Metal–Organic Frameworks

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Flexibility in a Metal–Organic Framework Material Controlled by Weak Dispersion Forces: The Bistability of MIL-53(Al)**

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Porous metal–organic frameworks (MOFs) display a tremendous range of crystal structures,[1] rich host–guest chemistry, and potential for major impact in adsorption and separation technologies[2] and catalysis.[3] A growing sub-class of "soft" MOFs behave in a remarkable guest-responsive fashion upon gas or solvent adsorption/desorption and have gained considerable attention, exhibiting a wide range of structural transitions[4,5] and the topic has been the subject of a recent review.[6] Here, we focus on the experimentally well-documented MIL-53(Al) material[6] known for its reversible switching between a large pore (**lp**) and a narrow pore (**np**) form upon gas or solvent adsorption. Interestingly, Liu et al.[7] have recently reported the occurrence of the **lp** to **np** transition *without* a guest molecule, establishing the intrinsic bistable behavior of the MIL-53(Al) host. While previous simulation studies[8] have examined the role of guest molecules in the **lp** to **np** transition, the driving force for the formation of the guest-free **np** structure has yet to be elucidated. More generally, the question of the origin of the intrinsic bistability of this topical MOF remains open. Here we show that dispersive interactions cause the **np** structure to stabilize at low temperature and entropy drives the structural transition to the **lp** phase.

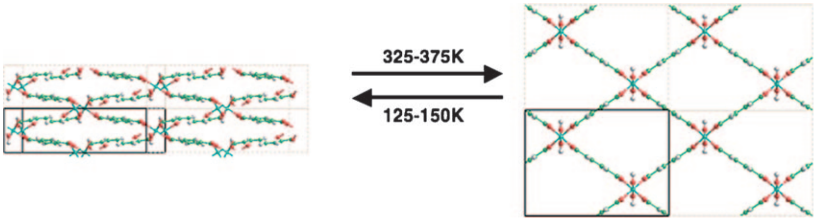

Figure 1. The remarkable expansion of MIL-53(Al) which undergoes a volume change from a narrow pore structure with a volume of 864 Å^3 (left) to a large pore structure with volume 1419 Å^3 (right) between 325 and 375 K. Color code: cyan Al, red O, white H, green C.

Figure 1 depicts the **np** and **lp** MIL-53(Al) structures: between 325 K and 375 K a marked transition occurs where the unit cell volume nearly doubles from 864 Å^3 in the **np** structure to 1419 Å^3 in the **lp** structure. It has been suggested that the driving force for this transition is provided by low energy phonon modes[7] and we speculate that dispersion interactions, potentially emanating from π–π stacking of the phenyl ligands may be important. Density functional theory (DFT) offers the possibility of probing the structure–energy relationship. However, previously reported DFT[7] and force-field[8] studies have been unable to stabilize the **np** structure. The **np** structure opens up on relaxation to give the **lp** form. A suspicion is that dispersive interactions, which are absent from "standard" GGA functionals used for DFT (e.g. leading to the exfoliation of graphite into unconnected sheets), may be key to understanding the bistability of this material. Here, we examine two complementary approaches to explore the role of dispersive effects within the DFT regime: 1) An efficient non-local functional,[9] vdW-DF, where dispersion is calculated self-consistently and depends on the unique electron density on each atom. 2) Dispersive interactions that depend on empirical $-C_6r^{-6}$ terms, the DFT-D method[10] and its solid-specific reparameterization.[11] Further details of the methods and settings used in this work are presented in the Supporting Information.

In Table 1, we present a summary of our results. In keeping with previous work, with a standard GGA functional the **np** structure yields no local minimum and the structure opens up to give the **lp** form. Furthermore, when the atomic

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Table 1: Comparison of **np** and **lp** MIL-53(Al) structures and energies calculated using various DFT methods.[a]

Technique	**np** Volume	**lp** Volume	ΔE (**np**−**lp**)	ΔD (**np**−**lp**)
Experiment[7]	863.9	1419.0	–	–
PBE[b]	–	1475.2	–	–
PBE//exp[b]	863.9	1419.0	+5.113	–
PBE//exp[c]	863.9	1419.0	+4.527	–
vdW-DF[c]	860.5	1473.4	−4.296	−13.912
PBE-D[b]	845.3	1455.4	−2.318	−8.982
B3LYP-D[b]	866.1	1429.6	−2.485	−10.988
B3LYP-D*[b]	879.6	1445.7	−2.018	−9.956
vdW-DF//cyc[c]	1072.6	1317.6	−1.218	−6.624

[a] Volumes refer to the crystallographic unit cell and are in Å^3. ΔE is the relative enthalpy and ΔD the difference in dispersion energy between **np** and **lp** phases, in kcal mol^{-1} per Al center. PBE//exp refers to PBE geometry optimization at experimental lattice parameters; vdW-DF, PBE-D, B3LYP-D and B3LYP-D* represent dispersion corrected functionals and vdW-DF//cyc indicates cyclohexane-substituted MIL-53 structures. [b] Calculations using CRYSTAL.[13] [c] Calculations using SIESTA.[14]

positions were optimized (neglecting dispersion) and with cell parameters constrained to the experimentally determined values,[7] the **lp** structure is more stable than **np**. This is in conflict with experiment where **np** is the low-temperature phase. By contrast, all calculations in which dispersion is included yield stable minima for both the **lp** and **np** forms in close agreement with the recent experimental structural data.[7] Moreover, when dispersion is included, the **np** form is more stable than the **lp** structure, reproducing the known order of stability.

These calculations reveal that it is dispersion that stabilizes the low temperature **np** phase—a result which is not sensitive to the methology by which the dispersion is calculated. To further probe the nature of the stabilizing interaction, and specifically to examine the π–π contribution, the phenyl groups were replaced with cyclohexane and the substituted **np** and **lp** structures geometry optimized using the vdW-DF scheme. After relaxation, **np** is still lower in energy than **lp** but the enthalpy and volume differences are smaller than those of the phenyl structures confirming that a significant component of the dispersion energy comes from π–π interactions. A comparison of the ΔD term in Table 1 between the phenyl and cyclohexane phases suggests that ca. 50% of the total dispersion energy arises from the phenyl rings. We note that a very recent study due to Devic et al.[12] on MIL53-Fe, where the ligand aromaticity was varied, demonstrated that the breathing behavior was influenced, which hints at a link between dispersion energy and bistability. Polarizable atoms, in closer proximity to one another in the dense phase, account for the remainder of the dispersion. The individual elemental contributions to the dispersion energy calculated using PBE-D, show that > 80% of the total is due to C−C, C−H, and C−O interactions.

There is a discrepancy of 6.6–8.6 kcal mol^{-1} between ΔE and ΔD that indicates that some non-dispersive interaction must counteract dispersion forces, tending to stabilize the **lp** form and thus facilitating the bistability of the structure. We performed a decomposition of the total energy with an approach used in other MOFs.[15] The relaxed **np** and **lp** cells were modified to yield cells containing just the organic subnetwork terminated by hydrogen atoms. Similarly, cells were prepared which contained the inorganic chains (and the C of the COOH group), again terminated by hydrogen atoms at C−H separation of 1.08 Å. Using the B3LYP-D and B3LYP-D* approaches, it was found that ΔE for the inorganic chain energies (**np**−**lp**) is +6.0 to +6.3 kcal mol^{-1}, whilst ΔE for the organic structures is −8.6 to −9.5 kcal mol^{-1} yielding an overall ΔE of −2.5 to −3.5 kcal mol^{-1}, c.f. −2.0 to −2.5 kcal mol^{-1} for the original MOF structures. The main difference between the inorganic chains in the **np** and **lp** forms is that the **np** structure contains very distorted octahedra with one short, one long and four approximately equivalent Al−O bonds. By contrast, the Al−O octahedra are close to regular in the **lp** form and hence lower in energy (by 6.0–6.3 kcal mol^{-1}). Thus, overall the **np** form is stable because the attractive dispersion interaction exceeds the penalty incurred for increased short-range repulsion and less favorable electrostatic interactions in the inorganic chains. The organic moiety separating the inorganic chains is relatively rigid and only internal deformation of the inorganic chains can facilitate the phase transition. Aluminium is known to adopt a range of coordination numbers (4, 5, and 6) in mineral phases suggesting its coordination sphere is quite pliable whilst other metals may be more discriminating, potentially inhibiting bistability in this and other MOF structures. Similarly, guest molecules may influence the flexibility of the Al (and other metals) coordination sphere.

Could vibrational entropy explain why the **lp** form stabilizes at high temperature? By taking the range of transition temperatures from experiment (125–375 K)[7] and the extrema of ΔE from the CRYSTAL B3LYP-D and B3LYP-D* calculations, we can estimate ΔS (**lp**−**np**) and find that ΔS is between 0.005 and 0.020 kcal mol^{-1} K^{-1}. The vibrational contribution to the entropy difference between phases were extracted from Γ point phonon calculations at 298 K, giving an estimate of ΔS to be 0.0033 kcal mol^{-1} K^{-1}. Using the latter values, the free energy of **lp** is lower than **np** at 300 K showing that the **lp** form is entropically stabilized. Analysis shows that the **lp** form has more low-frequency modes (associated with libration of the phenyl rings) than **np**, which drive the transition at higher temperatures.

In summary, we have shown that the exceptional bistable behavior of MIL-53(Al) is due to a competition between short-range and long-range interactions and entropic factors and this is key to further rationalization of guest-induced transformations in this material. More generally, our results highlight that dispersion-corrected DFT approaches are required to predict phase transition behavior and sorptive properties of MOF materials.

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