

Effect of the pillar ligand on preventing agglomeration of ZnO nanoparticles prepared from Zn(II) metal-organic frameworks

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ABSTRACT: Metal-Organic Frameworks (MOFs) represent a new class of highly porous materials. On this regard, two nano porous metal-organic frameworks of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**) and $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})] \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**), (1,4-bdc = benzene-1,4-dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane and DMF = N,N-dimethylformamide) were synthesized and characterized. They were used for preparation of ZnO nanomaterials. With calcination of **1**, agglomerated ZnO nanoparticles could be fabricated, but by the same process on **2**, the tendency of ZnO nanoparticles to agglomeration was decreased. In addition, the ZnO nanoparticles prepared from compound **2** had smaller diameter than those obtained from compound **1**. In fact, the role of organic dabco ligands in **2** is similar to the role of polymeric stabilizers in formation of nanoparticles. Finally, considering the various applications of ZnO nanomaterials such as light-emitting diodes, photodetectors, photodiodes, gas sensors and dye-sensitized solar cells (DSSCs), it seems that preparation of ZnO nanomaterials from their MOFs could be one of the simple and effective methods which may be applied for preparation of them.

Keywords: *Metal-organic framework; Nanomaterials; Zinc(II) oxide; Pillar*

INTRODUCTION

Metal-Organic Frameworks (MOFs) represent a new class of highly porous materials [1,2]. Crystal engineering based on metal-organic frameworks (MOFs) has recently attracted considerable interest and research on porous materials. MOFs is one of the most active endeavors among the inorganic and materials in chemistry community over the past two decades [3]. These porous compounds have potential applications in gas storage and capture, gas or liquid purification, catalysis, sensor devices or controlled drug release [4-6]. $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**), (1,4-bdc = benzene-1,4-dicarboxylate and DMF = N,N-dimethylformamide), also recognized as MOF-2, is one of the first MOFs exhibiting permanent porosity constructed from benzene-1,4-dicarboxylate (1,4-bdc). For the first time, it was reported by Yaghi *et al.* in 1998 [7]. Compound **1** is a 2D (4,4) layered framework consisting of paddle-wheel $\text{Zn}_2(\text{COO})_4$ SBUs which are bridged by 1,4-bdc linkers [8].

Chen *et al.* studied reversible structural transformation of **1** to $\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**), (dabco = 1,4-diazabicyclo[2.2.2]octane) too [8]. Compound **2** is one of the most recognized MOF constructed from 1,4-bdc, which for the first time was reported by Dybtsev *et al.* in 2004 [9]. This MOF has a jungle-gym-type structure in which a 2D square grid composed of dinuclear Zn_2 units is bridged by dabco molecules to extend the 2D layers into a 3D structure, thus affording wide open channels (with an area of $7.5 \times 7.5 \text{ \AA}^2$), which are large enough to allow the passage of small gas molecules. In spite of its fully connected 3D structure, compound **2** has enough flexibility around the coordination and single bonds to produce three different crystalline forms [10]. Furthermore, the host framework shrinks upon inclusion of organic guest molecules and expands upon guest removal [11]. Various different methods such as sol-gel [12,13], hydrothermal [12,13], pyrolysis of appropriate precursor [14], usage of copolymer agents [15] and *etc.* were applied in preparation of ZnO nanomaterials. Zn(II) coordination polymers were also used as new precursors for preparation of ZnO nanomaterials [16-18]. In addition, our

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studies on the case of fabrication nanomaterials from metal-organic frameworks, as new precursors, indicates that other nanomaterials such as Cu nanoparticles from the $[\text{Cu}_3(\text{btc})_2]$ (btc = benzene-1,3,5-tricarboxylate) MOF [19], ZnO nanoparticles from $\text{Zn}_4\text{O}(1,4\text{-bdc})_3$ (MOF-5) [20], 1D nano ZnO materials from $[\text{ZnF}(\text{AmTAZ})]$ -solvents (AmTAZ = 3-amino-1,2,4-triazole) [21] and PdO nanoparticles from a Pd(II) MOF, based on tetra-pyridyl porphyrin [22] have been prepared. In this work, we wish to report another potential application of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**) and $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})] \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**) in preparation of nano ZnO and also to investigate the role of presence and absence of pillar dabco ligand on agglomeration of nano ZnO prepared from these two MOFs.

EXPERIMENTAL

Materials and Physical Techniques

All reagents including benzene-1,4-dicarboxylic acid (98%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), 1,4-diazabicyclo[2.2.2]octane ($\geq 99\%$) and anhydrous N,N-dimethylformamide (99.8%) for the synthesis were commercially available from Sigma-Aldrich company and used as received. Microanalyses were carried out using a Heraeus CHN-O-rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Fourier transform infrared spectra were performed using KBr pellets on FT-IR spectrometer (Magna-IR, 550 Nicolet) in the range $400\text{-}4000\text{ cm}^{-1}$. The thermal behavior was measured with a PL-STA 1500 apparatus between 25 and $610\text{ }^\circ\text{C}$ in a static atmosphere of air. The molecular structure plot was prepared using Mercury software [23]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromatized Cu- K_α radiation. Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM).

Synthesis of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**) Metal-Organic Framework

White powder of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**) was synthesized by dissolving 5 mmol (0.831 g) benzene-1,4-dicarboxylic acid and 5 mmol (1.485 g) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 40 ml DMF. The resulting mixture was refluxed at 150

$^\circ\text{C}$ for 8 h. 4 h 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 $300\text{ }^\circ\text{C}$, yield: 1.433 g, 89.4% based on final product, Anal. Calcd. For **1**: C, 41.21; H, 4.09; N, 4.37; found: C, 41.33; H, 3.95; N, 4.25%.

Synthesis of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})] \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**) Metal-Organic Framework

White powder of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})] \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**) was synthesized by dissolving 10 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (33.6 mmol), 5.60 g of benzene-1,4-dicarboxylic acid (33.7 mmol) and 1.87 g of dabco (16.7 mmol) in 100 ml DMF and refluxing the resulting solution at $150\text{ }^\circ\text{C}$ for 8 h. 5 h 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. = about $120\text{ }^\circ\text{C}$, yield: 11.371 g, 78% based on final product, Anal. Calcd. For **2**: C, 46.80; H, 5.66; N, 9.63; Found: C, 47.10; H, 5.52; N, 9.68%.

Preparation ZnO Nanostructures from Compounds **1** and **2**

To prepare zinc oxide nanostructures, calcination of well scattered powder of compounds **1** and **2** as a very thin film was carried out at $550\text{ }^\circ\text{C}$ in a furnace and static atmosphere of air for 5 h.

RESULTS AND DISCUSSION

The reaction between 1,4- H_2bdc and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMF under reflux condition at $150\text{ }^\circ\text{C}$ results in formation of white powder which was dried at room temperature. Figure 1 shows unit cell of this MOF. A Comparison between the XRD patterns simulated from single crystal X-ray data (Fig. 2a) and that of the prepared powder (Fig. 2b), approved the formation of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2(\text{DMF})_2]_n$ (**1**). Figure 3a shows the thermo gravimetric analysis (TGA) of **1**. The TGA curve indicates that **1** loses its guest DMF and coordinated H_2O molecules in the temperature range of $60\text{-}170\text{ }^\circ\text{C}$. The experimental mass loss of 27.77% is consistent with the calculated value 28.42%. The resulting apohost framework is stable up to $400\text{ }^\circ\text{C}$. The TGA curve also indicates that the decomposition process of the apohost

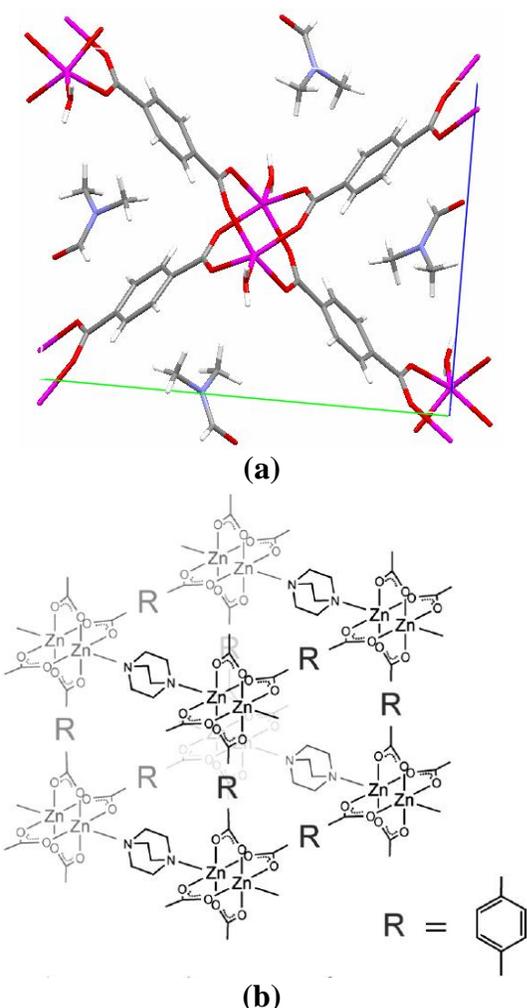


Fig. 1. a) Unit cell of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (**1**) with a guest DMF and coordinated water molecules, (Zn = violet, O = red, N = blue, C = gray and H = white) and b) schematic structure of $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})]$ framework in $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})]\cdot 4\text{DMF}\cdot\frac{1}{2}\text{H}_2\text{O}$ (**2**).

$[\text{Zn}_2(1,4\text{-bdc})_2]_n$ (**1**) framework is completed at 550 °C. The solid residue formed at around 550 °C is suggested to be ZnO (Calcd.: 25.38%, Obs.: 26.10%).

The reaction between 1,4- H_2bdc , dabco and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in DMF under reflux condition at 150 °C resulted in formation of the white powder which was dried at room temperature. Figure 1b shows the schematic structure of the compound **2** framework. Comparison between the XRD patterns simulated from single crystal X-

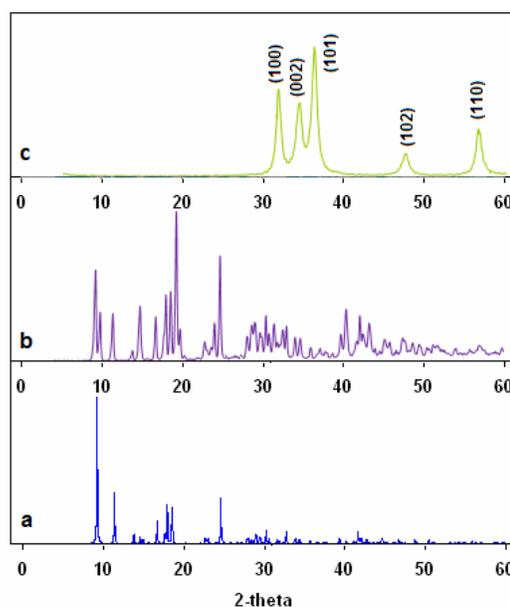


Fig. 2. XRD patterns; a) simulated pattern based on single crystal data of compound $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (**1**), b) white precipitate of **1**, c) ZnO nanoparticles fabricated from calcination of compound **1**.

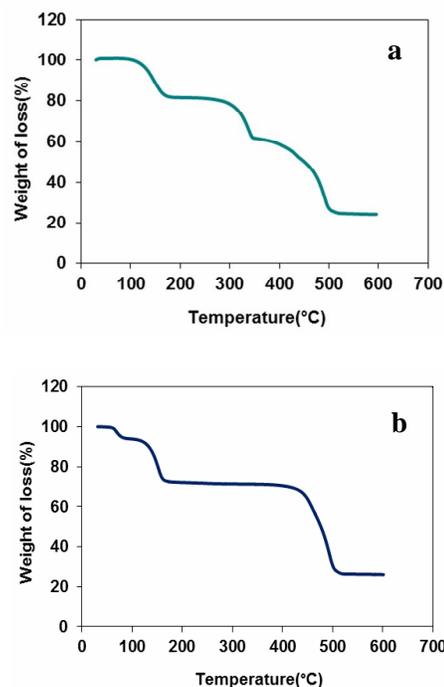


Fig. 3. Thermal behaviour of a) $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})_2]_n$ (**1**) and b) $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco})]\cdot 4\text{DMF}\cdot\frac{1}{2}\text{H}_2\text{O}$ (**2**).

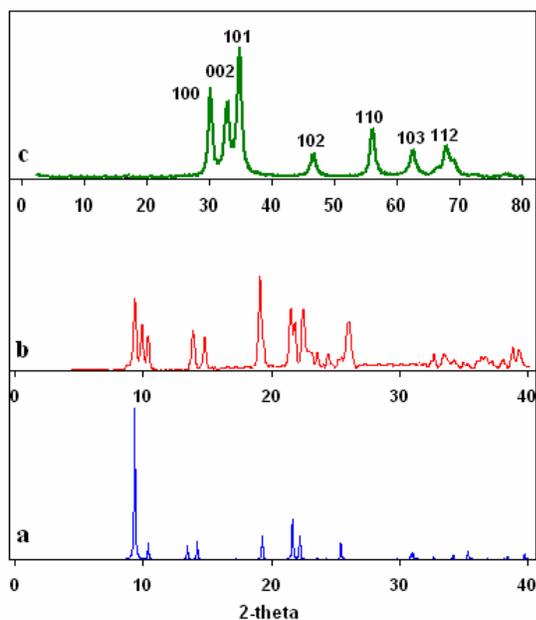


Fig. 4. XRD patterns; a) simulated pattern based on single crystal data of compound $[Zn_2(1,4\text{-bdc})_2(\text{dabco})] \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**), b) white precipitate of **2**, c) ZnO nanoparticles fabricated from calcination of compound **2**.

ray data (Fig. 4a) and that of the powder (Fig. 4b) approved the formation of **2**. Figure 3b shows the thermo gravimetric analysis (TGA) of **2**. The TGA data (Fig. 3b) indicate that **2** loses its guest molecules in the temperature range of 100-175 °C, and the resulting apohost framework starts to decompose after 250 °C. These TGA data indicate that the decomposition process of **2** has been completed at 550 °C.

Supramolecular polymers may be suitable precursors to the preparation of desirable nanoscale materials [24]. Thus, to prepare zinc oxide nanostructures and consideration the role of the pillar dabco ligand on formation of different morphologies of zinc oxide nanostructures, calcination of compounds **1** and **2** powders were carried out at 550 °C in static atmosphere of air. Figures 2c and 4c show the XRD patterns of zinc(II) oxide nanostructures prepared by this process. The XRD patterns are in agreement with the typical wurtzite structure of ZnO (hexagonal phase, space group $P6_3mc$, with lattice constants $a = 3.24982(9)$ Å, $c = 5.20661$ Å, $Z = 2$, JCPDS No. 36-1451). Figure 5a shows the SEM

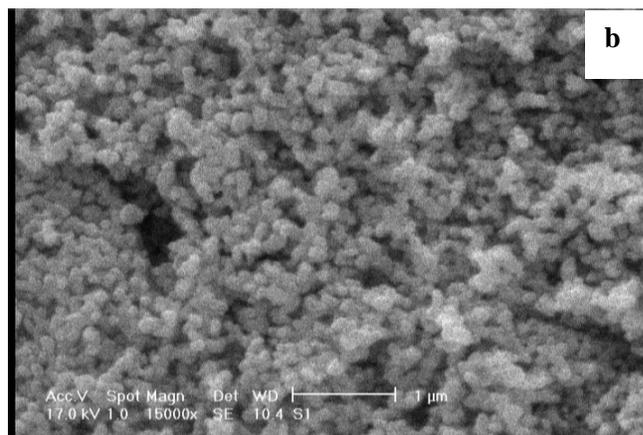
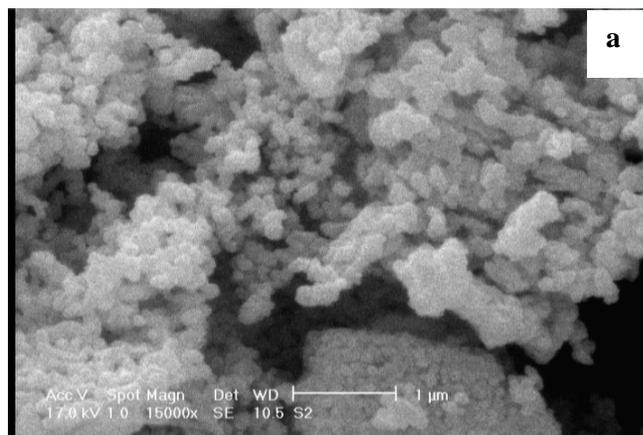


Fig. 5. SEM images of ZnO nanoparticles fabricated from calcinations process of a) **1** at 530 °C and b) **2** at 550 °C.

images of ZnO nanoparticles obtained from calcination of the **1**. The corresponding particle size distribution histogram of these nanoparticles could be observed in Fig. 6a. These nanoparticles have diameters between 60-100 nm, but the frequency (number of nanoparticles in each size distribution) of nanoparticles with 80-100 nm diameter are higher than others. SEM images of ZnO nanostructures, obtained from calcination of compound **2** framework (Fig. 5b), obviously show that the tendency of nanoparticles to agglomerate decreases. The corresponding particle size distribution histogram of these nanoparticles could be observed in Fig. 6b. These nanoparticles have diameters between 40-90 nm, but the frequency (number of

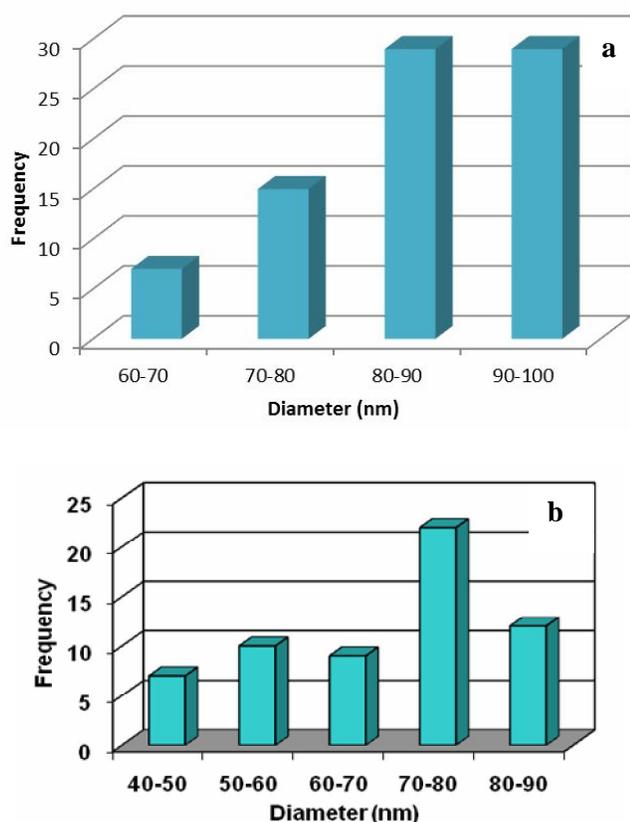


Fig. 6. The corresponding particle size distribution histograms of ZnO nanoparticles fabricated from calcination process of a) **1** and b) **2**.

nanoparticles in each size distribution) of nanoparticles with 70-80 nm diameter are higher than others.

Results of our work indicate that $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2 \cdot (\text{DMF})_2]_n$ (**1**) and $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}]$ (**2**) can be used for preparation of ZnO nanoparticles. It seems that removal of the pillar ligand from the structure of **2** enhances the tendency of nanoparticles to agglomerate and their particle sizes. Thus, the role of **1** in preparation of ZnO nanoparticles from it was reduced. In fact the role of organic dabco ligands **2** MOF is similar to the role of polymeric stabilizers in formation nanoparticles. Finally considering various applications of ZnO nanomaterials such as light-emitting diodes [25], photodetectors [26], photodiodes [27], gas sensors [28] and dye-sensitized solar cells (DSSCs) [29], it seems that preparation of ZnO nanomaterials from their MOFs could be one of the simple and effective

methods which may be applied for preparation of them.

CONCLUSIONS

In summary, the two MOFs $[\text{Zn}_2(1,4\text{-bdc})_2(\text{H}_2\text{O})_2 \cdot (\text{DMF})_2]_n$ (**1**) and $[\text{Zn}_2(1,4\text{-bdc})_2(\text{dabco}) \cdot 4\text{DMF} \cdot \frac{1}{2}\text{H}_2\text{O}]$ (**2**) were used for preparation of ZnO nanomaterials. With calcination of **1**, agglomerated ZnO nanoparticles could be fabricated. While by the same process on **2**, the tendency of ZnO nanoparticles to agglomerate was decreased. These results indicated that removal of the pillar dabco ligand from the structure of **2** increases the tendency of nanoparticles to agglomerate, and the role of this MOF (**1**) in preparation of ZnO nanoparticles is reduced. On the other hand, the ZnO nanoparticles prepared from compound **2** has smaller diameter than those obtained from compound **1**.

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