Figure S1 E: Schematic representation of 3D supramolecular MOF along [100], where the solid lines represent the 2₁ helices of the helical chains.
F: 3D supramolecular MOF with 1D channels running along [0-11-27].
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 zeotype 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 metanol 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 H$_2$ATIBDC (black), 1 (green), 2 (red), and 3 (blue). The excitation wavelength ($\lambda_{ex}$) is 290 nm for H$_2$ATIBDC and the complexes 1-3.