

## Supporting Information

**The interplay of coordinative and hydrogen-bonding in directing the [M(4,4'-bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] square-grid networks: Formation of 3D porous framework [Cd(4,4'-bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>(4,4'-bpy)(CH<sub>3</sub>OH)<sub>2</sub>**

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Fig. S1 Thermogravimetric curve of complex **1**.

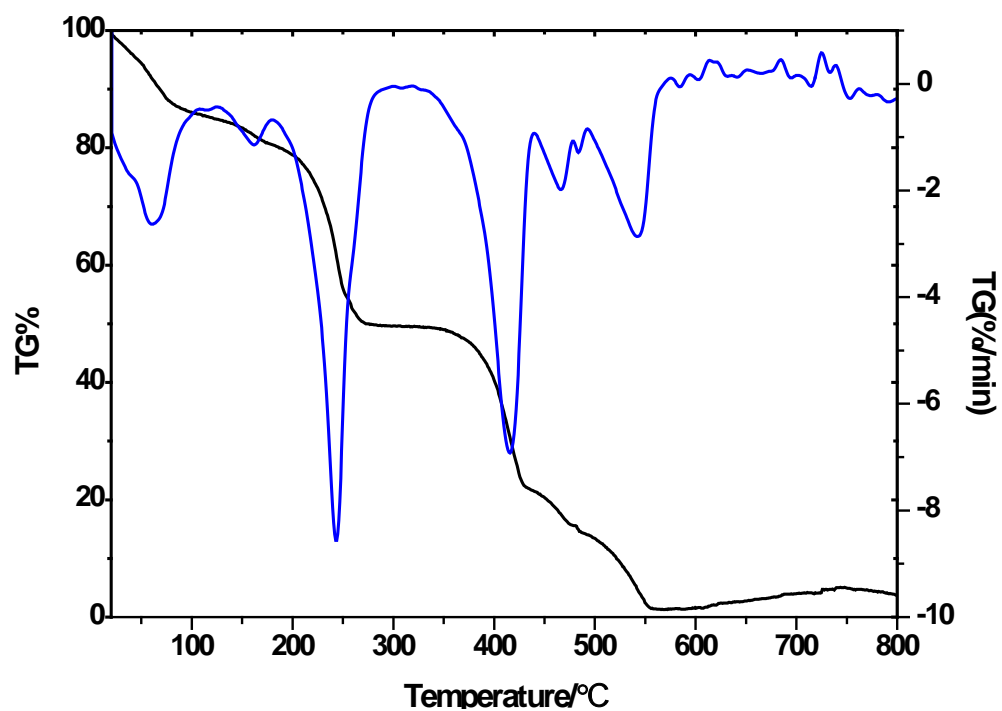
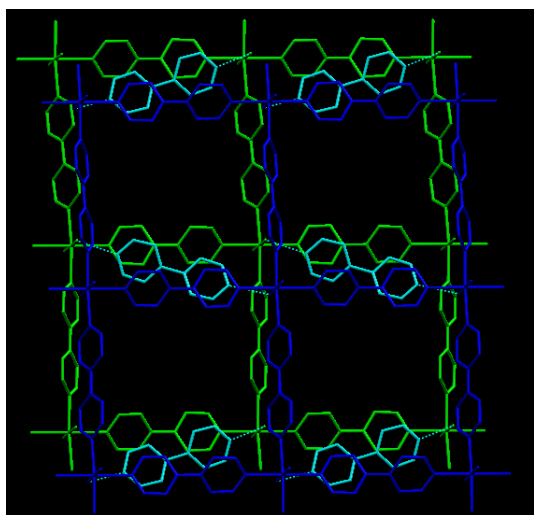
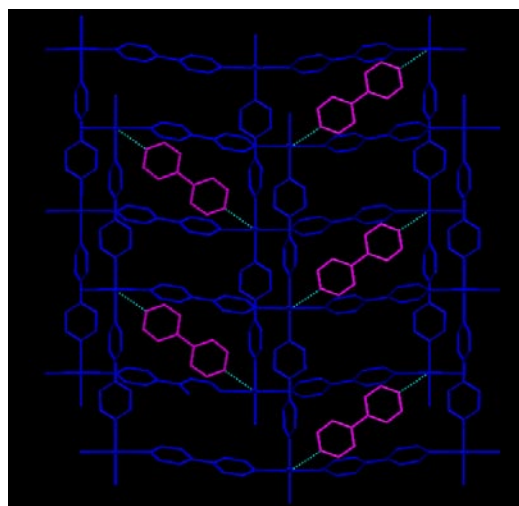


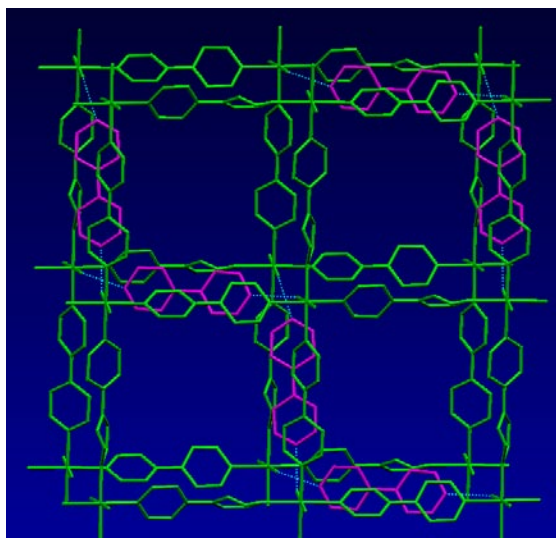
Fig. S2 The interplay of coordinative and hydrogen-bonding interactions in known examples containing square-grid  $[M(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]$  networks and hydrogen-bonding 4,4'-bpy.



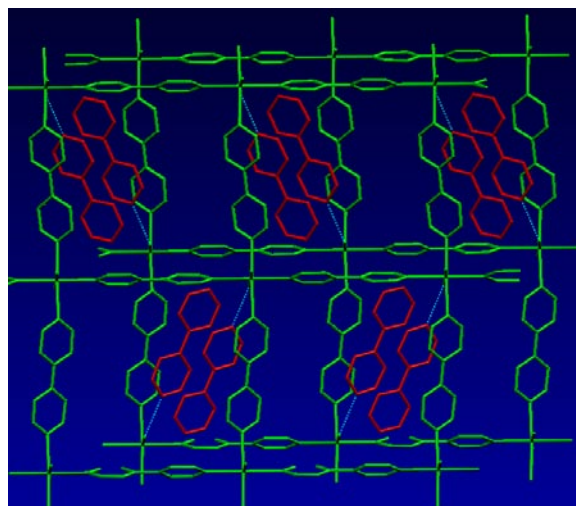
**a**



**b**



**c**



**d**

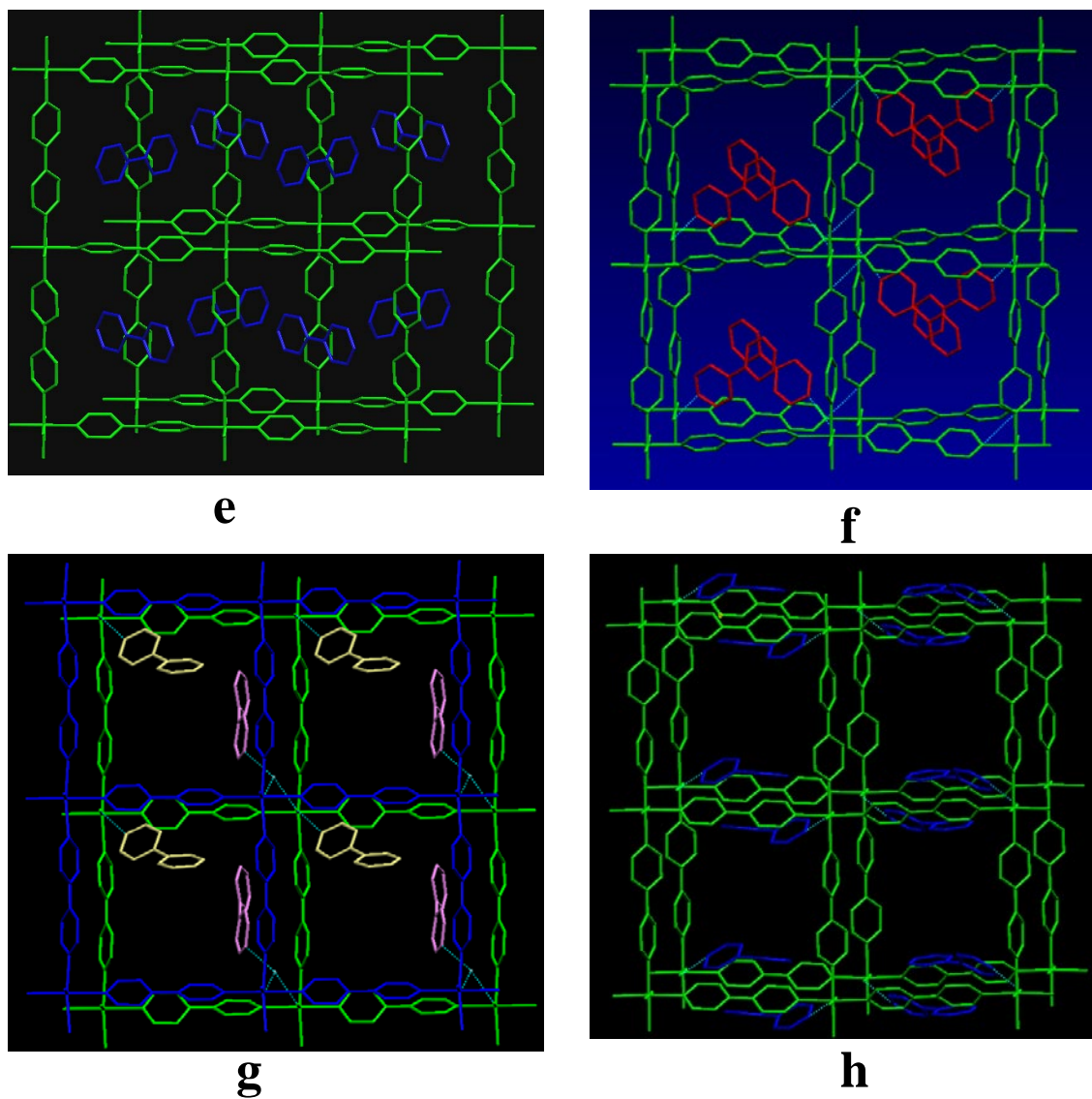


Fig. S3 Observed (black) and calculated (blue) powder X-ray diffraction patterns for complex 1.

