Supporting Information for

Ligand-concentration-dependent self-organization of Hoffman- and PtS-type frameworks from one-pot crystallization

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General Considerations. Unless otherwise mentioned, all reactants were used as purchased without further purification. IR spectra were measured on a Nicolet FT 1703X spectrophotometer in the form of KBr pellets in the 4000-400 cm^{-1} region. Thermogravimetric analysis was performed using Perkin Elmer Diamond TG/DTA instruments under nitrogen atmosphere at a heating rate of 5 °C·min^{-1}. Powder XRD pattern of compound **1** was collected with CuKα radiation using a Shimadzu XRD-6000 diffractometer.

X-ray crystallography. Diffraction data for **1-3** were collected on a Bruker Smart APEX diffractometer equipped with MoKα (λ = 0.71073 Å) radiation. Diffraction data analysis and reduction were performed within *SMART*, *SAINT*, and *XPREP*. Correction for Lorentz, polarization, and absorption effects were performed within *SADABS*. Structures were solved using Patterson method within *SHELXS-97* and refined using *SHELXL-97*. All non-hydrogen atoms were refined with anisotropic thermal parameters.

N_2 and H_2 sorption experiments. Gas adsorption measurements were performed on a Micromeritics ASAP 2020 analyzer. Sample tubes of a known weight were loaded and sealed using a transeal. Samples were degassed at 120 °C for 24 h, until the outgas rate was no more than 1 mTorr·min^{-1}. The degassed sample and sample tube were weighed and then transferred back to the analyzer (with the transeal preventing exposure of the sample to air after degassing). The outgas rate was again confirmed to be less than 1 mTorr·min^{-1}. Samples were maintained at constant

temperature by immersion in a liquid nitrogen bath (77 K). UHP grade N_2 and H_2 (99.999%) gases were used for all measurements.

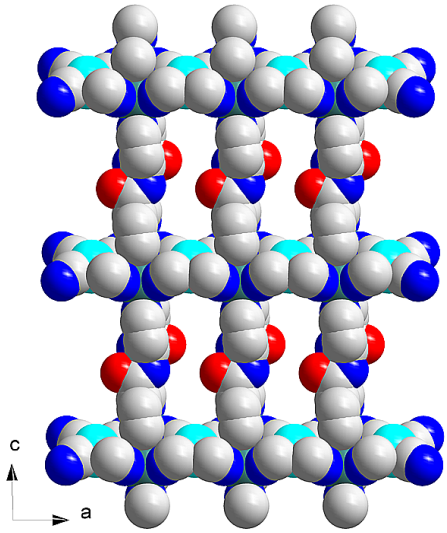


Figure S1. The 3D open framework of **1** veiwed along the *b* axis.

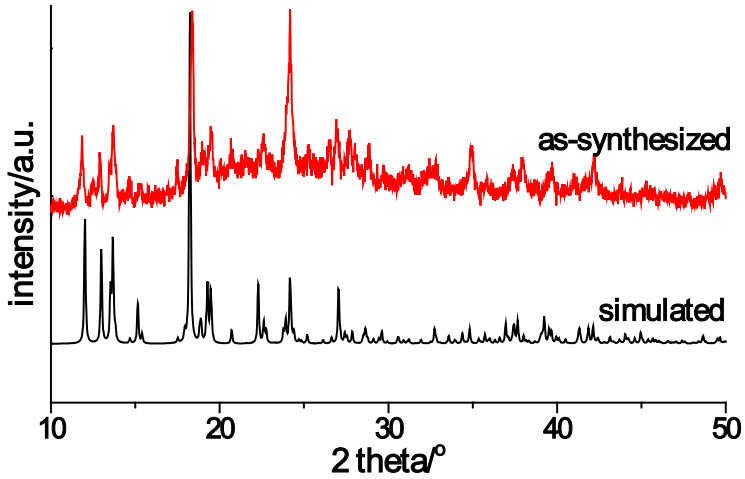


Figure S2. Powder XRD patterns of as-synthesized and simulated from single-crystal data of **1**.

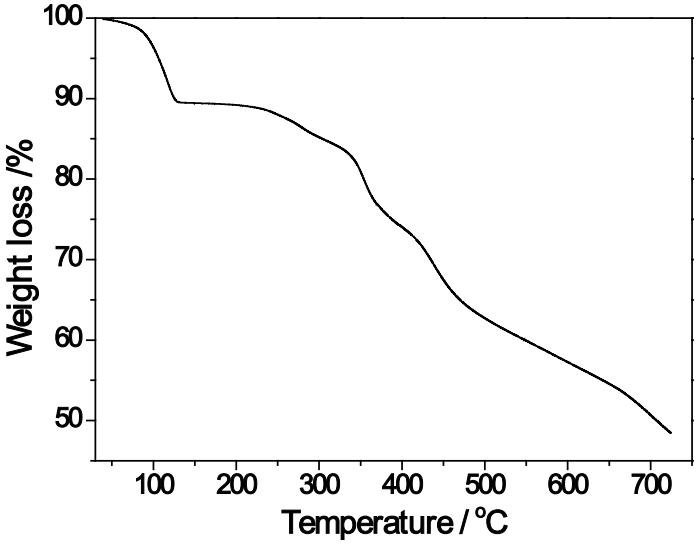
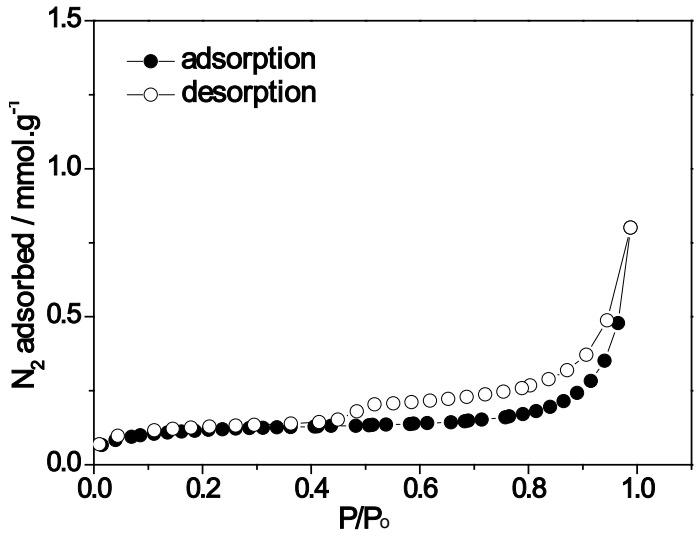
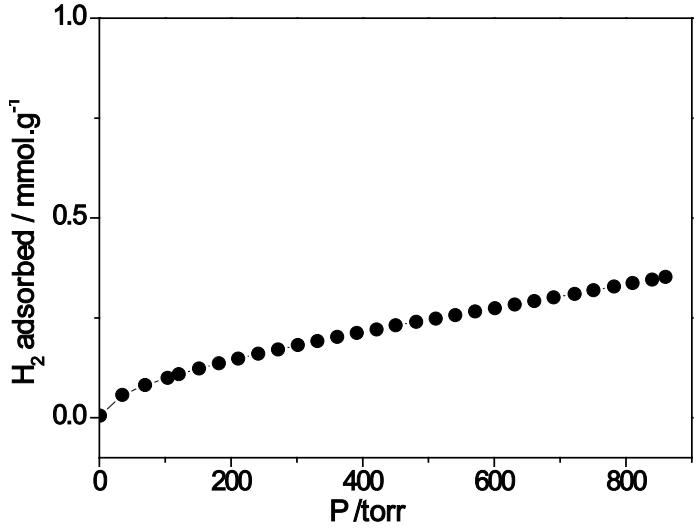


Figure S3. Thermogravimetric curve of **1**.



(a)



(b)

Figure S4. (a) N_2, and (b) H_2 sorption isotherms of **1** at 77 K.

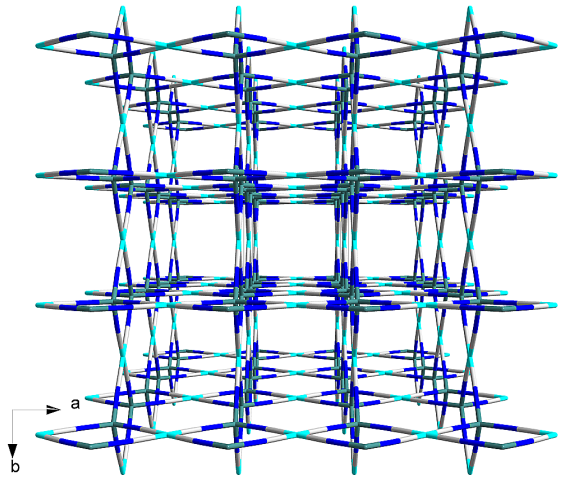
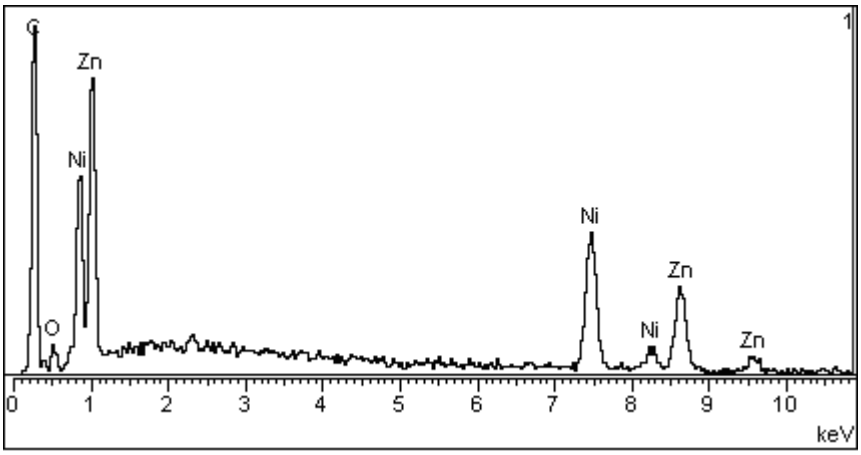
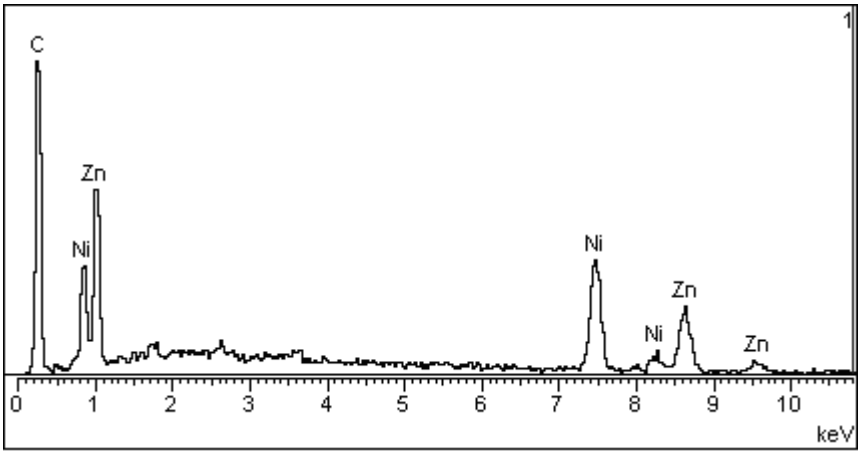


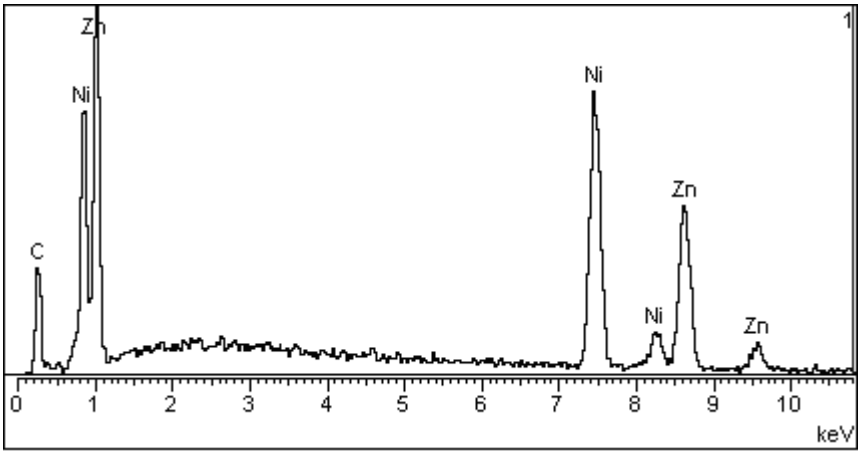
Figure S5. The 3D open framework of **2** viewed along the *a* axis.



(a)



(b)



(c)

Figure S6. EDS results of (a) **1**, (b) **2**, and (c) **3**.