

Porphyrin-based metal-organic frameworks for solar fuel synthesis photocatalysis: band gap tuning via iron substitutions

Supplementary Information

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PBE+U band structures

For the PBE+U band structures and DOS plots of Figure S1, a Γ -centred grid of k-points was used for integrations in the reciprocal space, where the smallest allowed spacing between k-points was set at 0.2 \AA^{-1} , which corresponds to 18 irreducible points in the Brillouin zone. This grid is much denser than the one used for the HSE06 calculations, where the spacing was 0.5 \AA^{-1} corresponding to only 3 irreducible points.

An additional linear mesh of 6 points along each interval in the high-symmetry paths was employed to plot the band structures. The reciprocal space coordinates of the high-symmetry Brillouin zone points are: Γ (0,0,0), S (0,0.5,0), R (0,0.5,0.5), Z (0,0,0.5), Y (-0.5,0.5,0), and T (-0.5,0.5,0.5).

Fe/Al distribution in the octahedral sites: the 1D Ising model

We show here how a 1D Ising model can be used to estimate that the equilibrium probability of Fe-Al pairs in nearest-neighbour (NN) positions at room temperature is $p=73\%$, as mentioned in the main text of the manuscript.

We can map the DFT energies of configurations 1 and 3 into an Ising model of the form:

$$E = E_0 - J \sum_{i=1}^N \sigma_i \sigma_{i+1}$$

where E_0 is a reference energy, J is the coupling constant, N is the cell length of the periodic chain, and σ_i represents the occupancy of site i : say $\sigma_i=1$ if the site is occupied by Fe, and $\sigma_i=-1$ if the site is occupied by Al. We define $\sigma_{N+1} = \sigma_1$ to impose periodic boundary conditions.

In the PMOF conventional cell, we have two parallel chains of $N=2$ sites each, so the Ising model can be written as:

$$E = E_0 - 2J \left[(\sigma_1 \sigma_2)_{\text{chain1}} + (\sigma_1 \sigma_2)_{\text{chain2}} \right]$$

Using the above equation for configurations 1 and 3 leads to:

$$E_1 = E_0 + 4J$$

$$E_3 = E_0 - 4J,$$

from where:

$$J = \frac{E_1 - E_3}{8} = -12.5 \text{ meV}$$

The negative value of the coupling constant reflects the preference for Fe-Al pairs over Fe-Fe or Al-Al pairs in NN positions.

By noting that

$$\frac{1}{2}(1 - \sigma_i \sigma_{i+1}) = \begin{cases} 0 & \text{for Fe-Fe or Al-Al pairs} \\ 1 & \text{for Fe-Al or Al-Fe pairs} \end{cases}$$

it is clear that the probability of NN Fe-Al can be calculated as:

$$p = \left\langle \frac{1}{2}(1 - \sigma_i \sigma_{i+1}) \right\rangle = \frac{1}{2}(1 - \langle \sigma_i \sigma_{i+1} \rangle)$$

where the $\langle \rangle$ brackets indicate average over all the NN pairs in an equilibrium system. For the one-dimensional Ising model with NN coupling, it is known that:¹

$$\langle \sigma_i \sigma_{i+1} \rangle = \tanh\left(\frac{J}{kT}\right)$$

where k is Boltzmann's constant and T is the equilibration temperature. Therefore:

$$p = \frac{1}{2} \left[1 - \tanh\left(\frac{J}{kT}\right) \right] = \frac{1}{1 + \exp\left(\frac{2J}{kT}\right)}$$

Substituting the J value and $T=298$ K in that expression leads to $p=0.73$, i.e. nearly three-quarters of all NN pairs along a chain in the mixed PMOF structure are Fe-Al.

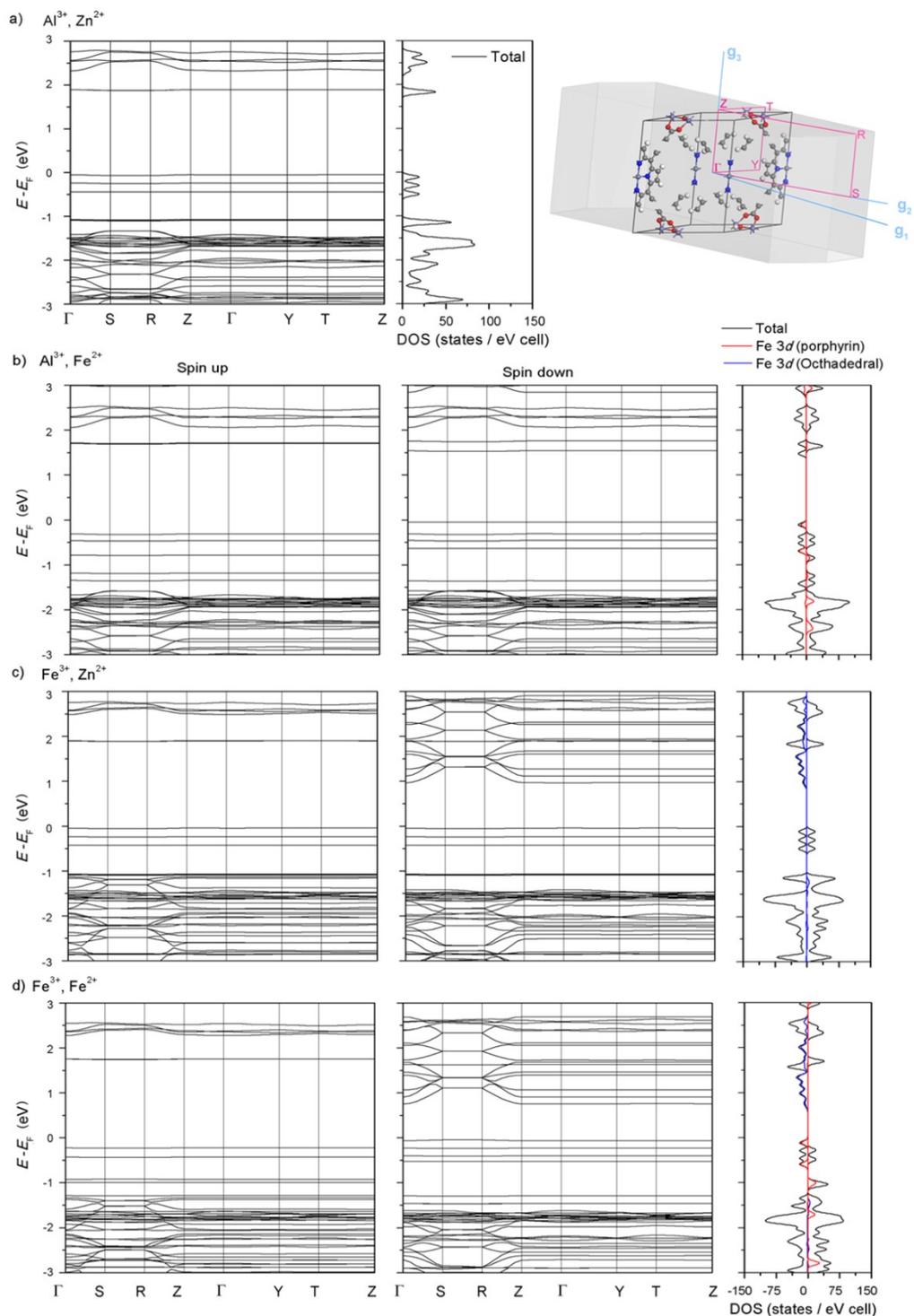


Figure S1: Electronic band structures and density of states (DOS) calculated using the PBE+U method for a) the “parent” structure (Al^{3+}, Zn^{2+})PMOF; b) for the structure with Fe in the porphyrin metal centres, (Al^{3+}, Fe^{2+})PMOF; c) for the structure with Fe in the octahedral metal centres, (Fe^{3+}, Zn^{2+})PMOF; and d) for the structure with Fe both in the porphyrin and the octahedral metal centres, (Fe^{3+}, Fe^{2+})PMOF.

References

1. F. Schwabl, *Statistical Mechanics*, Springer-Verlag, Berlin, 2006.