Supplement Information

Crystal morphology-directed framework orientation in porous coordination polymer films and freestanding membranes via Langmuir–Blodgettry

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**Fig. S1** Surface pressure isotherms of (a) $[\text{Cu}_3(\text{btc})_2]_n$ (octahedral morphology) and (b) $[\text{Cu}_2(\text{bdc})_2(\text{bpy})]_n$. 
**Fig. S2** Langmuir–Blodgett assembly of PCP crystals of [Cu₃(btc)₂]ₙ showing (a) truncated cubic morphology and (b) truncated octahedral morphology. The SEM images on the top show the assembled densely packed crystals with a preferential orientation. Below are the corresponding XRD out-of-plane diffraction patterns.
Fig. S3 Langmuir–Blodgett assembly of PCP crystals with different morphologies. (a) \([\text{Cu}_3(\text{btc})_2]_n\) showing Octahedral morphology; (b) \([\text{Cu}_3(\text{btc})_2]_n\) showing cubic morphology; (c) \([\text{Al}_{12}\text{O}(	ext{OH})_{18}(	ext{H}_2\text{O})_3(\text{Al}_2(	ext{OH})_4)(\text{btc})_6]_n\) showing a hexagonal prism like morphology (d) \([\text{Cu}_2(\text{bdc})(\text{bpy})]_n\) having plate-like morphology. The SEM images on the top show the crystal morphologies and the schematic representation. Below are the corresponding diffraction patterns. Upper: powder diffraction pattern; 2nd: simulated powder diffraction pattern; 3rd: out of plane; bottom: simulated preferential orientation (indicated in brackets for each case). The simulated patterns have been generated using Mercury 2.4 (The Cambridge Crystallographic Data Centre).
Fig. S4 SEM images at different magnifications showing the freestanding assemblies of (a) $\text{[Cu}_3\text{(btc)}_2]_n$ having cubic morphology, (b) $\text{[Al}_{12}\text{O(OH)}_{18}(\text{H}_2\text{O})_3\text{(Al}_2\text{(OH)}_4)\text{(btc)}_6]_n$ and (c) $\text{[Cu}_2\text{(bdc)}_2\text{(bpy)}]_n$ after transferring them from the water surface on top of a copper grid (shown empty in (d). Below the SEM images are the corresponding out-of-plane surface XRD pattern of the assembled freestanding crystals.