

An Electric Field Induced Breath for Metal–Organic Frameworks

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A detailed theoretical study demonstrates a new stimulus to change pore shape and size in MIL-53.

One of the reasons for the enormous interest in the class of porous metal organic frameworks (MOFs) is their structural flexibility, which is in contrast to the rather rigid zeolites. Kitagawa et al. have coined the term “third generation porous coordination polymers” for systems that undergo structural transformations in response to external stimuli, such as guest adsorption.¹ One of the most dramatic and intensively investigated transformation is the so-called “breathing” effect: an open pore contracts upon guest adsorption and reopens again at saturation load. The prototypical system for this breathing is the MIL-53 series of porous materials.² The large volume change of the breathing motion can not only be triggered by guest molecule adsorption (adsorption stress) but equally by mechanical pressure or temperature and is found for different MOFs with a “wine-rack” type structure.³

In their recent work, Ghoufi et al. have added to this list an additional interesting stimulus to trigger the breathing of MIL-53: namely, a (strong) homogeneous electric field.⁴ In a theoretical molecular dynamics investigation, they used their well tested force field to study the influence of such a field on MIL-53(Cr).⁵ Surprisingly, at ambient conditions and at a field strength of about 1.75 GV/m, the system closes in the same fashion as it does under pressure or guest molecule load. In addition, a hysteresis (e.g., lag) is observed, since the pores reopen at about 1.0 GV/m when reducing the field strength. The field induced polarization initially saturates already at about 0.1 GV/m (Figure S4 of ref 4) but increases again around 1.7 GV/m when the transformation is observed. By guest molecule adsorption in the presence of a field, the stimuli could be combined. When the authors maintained a system with narrow pores via the electric field, a size selective separation of carbon dioxide and methane was shown. This demonstrates the possibility to tune adsorption properties by the electric field.

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This first theoretical observation of an electric field-driven breathing opens numerous new possibilities for application, but—naturally—also raises new questions. In particular, the physical driving force behind the pore closing is not entirely clear, yet. Both hydrostatic pressure and host–guest interactions lead to opposing forces on neighboring pore walls, whereas for a centrosymmetric system like MIL-53(Cr) no direct interaction with the field is present in the first place, apart from an induced polarization in field direction. This polarization results from both electronic polarization and structural deformations. However, since a nonpolarizable force field (fixed atomic charges) was used in the present study, the former is not captured in the model, and the observed breathing must be thus due to the latter.

It is instructive to consider the atomistic structure of MIL-53(Cr). In Figure 1, a schematic representation of the

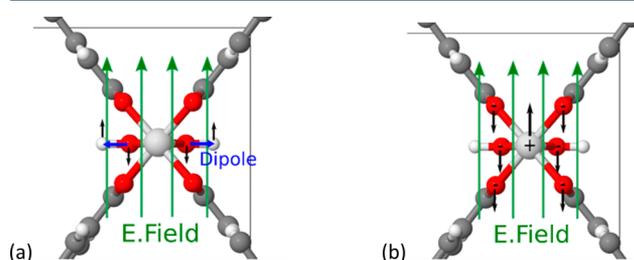


Figure 1. Potential deformations of the MIL-53(Cr) inorganic unit in a homogeneous electric field leading to an induced polarization: (a) orientation of O–H groups and (b) deformation of the coordination environment.

inorganic one-dimensional (1D) periodic strands of octahedrally coordinated Cr³⁺ ions is shown in a view along the

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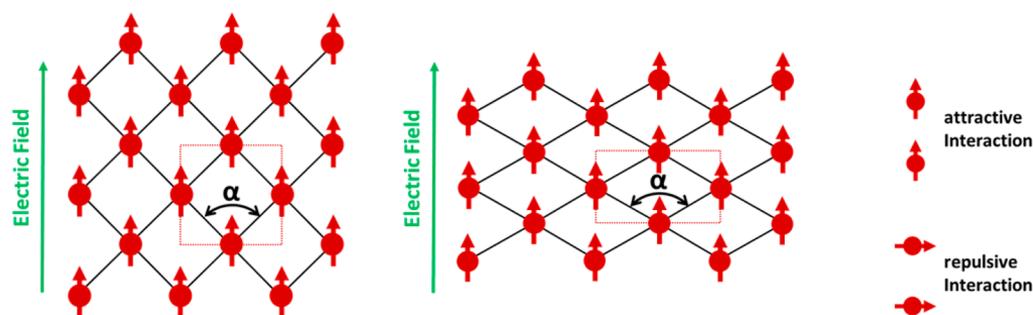


Figure 2. For a 2D lattice of induced (aligned) dipoles, the dipole–dipole interaction is stabilized by a factor of 1.22 when going from $\alpha = 90^\circ$ (left) to $\alpha = 120^\circ$ (right) (computed by a converged numerical integration).

crystallographic *c*-axis. The bridging O–H groups carry local dipole moments but point in alternating directions. As shown in Figure 1a an electric field could reorient these O–H groups and induce a local dipole moment. In addition, as in most carboxylate metal–organic frameworks, a positively charged metal ion is surrounded by negatively charged donor atoms like oxygen or nitrogen. A sufficiently strong electric field will deform this unit and induce a local dipole moment (Figure 1b). Note that these are not the only possibilities: e.g., deformation of the carboxylate units would also polarize the system. The exact nature of the local polarization will depend on the individual force constants of the corresponding deformation modes as well as the strength and orientation of the field vector (in the simulation a field with $E_x = E_y = E_z$ was used).

Materials that deform in an electric field serve as actuators in various technical applications (e.g., in inkjet printers). However, for this converse piezoelectric effect to occur, a non-centrosymmetric space group is necessary. In the case of a space group that is in addition polar, ferroelectricity with a spontaneous polarization can be observed, and MOFs with this interesting property have recently been synthesized.⁶ Interestingly, for the amine functionalized $\text{NH}_2\text{-MIL-53(Al)}$ in the closed pore form an ordering of the $-\text{NH}_2$ substituents is observed, resulting in such a polar space group.⁷ In contrast to that, for the centrosymmetric MIL-53(Cr) with its purely induced polarization, on the other hand, a transformation like the pore closing would not change the interaction of the induced dipole moments with the homogeneous field itself (see Figure 2). However, for any dielectric a (usually weak) deformation due to induced polarization is observed in an electric field, which is usually referred to as electrostriction. Because the system is symmetrical (due to the centrosymmetric space group), the direction of strain does not change upon reverting the field.

From these considerations, a hypothetical model is proposed here, which might be able to explain the observations: in a two-dimensional (2D) lattice of induced dipoles,

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resulting from a homogeneous electric field oriented along an axis of the unit cell (Figure 2), the electrostatic interaction between the induced dipoles depends on the shape of the grid. By a deformation to a rhombic shape it is stabilized, as the short ranged attractive interactions increase, meanwhile repulsive interactions decrease. The driving force for the breathing is then the mutual dipole–dipole interaction, whereas the electric field just acts as the source for the necessary polarization. The same deformation results in a reverted field. Thus, an electrostriction, amplified by cooperative effects in the “wine-rack” type architecture of MIL-53(Cr) , would be the origin for the pore contraction. An increased self-polarization in the denser narrow pore form could be the origin for the observed hysteresis. Note that if this scenario is correct, the same could be observed in a polar system after a ferroelectric ordering with a similar alignment of local dipoles. Obviously this is an oversimplified picture for MIL-53(Cr) with its already rhombic open pore, but it could still serve as a lead for further investigations of electric field induced breathing transformations in MOFs.

The work by Ghoufi et al. could be a “door-opener” for very interesting novel applications, as it shows that not only local rotations of dipolar groups,⁸ but a collective motion with a large volume change can be triggered by an electric field. In the context of host–guest systems this would allow for field switchable membranes or field enhanced pressure swing adsorption processes, but it should also be seen in the wider context of nanomechanical devices.⁹ The crystalline and porous MOFs are an interesting platform here, since the motion of molecular fragments affords free space.¹⁰

Like photons, electric fields can serve as a much more selective stimulus as compared to temperature and pressure allowing for more control in such devices. On the other hand, a detailed understanding of the driving force will be needed to design systems that can be stimulated at substantially lower field strength, since fields in the GV/m range are orders of magnitude above the breakthrough voltage of gases like CO₂. Without any doubt, the present study will initiate further work in this direction, and it will be very interesting to see if, e.g., NH₂-MIL-53(Al)⁷ or related systems would switch already at lower fields.

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