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Dynamic behaviours of a rationally prepared flexible MOF by postsynthetic modification of ligand struts†

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Through postsynthetic modification of ligand struts, controllable conversion of a Zr MOF between rigidity and flexibility is realized. The rationally prepared flexible MOF exhibits interesting dynamic behaviours, such as reversible structural deformation, vapour sorption hysteresis and unexpected adsorption of bulky guest molecules.

Large amplitude flexibility is one of the most intriguing advantages in the field of metal–organic framework (MOF) or porous coordination polymer (PCP) chemistry.[1] As proposed by Kitagawa and co-workers,[2] the third generation MOFs are defined as flexible MOFs or soft porous crystals, which can reversibly transform their structures in response to chemical guests and physical stimuli.[3] Such features of a host matrix may provide enzyme-like specificity, producing intelligent materials that have potential applications in guest storage, separation, release and sensing.[1–3] Compared with the well-studied rigid MOFs,[4,5] the rational construction of flexible third-generation MOFs is relatively more difficult. To date, only a few empirical rules involving deformation at the metal node have been proposed by Ferey[6] and Kitagawa *et al.*,[7] and the successful introduction of flexible factors into MOFs and the realization of the anticipated dynamic properties are somewhat random. An alternative approach for constructing flexible MOFs is to straightforwardly incorporate flexible ligands during the synthesis process, which has been summarized and reviewed by Fischer,[1b] Cao[1c] and Jenkins *et al.*[1d] Nevertheless, only limited success has been achieved using this strategy due to several unavoidable problems. First, flexible organic components tend to aggregate closely to form thermodynamically favoured condensed structures without the necessary flexibility. Second, the condensed structures could hinder the interior delivery of guest molecules, particularly bulky molecules, which limits the practical applications of flexible MOFs. Finally, the unfixed configuration of the flexible linkers usually leads to an undesirable and unpredictable framework topology. Therefore, the development of new strategies to rationally construct flexible MOFs is highly required.

Recently, postsynthetic modification (PSM) has been demonstrated as an attractive route for functionalization of MOFs.[8] Although the most PSM occurs on pendant moieties,[9] there have been several examples where PSM was carried out on ligand struts and resulted in a geometrical change of the linker.[10] For instance, Bauer *et al.* presented a facile conversion of the integral alkene unit in a Zn-MOF into a dibromoethane moiety by bromination, but no structural information on the PSM process could be reported.[10a] Forgan *et al.* modified a series of UiO-type MOFs containing integral unsaturated alkene and alkyne units using halogenation, and fully characterized them by single-crystal structural analyses.[10b–d] Although nanoindentation measurements showed that bromination resulted in a reduced elastic modulus,[10b] the dynamic behaviours were not reported in these cases. Inspired by these results, we expect that postsynthetic bromination of integral alkene moieties to generate rotatable C–C single bonds may endow ligand struts with great flexibility, and be capable of further changing the dynamic behaviours of the whole framework.

In this work, the controllable conversion of a UiO-type MOF between $[Zr_6O_4(OH)_4(L^1)_6]_n$ (**1**, L^1 = 4,4′-stilbenedicarboxylate) and $[Zr_6O_4(OH)_4(L^2)_6]_n$ (**2**, L^2 = meso-4,4′-(1,2-dibromoethane-1,2-diyl)dibenzoate) was realized by postsynthetic bromination and debromination[11,12] of ligand struts. Different from rigid **1**, brominated **2** exhibits a series of interesting dynamic behaviours. As demonstrated by X-ray diffraction (XRD) and solid-state ^{13}C NMR, structural deformation of **2** between single-crystallinity and non-crystallinity is solvent-triggered and completely reversible. The vapour sorption isotherm of desolvated **2** shows a marked hysteresis loop, displaying the flexible nature of the debrominated material. More interestingly, **2** can readily encapsulate a series of bulky guest molecules including porphyrin and phthalocyanine derivatives, chiral phosphoric acids and trinuclear gold(I) compounds that are much larger than the window size. Theoretical

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modeling shows that guest molecules can be accommodated in the octahedral cage of **2**. Furthermore, by heating in the presence of DMF or trimethylphosphine, **2** can be readily debrominated and converted back to **1**, which also provides a new strategy to immobilize functional molecules within the host matrix.

High quality cuboctahedron-shaped single crystals of **1** suitable for X-ray diffraction (XRD) studies were obtained by treating L^1, $ZrCl_4$, and benzoic and trifluoroacetic acid in DMF at 120 °C for 3 days. **1** was suspended in $CHCl_3$ with excess Br_2 and left to stand in the dark at 40 °C for 48 h to afford brominated **2**, which remained intact and transparent. The almost quantitative chemical transformation was proven by ^{1}H NMR, Raman and IR spectroscopy (see ESI†). When crystal **2** was sealed with solvents in a glass tube or exchanged with high boiling-point solvents such as DMF and DEF, full structural characterization could be achieved by single-crystal XRD, as has been reported by Forgan et al.[10c] Compared with **1**, the atoms in L^2 of **2** have much larger thermal parameters according to the single-crystal structure,[10b] implying a more versatile configuration of linkers. Taking the changeable carbon–carbon single bond in L^2 into account, the whole framework of **2** is expected to be endowed with great flexibility and potential structural deformation properties.

Although crystals of **2** became opaque when kept in air at room temperature for several minutes, the crystal shape and faces were retained without any cracking. Because single-crystal and powder XRD of desolvated **2** does not show any diffraction, non-crystalline **2** with a collapsed phase is thus denoted as **2-cp** hereafter. Interestingly, **2-cp** recovers its original crystallinity after being immersed in solvents, and this crystal deformation/recovery process with DMF removal/readsorption can be repeated no fewer than eight times, indicating a high degree of reversibility[13] (Fig. 1a). Notably, the rate of recovery is highly dependent on the nature of the solvents. As shown in Fig. 1b and c, the structure can be completely recovered in DMF within twenty minutes, while in mesitylene a long recovery time of more than four hours is required. This solvent-triggered dynamic behaviour suggests that **2** underwent a reversible phase transition between crystallinity and non-crystallinity (Scheme 1). As pointed out by Kitagawa *et al.*[2a] this non-crystallinity can be described as "imperfect crystallinity", which does not mean that the material is amorphous, just that long-range ordering of the framework is lost, without the collapse of the polymer network.

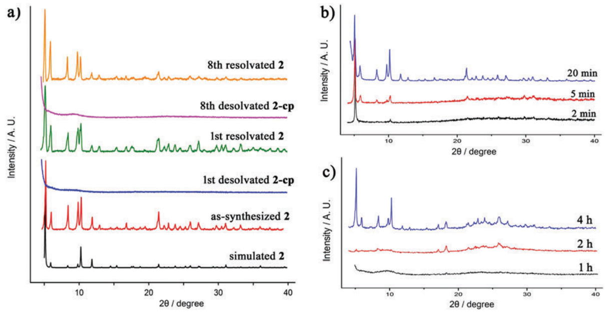
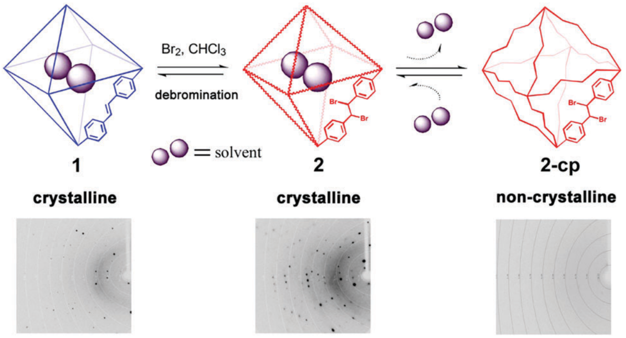


Fig. 1 (a) Powder XRD of **2** in the crystal deformation/recovery process. Structural recovery of **2-cp** in (b) DMF and (c) mesitylene.



Scheme 1 Reversible structural transition of **1**, **2** and **2-cp**.

The flexibility of **2** was also proven using vapour sorption measurements. As shown in Fig. 2a, the sorption isotherms of **2-cp** show a marked hysteresis loop between the adsorption and desorption branches. On the contrary, the sorption of **1** exhibits reversible isotherms without hysteresis under the same conditions (Fig. S13 in the ESI†). To understand the nature of the framework flexibility, the environmental change of the linkers in **2** and **2-cp** was probed by solid-state ^{13}C NMR. As shown in Fig. 2b, the sharp signals for solvated **2** are well separated, indicating a regular structure and uniform environment. In the **2-cp** spectrum, however, much broader resonances are found, which can be ascribed to the loss of long-range ordering in the framework upon solvent removal.[13] The sharp signals were re-obtained when **2-cp** was immersed in DMF solution, in accordance with the fine crystallinity observed by XRD measurements.

More interestingly, flexible **2** exhibits unexpected adsorption behaviour toward bulky guest molecules that is entirely different

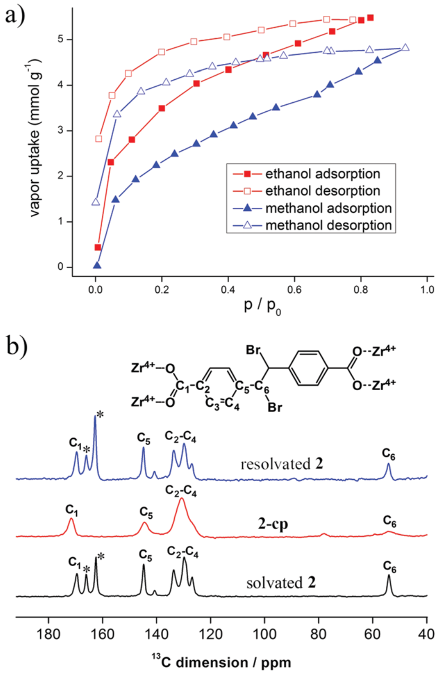
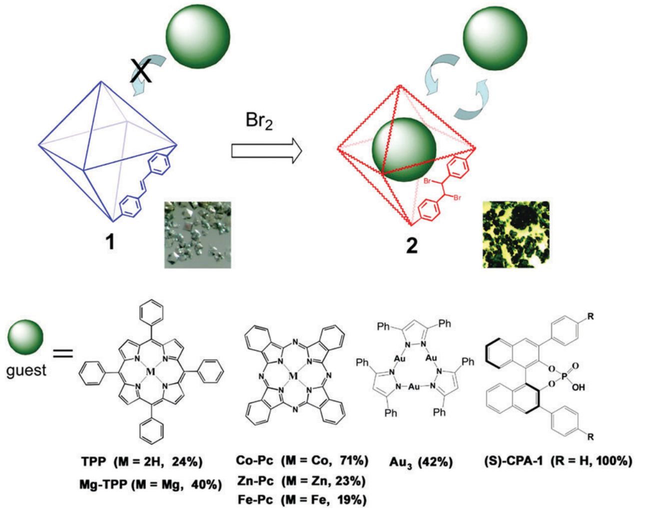


Fig. 2 (a) Vapor sorption of **2-cp** at room temperature. (b) Solid-state ^{13}C NMR spectra of **2**, **2-cp** and resolvated **2**. The asterisks mark the signals of the DMF solvent.

from the behaviour of rigid **1**. Because of its characteristic colour, tetraphenylporphyrin (TPP) was chosen as the adsorbate to conveniently visualize the accessibility of the interior porosity of **1** and **2**. When concentrated TPP solution in chloroform was added, **1** retained its colourless crystallinity without any UV-vis absorption. This may be ascribed to the large size of the TPP molecules ($\sim$16 Å), which exceeds the diameter of the framework windows ($\sim$10 Å). In striking contrast to **1**, **2** can be rapidly dyed by the macrocyclic TPP molecules and retains its transparent appearance. After carefully washing with pure chloroform, the colour of **2** was still retained, suggesting that the TPP molecules were not adsorbed onto the surface of the crystals. Interestingly, the adsorbed TPP molecules in **2** were released quite slowly in pure chloroform at ambient temperature, with only 3.12% TPP desorption after 170 hours (Fig. S23 in the ESI†). In fact, some MOFs with relatively high flexibility can exhibit a so-called "gate opening" effect,[14] allowing encapsulation of guest molecules that are obviously larger than the opening of the interior cavities. Therefore, we speculate that this unexpected sorption of **2** is derived from the great flexibility of this brominated MOF. To develop a better idea of the likely position of TPP in the interior cavities of **2**, we optimized the host–guest structure at the semi-empirical PM6 level.[15] The modeling result shows that TPP molecules can only be accommodated in the octahedral cages, and not the small tetrahedral ones (Fig. S24 in the ESI†). Therefore, this host–guest compound can be represented as TPP$\subset$**2**, and is a Class III hybrid PCP as proposed by Kitagawa and co-workers.[16] Using UV-vis absorption to determine the concentration of TPP, the porphyrin loading into the octahedral cages was estimated to be 24%. In addition, a series of bulky guest molecules such as magnesium tetraphenylporphyrin (Mg-TPP), metallophthalocyanine (M–Pc, M = Co, Zn, Fe), trinuclear gold(I) compounds (**Au$_3$**) and chiral phosphoric acids ((*S*)-CPA-1 and (*S*)-CPA-2) can be encapsulated by flexible **2** to form guest$\subset$**2** complexes, but no perceptible adsorption was observed for rigid **1** (ESI†). The guest loading ratios per octahedral cage in guest$\subset$**2** estimated by ^{1}H-NMR, UV-vis absorption and elemental analysis ranged from moderate to quantitative (Scheme 2 and ESI†).

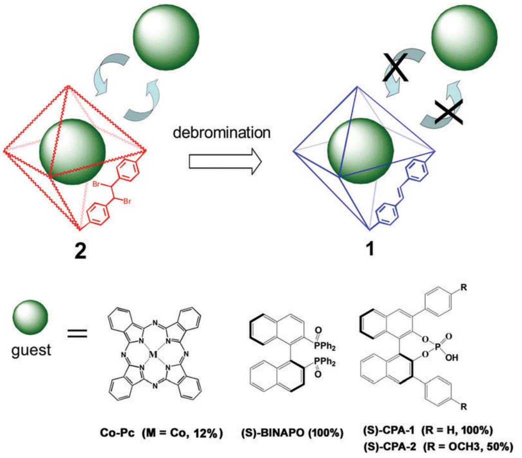
According to the literature, the dibromoethane moiety can be debrominated back to an alkene in the presence of DMF[11] or phosphine,[12] and we thus attempted to convert **2** back to **1** under similar conditions. After 12 hours at 80 °C in DMF, the obtained crystals were characterized by powder XRD, ^{1}H-NMR, Raman, IR, and BET, confirming the successful re-formation of the rigid porous **1′** (ESI†). Systematic investigations demonstrate that the debromination of **2** can also smoothly proceed in diluted trimethylphosphine solution under mild conditions at 40 °C within one day. Consequently, we realized reversible crystal-to-crystal conversion between rigid **1** and flexible **2** *via* two simple PSM reactions, namely bromine addition and elimination (Scheme 1).



Scheme 2 Adsorption behaviour of **1** and **2** toward bulky guest molecules. The guest loading ratios per octahedral cage are shown in brackets.

Furthermore, debromination of **2** in the presence of the above-mentioned guest molecules was investigated in order to immobilize them within the interior cavities. Fortunately, Co–Pc, (*S*)-CPA-1, (*S*)-CPA-2 and BINAPO[17] were proven to be trapped in the cavities even after complete debromination to afford guest$\subset$**1**, as characterized by powder XRD, UV-vis absorption and ^{1}H NMR (ESI,† and Scheme 3). Further purification of guest$\subset$**1** by Soxhlet extraction showed that the encapsulated guest molecules can be efficiently immobilized without any leaching, which is probably due to the rigid small openings of the interior cavities in guest$\subset$**1**. Notably, the circular dichroism signal of the digested (*S*)-CPA-1$\subset$**1** solution is consistent with that of pure (*S*)-CPA-1, which is known to be a highly effective organocatalyst (Fig. S29 in ESI†), and thus the further application of (*S*)-CPA-1$\subset$**1** as a heterogeneous catalyst in asymmetric synthesis is promising.

In conclusion, through postsynthetic modification of ligand struts, we provide a new protocol for controllable conversion between rigid second- and flexible third-generation MOFs. After bromination of the alkene units, the modified MOF **2** exhibits a series of interesting dynamic behaviours completely different from those of the parent rigid MOF **1**, such as reversible structural deformation between single-crystallinity and non-crystallinity, vapour sorption hysteresis and unexpected adsorption of bulky guest molecules that are much larger than the window size. Reversely, **2** can be readily



Scheme 3 Immobilization of bulky guest molecules *via* debromination. The guest loading ratios per octahedral cage are shown in brackets.

debrominated and converted back to **1**. During the debromination process, some functional guest molecules can be trapped within the interior cavities to form guest⊂**1**, which provides a new strategy to immobilize functional molecules within the host matrix. Future work will be directed towards the rational synthesis of more sophisticated flexible MOFs with enzyme-like specificity using this functionalization strategy.

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