

Electronic Supplementary Information

**Post-modified anionic nano-porous metal-organic framework
as novel catalyst for solvent-free Michael addition reactions**

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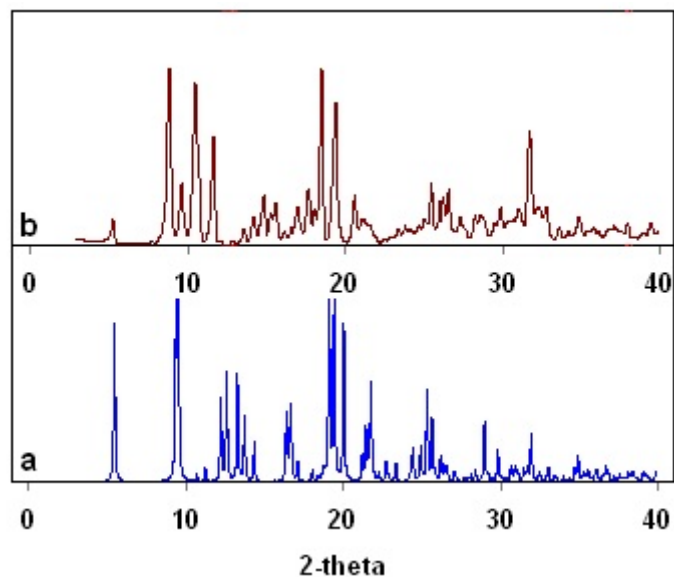


Figure S1. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1** and (b) colorless crystals of compound **1** prepared in the presence of terephthalodinitrile.

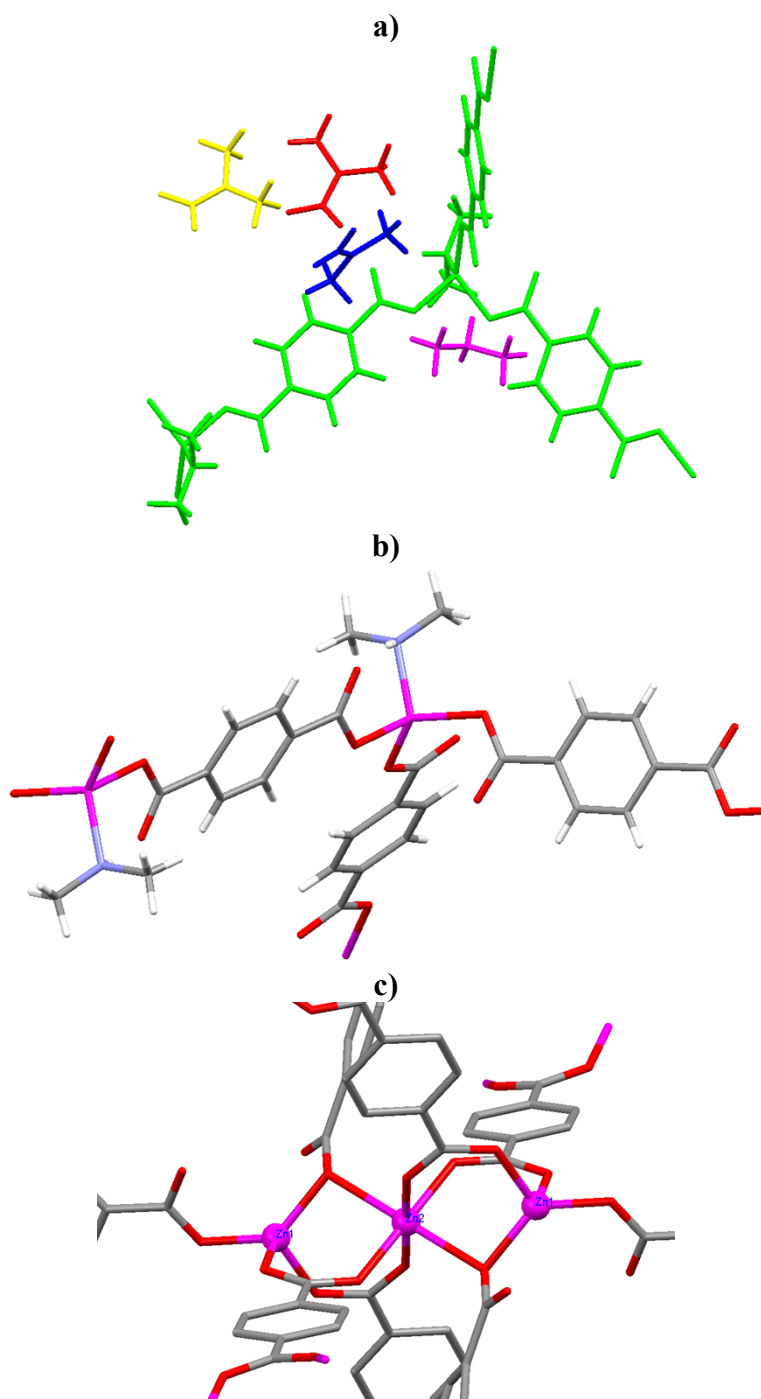


Figure S2. Showing the a) structure of the basic polymeric building block of compound **1** with three DMF molecules (red, blue and yellow species) and HDMA⁺ organic cation (violet species), b) coordination sphere around Zn^{II} ion in anionic MOF of **1** and c) trinuclear Zn₃ cluster unit which exists in anionic MOF of **4** (Zn = violet, O = red, N = blue, C = gray and H = white).

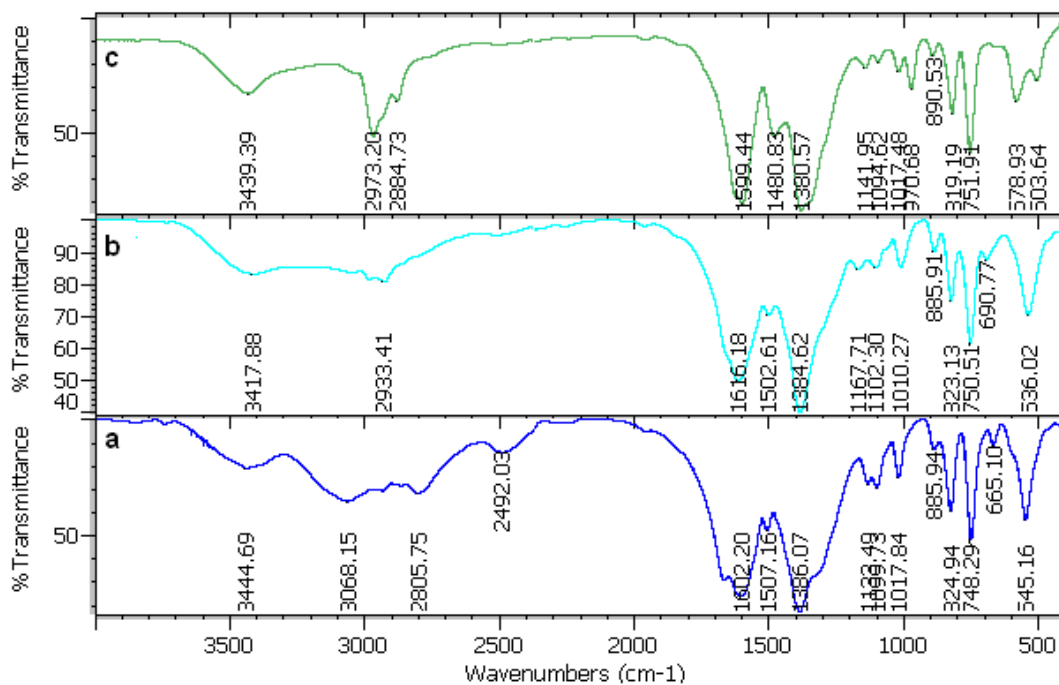


Figure S3. IR spectra of (a) colorless crystals of compound **1** prepared in the presence of terephthalodinitrile, (b) post-synthetic MOF material of **2** and (c) post-synthetic MOF material of **3**.

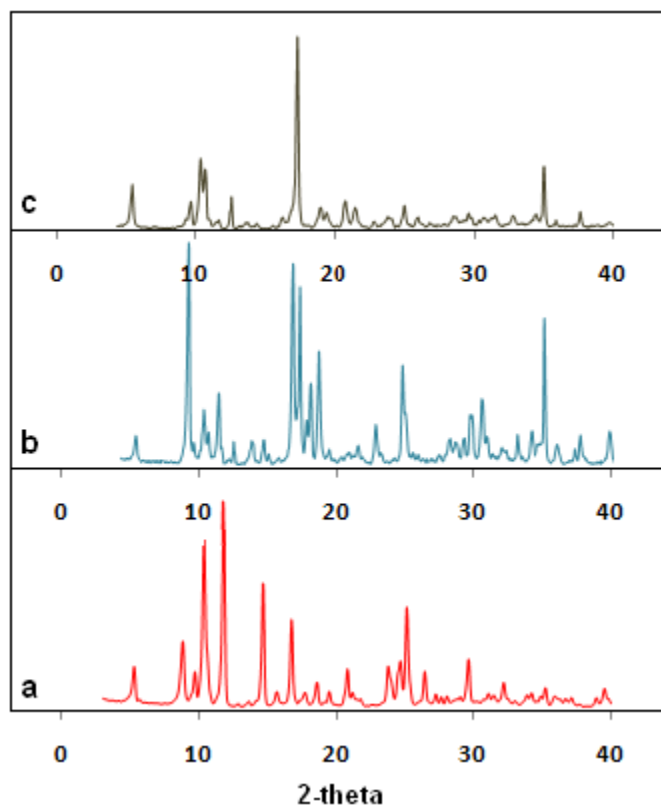


Figure S4. The XRD patterns of (a) colorless crystals of compound **1** prepared in the presence of terephthalodinitrile, (b) post-synthetic MOF material of **2** and (c) post-synthetic MOF material of **3**.

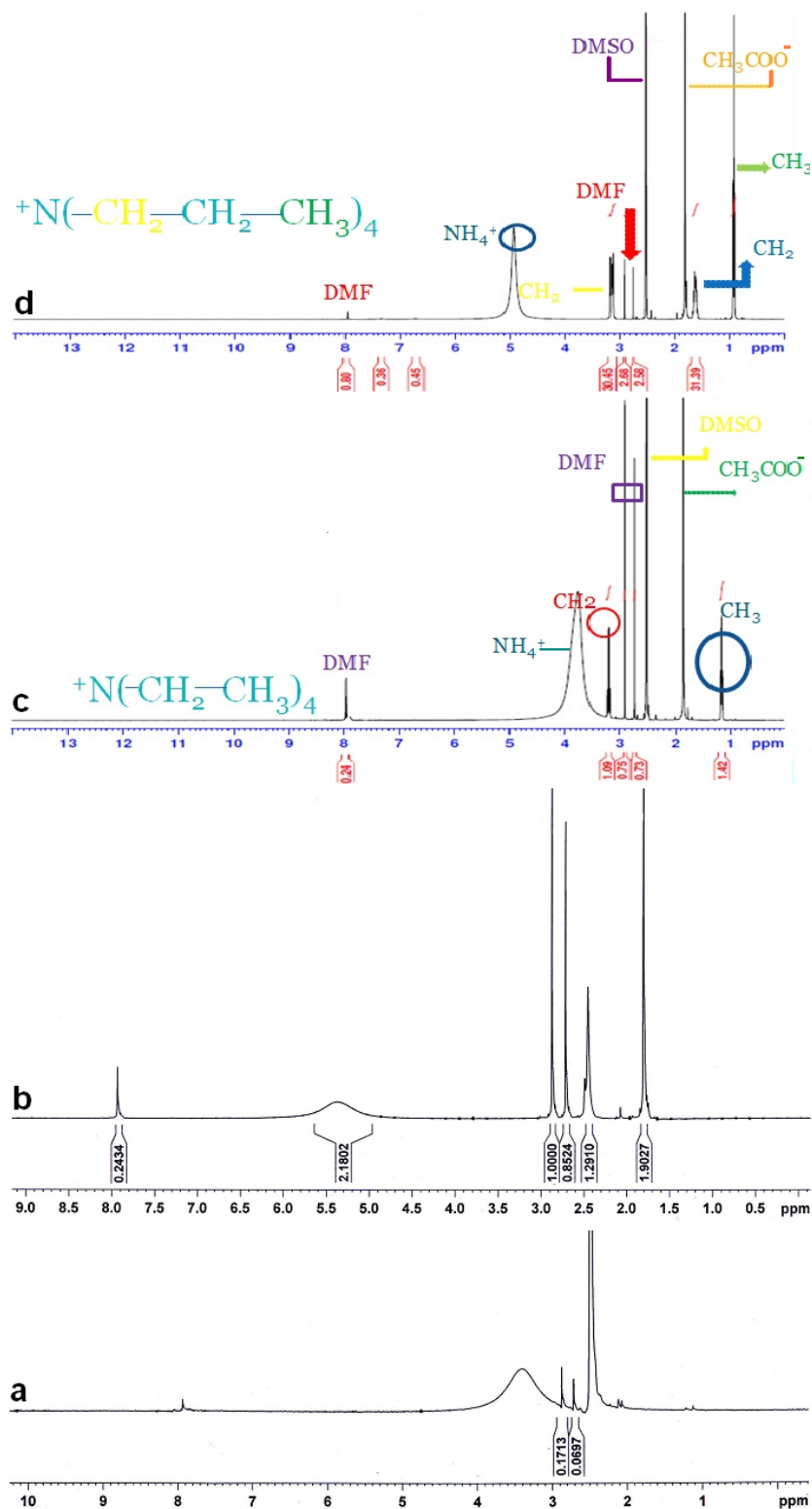


Figure S5. The $^1\text{H-NMR}$ spectra of (a) compound **1**, (b) compound **1** after addition of 5 mg ammonium acetate to the tube, (c) compound **2** after addition of 5 mg ammonium acetate to the tube and (d) compound **3** after addition of 5 mg ammonium acetate to the tube.

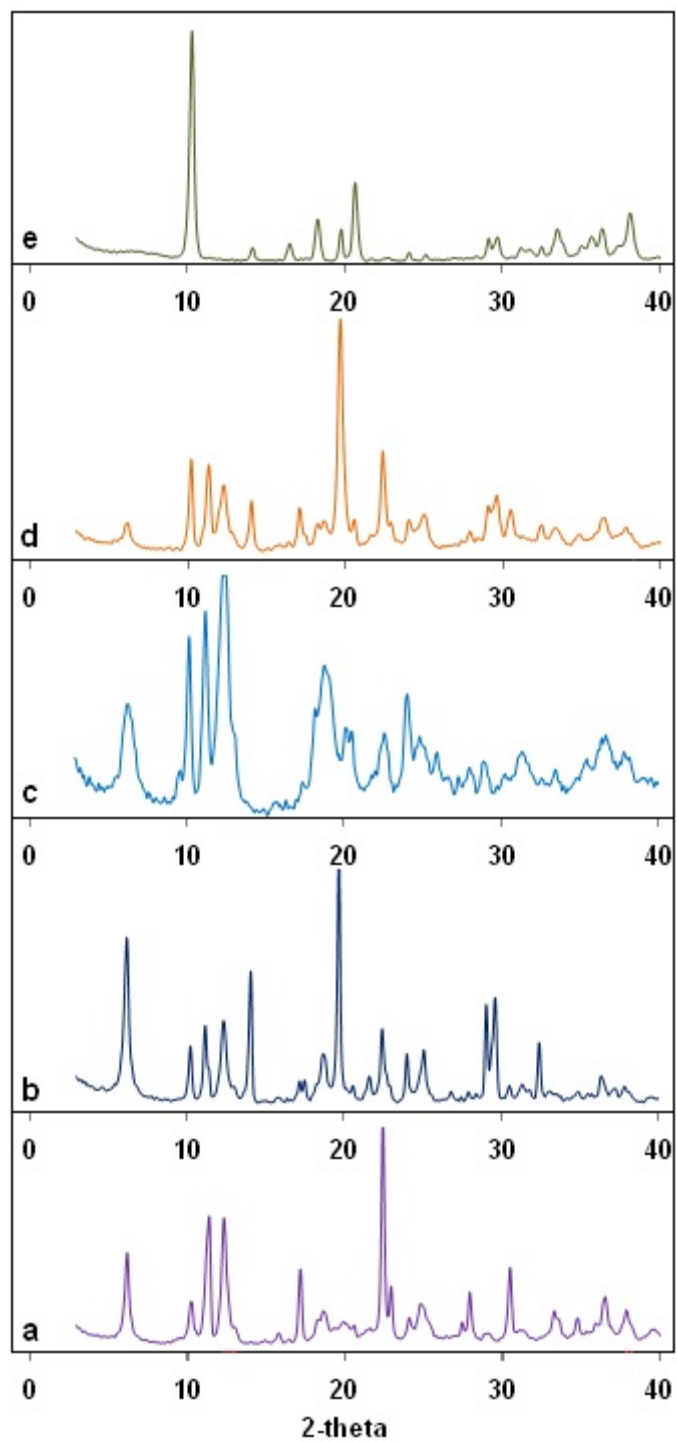


Figure S6. The XRD patterns of compound **3** samples which were immersed in (a) benzene, (b) toluene, (c) dichloromethane, (d) ethanol and (e) tetrahydrofuran (THF) after one week.

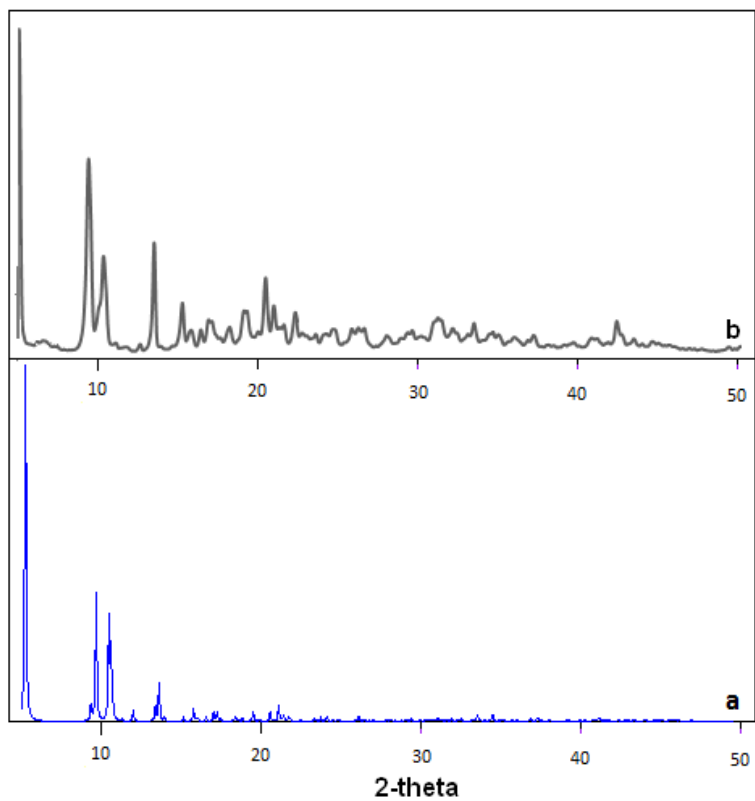


Figure S7. The XRD patterns of (a) simulated from single crystal X-ray data of compound **4** and (b) colorless crystals of compound **4** prepared in the presence of 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene).

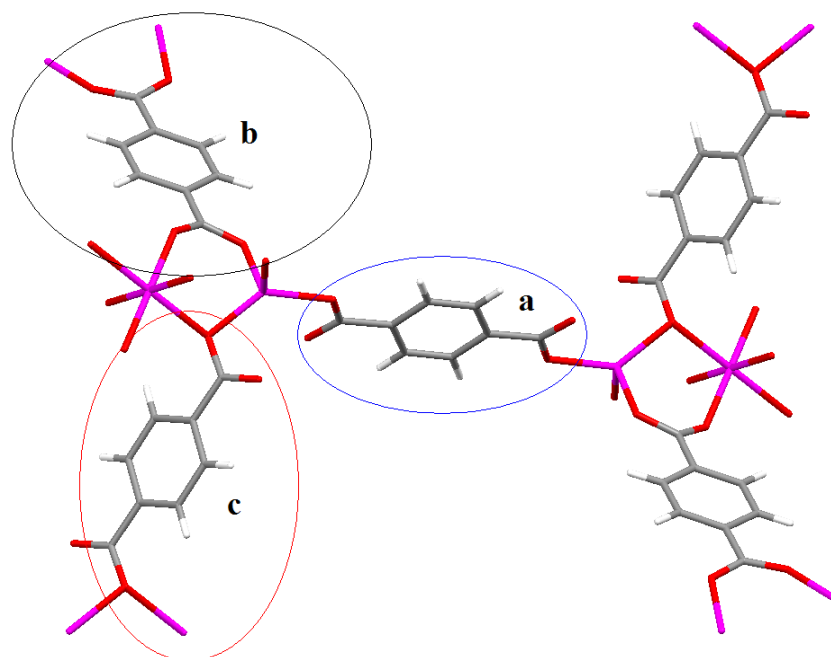


Figure S8. Showing three types of BDC²⁻ anions with a) μ_2 , b) μ_4 and c) μ_4 coordination modes in anionic MOF of **4**, (Zn = violet, O = red, C = gray and H = white).

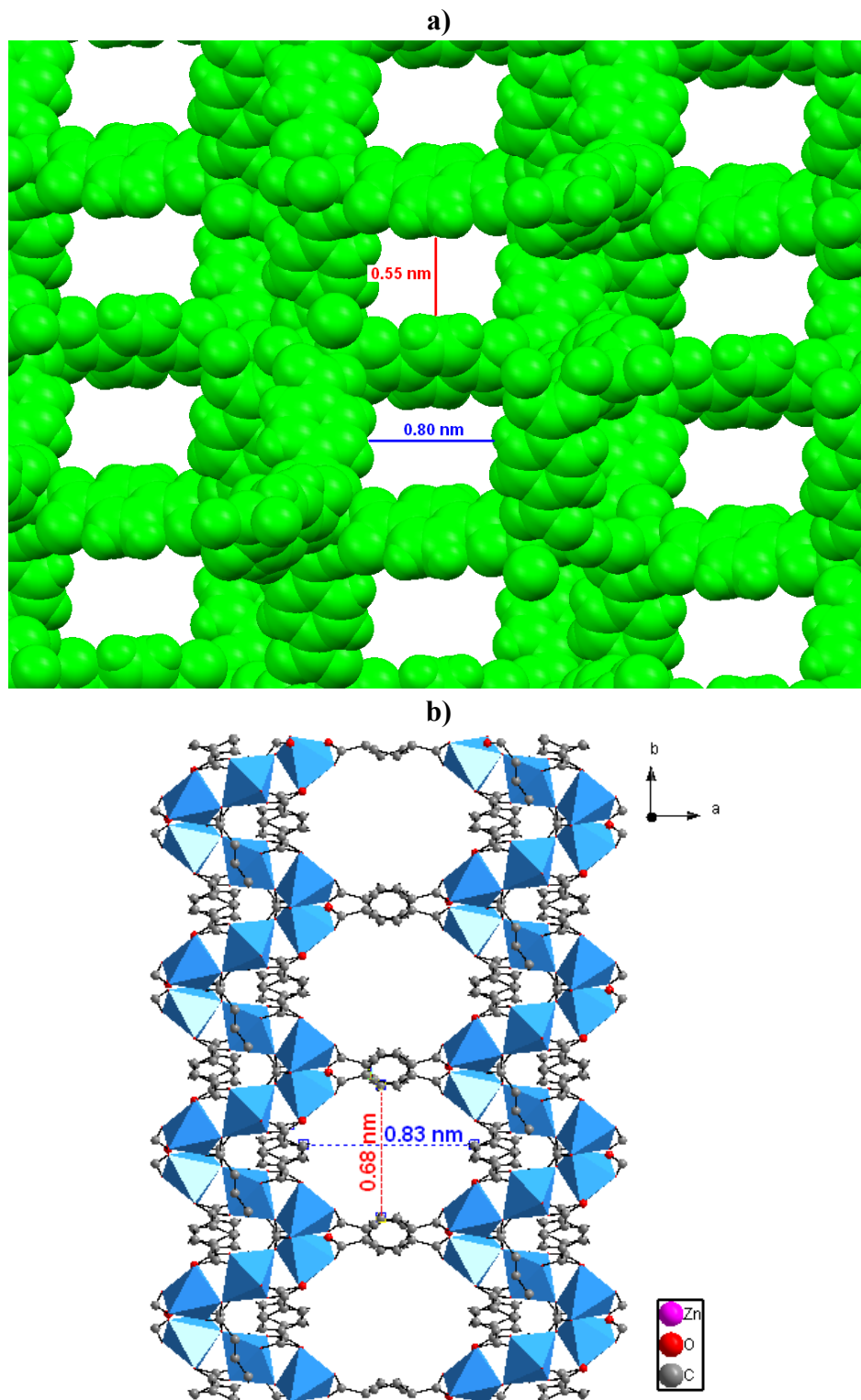


Figure S9. Showing the existence of one-dimensional channels along the crystallographic a) *b* axis and b) *c* axis in an anionic nano-porous MOF of 4.

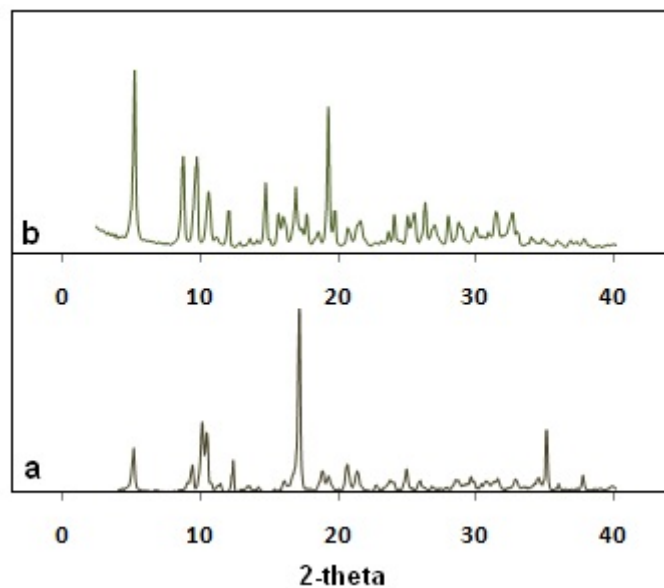


Figure S10. The XRD patterns of (a) colorless crystals of compound **3** prepared in the presence of terephthalodinitrile, (b) compound **3** after six successive runs.