Tuning the ferroelectric polarization in a multiferroic Metal-Organic Framework

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Supporting Information

Computational Methodology

Energy cutoff and k-point sampling

Computational results reported in the main text have been obtained by using density functional theory (DFT) simulations solving the Kohn-Sham equations in the projector augmented-wave (PAW) framework using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional as implemented in the VASP package.[1–3] The energy cutoff for the plane wave expansion was set to $400\,eV$; a $3 \times 4 \times 2$ Monkhorst-Pack grid of k-points was used.

We performed extensive tests in order to check the influence of computational paramenters on the relevant properties for the case of $[CH_3CH_2NH_3]Mn(HCOO)_3$ MOF. In particular, we will focus on the ferroelectric polarization and its dependence upon energy cutoff and k-points sampling.

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In Supplementary Table 1 we report the polarization for different input setups and the percentage difference with respect to the set-up used in the main text. For each set-up we included ionic relaxations.

Table 1: Convergence of the calculated ferroelectric polarization (P_z) with respect to input parameters.

	400 (eV)	600 (eV)
$3 \times 4 \times 2$	-1.64 μC/cm^2	-1.69 μC/cm^2 (3.0%)
$6 \times 8 \times 4$	-1.67 μC/cm^2 (1.8%)	-1.68 μC/cm^2 (2.4%)

It is clear that the computational parameters influence the polarization only to minor extend: variations with respect to the reference setup, *i.e.* energy cutt-off of 400 eV and k-point sampling with $3 \times 4 \times 2$, are within a few %.

Weak-interactions

Since we are dealing with ferroelectricity in hydrogen bonded systems, it may be interesting to test how different approximations may affect the h-bond description. The hydrogen bond interaction is realized by an attractive force between a polar D-H bond and a polar or region A (acceptor). Commonly, donor (D) is hydrogen and acceptor (A) atoms are C, N, O, F. In our case, the D-H$\cdots$A interaction is represented by C-H$\cdots$O or N-H$\cdots$O of the ethylammonium and the oxygen of the organic ligand.

An important characteristic of the h-bond is its directionality, *i.e.* the angle θ between the D-X and H$\cdots$A bonds. Tipical values range between $140°$ and $180°$:[4] the smaller is the angle, the weaker the interaction is. The complexity of the h-bond is also related to the fact that its nature is neither electrostatic or covalent but rather a mixture of the twos.[5] This makes the description based on density functional theory approximations very challenging. J. Ireta *et al.* have shown that the accuracy of standard DFT-PBE approximation for the description of the hydrogen-bond is closely connected to the bond directionality. In particular, with increasing deviation from linearity (i.e. from $180°$) the accuracy of the DFT-PBE decreases.[6,7] It is believed that for small angles the hydrogen-bond is mainly described by van der Waals interaction.[8,9]

In our case, the h-bonds are linear, with θ close to $180°$. Therefore, according to Ref.[6,7] we

expect a good description of the main properties related to the h-bond. For definiteness, we will focus on the main property we are interested in, *i.e.* the ferroelectric polarization. We performed test calculations using different van der Waals density functionals, from the DFT-D2 method which consists in adding a semi-empirical dispersion potential to the Kohn-Sham DFT energy,[10,11] to the more recent vdW-DF family of functionals proposed by Dion *et al.* where a nonlocal correlation functional approximately takes into account dispersion interactions.[12–14] Here we used the energy cutt-off of 400 eV and k-point sampling with $3 \times 4 \times 2$. We will compare our results to the reference density functional approaximation *i.e.* PBE.

Table 2: z-component P_z of the ferroelectric polarization as calculated by using different vdW-functionals after ionic relaxations at $400\,eV$ for the energy cutoff and $3 \times 4 \times 2$ Monkhorst-Pack grid for k-point sampling. Percentage differences with respect to the reference setup are reported in parenthesis.

	DFT-D2	vdW-DF	optPBE-vdW	optB88-vdW	optB86b-vdW
P_z (μC/cm^2)	-1.63 (0.6%)	-1.51 (7.7%)	-1.56 (4.7%)	-1.61 (1.8%)	-1.61 (1.8%)

As reported in the Supplementary Table 2, variations within different vdW functionals and with respect to the approximation in the main text are less than 8%, suggesting that dispersion interactions are weak in this class of MOF compounds and that results are robust with respect to different DFT approximations.

Estimation of the magnetic exchange constants

We performed total-energy calculations on the Mn-MOF with different spin configurations and for the non-magnetic state, but keeping the optimal lattice structure obtained by enforcing the G-type antiferromagnetic configuration. Supplementary Table 3 collects all the calculated energies, with the corresponding expression found when mapping onto a Heisenberg model with normalized spins, $H = -\sum_{ij} J_{ij} S_i S_j$, and taking into account only intra- and inter-chain coupling constants, J_c and J_a respectively (see the main text).

Furthermore, there is a direct coupling between the electronic orbital filling and the magnetic structure. The Goodenough-Kanamori-Anderson (GKA) rules[15,16] suggest that there is a strong

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Table 3: Calculated energy differences with respect to the AFM-G type configuration; the corresponding expressions obtained after the mapping onto Heisenberg model are given in the third column.

	ΔE(meV)	
AFM-G	0	
AFM-C	12.7	$\Delta E_1 = -4J_c$
AFM-A	25.4	$\Delta E_2 = -4J_a$
FM	38.7	$\Delta E_3 = -4J_c - 4J_a$

antiferromagnetic coupling if on corresponding sites the half-occupied orbitals are directed towards each other. Here, Mn^{2+} sites have all d orbitals singly-occupied which direct towards each other and interact *via* a superexchange mechanism mediated by molecular orbitals of the *HCOO* ligand groups. Thus, Mn sites are coupled antiferromagnetically (AFM) both in the *ab*-plane and along the *c*-axis, so that the ground state displays a G-type AFM spin configuration.

Born Effective Charges Analysis of the Ferroelectric Polarization

The first-principles calculation of the Born charge tensor is a useful tool to analyze the microscopic mechanism at the origin of the ferroelectric polarization. Generally, two opposite limits can be defined: in the extreme ionic limit, Born charges coincide with the nominal ions' charges, while in extreme covalent materials, Born charges can be significantly anomalous. This is the case of standard ferroelectrics as $BaTiO_3$ or hydrogen bonded organic ferroelectrics, where anomalous Born charges are intimately related to ferroelectric instabilities.[17,18] Usually, when dealing with materials belonging to low symmetry space-groups, the Born tensor is not symmetric. However, it's always possible to split it into symmetric and antisymmetric components, and the analysis can be carried on looking at the largest eigenvalue of the symmetric part.

   In the case of Mn-MOF, we studied the evolutions of Born charges along the λ-path from the paraelectric phase ($\lambda = 0$) to the ferroelectric one ($\lambda = 1$). No anomalous Born charge has been detected. In particular, for atoms belonging to the A-group in the ferroelectric phase, we find $Z^*_N \sim 4.75e$, $Z^*_C \sim 3.90e$ and $Z^*_H \sim 0.98e$, while for atoms in the framework we have $Z^*_{Mn} \sim 5.60e$, $Z^*_O \sim -2.55e$, $Z^*_C \sim 3.99e$ and $Z^*_H \sim 0.97e$. Very similar values are obtained for

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the paraelectric structure. This is in agreement with our expetection, since in this compound there is no covalency effects triggering the ferroelectric polarization, while the main contribution to the polarization comes from the dipole moment of the organic A-group embedded in the framework, as demonstrated in the main text.

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