \text{ \AA}^2$ (Fig. 4c)⁴⁶. This compound also has a movable component around Co^{2+} and the pyrazolate ligand; the degassed structure is totally different from the with-guest open phase, although the precise degassed crystal structure has not been elucidated. Importantly, this degassed Co framework adsorbs N_2 , showing five steps from zero to 0.1 bar at 77 K; the desorption profile

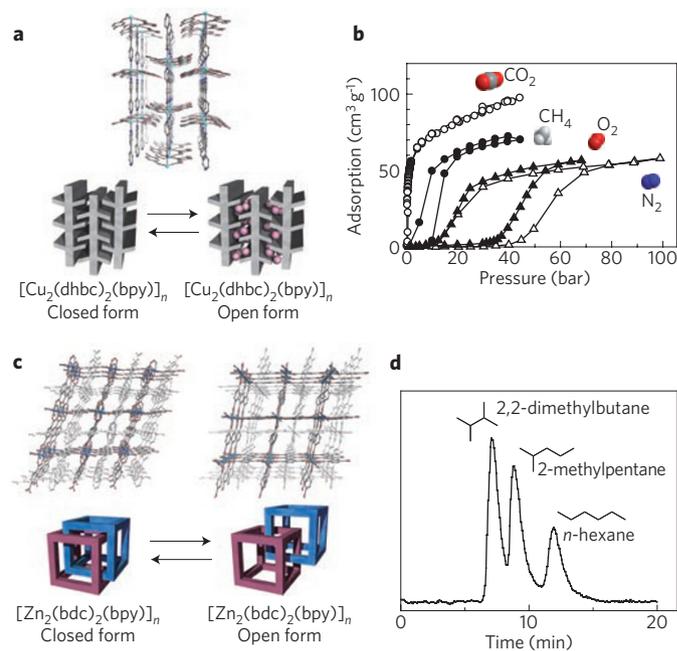


Figure 2 | Reorientation of porous networks for guest separation. **a**, 3D crystal structure of interdigitated framework $[\text{Cu}_2(\text{dhbc})_2(\text{bpy})]_n$ with illustrations of closed and open structures formed via guest sorption processes. **b**, Adsorption isotherms of gases for $[\text{Cu}_2(\text{dhbc})_2(\text{bpy})]_n$ at room temperature. Each gas is adsorbed at a different gate-opening pressure. (Open circles, CO_2 ; filled circles, CH_4 ; filled triangles, O_2 ; open triangles, N_2) **c**, 3D crystal structures and illustrations of the closed and open phases of $[\text{Zn}_2(\text{bdc})_2(\text{bpy})]_n$ (MOF-508). **d**, Chromatograms of alkane mixtures separated on a MOF-508 column: separation of 2,2-dimethylbutane, 2-methylpentane and *n*-hexane.

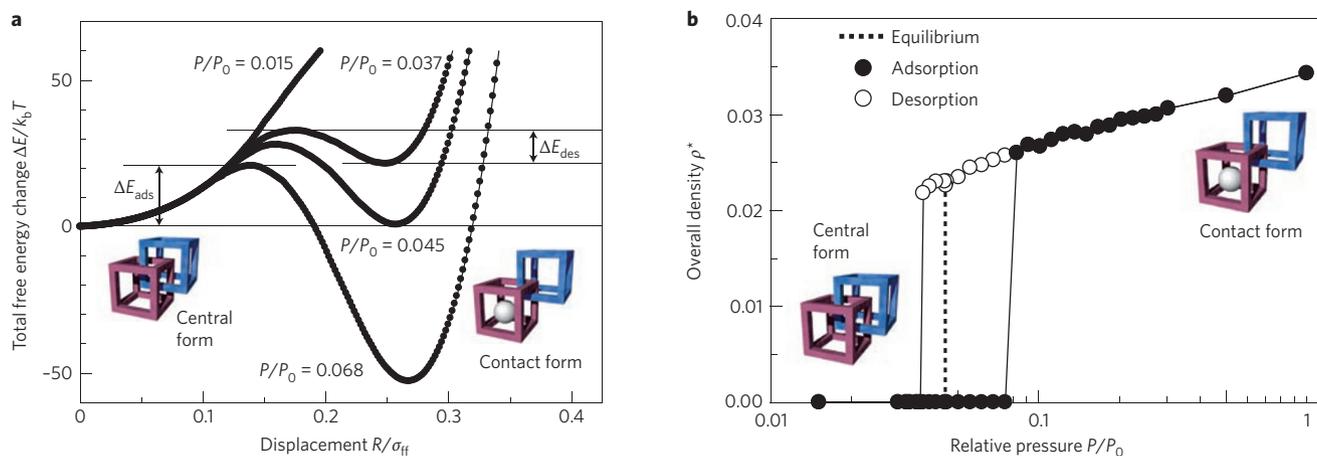


Figure 3 | Theoretical approach for hysteretic sorption by a gate-opening process of the interpenetrating system. **a**, Total free energy profiles of the interpenetrated framework along the displacement of one JG relative to the other. ΔE_{ads} and ΔE_{des} are the free barrier energies (in Joules) for the adsorption and desorption processes; k_b is the Boltzmann constant and T the temperature (in Kelvin); R is the position of one JG relative to the other; σ_{ff} is the Lennard-Jones parameter of the guest molecule (methane, 0.381 nm). The zero point of the free energy is set at the alignment between the centre of the two JGs; at this 'central alignment' guests cannot be accommodated. For a reasonably low pressure, the free energy increases on the approach of two JGs because of the steric repulsion between their rods. The closest position of the two JGs, which is referred to as the "contact configuration", has space available for Lennard-Jones methane adsorption. Thus, the guests get adsorbed in the framework, resulting in reduction in the free energy of the contact configuration and the appearance of a local minimum. **b**, A calculated adsorption isotherm for an interpenetrated framework composed of benzene rods, showing a stepwise uptake of guest molecules at the equilibrium transition pressure of $P/P_0 = 0.045$. The uptake is caused by the structural transition from a central to a contact configuration. The hysteresis loop is obtained assuming a threshold height of the energy barrier of $0.2 k_b T$ per molecule. ρ^* is the number of guest molecules in the available space of the framework.

shows hysteresis (Fig. 4d). This suggests that the adsorption occurs with multiple structural transformations because of the continuous phase transition of this framework. This compound also produces a large hysteretic adsorption curve for H_2 gas with gate-opening pressure (Fig. 4e). Even with a gas that has such little interaction, the compound can transform to another phase; the difference in free energy between the closed and open phases for H_2 is calculated to be very low (3.3 kJ mol^{-1})²⁹. Only a soft porous crystal can demonstrate H_2 hysteresis, and this suggests the potential of such compounds for hydrogen storage via a kinetics-based trapping mechanism.

Reversible bond cleavage and regeneration are also found in coordination bonds, and this contributes to the design of a soft porous framework. The copper pillared-layer-type compound, $[\text{Cu}_2(\text{pzdc})_2(\text{bpy})]_n$ (CPL-2), whose Cu and pzdc sheets are joined by linear bpy ligands, which act as pillars, has 1D micropores with a cross-section of $6 \times 8 \text{ \AA}^2$ (ref. 47). This framework contains a labile coordination moiety around the Cu^{2+} centres. The initial coordination geometry of Cu^{2+} in the sheet is square pyramidal (penta-coordination), and the coordination mode is crucial for softness. As guests are adsorbed, the apical Cu–O bond is cleaved, making the Cu^{2+} square planar (tetra coordinated; Fig. 4f), resulting in a large reduction in pore volume (Fig. 4g). This shrinking behaviour is observed only for specific guests that are suitable fits to the shape of the micropores. In this Cu compound, benzene is strongly bound inside the pores, which can be reversed by reorientation of the surrounding of Cu^{2+} ; the accommodation of benzene is anisotropically determined by X-ray analysis. In other words, this bond on–off-mediated transformation can selectively recognize and capture the guests in a specific manner⁴⁸. In addition to the metal–ligand bonding, a metal–metal interaction has been utilized as another key factor for guest-responsive frameworks. A dispersion-type attractive interaction of Au–Au occurs frequently. $\text{Cu}[\text{Au}(\text{CN})_2]_2$ provides a 2D framework whose Au–Au moiety changes its form to bind a guest organic vapour accompanying a crystal-to-crystal transformation⁴⁹. There are thus various types of softness that can be incorporated into porous frameworks.

Properties arising from the porous area

We have discussed the transformations between open and closed structures of soft porous crystals that give rise to the unique mechanism of separation and storage of gases. These structural changes have mainly been observed by X-ray crystallography and adsorption measurements. In addition to these systems, here we point out the time-dependent dynamics of porous coordination polymers as another motif of soft porous crystals⁵⁰. In porous coordination polymers, high porosity and crystallinity can spatially isolate organic linkers from each other and as a result, each linker can have enough space to allow free motion such as rotation and wobbling. Although the whole porous structure does not change, the dynamic motion of organic linkers has an important role for control of the physical and adsorption properties^{51–53}.

Some framework structures having mobile groups are shown in Fig. 5, with their activation energies listed in Table 1. For example, $[\text{Zn}_4\text{O}(\text{2-Br-bdc})_3]$ (IRMOF-2) has freely rotating 2-bromo-1,4-benzenedicarboxylate rings in the square-grid porous lattice⁵⁴ (Fig. 5b). The arrangement of the rotational group is well-ordered in a 3D scaffold and they can rotate independently in the solid. Because of the dipole moment of the rotational group, the dielectric response is observed at audio frequencies between 80 and 300 K; the rotational energy barrier was estimated to be $7.3 \text{ kcal mol}^{-1}$. The idea of incorporating into porous solids rotational dipole groups that would be responsive to an applied electric field is promising for the development of optically active sensors, or new types of adsorbents that would be controllable by external stimuli. The dynamic behaviour is derived not only from aromatic groups but also from alkyl groups in the framework. $[\text{Cu}(\text{etz})]_n$ (MAF-2) contains small pore apertures with pendant ethyl groups⁵⁵ that have a temperature-dependent dynamic motion, which results in effective pore opening for sorption. We can obtain the energetic aspect of the rotational motion of the framework's building blocks with the aid of theoretical approaches, by exploiting advanced methods such as the *ab initio* force field⁵⁶. Optimized motional mode, frequency and activation energy could be designed for further porous functions.

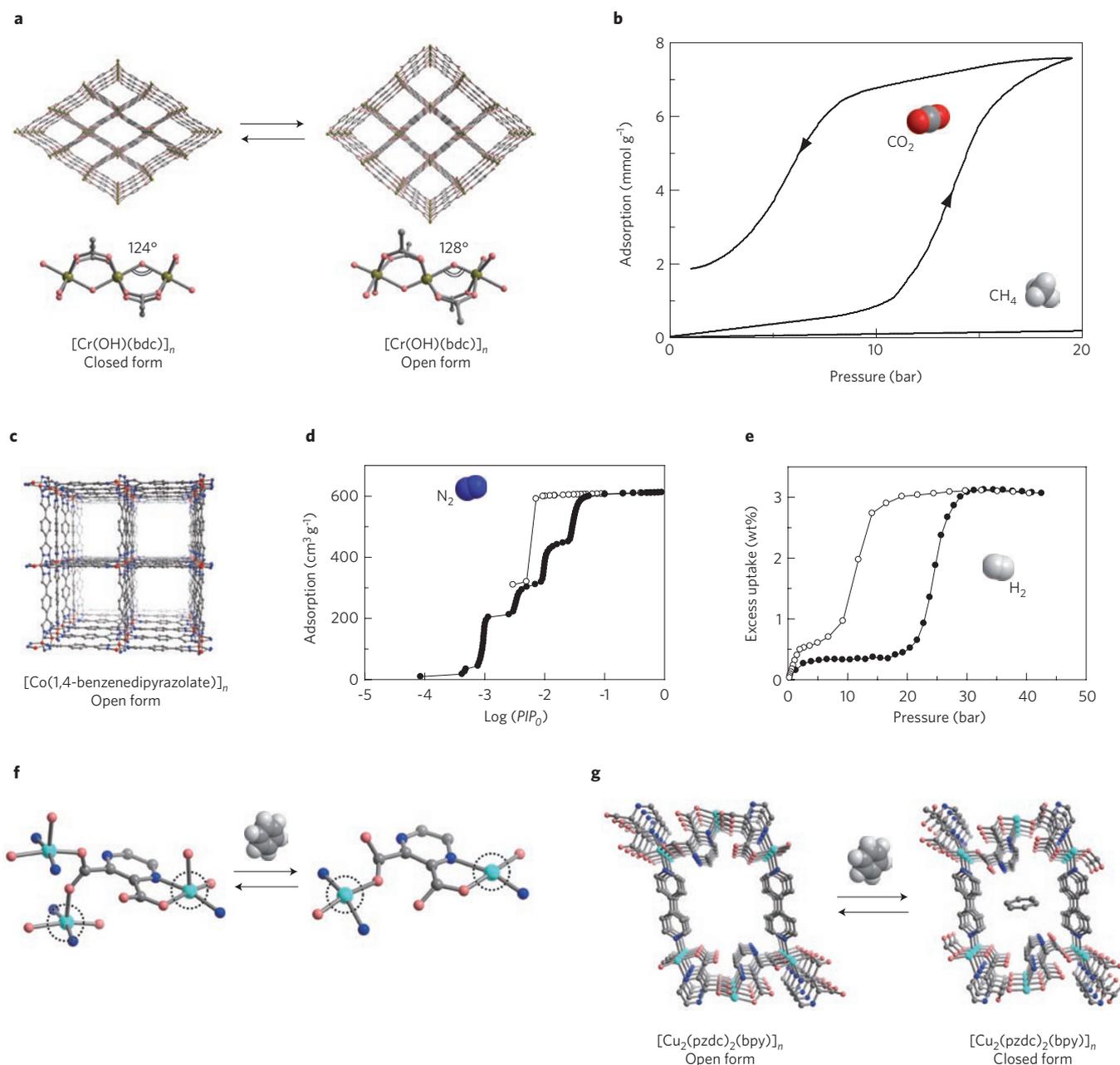


Figure 4 | Unique gas incorporation behaviour triggered by rearrangements of local structure. **a**, Crystal structures of the porous framework and local coordination environment around the Cr^{3+} centre of $[\text{Cr}(\text{OH})(\text{bdc})]_n$ (MIL-53(Cr)) for closed/open forms. **b**, Adsorption isotherms of hydrated MIL-53(Cr) for CO_2 and CH_4 at room temperature. **c**, 3D porous crystal structure of $[\text{Co}(1,4\text{-benzenedipyrzolate})]_n$ and the adsorption isotherms of **d**, N_2 and **e**, H_2 at 77 K. Filled circles are adsorption and open circles desorption. **f**, Coordination environment of Cu (circled) before and after benzene adsorption. The breakage of the apical Cu–O bond in CPL-2 gives rise to efficient host–guest interaction, resulting in the shrinkage of a pore space. **g**, Porous structures of $[\text{Cu}_2(\text{pzdc})_2(\text{bpy})]_n$ (CPL-2) before and after an adsorption of benzene.

Alteration of guest properties by the framework

The dynamic nanospace of soft porous crystals sometimes has a strong effect on the properties of guests; the polymerization of guest molecules is a good example. $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]_n$ (Zn-JAST-1) with 3D JG-like structure consisting of 2D-square-grid layers of $[\text{Zn}(\text{bdc})]_n$ and dabco as pillar ligands shows induced-fit guest accommodation⁵⁷. This guest-responsive transformation produces high adsorption capacity and reaction space for the selective topotactic radical polymerization of *p*-divinylbenzene (that is, a radical polymerization accompanied by the displacement of framework atoms; Fig. 6a,b) unlike the rigid isostructure $[\text{Cu}_2(\text{bdc})_2(\text{dabco})]_n$ (Cu-JAST-1) (ref. 58). The responsive crystalline framework arranges

the guest molecules uniformly in the channel and causes their crystallization. This effect brings the monomers, even the reaction parts, closer forcibly and regioselectively, and is how topotactic selective polymerization can be achieved. This is a representative example of how the flexibility of a channel contributes extensively to the diffusion of monomers. A moderate strength of confinement is required, but not so strong that monomers cannot diffuse to react with others.

Some compounds also show electronic flexibility and remarkable properties based on the coexistence with structural flexibility^{59–64}, as shown in Fig. 3. Treatment of pyrrole with the nano-slits of $\{[\text{Ni}(\text{dmen})_2]_2[\text{Fe}(\text{CN})_6](\text{PhBSO}_3)_n\}$ produces polypyrrole via oxidative polymerization⁶⁵. In this reaction, pyrrole monomers

are intercalated into the nanoslits, which results in expansion of the interlayers⁶⁶. The monomers are converted to polypyrrole, as a consequence of the effective host–guest redox reaction. During this process, the reduction in Fe³⁺ ions led to the release of the pillar counter anions to compensate the charges, accompanied by shrinkage of the intersheet distance, but with the whole network remaining intact. In this system, it is of interest that isolation of polypyrrole from the host framework allowed the formation of stacked sheet polymer objects whose orientation and morphology were directly related to the original coordination polymer template.

Guest-induced properties of the framework

The dynamic space of soft porous crystals is not just a container with unique guest accommodation. The strong interaction between the framework and guest molecules can create various states and multiple properties of the framework.

Magnetic properties are defined and dominated by the structure, on which structural transformation has a profound effect. In other words, soft porous crystals with a reversible crystalline transition could be a new platform of pluralistic magnetic properties. $\{[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4] \cdot (\text{EtOH})\}_n$ consists of the double interpenetration of 2D rhombic grids that are constructed by the linkage of Fe²⁺ centres by azpy units⁶⁷. This compound shows the spin crossover that is influenced by the reversible exchange of adsorbed guest molecules with considerable changes in the framework geometry. Following this compound, several others with guest-dependent magnetic properties have been synthesized and reported, however, there is a mismatch problem between the temperature regimes of guest adsorption and magnetic transition^{68–70}, that is, there is no overlap and so it has not been possible to control these processes at the same temperature.

The 3D breathing framework of $\{\text{Fe}(\text{pyz})[\text{Pt}(\text{CN})_4]\}_n$ (ref. 71) presents bidirectional chemo-switching of the spin state and the memory effect at room temperature, which is reversibly induced by coupling with accommodated guests⁷² (Fig. 6c,d). This framework normally shows expansion with guest accommodation, which results in a framework with a larger cell volume for which the high spin state is stabilized. In the case of guests with high affinity for the pore surface, which reduces the degree of freedom of surface molecular motion, the framework shrinks to accommodate and/or

complex with the guest, which results in a framework with a smaller cell volume and for which the low spin state of is stabilized. Each state (high or low spin) is maintained at room temperature, even if the guests are removed. This phenomenon is likely to be based on the cooperativity of the crystalline state transformation of soft porous crystals. The isostructural Ni complex also shows similar phenomena⁷³. By considering that spin crossover properties are also greatly associated with optical stimulus, it is possible to prepare a new material with multistability that responds to chemical guests and physical stimuli⁷⁴.

Conclusion and outlook

Soft porous crystals are materials with the potential to produce properties that are not observed in conventional materials. In the previous sections, on the concept of flexibility, we focused on the structures and properties of porous coordination polymers, which are representative of soft porous crystals. The functions of soft porous crystals are not necessarily restricted to structural properties, but also involve electric and magnetic properties as shown in Fig. 7. The electronic states definitely correlate with spatial structures, both of which provide a variety of chemical or physical stimulus-responsive properties. Understanding and control of the dynamic phenomena occurring in flexible frameworks and their pores could lead to unique properties and provide a significant development in the fields of chemistry and physics. Herein we give a future view of the chemistry and applications of soft porous crystals.

Structural transformations from a phase with guests to one without guests and *vice versa* create hysteretic isotherms (Fig. 7a). Understanding the processes enables us to control the hysteretic properties for adsorption/desorption. Tuning of hysteresis behaviour could ideally provide materials that are suitable for specific situations; the narrow hysteresis width around ambient pressure is ideal for use in fuel tanks, whereas a broader one would be useful for memory systems based on chemicals. Moreover, these are also applicable for controlled release or delivery processes with responsive properties⁷⁵. This could also be a way to external stimulus-responsive memory devices (temperature, photons, electric or magnetic field).

Pores in soft porous crystals are used not only for the inclusion of guests, but also for the rotation and/or translation of

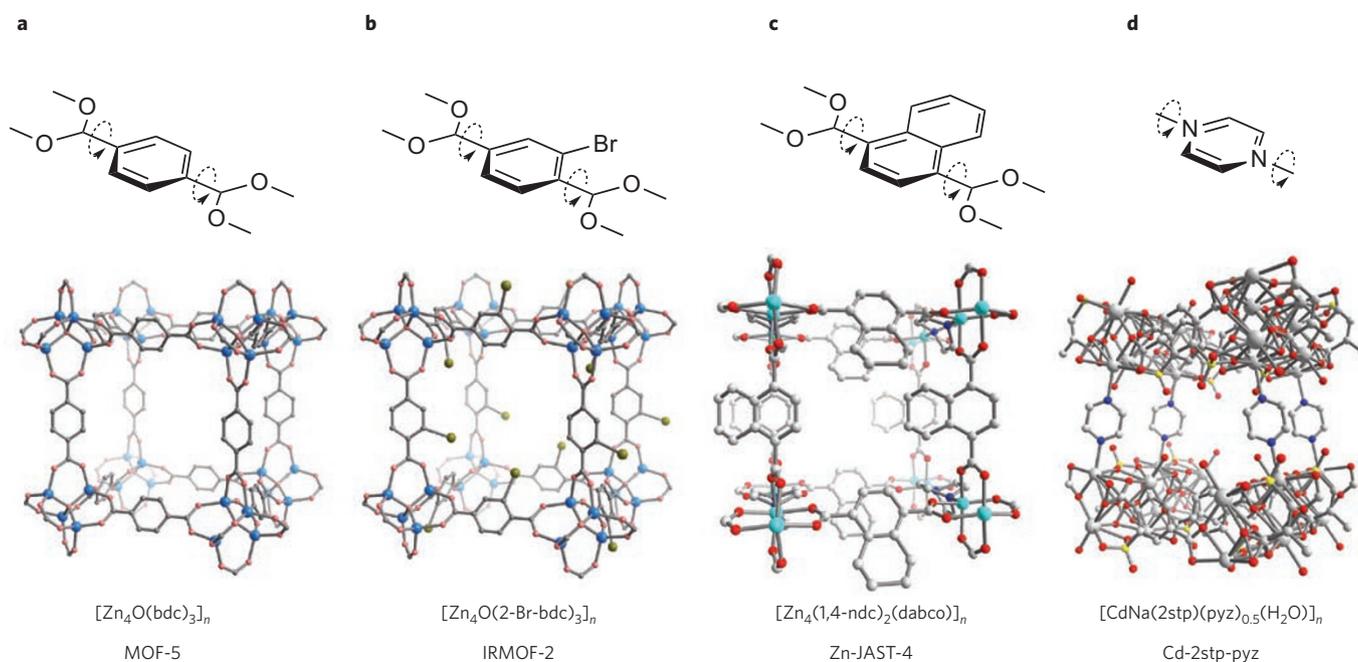


Figure 5 | Dynamic motions of porous coordination polymers. a–d, Illustrations of mobile groups and partial crystal structures of several compounds.

Table 1 | List of activation energy, frequency and mode of rotational motion for the four compounds shown in Fig. 5.

	Activation energy (kcal mol ⁻¹)	Frequency (MHz)	Rotational mode
MOF-5 (refs 51,54)	11.3 ± 2, 14–16	0.001 at 300 K	2 sites flip
IRMOF-2 (ref. 52)	7.3	-	-
Zn-JAST-4 (ref. 50)	12.7	50 at 223 K	4 sites flip
Cd-2stp-pyz (ref. 50)	1.8	0.1 at 293 K	4 sites flip

frameworks (Fig. 7b). Cooperative dynamics can also be achieved in the motion of each component of the framework. We can arrange each component at a suitable interval in space; then, individual motion of components such as rotation, will show cooperativity by achieving optimal interaction between them. In a Cu pillared-layer framework, the pyrazine pillars engage in a channel to give rise to rotation for the efficient confinement of acetylene⁷⁶. This kind of dynamic order–disorder system is also associated with the dielectric properties of the crystals^{34,77}. The post-synthetic modification approach is also powerful for incorporation of mobile moieties on the porous scaffold⁷⁸; this type of coherent motion would open new dimensions for physical stimulus-responsive systems, not only for optical switching devices, but also for dielectric materials.

Strong interaction between guests and the framework produces a variety of properties, such as electrical conductivity, luminescence and elasticity (Fig. 7c). Key elements are electron- or charge-transfer interactions of guests and surfaces by which conducting electrons or magnetic spins are generated on either or both sides, affording unique physical properties. Another case is the role of the framework by which guest molecules are confined in proximity to each other, and are aligned either in 1D or 2D. In particular, this idea is useful for paramagnetic (O₂, NO) or dipolar (CO, NO, SO₂) gas molecules⁷⁹. If polar or magnetic molecules are used in soft porous crystals, their unique dielectric or magnetic properties seem to be responsive to external stimuli, which affect the framework directly.

Control of open/closed phases of porous framework not by guest sorption processes, but by other external stimuli such as light, heat and charge-transfer is attractive for guest storage and release (Fig. 7d). We can store target molecules as long as the framework is open and we can release them by closing the system using external stimuli. Likewise, the on-demand guest transport inside the channels is feasible because the shrunk channels would be clogged by the adsorbed guests, which could then hardly move in the pores; once the channels expand, the guests start to diffuse smoothly and show high transportation within the solids. Several guests in porous coordination polymers have larger diffusion rates than in zeolites or metal oxides⁸⁰ and the control of these properties makes them suitable for practical applications.

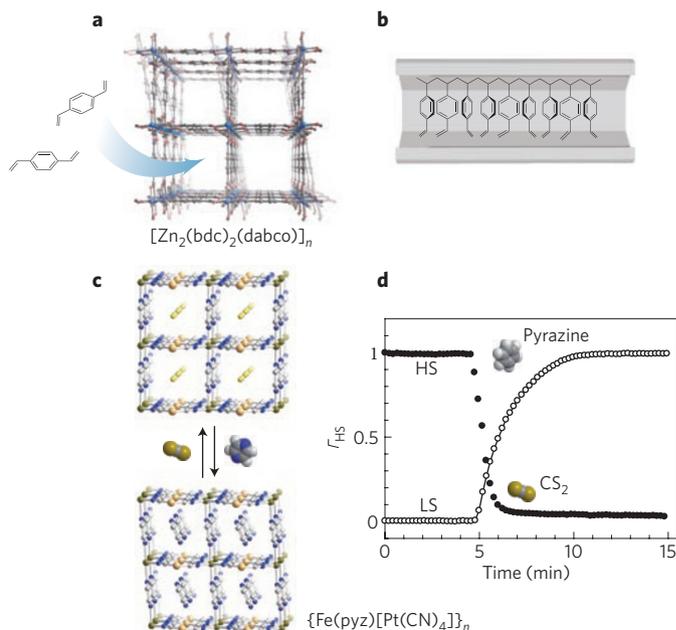
Structural transformations might also enable energy-related properties. With conventional porous materials, the energy generated on adsorption of guests is usually dissipated into the surrounding environment. In the case of soft porous crystals, however, part of this heat of adsorption can be absorbed by structural transformation, resulting, for instance, in distortion of the coordination geometry, rotational rearrangement of the organic moiety, and so on (Fig. 7e). In this sense, soft porous crystals could be effective adsorbents: they can use the energy stored in the framework to release guests, which means that they need less external energy than conventional absorbents.

Thermal conductivity is also a fundamental property of solid-state materials, in which it is governed by two mechanisms: phonon propagation and electron mobility. Generally, coordination

polymers are electric insulators, which means that their thermal conductivity is due to phonon propagation, for which the hardness or softness of the material is critical. Control of the framework's softness would therefore have a significant effect on heat transfer, which means that the transformation from a soft framework to a rigid framework using guest accommodation could create a new mechanism for the control of heat transfer⁸¹.

Conventional molecular sieving is attributed to the recognition of size and shape, that is, it has a spatial-dimension-governing system (classical channel). Rigid pore materials are classified in this category, where a smooth channel with a certain cross-section fulfils this condition. If the channel has a corrugated shape, such as an alternative arrangement of a large and a small cross-section, or non-uniform surface functionalities, the guest–surface interaction could show a rigorous recognition of guests (advanced channel). Soft porous crystals provide us with a dynamically responsive channel for guests because the local frame distortion occurs by an induced-fit mechanism⁸². This peristaltic motion induces more precise recognition of guests (evolving channel)⁸³. This system is a new approach for controlling the transfer of material in a solid — an avenue for superb molecular separation.

As shown in Fig. 7f, the controllable nanospace of soft porous crystals is a suitable candidate for an accurately controlled reaction field. Efficient reactant-accumulating pores in soft porous crystals work by overcoming the sacrifice of entropy. Moreover, the dynamic guest accommodation of soft porous crystals would enable the arrangement and orientation of the guest molecules uniformly, and even for gas molecules this is feasible. This flexible nature would be essential for producing superb molecular recognition and efficient conversion as in enzymes, which cannot be realized in conventional

**Figure 6 | Flexible pore spaces for polymerization and magnetic switching.**

a, Schematic representation of the topotactic radical polymerization reaction of *p*-divinylbenzene inside the one-dimensional channel of [Zn₂(bdc)₂(dabco)]_n (Zn-JAST-1), which has the flexible paddle-wheel Zn²⁺ dimer. **b**, Expected polymer structure of *p*-divinylbenzene inside the Zn-JAST-1. **c**, Alteration of the porous structure of {Fe(pyz)[Pt(CN)₄]}_n by exchange of guest molecules of CS₂ and pyrazine. **d**, The high-spin (HS) state of {Fe(pyz)[Pt(CN)₄]}_n can be converted to low-spin (LS) state by insertion of CS₂ at 298 K. Low-spin to high-spin can be achieved by accommodation of several guests. *T*_{HS} is the relative existence of high-spin state in the system.

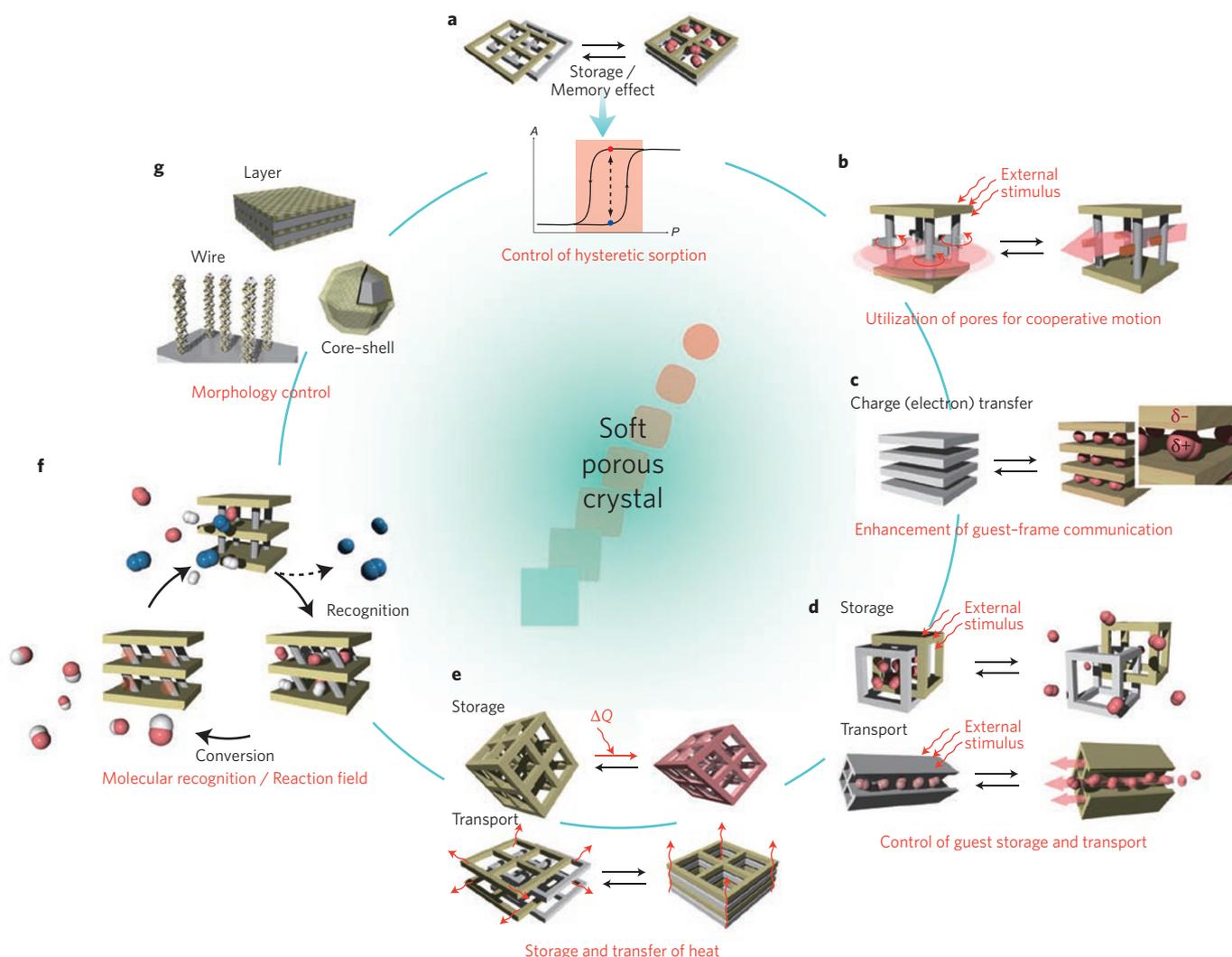


Figure 7 | Perspectives in functions of soft porous crystals with various properties. **a**, Control by external stimuli of hysteretic behaviour suitable for a storage/release system and a memory device. **b**, Utilization of the pore space for the cooperative motion manipulation of movable modules. **c**, Strong host-guest interaction leading to drastic change in physical properties caused by their electronic correlation. **d**, Control of the guest mobility and diffusivity by structural transformation in response to external stimuli. **e**, Transformable framework having the capability to act as a heat pump and a switcher of heat conduction. ΔQ is heat adsorbed; red arrows in the bottom diagram represent possible phonon paths. **f**, Control of nanospace for the target reaction with high recognition and conversion, without the encapsulation of product. **g**, Morphology control and combined architecture of crystals.

catalysts, that is, the reaction mechanism of the living system could be reproduced in an artificial system of soft porous crystals.

As soft porous crystals show expansion or shrinkage of crystal dimensions, their mechanical strength is important for maintaining their crystal integrity. In this sense, a 'proper' domain size (that is, one that is retained or recovered on repeated shrinking/expansion) could be an indication of the persistence of the structure. Therefore, development of the crystal size control is necessary^{84–86} (Fig. 7g). On the other hand, thin layer, nanowire or membrane-like crystal morphology are inevitably required for the creation of multifunctional features, such as catalyst, photo- or other physical properties^{87–89}. In addition, the combined technologies are available for core-shell crystals and multilayer crystals. The recent results for the so-called PCP on PCP (or MOF on MOF) are among promising examples of such combined technologies⁹⁰.

Glossary of compound and ligand abbreviations

CPL = coordination polymer with pillared-layer structure
 IRMOF = isoreticular metal-organic framework
 JAST = jungle-gym-analogous structure

MAF = metal azolate framework
 MIL = material of Institut Lavoisier
 MOF = metal-organic framework
 azpy = 4-(phenylazo)pyridine
 bdc = 1,4-benzenedicarboxylate
 bpe = 1,2-bipyridylethene
 bpy = 4,4'-bipyridine
 dabco = 1,4-diazabicyclo[2.2.2]octane
 dhbc = 2,5-dihydroxybenzoate
 dmen = 1,1-dimethylethylenediamine
 etz = 3,5-diethylethylenediamine
 1,4-ndc = 1,4-naphthalenedicarboxylate
 PhBSO₃⁻ = *p*-phenylbenzenesulfonate
 pyz = pyrazine
 2stp = 2-sulfonilyterephthalate

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