

Supplementary Information

Elucidating the Interaction of CO₂ in the Giant Metal-Organic Framework MIL-100 through Large- Scale Periodic Ab Initio Modelling

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Initial model for MIL-100(Fe) and MIL-100(Cr)

The initial geometry of MIL-100(Fe) F was created by starting from the optimized structure of MIL-100 (Sc) at the B3LYP/SVP-MINI1 level of theory and together with the account for some experimental evidence ¹ about iron-containing trimeric units in organometallic molecular clusters:

(i) Fe(III) is in a high-spin (HS) state;

(ii) there is an antiferromagnetic coupling between iron atoms in the trimeric unit;

According to this evidence two different electronic configurations can be designed:

(1) ferromagnetic unit cell:

- all iron atoms with 5 unpaired electrons ($S=5/2$), either all spin α or spin β , i.e. $|\alpha\alpha\alpha\rangle$ ($|\beta\beta\beta\rangle$);

- 68 trimeric units with 15 unpaired electrons each for a total of 1020 unpaired electrons in the unit cell;

(2) ferrimagnetic unit cell:

- antiferromagnetic coupling between two iron atoms in the trimeric unit;

- broken symmetry (BS) configuration with iron in $|\beta\alpha\alpha\rangle$ spin state where the β iron is the one linked to the fluorine atom. This choice allows us to keep the highest symmetry of the system preserving 16 symmetry operations.

- 68 iron atoms with 5 unpaired electrons each for a total number of 340 unpaired electrons.

Preliminary calculations with B3LYP/SVP-MINI-1 gave the BS configuration as the most stable one. This result were also confirmed for a larger basis set as pob-TVZP²/6-311G(d,p), hence we assumed a ferrimagnetic unit cell for further calculations.

The same strategy was applied to Cr(III) with three unpaired electrons ($S=3/2$).

Two initial configurations have been imposed corresponding to (1) and (2) as listed just above for iron. Even in that case preliminary calculations with B3LYP/SVP-MINI-1 give the BS configuration as the most stable one.

MPPcrystal scaling for MIL-100

To validate the efficiency of MPPCRYSTAL³⁴ and the optimal number of processors to run our calculations, we performed benchmark tests on an increasing number of processors to evaluate the scaling of wall-clock time needed to complete typical runs on MOFs under study.

To this purpose, a model system in which a nitrogen atom substitutes the oxygen at the centre of the inorganic unit, i. e. MIL-100(Al)-N, has been designed to avoid charge compensating ions. It consists of a unit cell containing 2720 atoms with P1 symmetry and with more than 44000 basis functions (BFs). Increasing the symmetry does not affect the scalability of the code. Running time scaling with the number of computing cores for MIL-100(Al)-N (2720 atoms) have been gathered on the SuperMUC HPC system⁵. **Figure S1** shows the scaling of the code up to 4096 cores when use is made of the B3LYP functional in combination with a basis set of 44606 atomic orbitals per unit cell. The wall-clock time speed-up (t_n/t_{1024} , with n the number of CPUs) refers to the wall-clock time (t_{1024}) required for a SCF+G calculation run performed by

1024 cores. SCF represents a single cycle for the calculations of the total energy of the system, while G indicates the gradient related to the evaluation of the forces acting on nuclei. Both SCF and G are important steps in more complex calculation like the relaxation of the crystalline structure. Overall, a very good scalability efficiency is reached because of the high degree of parallelization of CRYSTAL with the speed-up being 3.45 (86%) for 4096 cores.

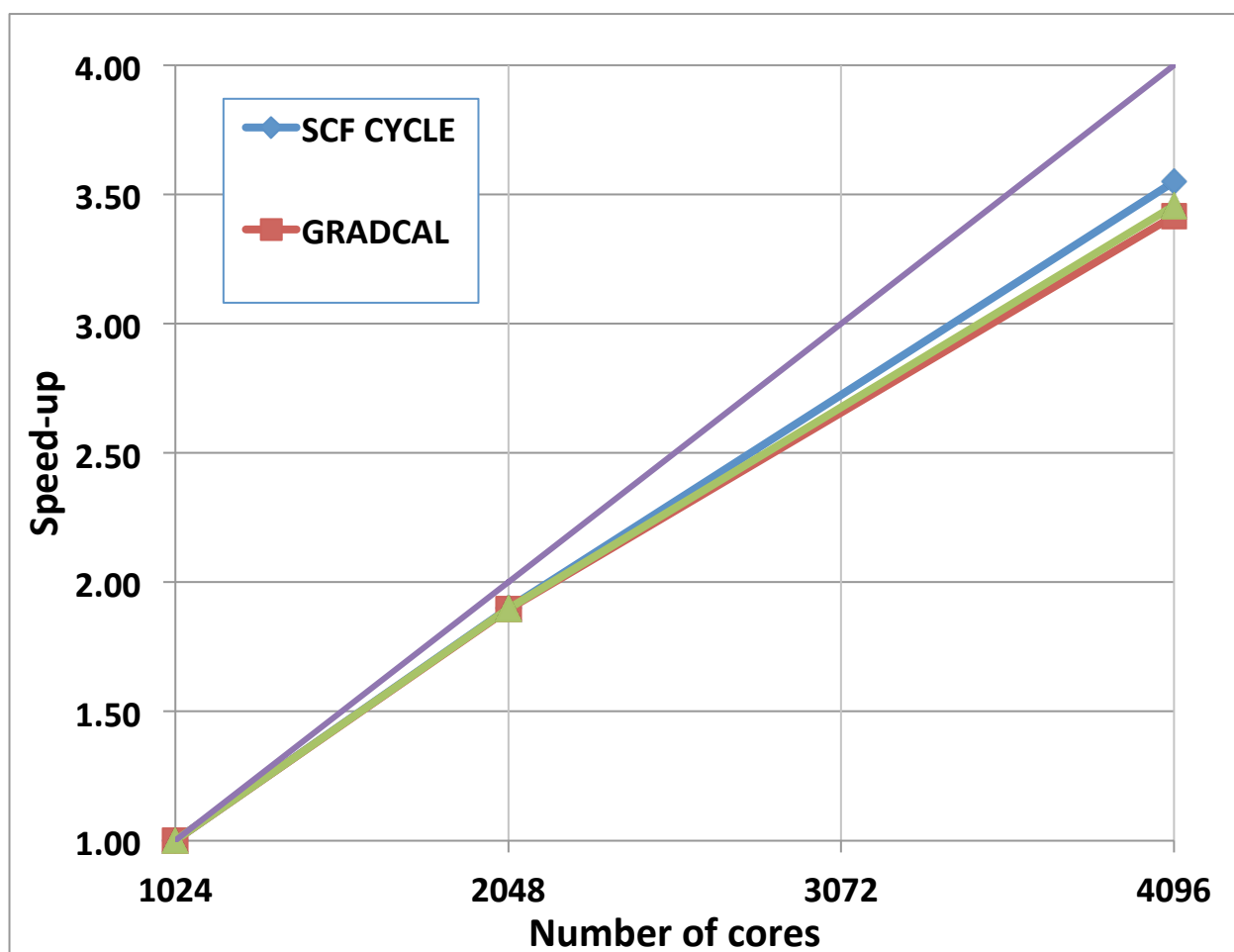


Figure S1. Wall-clock time speed-up (t_n/t_{1024} , with n the number of cores) for a SCF+G calculation performed on increasing number of CPUs at SuperMUC HPC center.

Crystallographic data

Crystallographic data of the B3LYP-D* optimized structures of MIL-100(Al), MIL-100(Sc), MIL-100(Cr) and MIL-100(Fe) are provided as supporting information.

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