Supporting information for the manuscript

An unprecedentedly robust microporous metal-organic framework constructed from a flexible organic linker for highly selective sorption of methanol over ethanol and water

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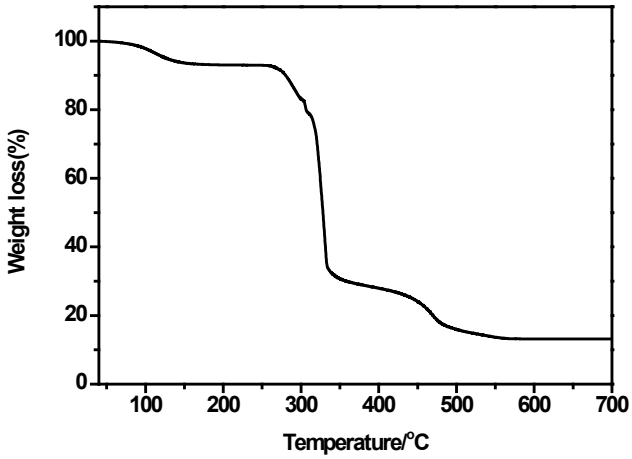

Figure S1 TGA of MOF **1**.

Powder x-ray diffraction studies

Activated MOF 1a: Majority of the XRD reflections in the MOF **1** pattern after activation can be indexed to a tetragonal structure with lattice parameters of approximately a=14.504Å and c=15.403Å. Assessment of the extinction symbol associated with the space group of the new phase indicated the most probable to be $P4_32_12$. Rietveld structural refinement was done using the GSAS package[i]. Due to the inadequate number of observations in the laboratory X-ray data, the organic linker were defined a rigid body with the C-C, C-O, C-H, and C-N bond lengths and bond

angles kept as the values determined from the single-crystal data. One linker rigid body and Zn cation positions together with the lattice parameters were refined, yielding the agreement factors of R_{wp}=11.70% and R_p=8.55%. The refined lattice parameters are a=14.4835(12) Å and 15.4118(16) Å, expanding along *a* and shrinking along *c* compared to the original MOF **1** (the lattice parameters of the original MOF **1** are a=14.3035(3) Å and c=15.9627(6) Å). The refined occupancy of the methanol CH_3OH molecule is closed to zero, indicating a complete activation of the MOF material. The refined XRD pattern is shown in Figure S2, and the determined crystal structure is in the attached CIF file.

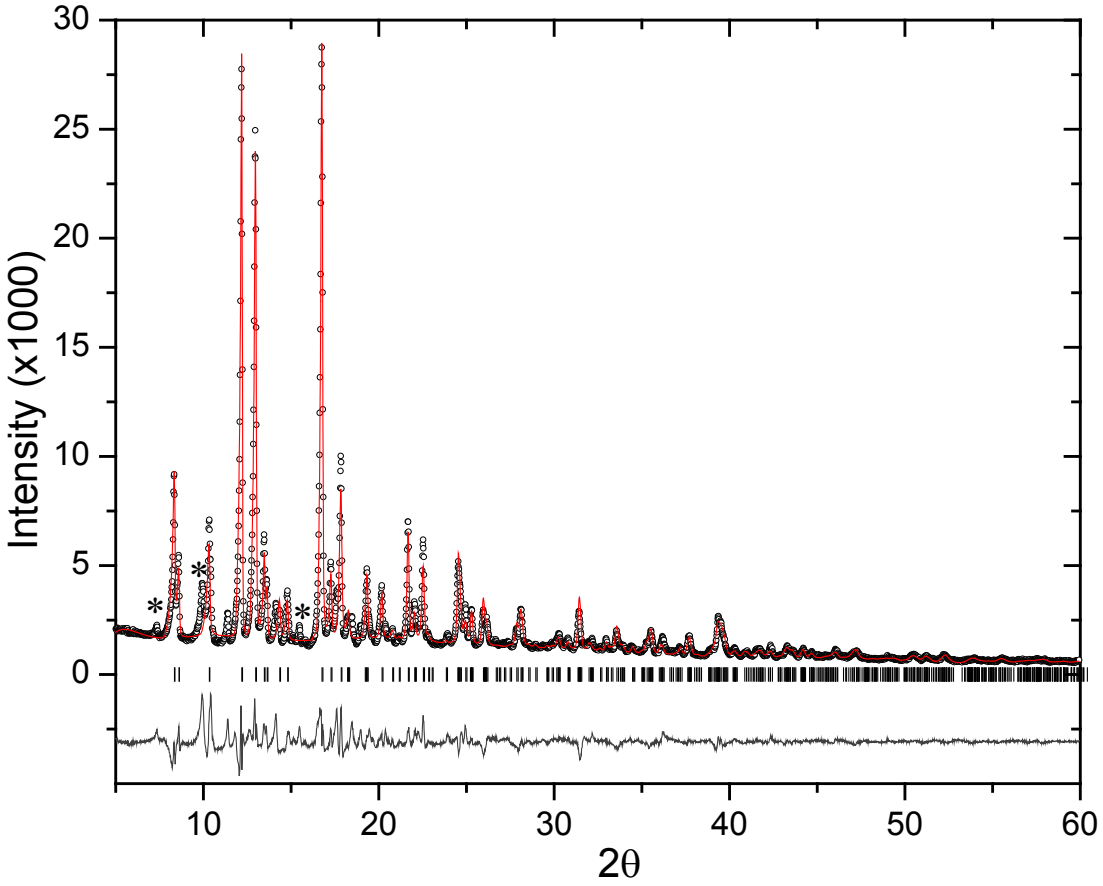

Figure S2 Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for the activated MOF **1a** at 298 K. Vertical bars indicate the calculated positions of Bragg peaks. There is also a small fraction of impurity phase(s) observed after activation as indicated by asterisks.

Methanol re-adsorbed MOF 1': The activated sample after re-adsorption of methanol is basically restored to the original structure in spite of the appearance of small extra peaks and slight loss of crystallinity. The refinement using the original MOF **1** model can essentially fit the whole pattern but with some poor fit on several broad peaks resulted from the poor crystallinity. The Rietveld fit is shown in Figure S3. The refined lattice parameters after re-adsorption are a=14.4395(23) Å and c=15.8028(36) Å.

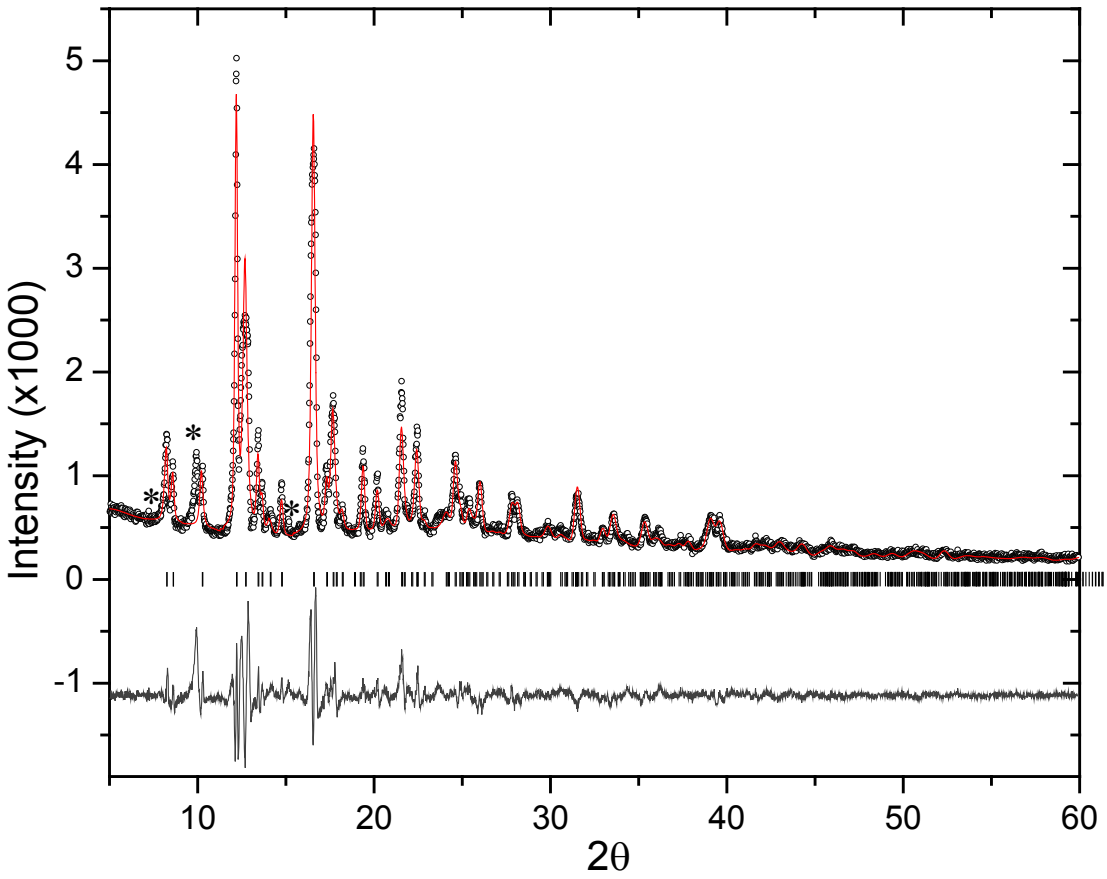

Figure S3 Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for the methanol re-adsorbed **MOF 1'**. Vertical bars indicate the calculated positions of Bragg peaks. There are also small amount of extra peaks which cannot be indexed to a single-phase due to the slight decomposition during the thermal activation under vacuum. A small amount of impurity phase(s) resulted from activation still persists after re-adsorption of methanol as indicated by asterisks.

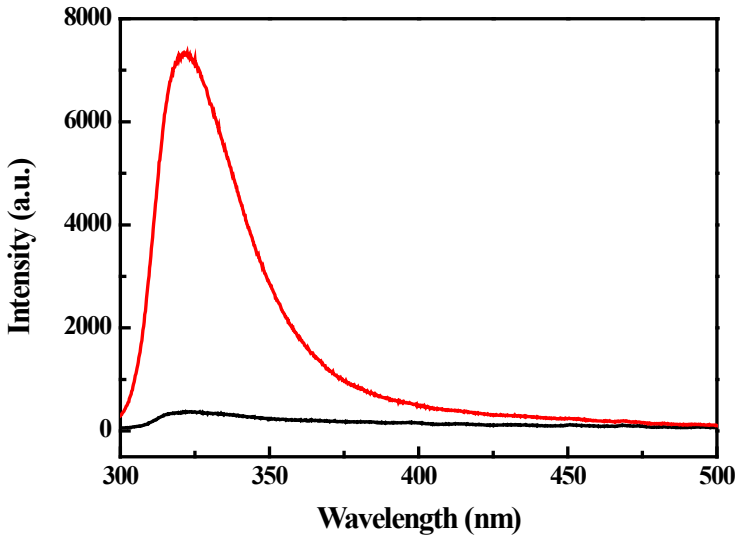

Figure S4 Photoluminescence spectra of MOF **1** (red) and L (black) in solid state at room temperature.

([i]) Larson A. C., Von Dreele, R. B. *General Structure Analysis System*, Report LAUR 86-748. Los Alamos National Laboratory, NM, 1994.