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# Electrically Induced Breathing of the MIL-53(Cr) Metal–Organic Framework

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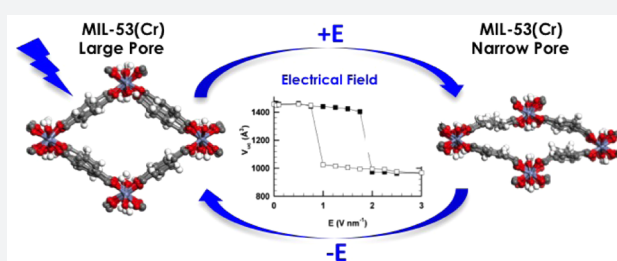
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## Supporting Information

**ABSTRACT:** The breathing behavior of the MIL-53(Cr) metal–organic framework (MOF) has been explored previously upon guest-adsorption and thermal and mechanical stimuli. Here, advanced molecular simulations based on the use of an accurate force field to describe the flexibility of this porous framework demonstrate that the application of an electrical field induces the structural switching of this MOF leading to a first-order transition and a volume change of more than 40%. This motivated us to electrically tune the pore size of MIL-53(Cr) with the idea to propose a new concept to selectively capture CO<sub>2</sub> over CH<sub>4</sub> via a molecular sieving that paves the way toward



the optimization of current separation-based processes.

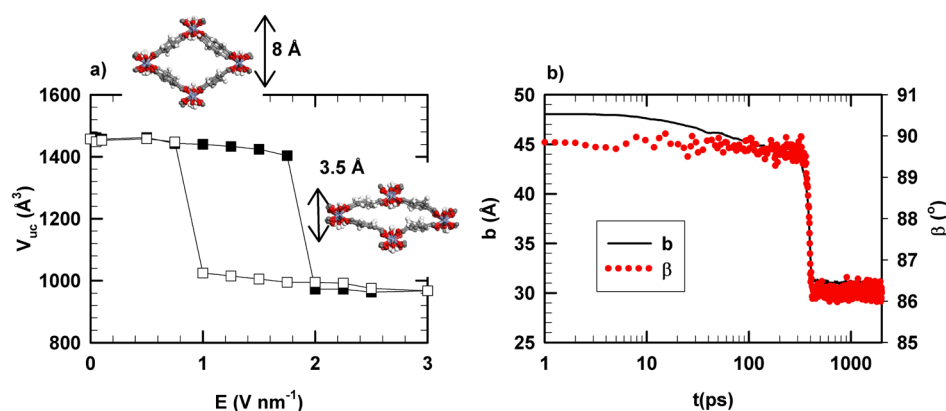
## INTRODUCTION

One fascinating property of many porous metal–organic frameworks (MOFs) is the diversity of their architectural flexibility, a unique feature in the field of nanoporous materials with respect to other reference materials such as active carbons and zeolites.<sup>1–5</sup> Guest-induced pore size/shape modulation of this class of porous solids (breathing, ligand flip, pore gating, etc.) has revealed unexpected adsorption/separation phenomena pointing toward new opportunities for adsorption-based technologies.<sup>1–11</sup> The breathing MOFs correspond to the most spectacular family of flexible porous solids. Among them, the 1D-type channel MIL-53 (MIL stands for Materials of Institut Lavoisier) built up from chains of metal octahedra sharing  $\mu_2$ -OH vertices linked by terephthalate groups has received the most attention with the evidence of a guest-assisted reversible structural transition between narrow pore (NP) and large pore (LP) forms.<sup>1,12,13</sup> This intriguing phenomenon was observed for a series of molecules implying a reversible expansion/contraction of the pore dimension up to 40% in unit cell volume. This arouses great interest not only for the selective capture of gas molecules via size exclusion effects but also for the progressive release of drugs.<sup>3,14</sup> Very recently such structural breathing was shown to be of real applicative interest.<sup>15–17</sup> The dipyrazolate based-Co(BDP) MOF owing to its structural transition from an LP form to a nonporous NP form associated with a unit cell volume change of 100% was revealed to show exceptional value of usable CH<sub>4</sub> storage capacity far beyond the record for a porous solid in the operating conditions of adsorbed natural gas vehicles.<sup>15</sup> Moreover, the Cu<sub>2</sub>-paddle-wheel based-DUT-49 shows an unprecedented negative gas adsorption (NGA) behavior for

CH<sub>4</sub> corresponding to a spontaneous desorption phenomenon caused by a spectacular guest-induced contraction of the framework corresponding to a unit cell variation of more than 60%.<sup>16,17</sup> Many of these breathing behaviors have been also pressure and temperature assisted.<sup>10,11</sup> Typically, MIL-53 breathes in the same manner as with chemical and thermal stimuli under external pressure that suggests the use of this family of materials for mechanical energy storage applications.<sup>18–20</sup> A few MOFs have been also reported to be photoswitchable with the use of azobenzene groups incorporated either as guest-molecules or in the organic node of the MOFs.<sup>21–23</sup> As a typical example, the light-induced trans–cis conformer transformation of the azobenzene function was shown to induce a pore size change of the IRMOF-74 of more than 20%.<sup>23</sup> More recently, the application of an electrical field was shown to induce some local intramolecular organization of the Cu(TCNQ) MOF (TCNQ = 7,7,8,8-tetracyanoquinodimethane) leading to a reversible transition from a high-resistance state to a conducting state.<sup>24</sup> However, this stimulus has never been explored so far to provoke the breathing of MOFs that might open new horizons for this class of nanoporous materials. In this context, here advanced molecular simulations tools explore first the electrical field-induced breathing of the empty and guest-loaded MIL-53 MOF in its Cr(III) version. The synergic combination of the application of the electrical field and the adsorption of guest molecules is then envisaged with the idea to propose new concepts to further optimize current gas separation-based processes. In particular,

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**Figure 1.** (a) Unit cell volume of the empty MIL-53(Cr) as a function of the external electrical field ( $E$ ). Full and empty symbols correspond to increasing and decreasing electrical field range, respectively. Temperature and pressure are 300 K and 1 bar, respectively. The provided values correspond to the pore size of both LP and NP forms. (b) Evolution of the unit cell parameters  $b$  and  $\beta$  as a function of time at  $E = 1.75$  V/nm at 300 K and 1 bar.

such a development could pave the way toward a variant of the electrical swing adsorption (ESA) process where the applied electrical current would favor the structural switching of the adsorbent to make optimal the separation steps rather than inducing an in situ heating of the conductive adsorbent as obtained in the existing technology for improving the regeneration.<sup>25</sup>

## RESULTS

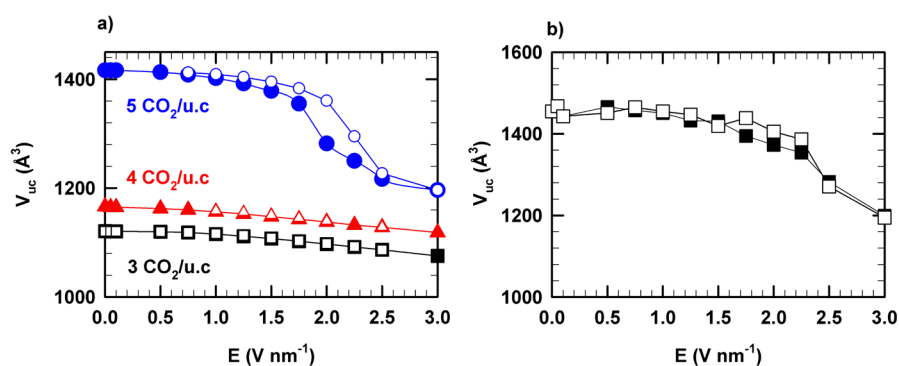
Figure 1a reports the evolution of the unit cell volume of the empty form of MIL-53(Cr) under the application of a gradual increase of the electrical field ( $E$ ) as predicted at room temperature by molecular dynamics (MD) simulations performed in the  $N\sigma T$  ensemble that allows both cell size and shape to vary. This plot reveals a structural switching between the initial LP form and a contracted pore (CP) form that occurs at  $E = 1.75$  V/nm associated with a unit cell volume change of 35% and a drastic drop of the aperture of the channel from 12.8 to 7.9 Å. As shown in Table S1 the CP form corresponds to a volume of 967.2 Å<sup>3</sup> at  $E = 3.00$  V/nm, very similar to the value previously reported for the same structure under an applied external pressure (931.0 Å<sup>3</sup>) and thermal stimuli (927.9 Å<sup>3</sup>).<sup>10</sup> Figure 1a provides further evidence that the structural transformation is fully reversible with a hysteresis of 1.00 V/nm, such a behavior being again reminiscent of the pressure and thermal-induced profile.<sup>10</sup>

Indeed, when the electric field is high enough, the MOF framework undergoes a reversible structural shrinkage driven by a rotation of the linker about the Oc–Oc axis as evidenced by a significant change of the torsion angle distribution (Cr–Oc–Co–C; this angle is described in Figure S1b) with a sharp peak centered at 180° for the LP form and a broad band that spans between 120° and 160° for the CP form (see Figure S1a). This LP–NP structural switching induces a sudden change of the energetics of the intramolecular torsion angle contribution (see Figure S2). This behavior is the same as that already pointed out for the structural transition triggered by chemical and mechanical stimuli. Figure S3a,b shows that during the structural transition, the cell dimensions  $a$  and  $b$  as well as the angles undergo changes with a hysteresis, while the  $c$  parameter orientated along the channel is only slightly affected. This emphasizes an anisotropic transition due to the anisotropy in the constraint and elastic tensor of the LP form as already mentioned in ref 26. This hysteretic behavior is probably due to

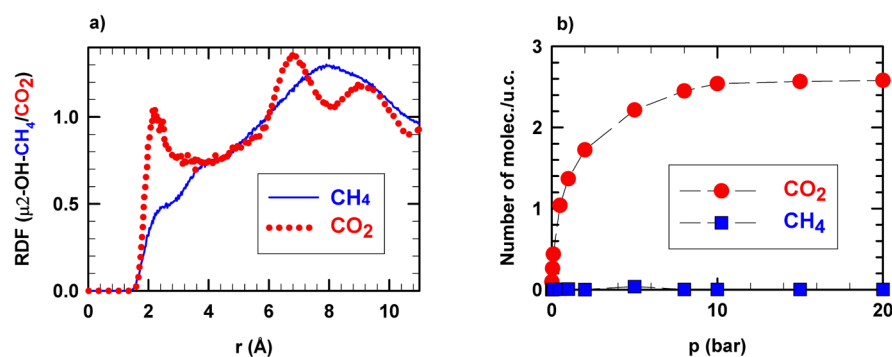
a difference in the structural response between NP and LP forms caused by the electrical constraint. Indeed, as shown in Figure S4 there is a significant modification of the polarization density when one switches from the LP to the NP form that highlights a different critical stress in the two structures that triggers the transition.

Interestingly, a sudden decrease in volume is shown in Figure 1a and suggests a first order transition probably due to a symmetry breaking leading to an unstable LP form. It was previously reported that the mechanism of the guest-induced structural LP–CP transition is decomposed into two stages, a shear displacement following a compression process.<sup>10,27</sup> Here the scenario slightly differs with the shear and compression stages occurring concomitantly as evidenced in Figure 1b that reports the evolution of the unit cell parameters  $b$  and  $\beta$  as a function of MD time for MIL-53(Cr) under the application of an electrical field of 1.75 V/nm. This graph clearly shows that both parameters simultaneously drop beyond 400 ps. Indeed, the electrical field can be seen as an external electrostatic pressure exerting on the MIL-53(Cr), which induces a collective motion in such a way that the shear and the compression processes occur simultaneously. Upon adsorption the constraint due to the adsorbed molecules is exerted from the inside of MIL-53(Cr) by a heterogeneous distribution of the guests in the pore of the material. This leads to an anisotropic constraint at the origin of a mechanism of transition in a two-stage transition.<sup>10,27</sup> Interestingly, we report in Figure S3 the total polarization ( $P$ ) of the MIL-53(Cr) as a function of  $E$ . A discontinuity at  $E = 1.75$  V/nm is observed that highlights a second order polarization transition that is in line with the structural one. Additionally, by minimizing the free energy that is a function of the polarization (Landau's hypothesis), we show that  $E$  is a function of  $P$ . This result in polarization bears out the displacive-type of LP  $\rightarrow$  NP transition rather than a disorder/order one.

As a further step, we envisaged the control of both the electrical field and adsorption simultaneously acting as an internal and external pressure on the MOF, respectively, their synergic combination being expected to fine-tune the pore size of MIL-53(Cr). As a typical illustration, we investigated the adsorption of CO<sub>2</sub> and CH<sub>4</sub> gases that are of prime importance in the context of the CO<sub>2</sub> capture from natural gas streams.<sup>28</sup>  $N\sigma T$  MD simulations were then run starting with the LP structure loaded with 5 CO<sub>2</sub>/u.c. at 300 K where MIL-53(Cr)



**Figure 2.** Evolution of the unit cell volume of (a) CO<sub>2</sub> loaded MIL-53(Cr) with different CO<sub>2</sub> concentrations, circle, triangle, and square symbols for 5, 4, and 3 CO<sub>2</sub>/u.c. where full and empty symbols correspond to increasing and decreasing electrical field range, respectively, and (b) CH<sub>4</sub> loaded MIL-53(Cr) as a function of the electrical field.



**Figure 3.** (a) Radial distribution function between the center of mass of CO<sub>2</sub> and CH<sub>4</sub> and the hydrogen atom of the  $\mu_2$ -OH groups present at the MIL-53(Cr) surface. (b) Simulated adsorption isotherm of CO<sub>2</sub> (circle) and CH<sub>4</sub> (square) of 50:50 CO<sub>2</sub>/CH<sub>4</sub> mixture at 300 K. Isotherms were obtained by using hybrid osmotic Monte Carlo simulations with the application of an electrical field of 2.0 V/nm.

is known to remain in the LP form.<sup>12</sup> Figure 2a shows that the unit cell volume of MIL-53(Cr) initially smoothly decreases up to 1.75 V/nm, and there is a step-change above with a more pronounced decrease that leads to a structural switching of the LP phase toward a NP form corresponding to a unit cell volume of 1154  $\text{\AA}^3$  under 3.00 V/nm. This observation emphasizes that the application of an electrical field creates an additional external constraint to the internal adsorption that enables the structural contraction of MIL-53(Cr) that is not possible only considering the chemical stimulus. The corresponding unit cell volume of this NP form is significantly higher than that observed upon the adsorption of a lower concentration of CO<sub>2</sub> (1132.8 and 1422.1  $\text{\AA}^3$  for 3 and 4 CO<sub>2</sub> molecules per unit cell respectively) as reported in Figure 2a. In comparison with the empty LP form, a more continuous transition occurs due to the internal pressure exerted by this concentration of guest molecule. This is attributed to the relatively strong CO<sub>2</sub>/MOF interactions that tend to resist to the contraction of the structure under the application of the electrical field. This leads to a fully reversible structural transition with the absence of hysteresis with 3 and 4 CO<sub>2</sub>/u.c., while a small hysteresis is observed with 5 CO<sub>2</sub>/u.c. This hysteretic behavior is probably due to the large difference in volume between the initial (LP form) and final (NP form) structures in contrast with 3 and 4 CO<sub>2</sub>/u.c. whereby the MIL-53(Cr) remains always in a NP form. Relatively strong CO<sub>2</sub>/MOF interactions are highlighted through the calculation of the radial distribution function between the center of mass of CO<sub>2</sub> and the hydrogen atom of the  $\mu_2$ -OH groups of the MIL-53(Cr) in Figure 3a with the evidence of short interacting

distances with an average value of 2.2  $\text{\AA}$  that corresponds to the strength of a hydrogen bond. The orientation of CO<sub>2</sub> in the pore was further explored. Indeed, we calculated the angular distribution between the vector connecting both oxygen atoms of CO<sub>2</sub> and the unit vector in the  $z$  direction corresponding to the axis of the channel (Figure S5). It was shown that without the application of the electrical field, the orientation of the CO<sub>2</sub> molecules is along along the axis of the channel ( $z$  direction) consistent with our previous findings.<sup>6,7,9–11</sup> When  $E = 3.0$  V/nm another preferential orientation parallel to the  $x$ -direction appears for CO<sub>2</sub>. This orientation is induced by the contraction of the pore into the  $y$  direction that changes the orientation of the CO<sub>2</sub> molecules in order to favor the optimal interaction with both the other guest molecules and the host framework.

This behavior also holds true when we consider the adsorption of CH<sub>4</sub>. Indeed, it is well documented that the adsorption of CH<sub>4</sub> at ambient temperature does not lead to any structural change of MIL-53(Cr). As depicted in Figure 3a methane molecules weakly interact with the  $\mu_2$ -OH present at the MIL-53(Cr) surface since only a broad peak is observed in the corresponding radial distribution function. Thus, the internal pressure exerted by CH<sub>4</sub> molecules is then not sufficient to trigger the structural transition. Figure 2b shows that for a given concentration of CH<sub>4</sub>, i.e., three molecules/u.c., a smooth structural transition starts to be initiated at 2.00 V/nm, an electrical field of slightly higher magnitude than the value observed for the empty material. Here, the relatively large dimension of methane prevents the sudden transition as observed for the empty case. The resulting unit cell volume of the electrical field ( $E = 3$  V/nm) induced CH<sub>4</sub> loaded NP form



(1090 Å<sup>3</sup>) is indeed higher than the CP (960 Å<sup>3</sup>) mentioned above.

Furthermore, we evidenced that MIL-53(Cr) initially present in the NP form upon the adsorption of 3 and 4 CO<sub>2</sub>/u.c. remains in this monoclinic symmetry phase when the electrical field is applied (Figure 2a), the associated volume being only slightly more contracted when increasing the magnitude of the electrical field (from 1121 Å<sup>3</sup> to 1075 Å<sup>3</sup> and from 1166 Å<sup>3</sup> to 1118 Å<sup>3</sup> for 3 and 4 CO<sub>2</sub>/u.c. respectively). This whole observation highlights that the application of an electrical field about 2.00 V/nm is able to induce the structural closing of both the empty and the guest-loaded MIL-53(Cr) LP form. This external electrical field control might thus help to maintain the breathing MOF in the NP form during adsorption to selectively capture CO<sub>2</sub> over CH<sub>4</sub> via a size exclusion effect. To confirm this, hybrid osmotic Monte Carlo simulations were further performed to predict the adsorption isotherm for the CO<sub>2</sub>/CH<sub>4</sub> mixture in MIL-53(Cr) at 300 K under the application of an electrical field of 2.00 V/nm. The corresponding data are reported in Figure 3b. As shown in this figure, the amount of CH<sub>4</sub> adsorbed is negligible, whereas we obtain a reasonable amount of CO<sub>2</sub> adsorbed resulting from a relatively high affinity between this gas and the μ<sub>2</sub>-OH groups present at the pore wall of the MOF (Figure 3a). In this condition, MIL-53(Cr) is maintained in a NP corresponding to a unit cell volume of 1084 Å<sup>3</sup> and a pore size of 3.5 Å. Since the kinetic diameter of methane is 3.8 Å there a size exclusion effect that hampers the adsorption of this molecule into the pore of the NP form. This result emphasizes an almost infinite selectivity for the CO<sub>2</sub>/CH<sub>4</sub> mixture. This clearly suggests that the application of an external electrical field can allow fine tuning of the pore size of MIL-53(Cr) allowing a spectacular gas separation with a selective adsorption of CO<sub>2</sub> over CH<sub>4</sub>.

## CONCLUSION

In this work MD simulations have been performed to show that the MIL-53(Cr) MOF undergoes a reversible structural transition by applying an electrical field. While a hysteresis and a first order transition are observed for the empty material, transition of the CO<sub>2</sub> and CH<sub>4</sub> loaded MIL-53(Cr) is found to be continuous and without hysteresis whatever the loading. Hybrid osmotic Monte Carlo simulations demonstrated that the application of an external electrical field can maintain the structure in the NP form during the adsorption leading to a full separation of CO<sub>2</sub> over CH<sub>4</sub> via a size exclusion effect. Such electrically switchable flexible MOFs pave the way toward novel perspectives for separation-based technology. This property can be also of interest for a potential use as sensors and/or switching devices in diverse fields including nanomedicine. However, the electrical field used in our MD simulations on the order of V/nm is relatively large due to the resilience of the MOF framework to the electrically induced structure polarization. Since the conventional field strength is MV/m, future experiments will be performed to evaluate the correct magnitude of the electrical field to induce such a structural transition.

## METHODS

The simulation box consisted of 32 unit cells of the LP-MIL-53(Cr) deployed according to the *x*, *y*, and *z* directions and built from the crystallographic coordinates previously reported by powder X-ray diffraction study.<sup>12</sup> Thus, the box lengths are

$L_x = 33.2$  Å,  $L_y = 52.8$  Å, and  $L_z = 26.8$  Å. MD simulations were performed in the  $N\sigma T$  ensemble where  $N$  is the number of molecules,  $T$  is the temperature, and  $\sigma$  is the isotropic constraint. A Nose–Hoover thermostat and barostat were used with a relaxation time of 0.5 ps. MD simulation runs were conducted for 10 ns with a time step of 1 fs with 10 ns of equilibration. The equations of motion were integrated using the velocity Verlet scheme. The Ewald summation was used for calculating the electrostatic interactions, and the short-range interactions were truncated at 12 Å. The MIL-53(Cr) framework was considered as flexible with intramolecular and intermolecular potentials of MIL-53(Cr) were taken from ref 10. External electrical field was applied on each atom  $i$  of the MOF such as that  $F_i = -q_i E$  where  $F_i$  is the force on each atom  $i$ ,  $E$  is the electrical field, and  $q_i$  is the partial charge on  $i$  atom. The electrical field has been applied equally along the three directions, i.e.,  $E_x = E_y = E_z$ . Similar structural transitions have been observed when applying an electrical field along the  $x$  and  $y$  directions. The electrical field was also applied along the  $z$ -axis ( $E_z$ ) but no transition was evidenced. Indeed, under the application of  $E_z$  only the shear motions are possible in the  $z$  direction, while compression along the  $x$  and  $y$  axes cannot be triggered.<sup>10</sup> Furthermore, from an experimental viewpoint the MIL-53(Cr) material can only be investigated as a powder and not as a single crystal, and therefore application of an oriented electrical field is impossible from an experimental point of view. To be electrically stimulable a flexible charged model of methane was considered,<sup>29</sup> while a rigid charged model was considered for CO<sub>2</sub>.<sup>30</sup> The electrical force is modulated by the partial charges on each atom, and the amplitude of the electrically induced structural modifications of MIL-53(Cr) depends on these partial charges. The flexible force field and the partial charges have already been trained and validated in previous studies.<sup>10</sup> Indeed here the objective of this work is to study the electrically induced breathing phenomena of the MIL-53(Cr) using this validated full flexible force field. The rigid case would be inappropriate because for a rigid neutral system there is zero net force from an electric field. Methane-MIL-53(Cr) interactions were considered by means of the mixing Lorentz–Berthelot rules. Hybrid osmotic Monte Carlo simulations were carried out with the same parameters as those used in ref 31.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00392.

Unit cell parameters as a function of  $E$ , angular distribution of the dihedral angle represented and torsional energy of the dihedral angle as a function of  $E$  (PDF)

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### Notes

The authors declare no competing financial interest.

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## DEDICATION

Dedicated to the 75th birthday of Professor Gérard Férey.

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