Electronic Supplementary Information

Solid-state Thermal Conversion of a Nanoporous Metal-Organic Framework to a Nonporous Coordination polymer

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Synthesis of $[\text{Zn}_2(\text{BDC})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (3·2H$_2$O·2DMF) metal-organic framework.

White powder of $[\text{Zn}_2(\text{BDC})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (3·2H$_2$O·2DMF) was synthesized by dissolving 5 mmol (0.831 g) benzene-1,4-dicarboxylic acid (H$_2$BDC) and 5 mmol (1.485 g) Zn(NO$_3$)$_2$·6H$_2$O in 40 mL DMF. The resulting mixture was refluxing at 150 °C for 8 hours. 4 hours after beginning of the reflux reaction, white precipitate was formed. After filtering, the white precipitate was washed with DMF, and dried at room temperature for 2 days, d.p. = above 300 °C, yield: 1.433 g, 89.4 % based on final product, IR (selected bands; in cm$^{-1}$): 543 m, 678 w, 749 s, 826 m, 1016 w, 1108 m, 1385 vs, 1603 vs, 1658 vs and 2700-3700 br. Anal. calc. For C$_{11}$H$_{13}$NO$_6$Zn: C, 41.21; H, 4.09; N, 4.37 found; C, 41.33; H, 3.95; N, 4.25 %. A Comparison between the XRD patterns simulated from single crystal X-ray data (Figure S7a) and that of the prepared powder (Figure S7b), approved the formation of $[\text{Zn}_2(\text{BDC})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (3·2H$_2$O·2DMF).

Preparation apohost framework of $[\text{Zn}_2(\text{BDC})_2]_n$ (3) by removal of guest DMF and coordinated water molecules.

White powder of $[\text{Zn}_2(\text{BDC})_2]_n$ (3) was prepared by heating half of the 3·2H$_2$O·2DMF powder at 180 °C for 8 hours. d.p. = above 300 °C, IR (selected bands; in cm$^{-1}$): 545 m, 678 w, 750 s, 820 m, 1020 w, 1382 vs and 1660 vs. Anal. calc. For C$_8$H$_4$O$_4$Zn: C, 41.87; H, 1.76; N, 0.00 found; C, 42.01; H, 1.81; N, 0.11 %. XRD pattern of the resulting powder (Figure S7c) approximately matches with the simulated XRD pattern from single crystal X-ray data (Figure S7a). The differences between these two patterns is due to removal of DMF and coordinated H$_2$O molecules which can be considered as a template in formation of 3·2H$_2$O·2DMF. Other studies such as gas adsorption analyses$^{1,2}$ were approved that the structure of compound 3 does not change or collapse during thermal treatment of 3·2H$_2$O·2DMF at 180 °C.

References:
Figure S1. a) A fragment of Zn(BDC)(4,4'-Bipy)$_{0.5}$ MOF with pillared 2D Kagomé net; b) MOF-508a (1.DMF.H$_2$O) primary structural building unit; c) guest-free phase of MOF-508b (1) primary structural building unit, d) a fragment of the apohost framework of 1 along the crystallographic $b$ axis and e) primary structural building unit of 2 (Zn= violet, O = red, C = gray, N = blue and H = white).
Figure S2. XRD patterns; a) simulated pattern based on single crystal data of compound Zn(BDC)(4,4'-Bipy)$_{0.5}$·(DMF)$_{0.5}$·(H$_2$O)$_{0.5}$ (1.DMF.H$_2$O) with pillared 2D Kagomé network, b) simulated pattern based on single crystal data of compound 1.DMF.H$_2$O with pillared 2D square-grid network, c) microrods of 1.DMF.H$_2$O prepared under reflux condition, d) simulated pattern based on single crystal data of guest-free phase of MOF-508b (1), e) the apohost framework of Zn(BDC) (3), f) simulated pattern based on single crystal data of compound Zn(BDC)(4,4'-Bipy) (2) and g) the obtained powder after thermal treatment of 1.DMF.H$_2$O at 350 °C.
Figure S3. XRD patterns; a) simulated pattern based on single crystal data of guest-free phase of MOF-508b (1) and b) the obtained powder after thermal treatment of 1.DMF.H₂O at 350 °C.
Figure S4. Thermal behaviour of compounds 2;3 mixture.
Figure S5. XRD patterns; a) ZnO nanoparticles, fabricated from calcination process of 1.DMF.H₂O microrods at 550 °C and b) agglomerated nanoparticles of ZnO fabricated from calcination process of compounds 2 and 3 microrods at 550 °C.
Figure S6. The corresponding particle size distribution histograms of ZnO nanoparticles fabricated from calcination process of a) 1.DMF.H$_2$O microrods and b) compounds 2 and 3 microrods.
Figure S7. XRD patterns; a) simulated pattern based on single crystal data of compound [Zn$_2$(BDC)$_2$(H$_2$O)$_2$·(DMF)$_2$]$_n$ (3·2H$_2$O·2DMF), b) white precipitate of 3·2H$_2$O·2DMF and c) apohost framework of 3.