Electronic Supplementary Information (8 pages)

Synthesis and hydrogen adsorption properties of internally polarized 2,6-azulenedicarboxylate based metal-organic frameworks

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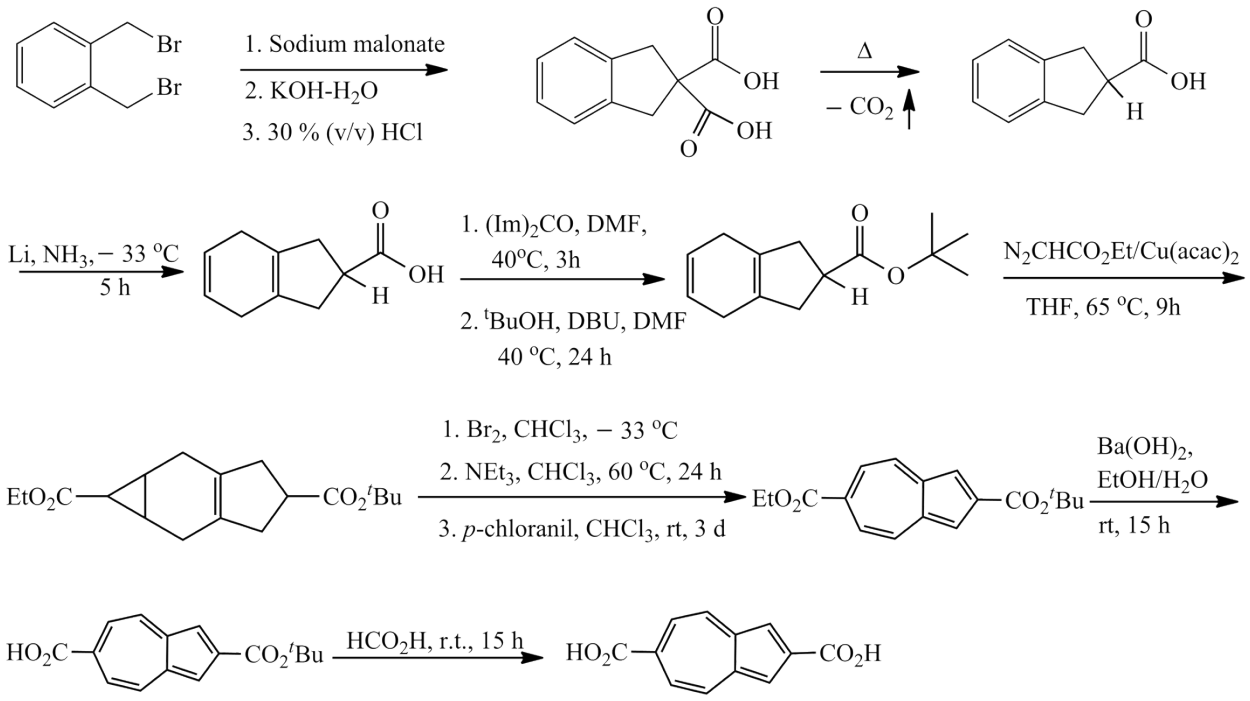
Synthesis Scheme



Scheme S1. Scheme for Synthesis of 2,6-azulenedicarboxylic acid

Single-Crystal X-Ray Diffraction

Single-crystal X-ray diffraction (SXRD) data for MOF-649 and MOF-650 were collected on a Xcalibur diffractometer (Agilent Technologies, Ruby CCD detector) using a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å.[S1] The selected single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, analytical absorption correction,[S2] and data reduction were performed with the Oxford program suite CrysAlisPro.[S1] The crystal structures were solved with SHELXS97[S3] using direct methods and was refined by full-matrix least-squares methods on F2 with SHELXL97.[S3] All programs used during the crystal structure determination process are included in the WINGX software.[S4] The program PLATON[S5] was used to check the results of the X-ray analyses. The electron densities corresponding to the disordered guest molecules of MOF-649 and MOF-650 were flattened using 'SQUEEZE'[S6] option of PLATON. The chemical formula of MOF-649 and MOF-650 were determined

using a combination of single-crystal X-ray diffraction, thermogravimetric analysis, and elemental analysis studies. The crystallographic details of both the MOFs are summarized in Table 1. CCDC 922543-922544 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

MOF-649: The title compound, $[Zn_2(C_{24}H_{12}O_8)_2(C_6H_{12}N_2)].(DMF)_4.(H_2O)_2$, crystallized in the orthorhombic *C*mmm space group. The crystal structure exhibits a three-dimensional framework with wide open channels of approximately 15.7 × 9.0 Å running along the crystallographic *c* axis. Most of the structure is disordered over two sets of positions since it lies about several symmetry elements, inversion centers, two-fold axes and mirror planes. Some soft *SHELXL* restraints (*DELU*, *SADI*, *SIMU*) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, and with C-H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methyl H atoms. The presence of solvent molecules could easily be seen by the residual peaks located in the open channels. Unfortunately, they were disordered so badly that it could not be modeled even with restraints. Consequently, SQUEEZE (from PLATON) was used to calculate the void space, the electron count and to get a new *HKL* file. According to the SQUEEZE results and the different experimental evidences (see manuscript), a total number of 8 *N*,*N*-dimethylformamide (DMF) and 4 water solvent molecules (360 electrons) was considered per unit cell. All parameters reported in the CIF take the solvent molecules into account, leading to many alerts level A in the checkCIF report. Without solvent molecules: $R_1 = 0.115$ for 1337 reflections of $I > 2\sigma(I)$ and $wR_2 = 0.360$ for all data. With solvent molecules (SQUEEZE): $R_1 = 0.072$ for 1337 reflections of $I > 2\sigma(I)$ and $wR_2 = 0.214$ for all data, the volume fraction was calculated to 2158 $Å^3$ which corresponds to 66% of the unit cell volume, and to 359 electrons per unit cell allocated to solvent molecules.

MOF-650: The title compound, $[Zn_4O(C_{12}H_6O_4)_3].(DMF)_4.(NMP)_4(H_2O)_{13}$, crystallized in the cubic *F*m-3m space group. The crystal structure has two large cavities having approximate diameter 15 and 18.2 Å and the pore apertures of the later is about 9.8 Å in diameter. Most of the structure is disordered over two sets of positions since it lies about several symmetry elements, inversion centers, two-fold axes and mirror planes. Some *SHELXL* restraints (*DFIX*, *DANG*, *SIMU*) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms. All hydrogen

positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms. The presence of solvent molecules could easily be seen by the residual peaks located in the open channels. Unfortunately, they were disordered so badly that it could not be modeled even with restraints. Consequently, *SQUEEZE* (from *PLATON*) was used to calculate the void space, the electron count and to get a new *HKL* file. According to the *SQUEEZE* results and the different experimental evidences (see manuscript), a total number of 4 *N*,*N*-dimethylformamide (DMF), 4 N-Methyl-2-pyrrolidone (NMP), and 13 water solvent molecules (3920 electrons) was considered per unit cell. In comparison with the 10106 electrons calculated by SQUEEZE, we consider that only one third of the accessible void is filled by solvent molecules. More solvent molecules will not be in agreement with the elemental analysis. All parameters reported in the CIF take the solvent molecules into account, leading to many alerts level A in the checkCIF report. Without solvent molecules: R_1 = 0.340 for 744 reflections of $I > 2\sigma(I)$ and wR_2 = 0.653 for all data. With solvent molecules (SQUEEZE): R_1 = 0.144 for 744 reflections of $I > 2\sigma(I)$ and wR_2 = 0.376 for all data, the volume fraction was calculated to 23342 Å^3 which corresponds to 82% of the unit cell volume, and to 10106 electrons per unit cell allocated to solvent molecules.

References

[S1] Agilent Technologies (formerly Oxford Diffraction), Yarnton, England, 2011.

[S2] R. C. Clark and J. S. Reid, *Acta Cryst.*, 1995, **A51**, 887.

[S3] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

[S4] L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837.

[S5] A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.

[S6] A. L. Spek, PLATON99 A Multipurpose Crystallographic Tool, Utrecht University: Utrecht, 1999.

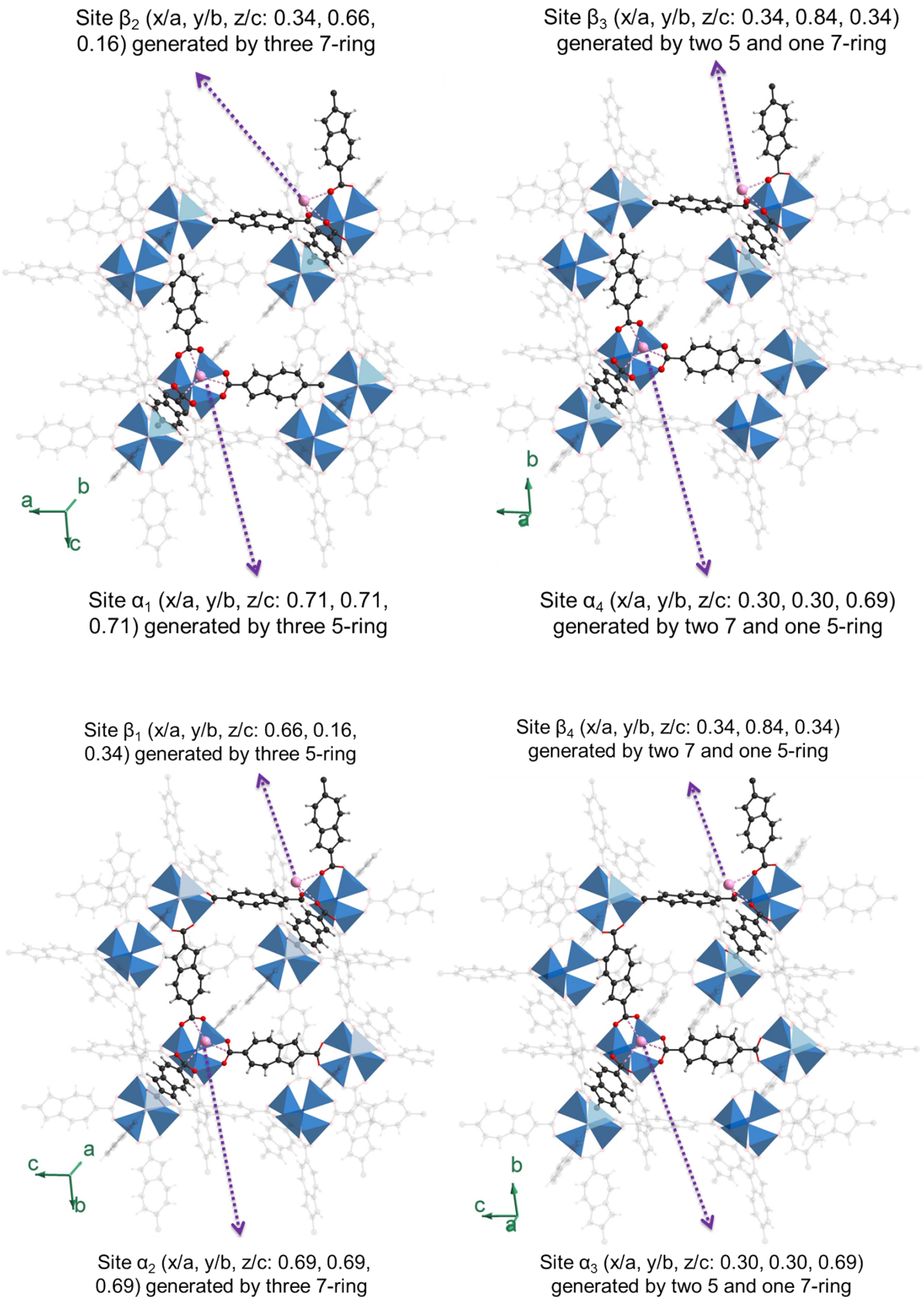


Figure S1. Ball and stick presentation of the modelled structures of MOF-650 in *Pa*-3 which incorporates four different possible alpha sites i.e. α_1 (top, left), α_2 (down, left), α_3

(down, right), α_4 (top, right) and beta sites i.e. β_1 (down, left), β_2 (top, left), β_3 (top, tight) and β_4 (down, right). Atom colors: Zn, blue polyhedra; O, red; C, black and H, light grey. The sites are visualized with light-pink spheres.

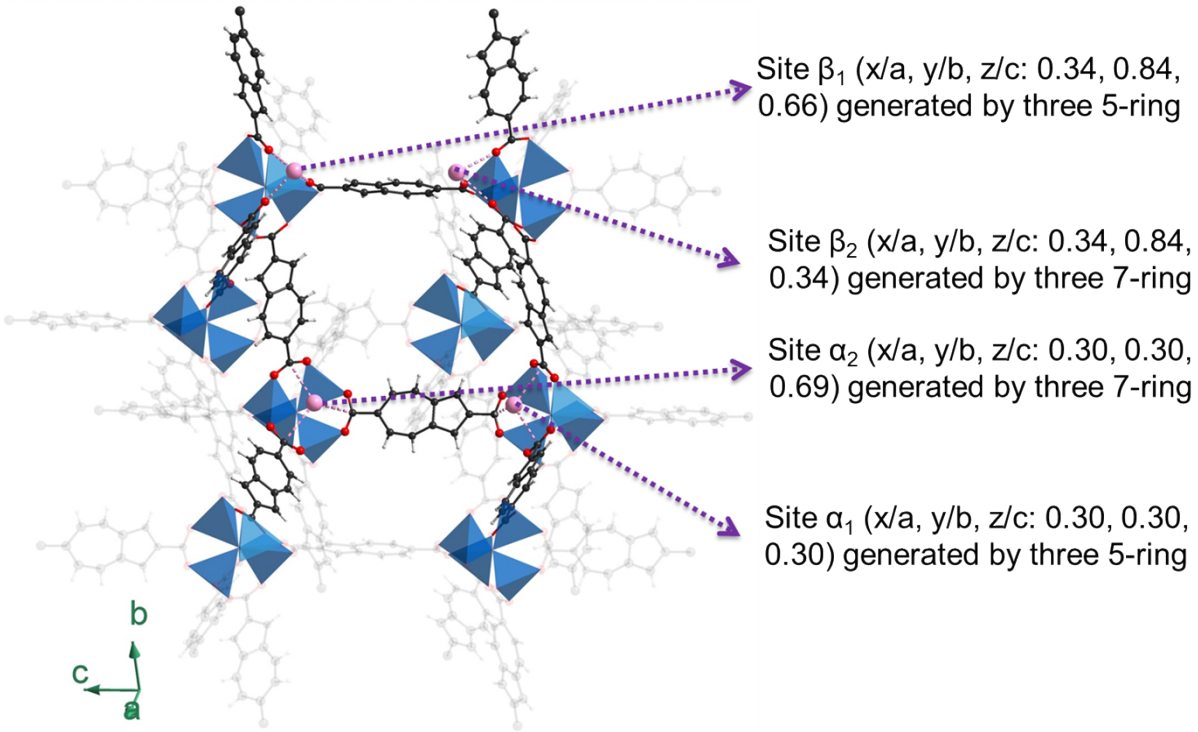


Figure S2. A ball and stick presentation of the modelled structure in *F*-43*m* which incorporate sites α_1, α_2, β_1 and β_2 where the linkers are in antiparallel orientation with respect to the opposite edge of the square faces of both the cavity (only the large cavity is shown for simplicity). Atom colors: Zn, blue polyhedra; O, red; C, black and hydrogen, light grey. The sites are visualized with light-pink spheres.

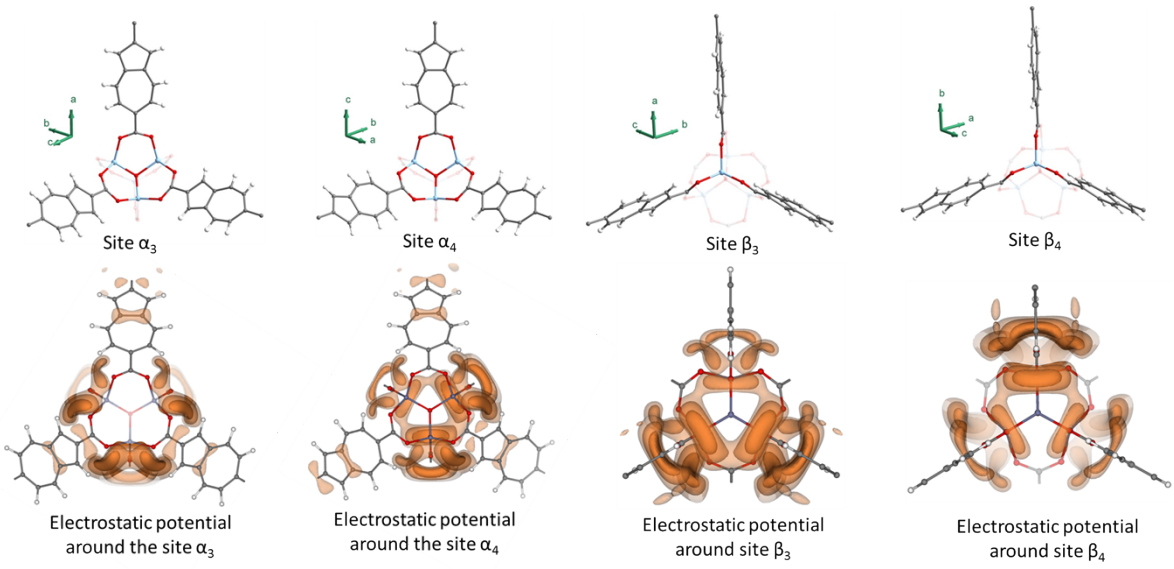


Figure S3. Partial view of the modeled structure in *Pa*-3 which incorporates site α_3, α_4, β_3 and β_4 depending on the number of carboxylate of 5 or 7-membered ring sides of azulene linkers are connecting at their edges and their corresponding calculated electrostatic potential (down). Atom colors: Zn, blue; O, red; C, black and H, light grey.

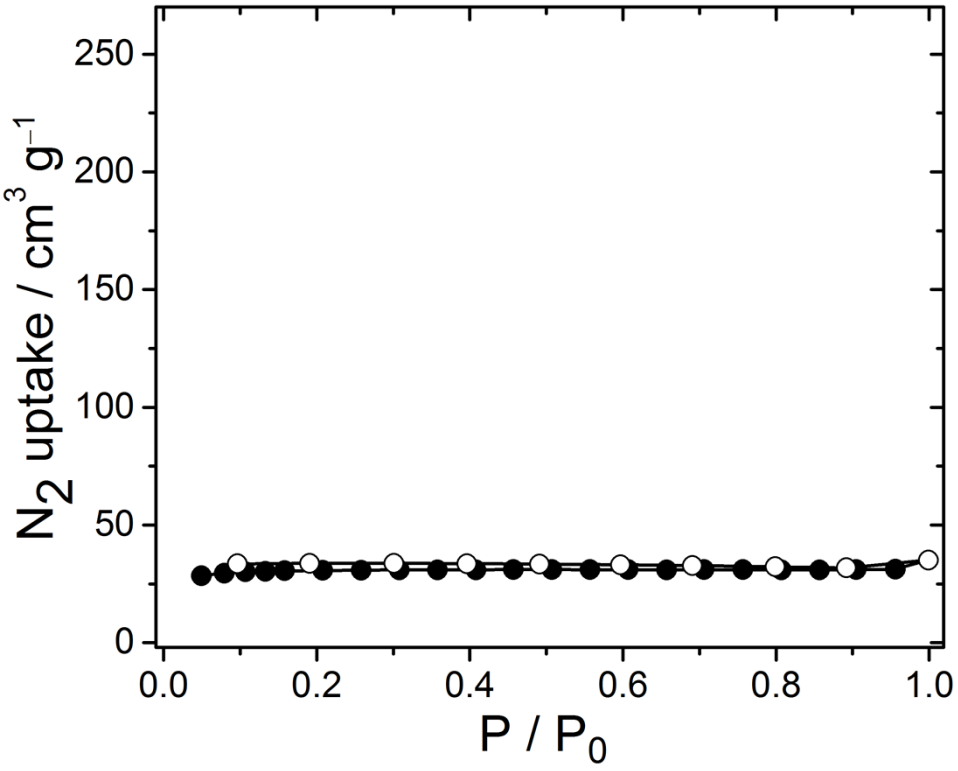


Figure S4. N_2 isotherm at 77 K: activated MOF-649 prepared after degassing the chloroform exchanged materials at room temperature for 12 h. Filled and open circles represent adsorption and desorption branches, respectively. Connecting traces are guides for the eyes.

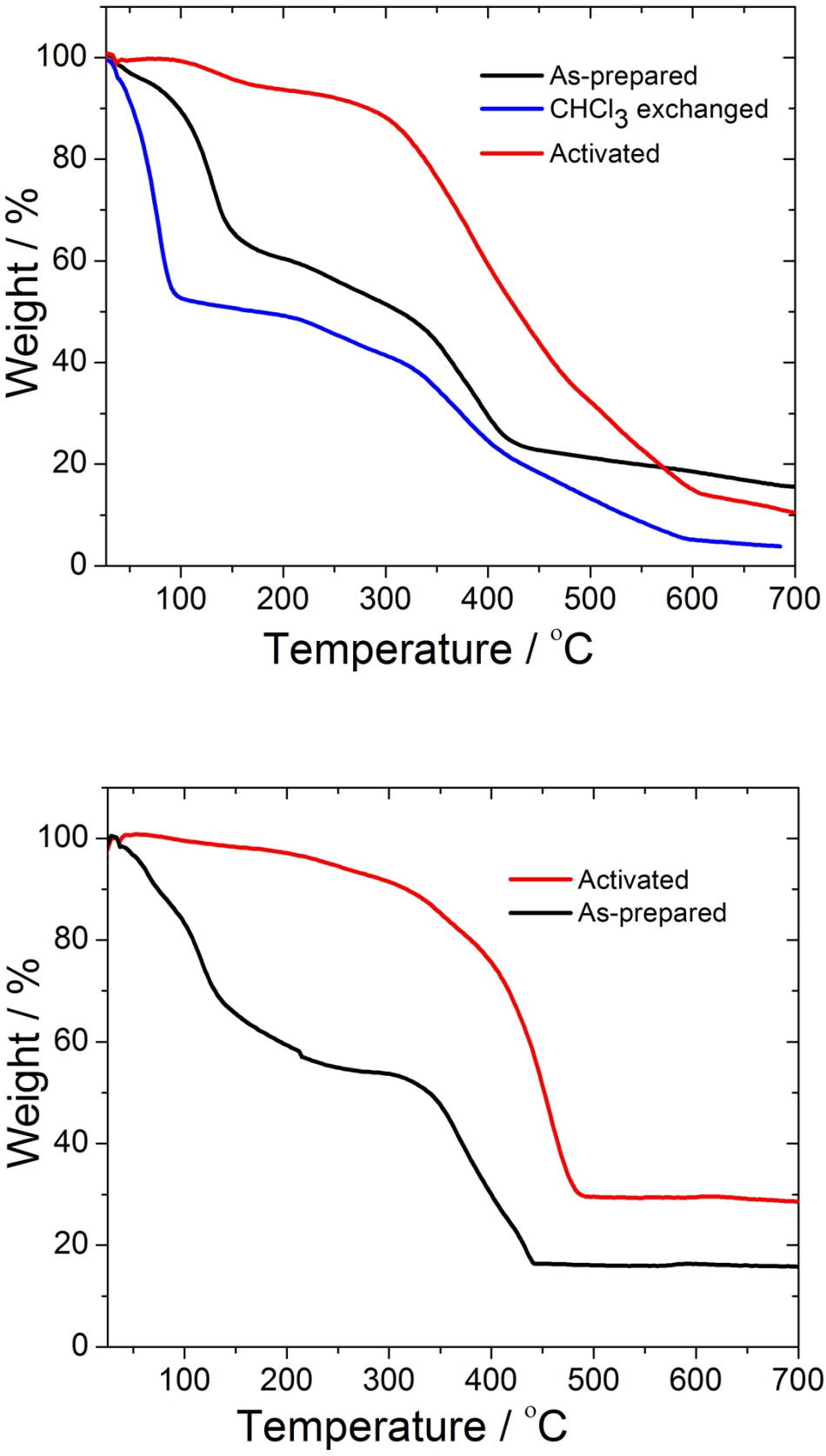


Figure S5. TGA plot for MOF-649 (top) and for MOF-650 (bottom).