Electronic Supplementary Information

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

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Synthesis of $[Zn_2(BDC)_2(H_2O)_2\cdot(DMF)_2]_n$ ($3\cdot2H_2O\cdot2DMF$) metal-organic framework.

White powder of $[Zn_2(BDC)_2(H_2O)_2\cdot(DMF)_2]_n$ (**3**$\cdot2H_2O\cdot2DMF$) was synthesized by dissolving 5 mmol (0.831 g) benzene-1,4-dicarboxylic acid (H_2BDC) and 5 mmol (1.485 g) $Zn(NO_3)_2,6H_2O$ 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 $C_{11}H_{13}NO_6Zn$: 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 $[Zn_2(BDC)_2(H_2O)_2\cdot(DMF)_2]_n$ (**3**$\cdot2H_2O\cdot2DMF$).

Preparation apohost framework of $[Zn_2(BDC)_2]_n$ (3) by removal of guest DMF and coordinated water molecules.

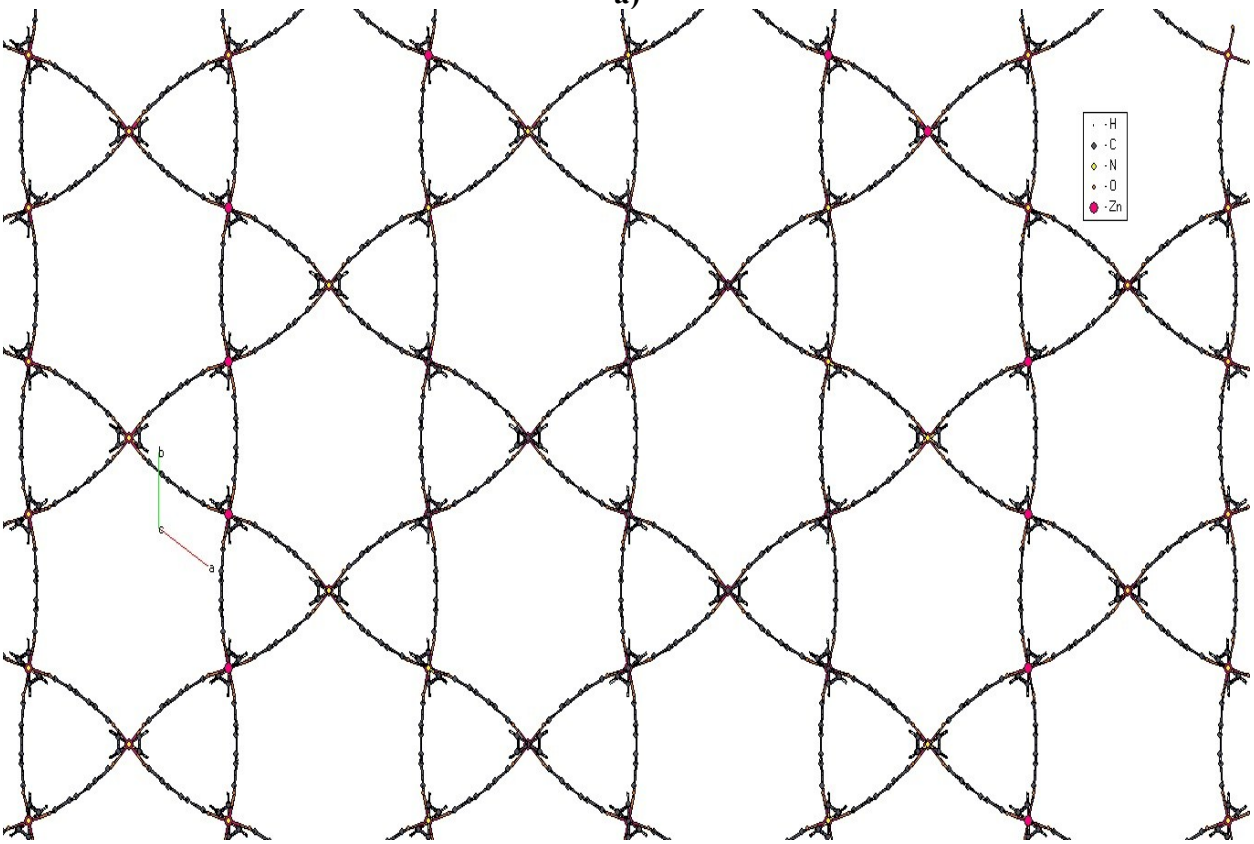
White powder of $[Zn_2(BDC)_2]_n$ (**3**) was prepared by heating half of the **3**$\cdot2H_2O\cdot2DMF$ powder at 180 °C for 8 hours. d.p. = above 300 °C, IR (selected bands; in cm^{-1}): 545 m, 678 w, 750 s, 820 m, 1020 w, 1382 vs and 1660 vs. Anal. calc. For $C_8H_4O_4Zn$: C, 41.87; H, 1.76; N, 0.00 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_2O molecules which can be considered as a template in formation of **3**$\cdot2H_2O\cdot2DMF$. 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**$\cdot2H_2O\cdot2DMF$ at 180 °C.

References:

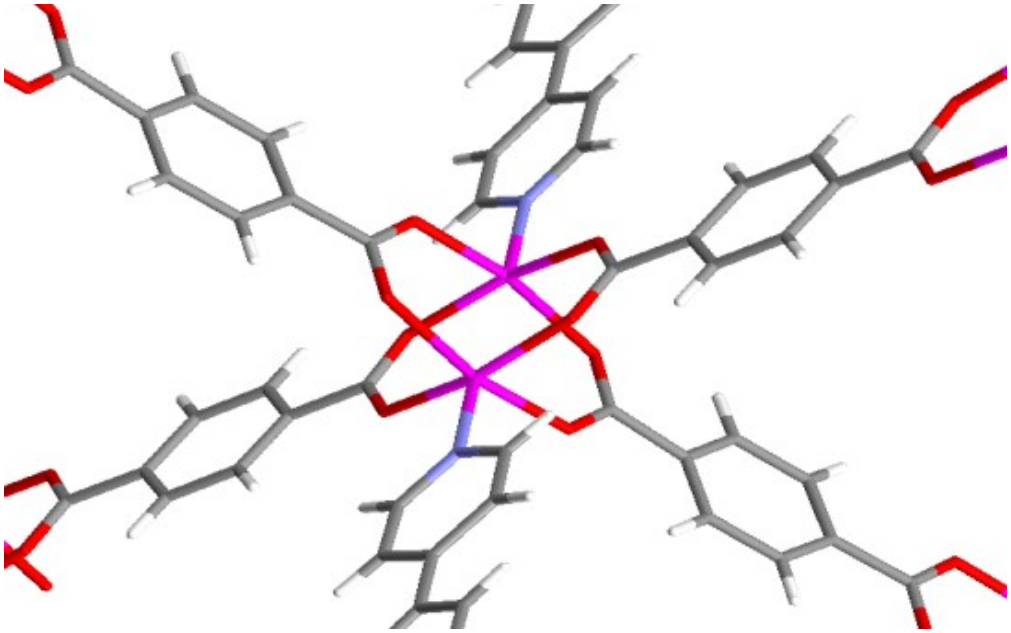
1. H. L. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, J. Am. Chem. Soc. 1998, 120, 8571.

2. Z. Chen, S. Xiang, D. Zhao, B. Chen, Cryst. Growth Des. 2009, 9, 5293.

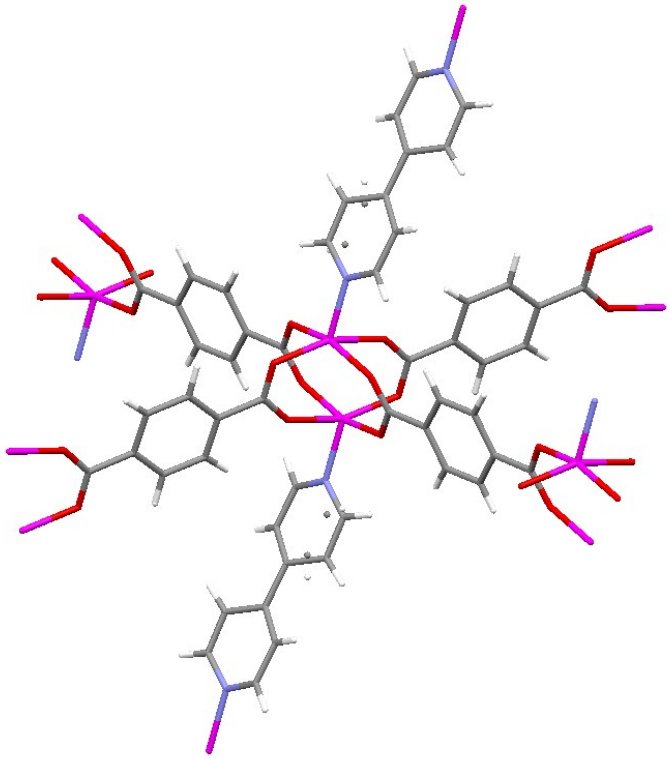
a)



b)



c)



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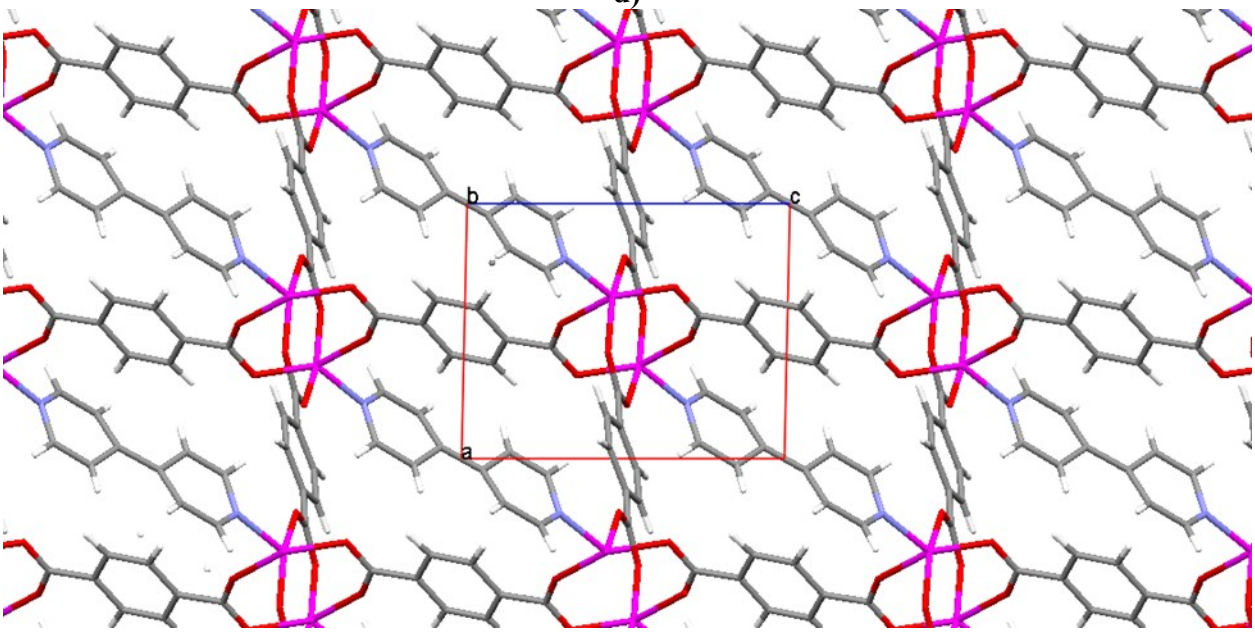

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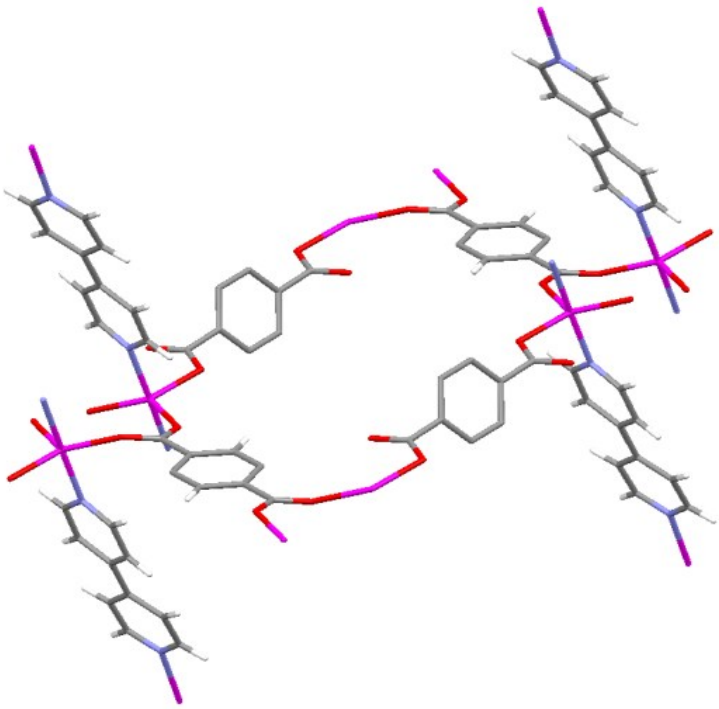

Figure S1. a) A fragment of Zn(BDC)(4,4'-Bipy)$_{0.5}$ MOF with pillared 2D Kagomé net; b) MOF-508a (**1**.DMF.H_2O) primary structural building unit; c) guest-free phase of MOF-508b (**1**) primary structural building unit, d) a fragment of the apohost framework of **1** along the crystallographic *b* axis and e) primary structural building unit of **2** (Zn= violet, O = red, C = gray, N = blue and H = white).

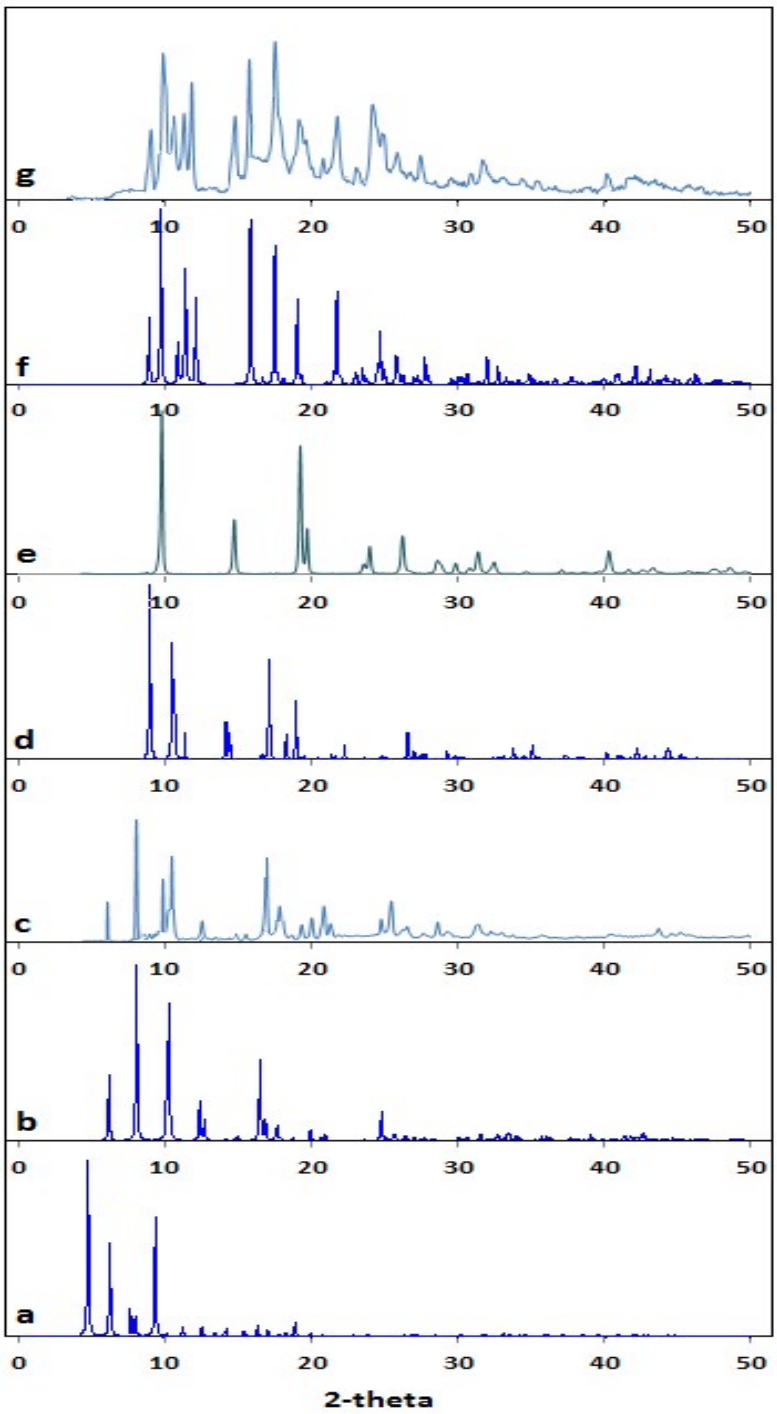

Figure S2. XRD patterns; a) simulated pattern based on single crystal data of compound $Zn(BDC)(4,4'\text{-Bipy})_{0.5}\cdot(DMF)(H_2O)_{0.5}$ (1.DMF.H_2O) with pillared 2D Kagomé network, b) simulated pattern based on single crystal data of compound 1.DMF.H_2O with pillared 2D square-grid network, c) microrods of 1.DMF.H_2O 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_2O at 350 °C.

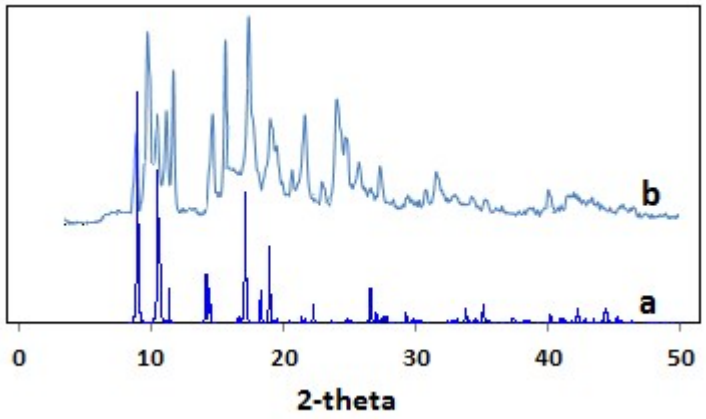

Figure S3. XRD patterns; a) simulated pattern based on single crystal data of guest-free phase of MOF-508b (**1**) and b) the obtained powder after thermal treatment of **1**.DMF.H_2O at 350 °C.

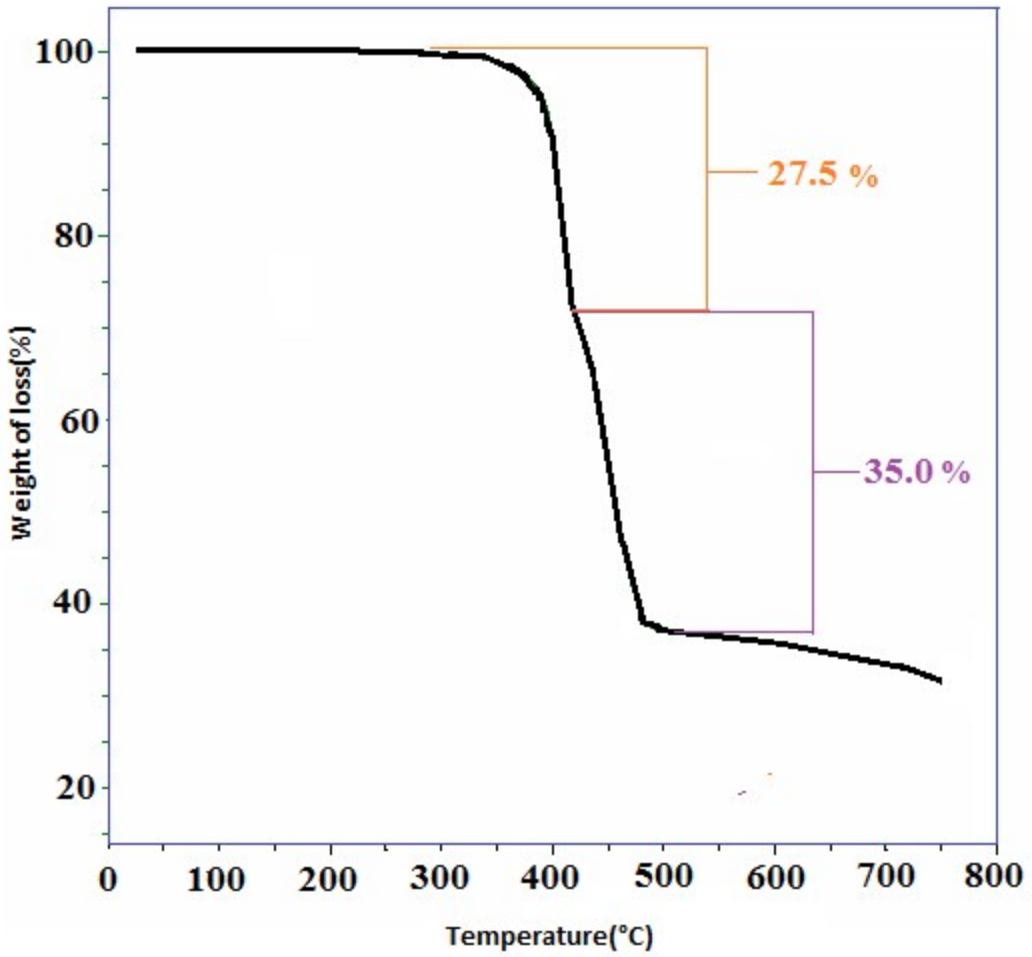

Figure S4. Thermal behaviour of compounds **2**;**3** mixture.

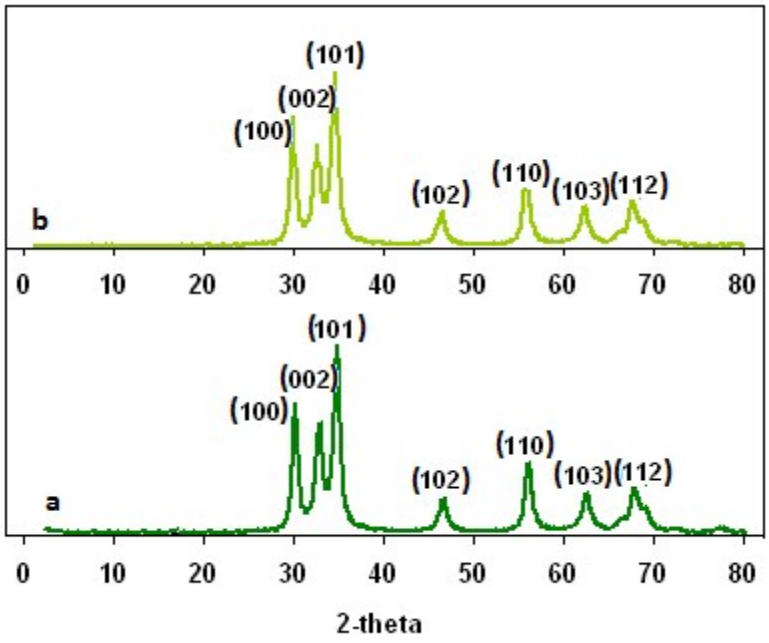

Figure S5. XRD patterns; a) ZnO nanoparticles, fabricated from calcination process of **1**.DMF.H_2O microrods at 550 ˚C and b) agglomerated nanoparticles of ZnO fabricated from calcination process of compounds **2** and **3** microrods at 550 ˚C.

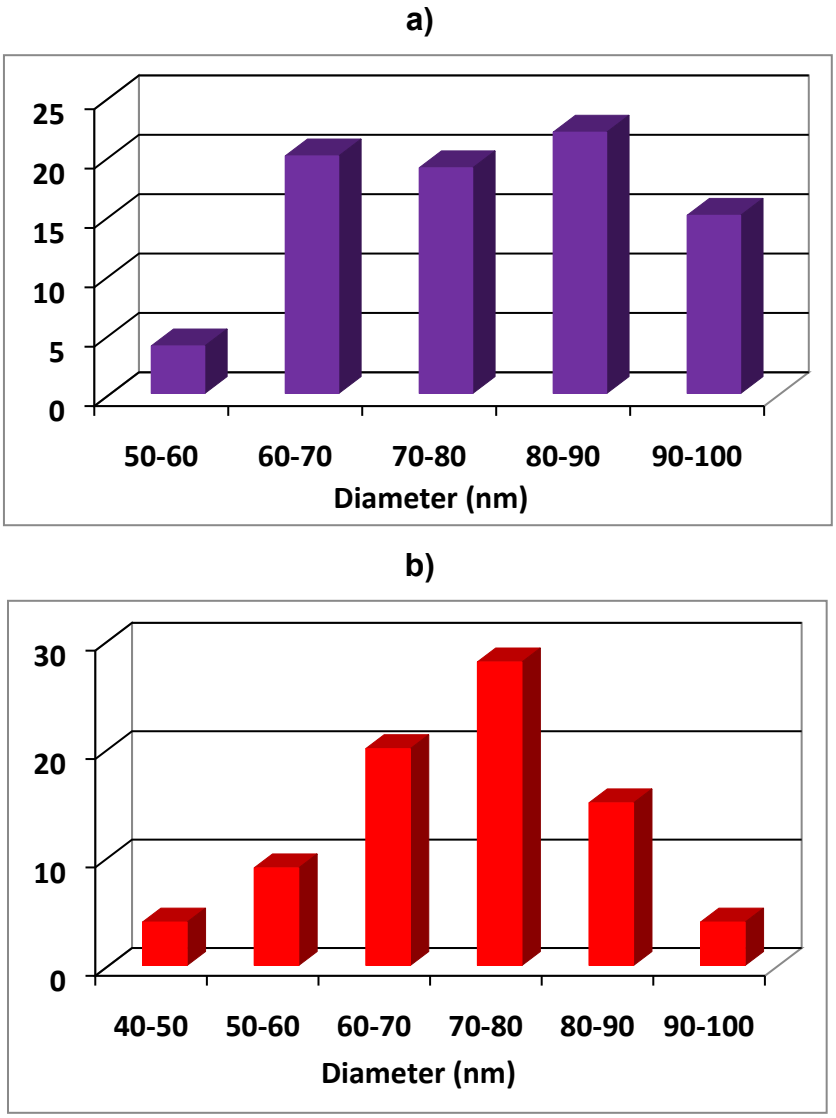

Figure S6. The corresponding particle size distribution histograms of ZnO nanoparticles fabricated from calcination process of a) **1**.DMF.H_2O microrods and b) compounds **2** and **3** microrods.

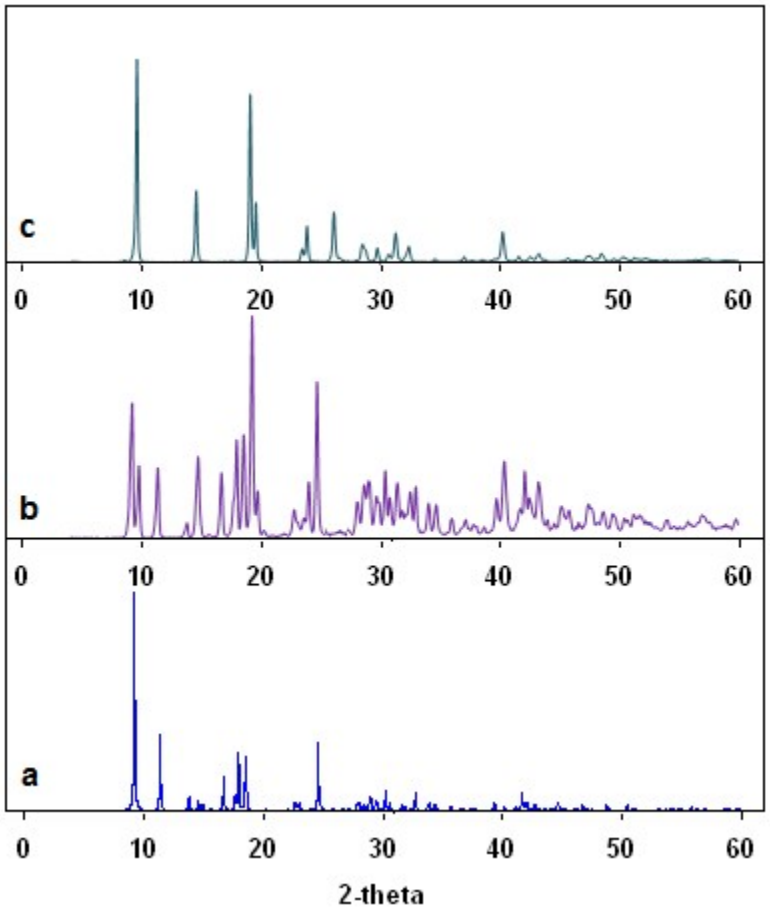

Figure S7. XRD patterns; a) simulated pattern based on single crystal data of compound $[Zn_2(BDC)_2(H_2O)_2 \cdot (DMF)_2]_n$ (**3**·2H_2O·2DMF), b) white precipitate of **3**·2H_2O·2DMF and c) apohost framework of **3**.