

Figure S1: X-ray powder diffraction pattern (Huber G670,  $\text{CuK}\alpha_1$  radiation, flat sample, 30 min) of  $^3[\text{Tl}_2(\text{tfBDC})]$  (**1**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

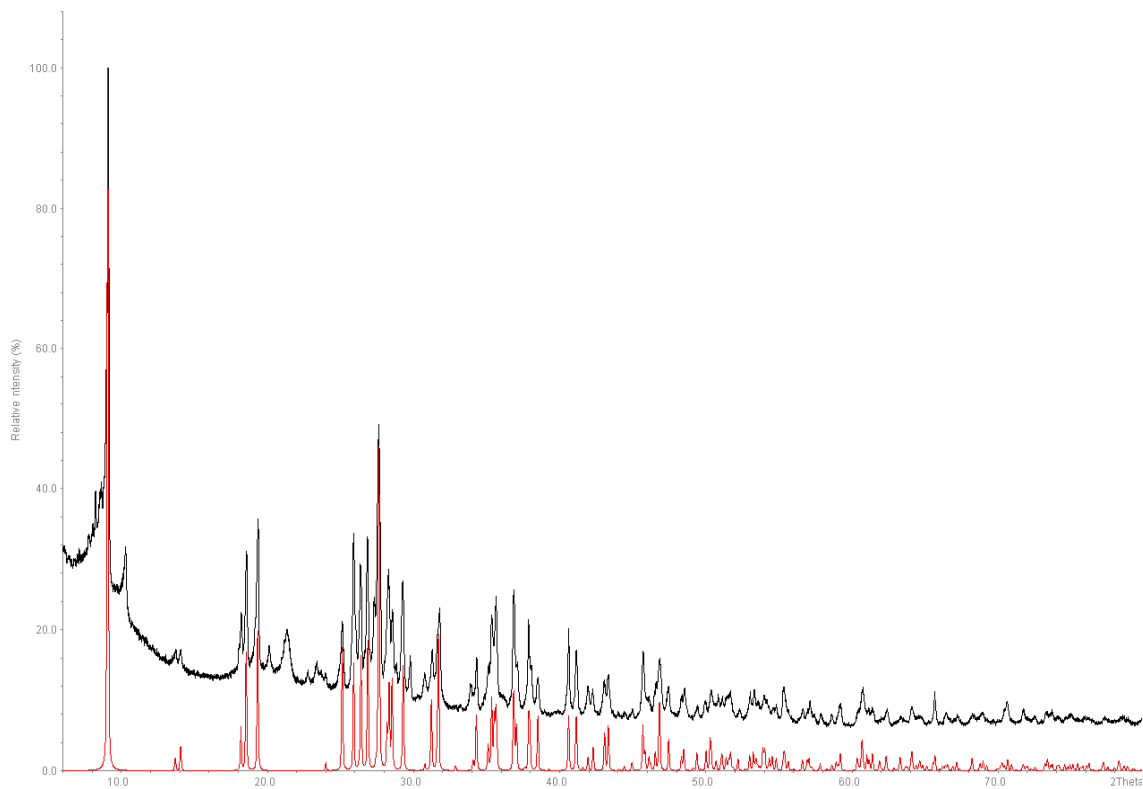


Figure S2: X-ray powder diffraction pattern (Huber G670,  $\text{CuK}\alpha_1$  radiation, flat sample, 30 min) of  ${}^2[\text{Pb}(\text{tfBDC})(\text{H}_2\text{O})_3] \cdot \frac{1}{2} \text{H}_2\text{O}$  (**2**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

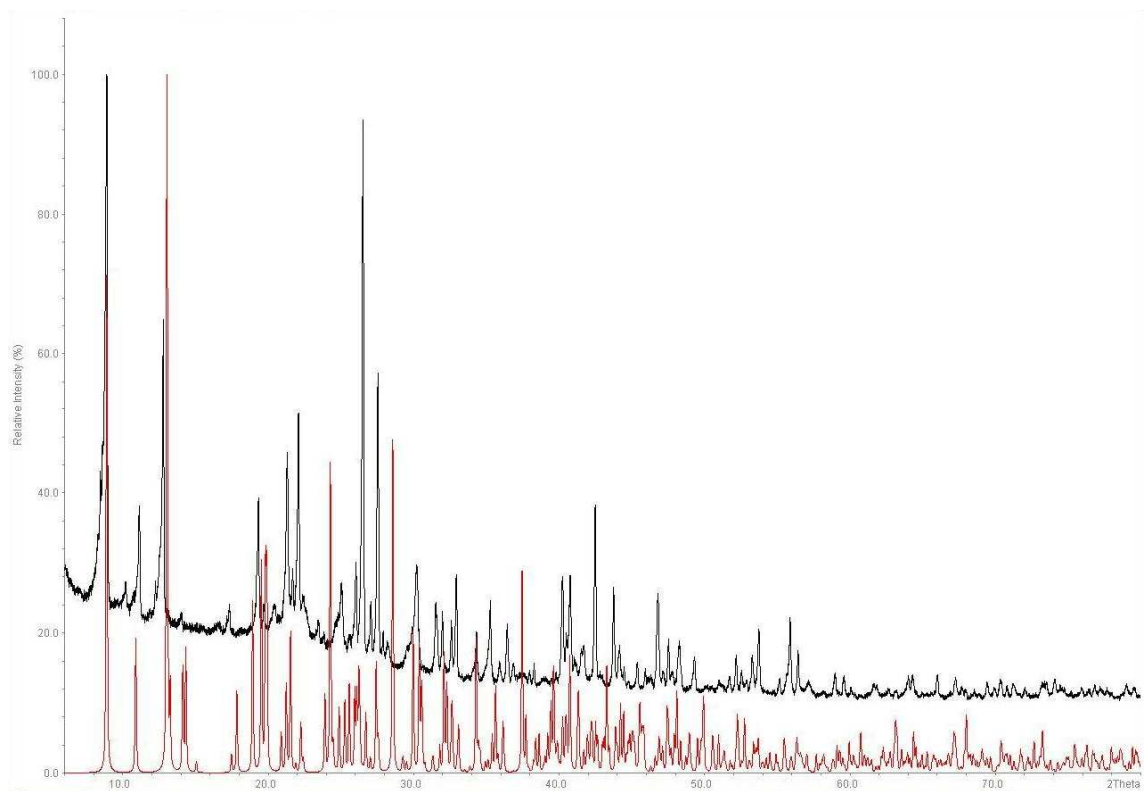


Figure S3: X-ray powder diffraction pattern (Huber G670,  $\text{CuK}\alpha_1$  radiation, flat sample, 30 min) of  $[\text{Zn}(\text{tfBDC})(\text{H}_2\text{O})_4]$  (**3**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

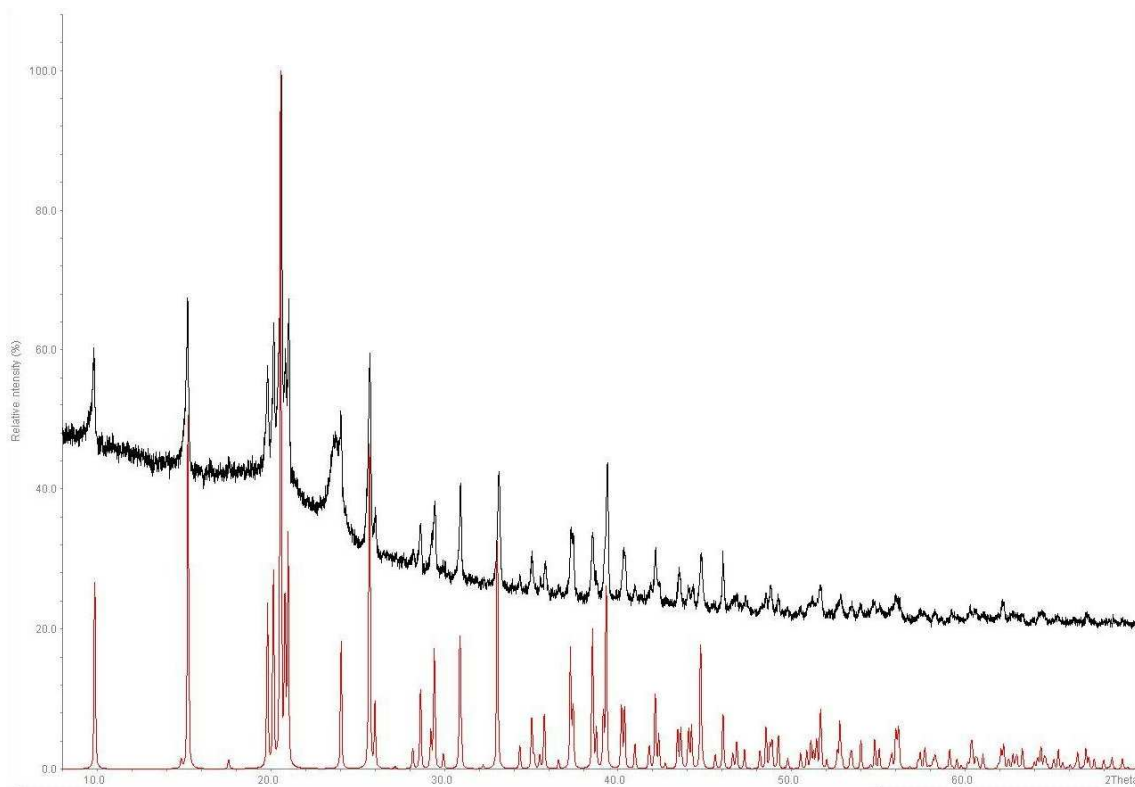


Figure S4: X-ray powder diffraction pattern (Huber G670, MoK $\alpha$  radiation, capillary, 60 min) of  $[\text{Co}(\text{tfBDC})(\text{H}_2\text{O})_4]$  (**4**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

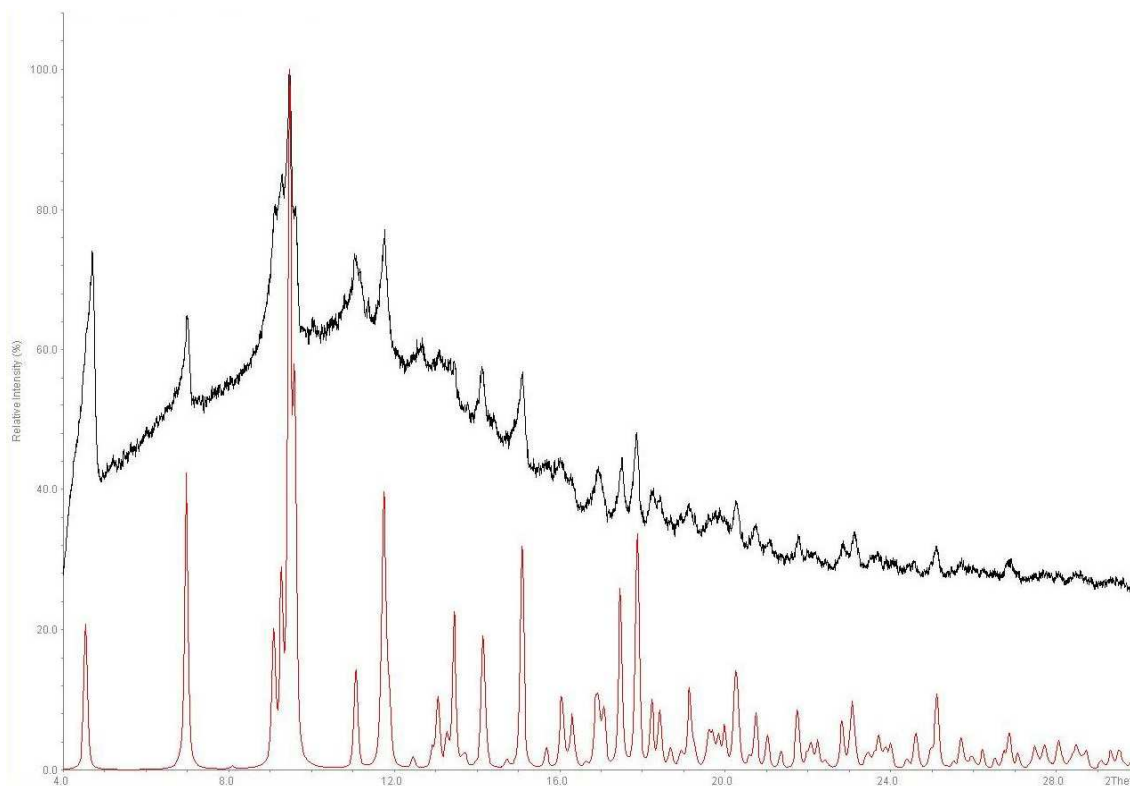


Figure S5: X-ray powder diffraction pattern (Huber G670,  $\text{CuK}\alpha_1$  radiation, capillary, 800 min) of  $^1[\text{Ni}(\text{tfBDC})(\text{H}_2\text{O})_4]$  (**5**, black) compared to a theoretical pattern calculated from the refined lattice parameters of **5** and the atomic positions of **3** (red).

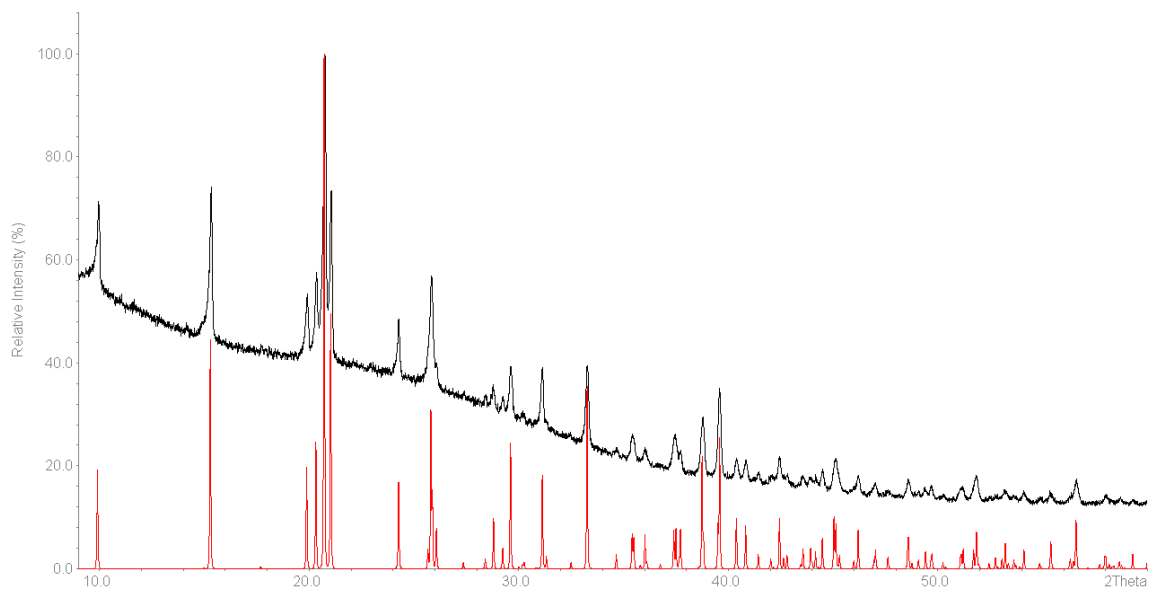


Figure S6: X-ray powder diffraction pattern (Huber G670, CuK $\alpha_1$  radiation, capillary, 120 min) of  $^3[\text{Zn}_2(\text{tfBDC})_2(\text{DMF})_2(\text{EtOH})]$  (**6**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

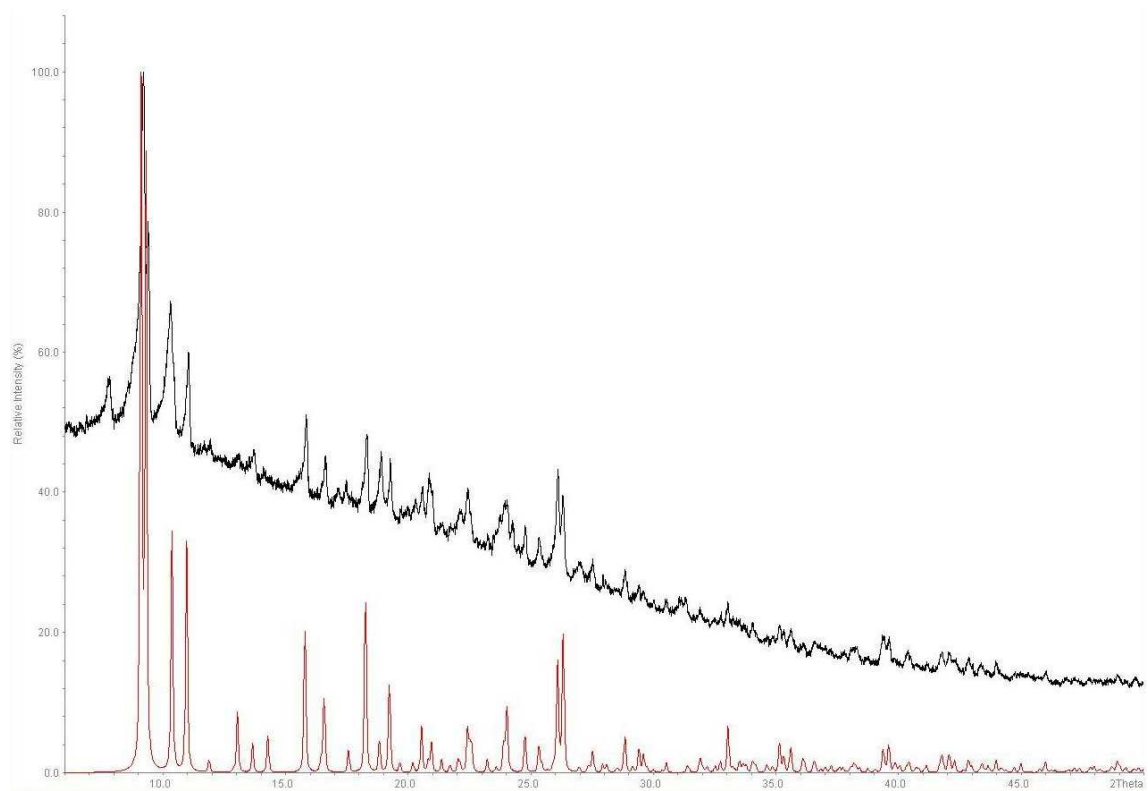


Figure S7: X-ray powder diffraction pattern (Huber G670, CuK $\alpha_1$  radiation, capillary, 120 min) of  $^3[\text{Mn}_2(\text{tfBDC})_2(\text{DMF})_2(\text{EtOH})]$  (**7**, black) compared to a theoretical pattern calculated from single crystal structure data (red).

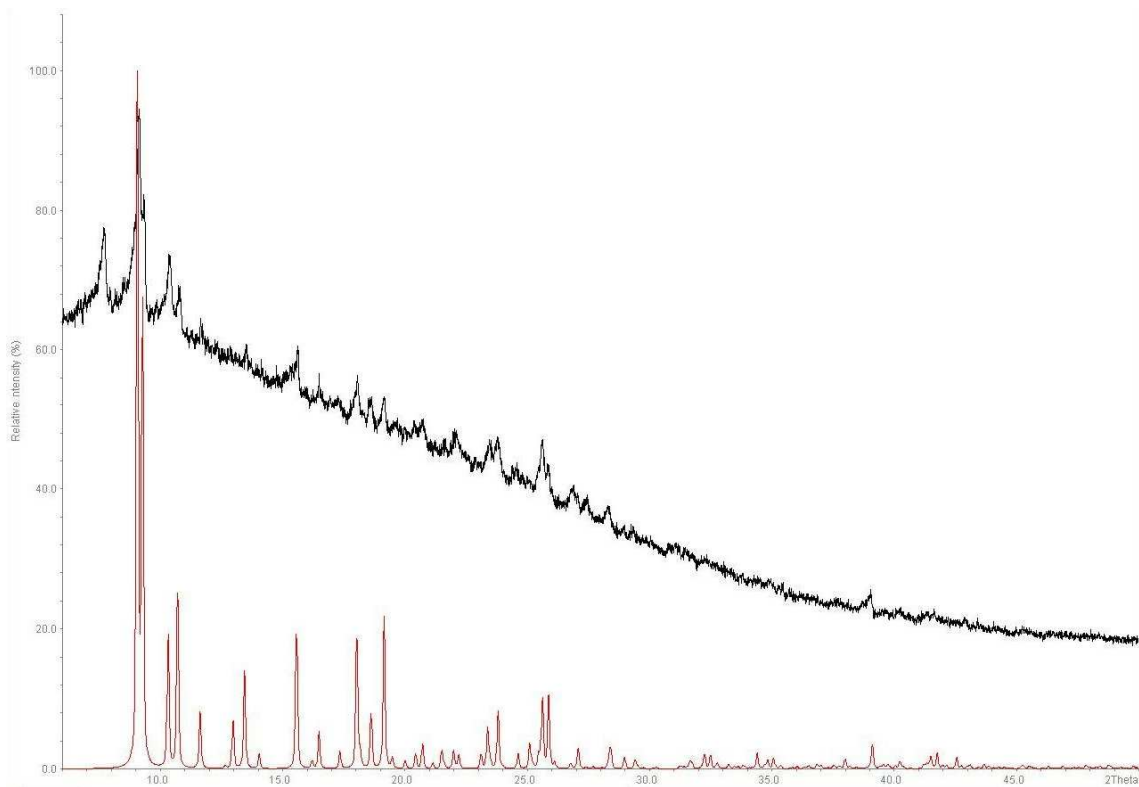


Figure S8: IR spectrum of  ${}^3[\text{Ti}_2(\text{tfBDC})]$  (1).

