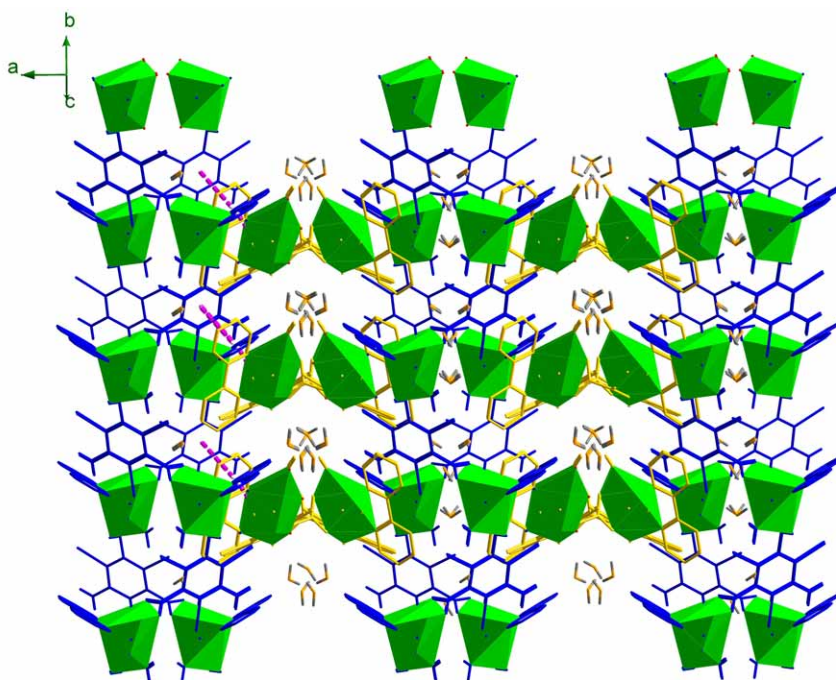


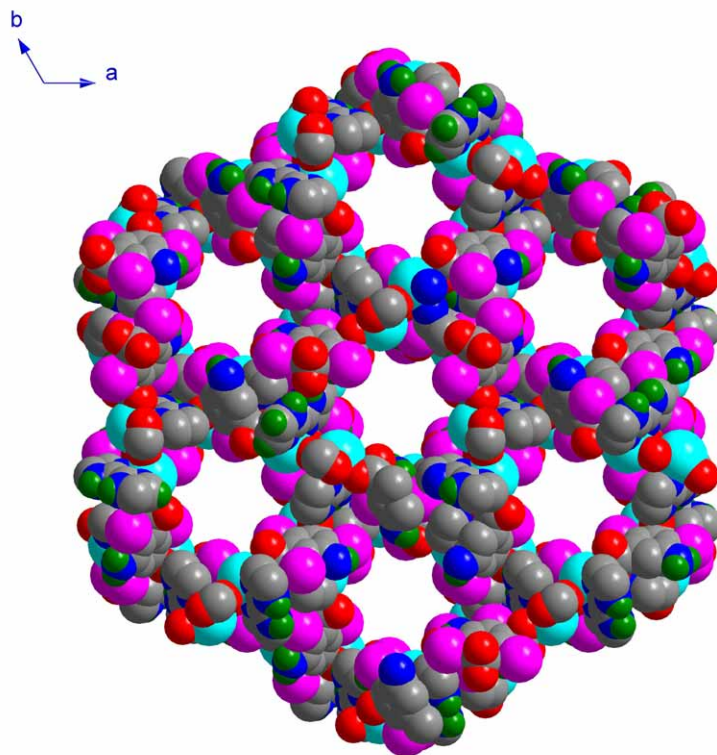
E



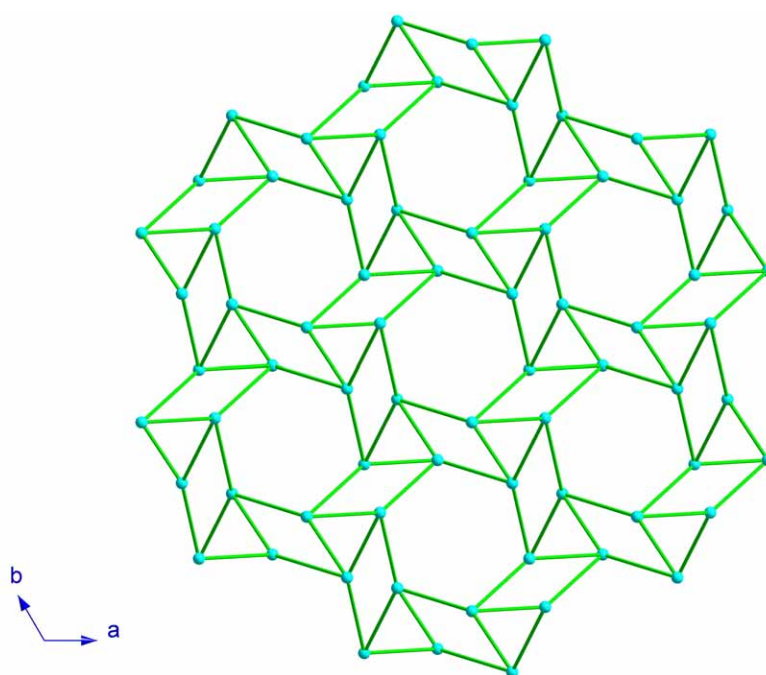
F

Figure S1 E: Schematic representation of 3D supramolecular MOF along [100], where the solid lines represent the 2_1 helices of the helical chains.

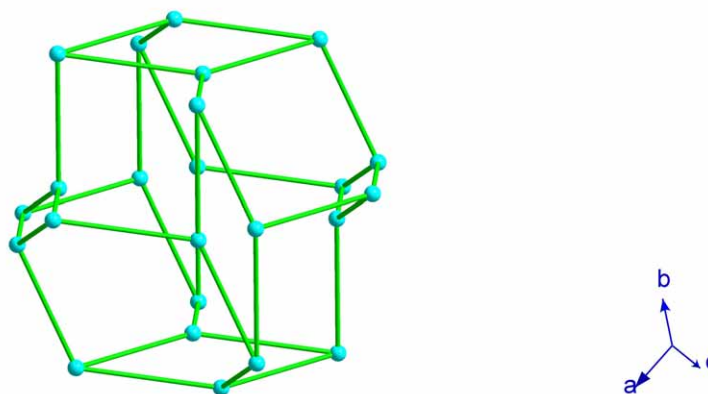
F: 3D supramolecular MOF with 1D channels running along [0-11-27].



D



E



F

Figure S2 D Space-filling diagram of the framework showing the large cavities, the guest water molecules were omitted for clarity.

E Schematic representation of sodalite-like zeolite framework found in **2**.

F The sodalite-like β -cage ($4^6, 6^8$).

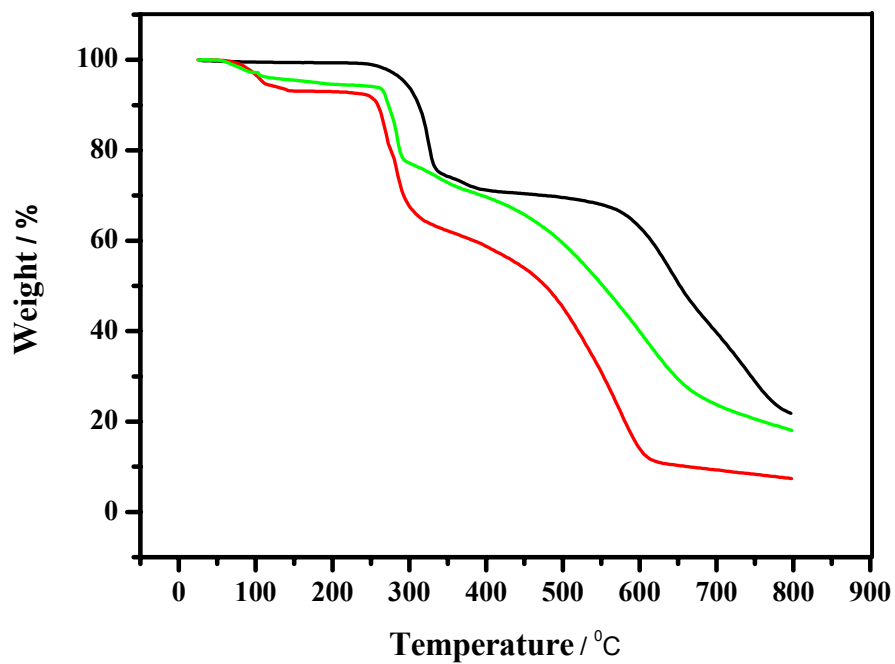


Figure S3 TG curves of **1** (red), **2** (green), and **3** (black).

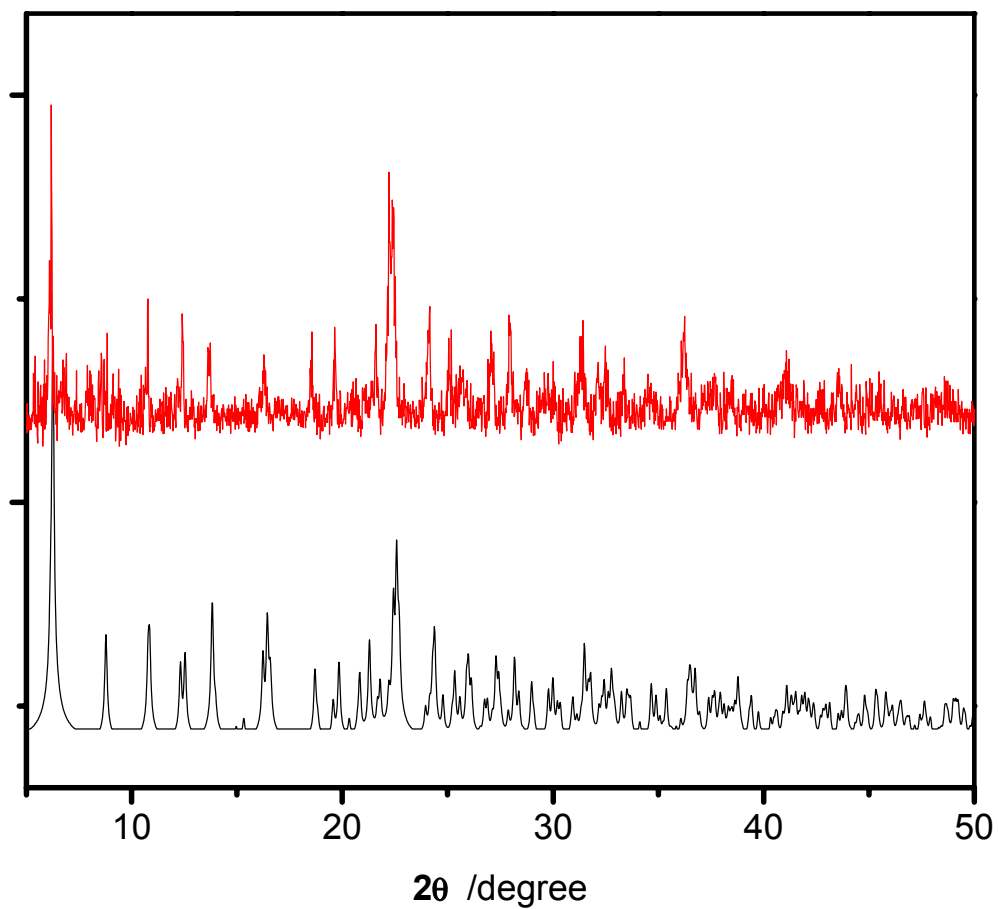


Figure S4. XRPD patterns for **2** recorded (red) after removal of the water molecules at 120 °C, and (black) the simulated XRPD pattern calculated from single-crystal data of **2** with Mercury 1.4.2.

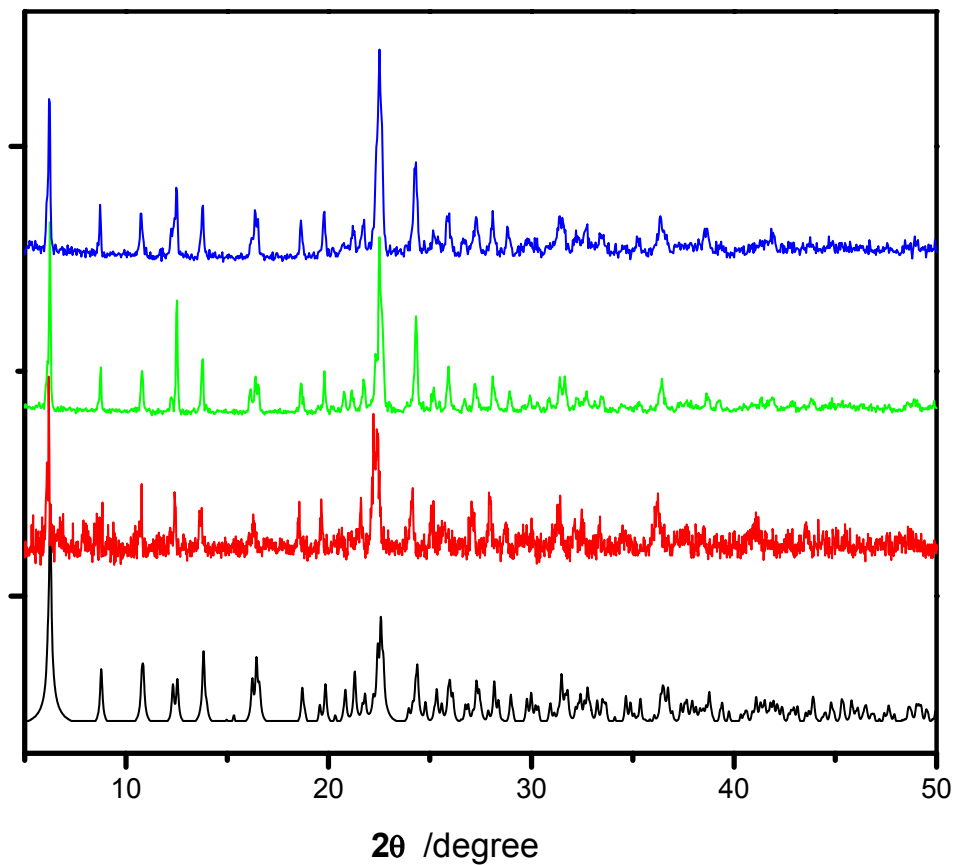


Figure S5. XRPD patterns for **2** recorded (red) after removal of the water molecules at 120 °C, (blue) after introduction of the methanol molecules into the desolvated material at room temperature, (green) after removal of the methanol molecules at 120 °C, and (black) the simulated XRPD pattern calculated from single-crystal data of **2** with Mercury 1.4.2.

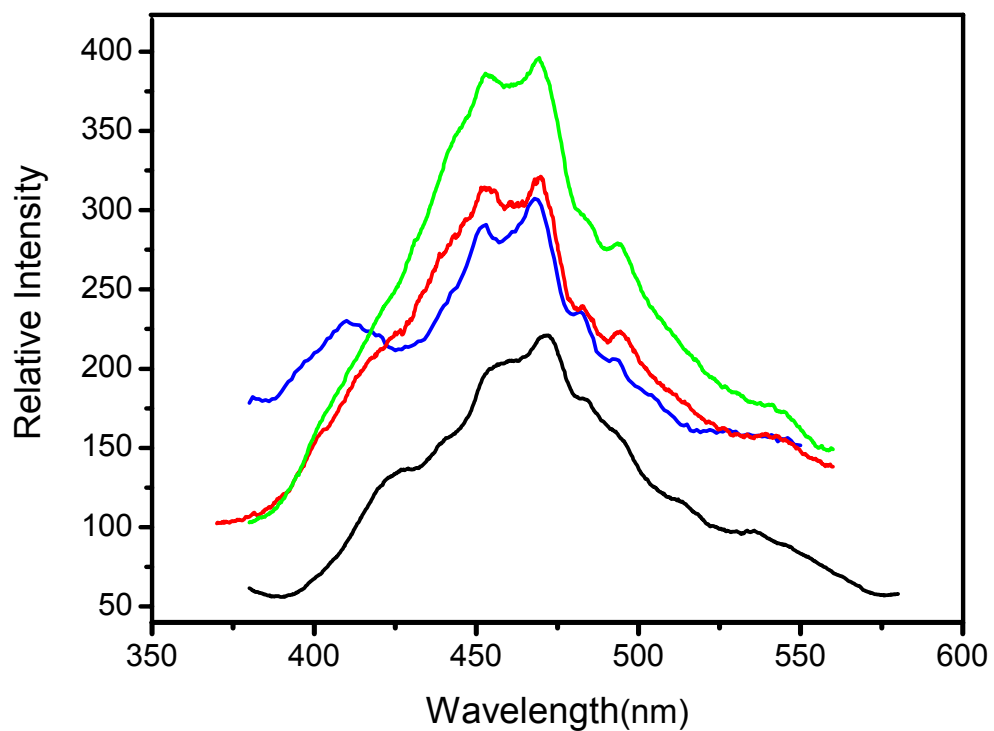


Figure S6 Solid-state fluorescence emissions recorded at room temperature for H₂ATIBDC (black), **1** (green), **2** (red), and **3** (blue). The excitation wavelength (λ_{ex}) is 290 nm for H₂ATIBDC and the complexes 1-3.