

## Electronic structure of porphyrin-based metal-organic frameworks and their suitability for solar fuel production photocatalysis

### Supplementary Information

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### Effects of Hubbard and dispersion corrections on the results

In our simulations, we used the GGA-PBE functional to optimise the geometries, while the electronic structures were calculated using single-point runs with the HSE06 functional. We have followed this approach because we are dealing with large simulation cells, where it becomes very computationally expensive to carry out the optimisations at the HSE06 level.

Here we provide evidence to show that the errors in the PBE optimisation are not expected to carry over to the electronic structure calculation. We have selected one of the structures (the one with Ni, which in this case is non spin-polarised, and therefore easier to calculate) for the test calculations.

In Table S1, we compare the geometries obtained with the following methods: a) PBE, b) PBE-D2, where the van der Waals interactions are taken into account via the DFT-D2 method of Grimme, c) PBE+U, where the  $U_{\text{eff}}$  parameter that describe the on-site Coulomb interaction of d electrons is set at 3 eV, and d) PBE-D2+U (i.e., both corrections applied).

Table S1. Calculated lattice parameters, cell volume and the two perpendicular N-N distances inside the porphyrin for the Ni-Al-PMOF structure, using different DFT functionals for the optimisation. As in Table 1 of the manuscript, in all cases the structures adopt the orthorhombic space group  $Cmmm$  (65), where  $\alpha=\beta=\gamma=90^\circ$ .

Functional	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$d$ [N-N] (Å)
PBE	31.995	6.723	16.964	3649.2	3.91/3.91
PBE-D2	31.920	6.641	16.949	3592.6	3.91/3.91
PBE+U	31.999	6.722	16.969	3649.8	3.92/3.93
PBE-D2 + U	31.917	6.644	16.956	3595.4	3.92/3.92

The cell parameters exhibit little deviation from one calculation to the other (maximum discrepancy is  $\sim 1\%$  along the  $b$  axis). The small effect of the U correction on the cell parameters is due to the fact that it only affects the metal at the centre of the rigid porphyrin ligand. On the other hand, the effect of the D2 correction is also small (although larger than for the U correction) because the whole structure is covalently linked.

The question remains on whether these small geometric changes can affect the final electronic structure. Figure S1 shows the positions of the band edges, as calculated with an HSE06 single point on the geometries optimised with different functionals. Clearly the variations in the positions of the band edges are very small (less than 0.04 eV).

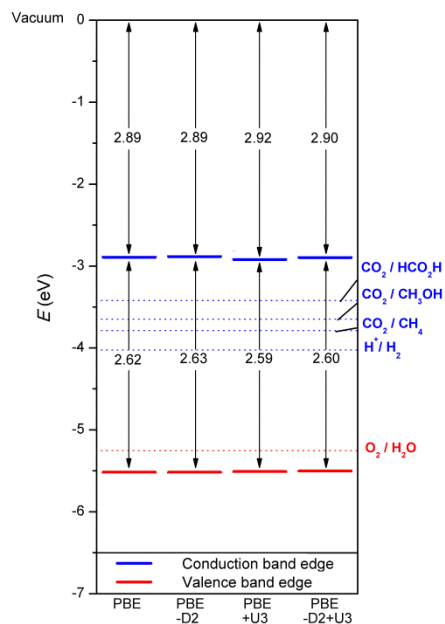


Figure S1. Bandgaps and band edge positions of the Ni-Al-PMOF system with respect to the vacuum level, as calculated with the HSE06 functional on geometries optimised at different levels of calculations (PBE, PBE-D2, PBE+U with U=3 eV, and PBE-D2+U). Energy levels corresponding to redox potentials of water splitting and carbon dioxide reduction reactions producing methane, methanol, and formic acid at pH = 7 are also shown with dotted lines.