

# Supporting information for: Ligand-assisted enhancement of CO<sub>2</sub> capture in metal organic frameworks

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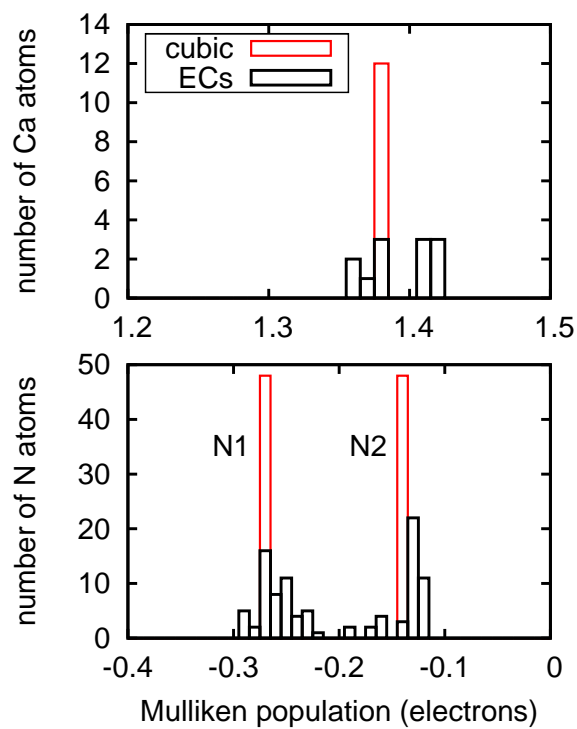


Figure S 1: Histogram of Mulliken charge population for Ca and N atoms in CaBTT MOF. Red and black data correspond to a cubic crystal in absence of  $M'$  atoms and to CaBTT with  $M'=Na$ , respectively. The presence of a neighboring  $M'$  atoms reduces the charge difference between N1 and N2 and as a consequence neighboring Ca atoms have a lower positive charge.

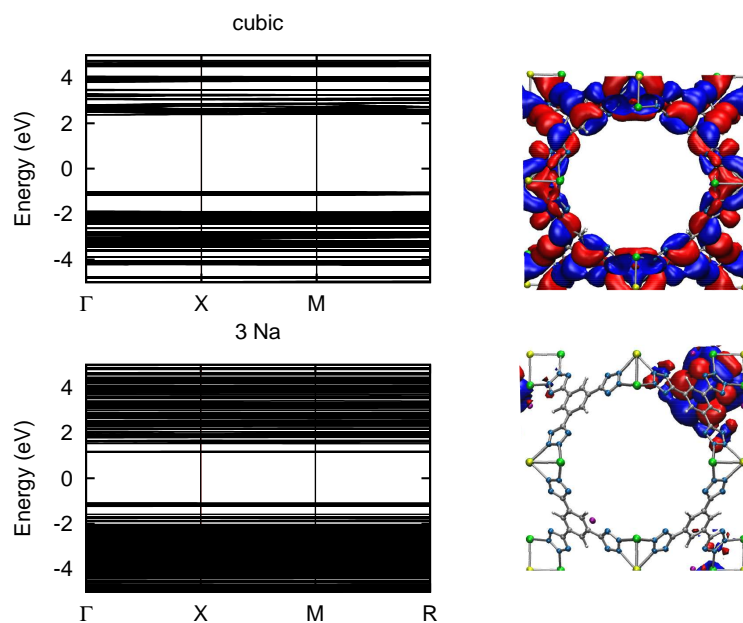


Figure S 2: Left panels: Electronic band structure for cubic CaBTT (upper panel) and monoclinic CaBTT where charge is balanced by 3  $M' = Na$  (lower panel). Right panels: Corresponding wavefunction of the lowest unoccupied band. The presence of  $M'$  atoms removes the degeneracies of the electronic structure with the wavefunction exhibiting a defect-like character.

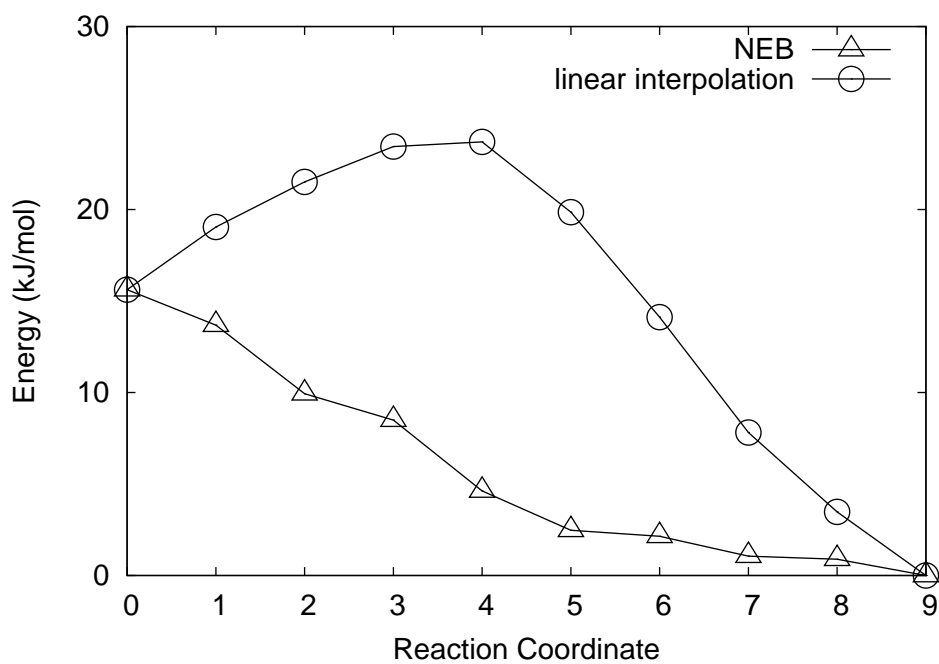


Figure S 3: Total energy at intermediate images between the CO<sub>2</sub> binding geometry at the Ca and N sites. The images have been computed as a linear interpolation between the two geometries (x coordinate in Figure). After the nudged elastic band calculation the minimum energy path shows absence of an energy barrier between the two configurations.

## Extraframework cations

When smaller M' atoms are used, CO<sub>2</sub> binding is significantly enhanced for M' at the A2 site: a smaller ionic bond distance between the CO<sub>2</sub> oxygen and M' is predicted, as well as a larger O-Ca distances. This suggests that a stronger O-M' interaction weakens O-Ca, resulting in a more attractive CO<sub>2</sub> interaction energy. Bond lengths, bond angle and binding energies are reported in Table 1. For M'=K, although CO<sub>2</sub> is found to bind with the MOF, the total binding energy shows a less stable complex upon CO<sub>2</sub> adsorption. This destabilization is due to the CO<sub>2</sub>-K(A2) interaction with result in a different location of the M' atom as shown in Figure S4. A negligible dependence of the M' atom choice is found when the neighboring M' atom is located at A1 due to the larger CO<sub>2</sub>-M' distance (O-Na(A2) is 2.393 Å while O-Na(A1) is 5.060 Å).

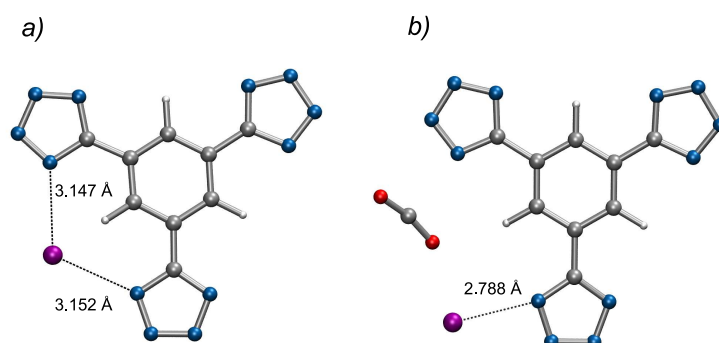


Figure S 4: Fragments of the crystal structure of CaBTT before and after CO<sub>2</sub> adsorption with M'=K at the A2 site

Table S 1: PBE binding energies, bond distances and the O-C-O bond angle of CO<sub>2</sub> are also reported for the different M' atoms at the A2 site.

FC	$E_{ads}$ (kJ/mol)	O-C-O(°)	O-FC(Å)	C-N(Å)	O-H(Å)	O-M'(Å)
Li	59.9	169.1	2.634	2.657	2.647	2.447
Na	48.5	171.4	2.476	2.741	2.682	2.393
K	N.B.	165.5	2.471	2.573	2.516	2.623

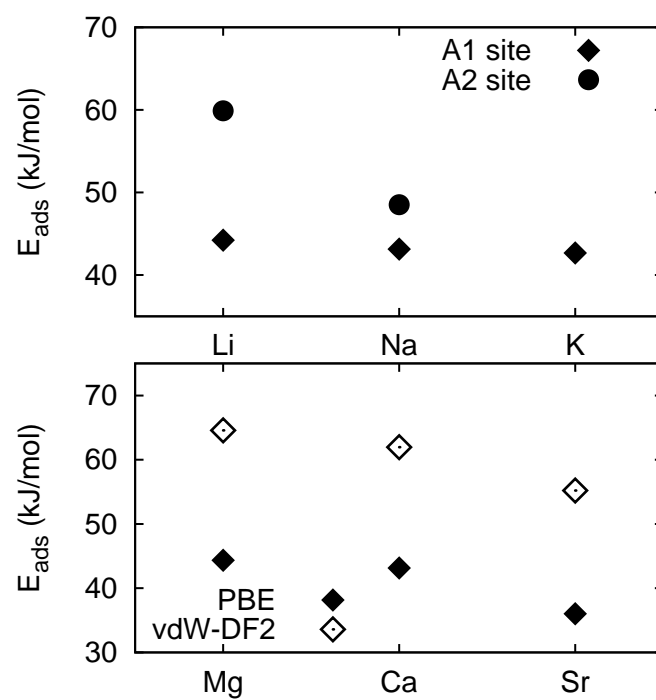


Figure S 5: Upper panel: Evolution of the PBE CO<sub>2</sub>-MOF interaction energy as a function of the extraframework at both A1 (diamond) and A2 (circle) geometry. Lower panel: Evolution of the PBE and vdW-DF2 CO<sub>2</sub>-MOF interaction energies as a function of the metal atom, with M<sup>2</sup>=Na at the A1 geometry.