# Chemical bonding at the metal-organic framework / metal oxide interface: simulated epitaxial growth of MOF-5 on rutile $TiO_2$

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## 1 Supplementary Information

### 1.1 Lattice mismatch

The lattice matching data for possible interfaces between metal-organic frameworks and binary inorganic materials within an 8 % mismatch is given in Tables S1, S2, S3 and S4. All binary materials are the experimental structures as taken from the ICSD [1]. All MOF structures were cleaned of disorder from experimental .CIF files and converged with the PBEsol+D3 functional using VASP. The planewave cut-off was set to 500 eV and forces converged to 0.001 eV/Å.

**Table S1** Lattice matching data for between the surface unit cells of the given binary materials (BM) and MOFs. Given are the Miller indices (*hkl*), cell expansions, and lattice mismatch percentages between the interfacing surfaces.

| BM | MOF | BM index | MOF index | Expansion BM(*x,y*), MOF(*x,y*) | Mismatch BM,MOF (%) |
|---|---|---|---|---|---|
| $SnS_2$ | UiO-66 (Zr) | (010) | (110) | (4,5) (1,2) | 0.1, 1.1 |
| ZnSe | UiO-66 (Zr) | (001) | (110) | (5,5) (2,2) | 2.2, 2.2 |
| $Al_2O_3$ | UiO-67 (Zr) | (010) | (011) | (4,3) (1,2) | 2.6, 2.5 |
| | | (110) | (011) | (4,3) (1,2) | 2.6, 2.5 |
| $TiO_2$ (A) | UiO-67 (Zr) | (001) | (001) | (5,3) (1,2) | 2.7, 0.7 |
| | | (101) | (011) | (5,5) (1,4) | 2.6, 0.7 |
| $SiO_2$ | UiO-67 (Zr) | (001) | (111) | (4,4) (1,1) | 3.6, 3.6 |
| ZnS | UiO-67 (Zr) | (111) | (111) | (5,5) (2,2) | 1.6, 1.6 |
| $SnS_2$ | UiO-66 (Ti) | (010) | (110) | (4,5) (1,2) | 3.1, 1.8 |
| ZnSe | UiO-66 (Ti) | (001) | (110) | (5,5) (2,2) | 0.7, 0.7 |
| $Al_2O_3$ | MIL-125(Ti) | (010) | (001) | (4,3) (1,2) | 2.7, 0.5 |
| | | (100) | (001) | (4,3) (1,2) | 2.7, 0.5 |
| | | (010) | (011) | (4,2) (1,1) | 0.6, 0.5 |
| | | (100) | (010) | (4,2) (1,1) | 0.6, 0.5 |
| $TiO_2$ (R) | MIL-125(Ti) | (011) | (110) | (4,5) (1,1) | 2.2, 2.2 |
| $TiO_2$ (A) | MIL-125(Ti) | (001) | (001) | (5,3) (1,2) | 2.4, 0.5 |
| | | (101) | (001) | (5,5) (1,4) | 2.8, 0.5 |
| | | (100) | (011) | (5,4) (1,1) | 1.4, 0.5 |
| | | (101) | (011) | (5,5) (1,3) | 0.5, 0.5 |
| $SiO_2$ | MIL-125(Ti) | (010) | (011) | (4,5) (1,1) | 3.1, 3.3 |
| $SnS_2$ | MIL-125(Ti) | (110) | (010) | (3,3) (1,1) | 0.3, 1.8 |
| $Al_2O_3$ | MOF-5(Zn) | (010) | (011) | (4,3) (1,2) | 6.2, 4.0 |
| | | (110) | (011) | (4,3) (1,2) | 6.2, 4.0 |
| | | (010) | (110) | (4,3) (1,2) | 6.2, 4.0 |
| | | (100) | (100) | (4,3) (1,2) | 6.2, 4.0 |
| $TiO_2$ (R) | MOF-5(Zn) | (001) | (011) | (4,4) (1,1) | 3.9, 3.9 |
| | | (001) | (110) | (4,4) (1,1) | 3.9, 3.9 |
| | | (110) | (011) | (6,4) (1,1) | 3.0, 4.9 |
| | | (110) | (110) | (6,4) (1,1) | 3.0, 4.9 |
| $TiO_2$ (A) | MOF-5(Zn) | (001) | (011) | (5,3) (1,2) | 1.0, 3.0 |
| | | (001) | (110) | (5,3) (1,2) | 1.0, 3.0 |
| $SnS_2$ | MOF-5(Zn) | (010) | (011) | (5,3) (1,1) | 3.5, 0.7 |
| | | (010) | (110) | (5,3) (1,1) | 3.5, 0.7 |
| | | (110) | (011) | (3,3) (1,1) | 3.5, 3.2 |
| | | (110) | (110) | (3,3) (1,1) | 3.5, 3.2 |
| ZnSe | MOF-5(Zn) | (001) | (110) | (3,3) (1,1) | 5.9, 5.9 |
| | | (001) | (110) | (3,3) (1,1) | 5.9, 5.9 |

**Table S2** Lattice matching data for between the surface unit cells of the given binary materials (BM) and MOFs. Given are the Miller indices (*hkl*), cell expansions, and lattice mismatch percentages between the interfacing surfaces.

| BM | MOF | BM index | MOF index | Expansion BM(*x,y*), MOF(*x,y*) | Mismatch BM,MOF (%) |
|---|---|---|---|---|---|
| $TiO_2$ (R) | MOF-646(Zn) | (001) | (001) | (4,4) (1,1) | 0.0, 2.2 |
| | | (001) | (100) | (4,4) (1,1) | 2.2, 2.2 |
| $SnS_2$ | MOF-646(Zn) | (110) | (101) | (3,4) (1,1) | 3.4, 2.6 |
| ZnSe | MOF-646(Zn) | (001) | (001) | (3,3) (1,1) | 2.0, 0.2 |
| | | (001) | (100) | (3,3) (1,1) | 0.2, 0.2 |
| | | (011) | (101) | (3,3) (1,1) | 0.2, 0.2 |
| $ZrO_2$ | DMOF-1(Zn)(orth) | (001) | (001) | (3,3) (1,1) | 1.5, 0.2 |
| | | (110) | (001) | (3,3) (1,1) | 1.8, 2.2 |
| | | (101) | (001) | (3,2) (1,1) | 2.2, 2.2 |
| | | (101) | (010) | (3,5) (1,2) | 1.4, 1.5 |
| | | (101) | (100) | (3,5) (1,2) | 1.4, 2.2 |
| $Al_2O_3$ | DMOF-1(Zn)(orth) | (010) | (110) | (4,5) (1,3) | 1.1, 2.7 |
| | | (110) | (110) | (4,5) (1,3) | 1.1, 2.7 |
| $TiO_2$ (A) | DMOF-1(Zn)(orth) | (001) | (001) | (4,5) (1,4) | 0.8, 2.2 |
| | | (101) | (001) | (4,1) (1,1) | 0.5, 2.2 |
| | | (100) | (010) | (4,3) (1,1) | 1.6, 2.9 |
| | | (101) | (010) | (4,5) (1,4) | 0.4, 2.9 |
| | | (001) | (011) | (4,2) (1,1) | 1.1, 2.9 |
| | | (100) | (100) | (4,3) (1,1) | 1.6, 2.2 |
| | | (101) | (100) | (4,5) (1,4) | 0.4, 2.2 |
| | | (001) | (101) | (4,2) (1,1) | 1.3, 2.2 |
| $SiO_2$ | DMOF-1(Zn)(orth) | (010) | (011) | (2,4) (1,1) | 1.2, 0.8 |
| ZnO | DMOF-1(Zn)(rhom) | (010) | (001) | (3,5) (1,2) | 1.9, 0.3 |
| | | (010) | (101) | (4,4) (1,1) | 3.8, 0.9 |
| $ZrO_2$ | DMOF-1(Zn)(rhom) | (101) | (101) | (5,5) (2,2) | 1.3, 2.6 |
| $Al_2O_3$ | DMOF-1(Zn)(rhom) | (010) | (001) | (2,1) (1,1) | 1.1, 1.4 |
| | | (100) | (001) | (2,1) (1,1) | 1.1, 1.4 |
| | | (010) | (010) | (2,4) (1,3) | 1.8, 1.4 |
| | | (100) | (010) | (2,4) (1,3) | 1.8, 1.4 |
| | | (010) | (011) | (2,5) (1,3) | 0.7, 1.4 |
| | | (100) | (011) | (2,5) (1,3) | 0.7, 1.4 |
| | | (110) | (100) | (3,4) (2,3) | 1.8, 3.4 |
| | | (110) | (101) | (3,3) (2,2) | 1.8, 3.4 |
| | | (110) | (110) | (2,4) (1,3) | 1.8, 2.8 |
| $TiO_2$ (R) | DMOF-1(Zn)(rhom) | (011) | (110) | (3,4) (1,1) | 0.2, 3.1 |
| $TiO_2$ (A) | DMOF-1(Zn)(rhom) | (001) | (001) | (5,1) (2,1) | 1.4, 2.8 |
| | | (100) | (001) | (5,2) (2,1) | 3.4, 2.4 |
| | | (101) | (001) | (5,4) (2,5) | 2.5, 2.4 |
| $SiO_2$ | DMOF-1(Zn)(rhom) | (010) | (110) | (4,4) (1,1) | 1.3, 0.0 |
| $SnS_2$ | DMOF-1(Zn)(rhom) | (110) | (001) | (5,2) (3,1) | 1.6, 16 |
| GaN | DMOF-1(Zn)(rhom) | (010) | (001) | (3,5) (1,2) | 2.4, 0.0 |
| | | (010) | (011) | (3,4) (1,1) | 3.7, 0.0 |
| ZnSe | DMOF-1(Zn)(rhom) | (001) | (010) | (5,3) (3,1) | 2.1, 0.8 |

**Table S3** Lattice matching data for between the surface unit cells of the given binary materials (BM) and MOFs. Given are the Miller indices (*hkl*), cell expansions, and lattice mismatch percentages between the interfacing surfaces.

| BM | MOF | BM index | MOF index | Expansion BM(*x,y*), MOF(*x,y*) | Mismatch BM,MOF (%) |
|---|---|---|---|---|---|
| ZnO | MOF-649(Zn) | (010) | (001) | (5,4) (1,1) | 1.9, 0.0 |
| | | (010) | (010) | (3,3) (1,1) | 3.0, 0.2 |
| | | (010) | (100) | (3,4) (1,1) | 1.9, 0.2 |
| | | (010) | (110) | (3,5) (1,1) | 2.3, 0.2 |
| $ZrO_2$ | MOF-649(Zn) | (001) | (001) | (3,4) (1,1) | 1.0, 2.3 |
| | | (101) | (011) | (3,3) (1,1) | 1.8, 2.3 |
| $Al_2O_3$ | MOF-649(Zn) | (110) | (001) | (2,5) (1,3) | 1.7, 2.2 |
| | | (010) | (010) | (2,5) (1,4) | 0.6, 1.6 |
| | | (100) | (010) | (2,5) (1,4) | 0.6, 1.6 |
| | | (010) | (100) | (2,5) (1,3) | 1.7, 1.6 |
| | | (100) | (100) | (2,5) (1,3) | 1.7, 1.6 |
| | | (010) | (101) | (4,5) (1,3) | 1.7, 1.2 |
| | | (100) | (101) | (4,5) (1,3) | 1.7, 1.2 |
| | | (010) | (110) | (2,2) (1,1) | 2.8, 1.6 |
| | | (100) | (110) | (2,2) (1,1) | 2.8, 1.6 |
| $TiO_2$ (A) | MOF-649(Zn) | (001) | (010) | (5,4) (2,3) | 1.8, 2.5 |
| | | (100) | (010) | (5,5) (2,2) | 2.5, 2.6 |
| | | (101) | (010) | (5,1) (2,1) | 3.4, 2.5 |
| | | (001) | (100) | (5,5) (2,3) | 3.5, 2.5 |
| | | (101) | (100) | (5,4) (2,3) | 2.3, 2.5 |
| | | (001) | (101) | (5,5) (1,3) | 3.5, 0.3 |
| | | (101) | (101) | (5,4) (1,3) | 2.3, 0.3 |
| | | (001) | (110) | (5,4) (2,1) | 0.8, 2.5 |
| | | (101) | (110) | (5,5) (2,3) | 2.7, 2.5 |
| $SiO_2$ | MOF-649(Zn) | (010) | (010) | (2,3) (1,1) | 1.1, 0.4 |
| | | (010) | (100) | (2,4) (1,1) | 1.1, 1.5 |
| | | (010) | (101) | (4,4) (1,1) | 3.9, 1.5 |
| | | (010) | (110) | (2,5) (1,1) | 1.1, 1.1 |
| | | (110) | (001) | (3,5) (1,2) | 0.4, 0.5 |
| $SnS_2$ | MOF-649(Zn) | (110) | (011) | (3,3) (1,2) | 2.5, 0.2 |
| GaN | MOF-649(Zn) | (010) | (001) | (5,4) (1,1) | 1.4, 0.2 |
| | | (010) | (010) | (3,3) (1,1) | 2.4, 0.1 |
| | | (010) | (100) | (3,4) (1,1) | 1.4, 0.1 |
| | | (010) | (110) | (3,5) (1,1) | 1.8, 0.1 |
| ZnS | MOF-649(Zn) | (001) | (001) | (3,4) (1,1) | 2.3, 1.5 |
| | | (011) | (011) | (3,3) (1,1) | 0.9, 1.5 |
| ZnSe | MOF-649(Zn) | (011) | (010) | (5,2) (3,1) | 0.8, 0.9 |

**Table S4** Lattice matching data for between the surface unit cells of the given binary materials (BM) and MOFs. Given are the Miller indices (*hkl*), cell expansions, and lattice mismatch percentages between the interfacing surfaces.

| BM | MOF | BM index | MOF index | Expansion BM(*x,y*), MOF(*x,y*) | Mismatch BM,MOF (%) |
|---|---|---|---|---|---|
| ZnO | IRMOF-16(Zn) | (110) | (001) | (4,4) (1,1) | 3.7, 3.2 |
| | | (110) | (010) | (4,4) (1,1) | 3.7, 3.2 |
| | | (110) | (100) | (4,4) (1,1) | 3.7, 3.2 |
| $ZrO_2$ | IRMOF-16(Zn) | (100) | (001) | (4,4) (1,1) | 2.2, 2.5 |
| | | (100) | (010) | (4,4) (1,1) | 2.2, 2.5 |
| | | (100) | (100) | (4,4) (1,1) | 2.2, 2.5 |
| $TiO_2$ (R) | IRMOF-16(Zn) | (001) | (001) | (5,5) (1,1) | 2.0, 2.0 |
| | | (011) | (001) | (5,4) (1,1) | 2.8, 2.0 |
| | | (001) | (010) | (5,5) (1,1) | 2.0, 2.0 |
| | | (011) | (010) | (5,4) (1,1) | 2.7, 2.0 |
| | | (001) | (100) | (5,5) (1,1) | 2.0, 2.0 |
| | | (011) | (100) | (5,4) (1,1) | 2.7, 2.0 |
| $SiO_2$ | IRMOF-16(Zn) | (110) | (001) | (4,5) (1,2) | 0.2, 1.8 |
| | | (110) | (010) | (4,5) (1,2) | 0.2, 1.8 |
| | | (110) | (100) | (4,5) (1,2) | 0.2, 1.8 |
| GaN | IRMOF-16(Zn) | (110) | (001) | (4,4) (1,1) | 3.5, 2.7 |
| | | (110) | (010) | (4,4) (1,1) | 3.5, 2.7 |
| | | (110) | (100) | (4,4) (1,1) | 3.5, 2.7 |
| ZnS | IRMOF-16(Zn) | (001) | (001) | (4,4) (1,1) | 1.3, 1.3 |
| | | (001) | (010) | (4,4) (1,1) | 1.3, 1.3 |
| | | (011) | (011) | (4,4) (1,1) | 1.3, 1.3 |
| | | (001) | (100) | (4,4) (1,1) | 1.3, 1.3 |
| | | (011) | (101) | (4,4) (1,1) | 1.3, 1.3 |
| | | (011) | (110) | (4,4) (1,1) | 1.3, 1.3 |
| $SnS_2$ | IRMOF-14(Zn) | (110) | (011) | (4,4) (1,1) | 3.4, 3.3 |
| | | (110) | (101) | (4,4) (1,1) | 3.4, 3.3 |
| ZnSe | IRMOF-14(Zn) | (001) | (110) | (4,4) (1,1) | 5.9, 5.9 |
| | | (001) | (110) | (4,4) (1,1) | 5.9, 5.9 |
| | | (011) | (011) | (4,3) (1,1) | 5.9, 0.3 |
| | | (001) | (101) | (4,3) (1,1) | 5.9, 0.3 |
| | | (111) | (001) | (4,4) (1,1) | 0.3, 0.3 |
| | | (111) | (010) | (4,4) (1,1) | 0.3, 0.3 |
| | | (111) | (100) | (4,4) (1,1) | 0.3, 0.3 |
| | | (111) | (111) | (4,4) (1,1) | 0.3, 0.3 |
| $TiO_2$ (A) | HKUST-1(Cu) | (001) | (011) | (5,3) (1,2) | 0.7, 1.3 |
| | | (001) | (110) | (5,3) (1,2) | 0.7, 1.3 |
| ZnS | HKUST-1(Cu) | (111) | (001) | (5,5) (2,2) | 3.5, 2.5 |
| | | (111) | (100) | (5,5) (2,2) | 3.5, 3.5 |

**Table S5** Lattice matching data for between the surface unit cells of the given binary materials (BM) and MOFs. Given are the Miller indices (*hkl*), cell expansions, and lattice mismatch percentages between the interfacing surfaces.

| BM | MOF | BM index | MOF index | Expansion BM(*x,y*), MOF(*x,y*) | Mismatch BM,MOF (%) |
|---|---|---|---|---|---|
| ZnO | COF-1(-) | (110) | (010) | (3,1) (2,4) | 1.3, 1.5 |
| | | (110) | (100) | (3,1) (2,4) | 1.3, 1.5 |
| $ZrO_2$ | COF-1(-) | (101) | (110) | (2,5) (3,1) | 1.1, 0.8 |
| $Al_2O_3$ | COF-1(-) | (010) | (110) | (3,3) (4,1) | 0.8, 1.2 |
| | | (100) | (110) | (3,3) (4,1) | 0.8, 1.2 |
| $TiO_2$ (R) | COF-1(-) | (001) | (010) | (4,5) (5,1) | 3.0, 0.3 |
| | | (010) | (010) | (5,5) (4,1) | 3.0, 0.9 |
| | | (001) | (100) | (4,5) (5,1) | 3.0, 0.3 |
| | | (010) | (100) | (5,5) (4,1) | 3.0, 0.9 |
| $SnS_2$ | COF-1(-) | (010) | (010) | (1,4) (1,1) | 3.9, 2.9 |
| | | (010) | (100) | (1,4) (1,1) | 3.9, 2.9 |
| GaN | COF-1(-) | (110) | (010) | (2,4) (3,1) | 1.6, 0.9 |
| | | (110) | (110) | (2,4) (3,1) | 1.6, 0.9 |
| ZnS | COF-1(-) | (001) | (010) | (2,4) (3,1) | 3.8, 3.0 |
| | | (011) | (010) | (2,3) (3,1) | 2.1, 3.0 |
| | | (001) | (100) | (2,4) (3,1) | 3.8, 3.0 |
| | | (011) | (100) | (2,3) (3,1) | 2.1, 3.0 |
| | | (011) | (110) | (2,5) (3,1) | 1.7, 3.0 |
| ZnSe | COF-1(-) | (001) | (010) | (3,4) (5,1) | 1.5, 2.3 |
| | | (001) | (100) | (3,4) (5,1) | 1.5, 2.3 |
| | | (011) | (110) | (3,5) (5,1) | 3.5, 2.3 |

### 1.2 First principles reference state energies

The total energy of reference states considered for the calculation of binding energies of BDC on the surface of $TiO_2$ are given in Table S6.

**Table S6** First-principles reference energies used for calculating reported binding energies of BDC ligand to $TiO_2$ (110) surface.

| System | Energy (eV) |
|---|---|
| BDC-$H_2$ | -3070.515 |
| BDC-$H_1^-$ | -3056.345 |
| $TiO_2$ (110) surface | -442099.193 |
| $TiO_2$ (110) surface + $H^+$ | -442114.702 |

### 1.3 Coulomb energy correction

An electrostatic energy correction was required for calculating the proton transfer energy between BDC ligand and $TiO_2$ surface. We place an $F^-$ anion in the centre of a cubic unit cell and calculate the internal energy as a function of inverse unit cell length, $a$. The internal energy of a charged unit cell with infinite dimensions can be extrapolated from the intercept of $1/a$ *vs* internal energy plot. The difference in energy of an $F^-$ anion in the unit cell used for the BDC on $TiO_2$ surface calculations and the total energy of the charged unit cell with infinite dimensions is the correction per +/- 1 charge on a system (-0.408 eV). As two charges need to be accounted for (from surface and ligand charged reference states) in the correction, a factor of two is applied when calculating the final proton transfer energy. The charge correction was calculated as the difference between the infinite box limit (intercept of the plot given in Figure S1) and the energy of the anion in the unit cell used for the first-principles calculations of BDC on $TiO_2$.

**Table S7** Total energy of $F^-$ anion in a cubic unit cell of dimensions ($a$) used to calculate the electrostatic Coulomb energy correction of charged reference states.

| $a$ | $1/a$ ( $Å^{-1}$) | Total energy (Ha) | Total energy (eV) |
|---|---|---|---|
| 10 | 0.1 | -24.227 | -659.253 |
| 15 | 0.066666667 | -24.205 | -658.660 |
| 20 | 0.05 | -24.194 | -658.341 |
| 25 | 0.04 | -24.186 | -658.145 |
| 30 | 0.033333333 | -24.182 | -658.012 |
| 35 | 0.028571429 | -24.178 | -657.916 |
| 40 | 0.025 | -24.175 | -657.844 |
| 45 | .022222222 | -24.173 | -657.788 |
| 50 | 0.02 | -24.172 | -657.743 |

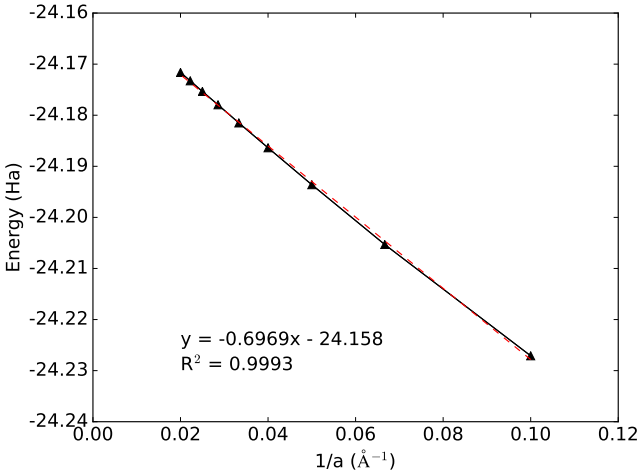


**Fig. S1** Electrostatic Coulomb energy correction plot from data given in Table S7.

**Table S8** Calculation of electrostatic Coulomb energy correction from the infinite box limit as determined from data reported in Table S7.

| Description | Energy |
|---|---|
| Intercept (infinite box limit) energy (Ha) | -24.158 |
| In box same size as simulations (Ha) | -24.173 |
| Δ E (Coulomb) (Ha) | 0.015 |
| Δ E (Coulomb) (eV) | 0.408 |

### 1.4 Thermodynamic cycle of proton transfer

The thermodynamic cycle considered for calculating the proton transfer energy between a BDC ligand and $TiO_2$ surface is given in Figure S2. Note the inclusion of the electrostatic Coulomb energy correction.

### 1.5 Forcefield parameters and structure files

All forcefield parameter files can be obtained from `https://github.com/WMD-group/VMOF`. The charges of the BDC ligands depending on where they are located in relation to the surface and charge terminating ends are given in Figure S3.

### 1.6 Proton migration across the surface of $TiO_2$

The energy required to move the protons from ligand a and ligand b across the surface of $TiO_2$ was calculated (Table S9), with trialled positions depicted in Figure S4. Two different structure models were considered and are depicted in Figure S5. For ligand b, reconstruction of the surface was observed when the proton was moved around neighbouring oxide sites

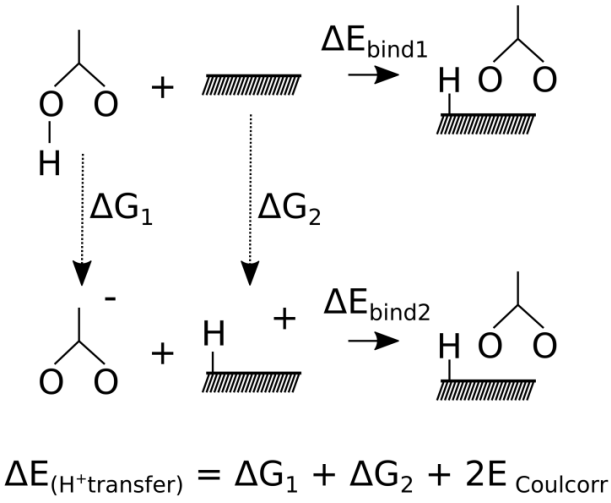


**Fig. S2** Thermodynamic cycle considered for calculating proton transfer energies between BDC and the $TiO_2$ surface.

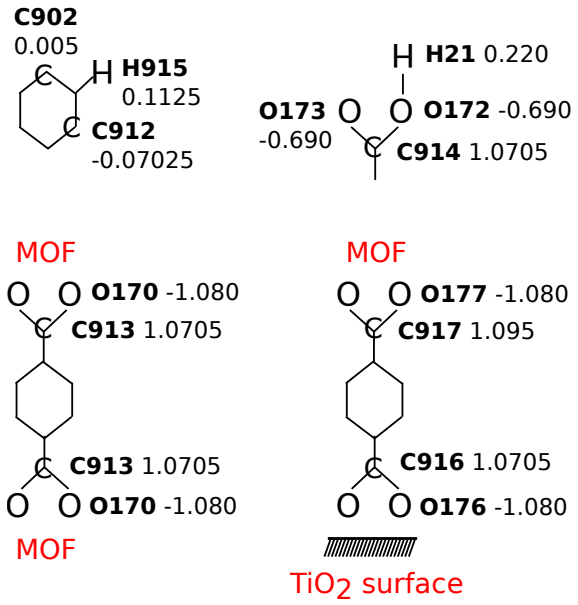


**Fig. S3** Charges and atom types correlating to supplied parameter files of the BDC ligand in different regions of the MOF with regards to distance from the $TiO_2$ surface and charge terminating ends of the ligand.

to the BDC ligand position, which has resulted in the large differences in energies for the reconstructed and un-reconstructed surfaces.

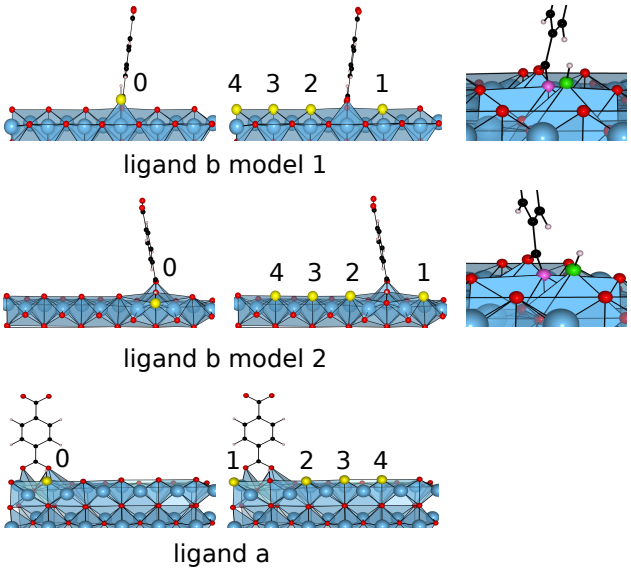


**Fig. S4** Locations considered for the movement of a proton across the surface for ligand **b** model 1 and 2 and ligand **a**. Initial converged geometries are given, where the proton is located on the displaced oxide anion (left) with proton movements across the oxide bridge shown (centre). The closer view of the reconstruction at the site of ligand **b** models is given (right), where the protonated oxide is highlighted in green and O (carb) that has become incorporated into the surface is highlighted in pink. Note that the labels of ligand **a** and ligand **b** correspond to Figure 5 in the main manuscript text but the orientation of the cell is rotated.

**Table S9** Energy of moving protons associated with ligand **a** and **b** considering structures 1 and 2 (Figure S5) of MOF-5 on $TiO_2$. Positions 1–4 refer to an increasing distance of the proton from the ligand along down the oxide bridge as depicted in Figure S4.

| Ligand **a** proton movement | Relative energy (eV) | | | |
|---|---|---|---|---|
| | Structure 1 | | Structure 2 | |
| Proton position | Ligand **b** model 1 | Ligand **b** model 2 | Ligand **b** model 1 | Ligand **b** model 2 |
| 0 | 0.000 | 0.000 | 0.000 | 0.000 |
| 1 | 0.018 | 0.001 | 0.077 | 0.005 |
| 2 | 0.235 | 0.234 | 0.236 | 0.334 |
| 3 | 0.401 | 0.402 | 0.408 | 0.374 |
| 4 | 0.446 | 0.446 | 0.447 | 0.413 |
| Ligand **b** proton movement | Relative energy (eV) | | | |
| | Structure 1 | | Structure 2 | |
| Proton position | Ligand **b** model 1 | Ligand **b** model 2 | Ligand **b** model 1 | Ligand **b** model 2 |
| 0 | 0.000 | 0.018 | 0.000 | 0.000 |
| 1 | 2.218 | 0.202 | 2.267 | 0.234 |
| 2 | 2.300 | 0.000 | 2.349 | 0.025 |
| 3 | 2.372 | 2.681 | 2.410 | 2.541 |
| 4 | 2.346 | 2.797 | 2.381 | 2.471 |

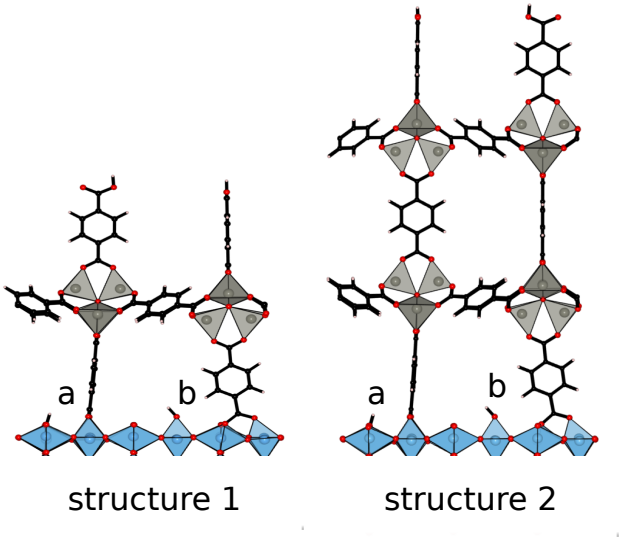


**Fig. S5** Structure models considered for different layer thickness of MOF-5 on the (110) surface of $TiO_2$ with ligand **a** and ligand **b** labelled. Note that the full thickness of the $TiO_2$ has not been depicted but is identical for both models as described in the main manuscript.

### 1.7 Energy of adsorption of MOF-5 on $TiO_2$

To calculate the energy of adsorption of MOF-5 on $TiO_2$ with the forcefield, the thickness of the two layers were incrementally increased. The extrapolation of a plot of internal energy as a function of layer thickness (Figure S6) allows the bare adsorption energy of the interfacing layers to be calculated.

**Table S10** Calculation of the energy of adsorption between the interfacing surfaces of MOF-5 and $TiO_2$.

| Number of layers | Internal energy (eV) |
|---|---|
| 2 | -3525.369 |
| 3 | -5439.346 |
| 4 | -7357.126 |
| Surface area of interface ($m^{-2}$) | $3.449\times10^{-17}$ |
| Intercept (zero interface limit) | 307.020 |
| Energy of adsorption ($Jm^{-2}$) | 1.426 |

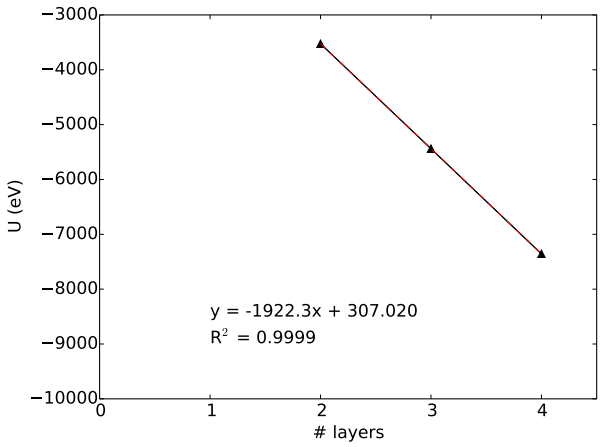


**Fig. S6** Thickness of MOF-5 and $TiO_2$ *vs* internal energy of the interfacing systems plot used to calculate the energy of adsorption between the interfacing surfaces.

## References

1 A. Belsky, M. Hellenbrandt, V. L. Karen and P. Luksch, *Acta Cryst. B*, 2002, **58**, 364–369.