



Short communication

Coexistence of sorption behavior and magnetic property in heterometallic cluster-based frameworks

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ABSTRACT

Based on the Bifunctional Method, a new heterometallic cluster-based framework (**FJI-7**) with the coexistence of Cu₄I₄ cluster and binuclear [(Dy)₂(COO)₃(DMF)₂], has been successfully synthesized and structurally characterized. This **FJI-7** structure exhibits a 3-dimensional framework with Lewis basic pyridinyl sites and magnetic centre simultaneously. Additionally, its sorption behavior and magnetic property are also investigated.

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Heterometallic cluster-based frameworks, recognized as its multifunctionality, are usually constructed by postsynthetic method, transmetalation method, one-pot method and so forth [1–6]. Despite some success cases, it remains the necessity to develop more convenient and effective synthetic methods for the preparation of heterometallic cluster-based frameworks [7–10]. Previously, we have conceived and developed the ligand-directed Bifunctional Method, in which the carboxylate-affinitive metal ions only bind to carboxylate groups, whereas the N-affinitive counterparts only connect to aromatic N-centers with unpaired electrons. It has been realized to effectively synthesize heterometallic indium-organic frameworks by Bifunctional Method, in which the bifunctional isonicotinic acid, nicotinic acid and 3,5-pyridinedicarboxylic acid have been utilized for the assembly of **InOF-5 (BMM-1)**, **InOF-6 (BMM-2)**, **InOF-7 (BMM-3)** and **InOF-8 (BMM-4)** [11,12]. Afterwards, a photoluminescent **InOF-14 (BMM-5)** based on the mutually competitive [In(COO)₄] and [Eu₂(COO)₄(H₂O)₄] units is unexpectedly obtained by the modified Bifunctional Method, where the pure multi-carboxylic ligands (i.e., 1,3,5-benzenetricarboxylic acid) are used [13].

In this work, a new heterometallic cluster-based framework, which formulated as [Dy₂(Cu₄I₄)(nia)₆(DMF)₂] (**FJI-7** = **BMM-6**,

Hnia = nicotinic acid), has been successfully synthesized and structurally characterized. Moreover, its synthesis, crystal structure, magnetic property and sorption behavior are discussed in detail.

The light yellow crystals were solvothermally prepared by heating the mixture of DyCl₃, CuI and Hnia ligand in a 1: 2: 4 M ratio in 6 ml DMF/MeCN mixed solution (1: 1, v/v, DMF = N,N-Dimethylmethanamide) at 120 °C for one week. The microcrystal phase purity of **FJI-7** was confirmed by the powder X-ray diffraction analysis (Fig. S1) and the molecular formula of **FJI-7** was calculated from the combination of thermogravimetric analysis curve and elemental analysis data (Fig. S2) and the Cu(I) and Dy(III) ions were confirmed by the elemental mapping (Fig. S4).

Single crystal X-ray diffraction analysis reveals that it is crystallized in the tetragonal space group *I*4̄2d with cell parameters of a = b = 25.2901(4) Å, c = 9.0497(3) Å, V = 5788.1(3) Å³. Its asymmetric unit constitutes one Dy(III) centre, one quarter of Cu₄I₄-based cluster, one and a half nia⁻ ligands (one ina⁻ is connected to Dy(III) as well as Cu₄I₄ cluster, while the half is only terminally coordinated to the Dy(III) centre), and one coordinated DMF molecule as depicted in Fig. 1a. In the coordination environment, four Cu(I) ions is bonded to four I(1) ions, to generate a typical cubane-like Cu₄I₄ cluster, which can be further linked by four pyridinyl nitrogen atoms from four independent nia⁻ ligands. The central Dy(III) ion is seven-coordinated with the pentagonal bipyramidal geometry, surrounded by six carboxylate O atoms from six different nia⁻ ligands and one O atom from the coordinated DMF

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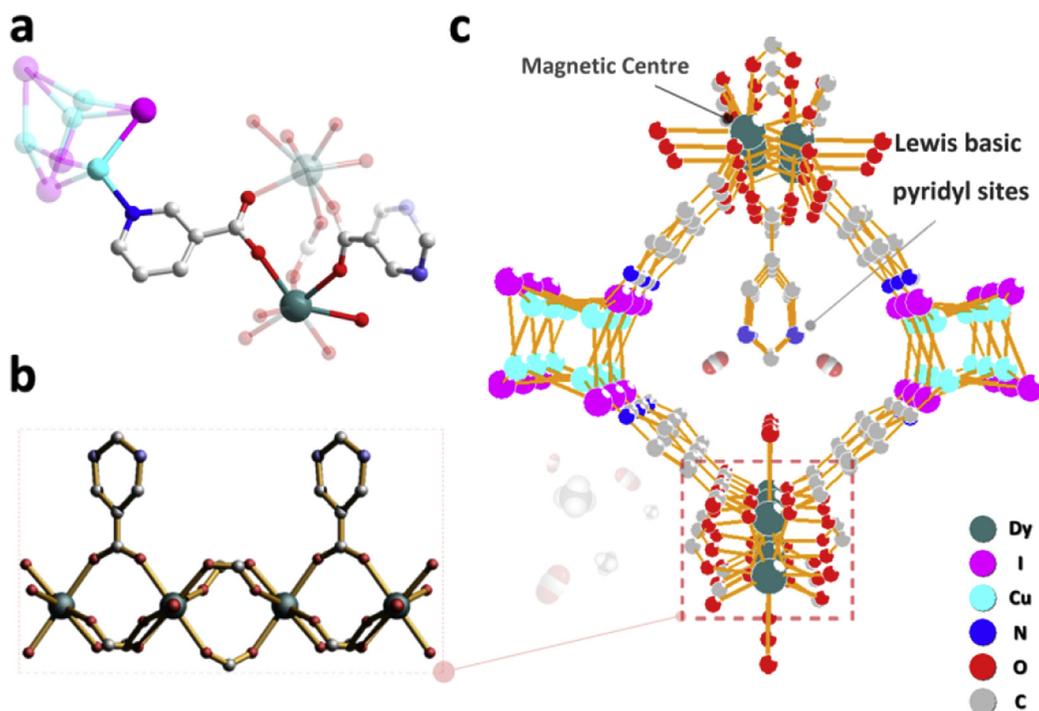


Fig. 1. (a) The coordination environment of nia⁻ligand, [Cu₄L₄] moiety and binuclear [(Dy)₂(COO)₃(DMF)₂] in FJI-7. (b) The 1-dimensional Dy-carboxylate chains. (c) The 3-dimensional framework embedded with the Lewis basic pyridinyl sites and magnetic centre (Hydrogen atom omitted for clarity).

solvent molecule. Meanwhile, each nia⁻ ligand connect to one N-affinitive Cu₄L₄ cluster and two carboxylate-affinitive Dy(III) ions with a $\kappa^1-(\kappa^1-\kappa^1)-\mu_3$ coordination mode, whereas another nia⁻ ligand only links two neighboring Dy(III) ions with a $(\kappa^1-\kappa^1)-\mu_2$ coordination mode (Fig. 1a). Between the Cu₄L₄ cluster and binuclear [(Dy)₂(COO)₃(DMF)₂], the observed Dy–O, Cu–I and Cu–N bond lengths are in the range of 2.16–2.47 Å, 2.625–2.746 Å and 2.057 Å, respectively. In addition, the adjacent seven-coordinated Dy(III) ions are further bridged by carboxylate groups, to

construct an infinite 1-dimensional Dy(III) carboxylate chain (Fig. 1b), which can be expanded into a 3-dimensional network by the copper(I) halide clusters and nia⁻ ligands together (Fig. 1c).

In this 3-dimensional structure, the Lewis basic pyridinyl sites and magnetic centre coexist [14]. The adjacent binuclear [(Dy)₂(COO)₃(DMF)₂] with the approximate size of 10.42 Å (the shortest Dy–Dy distance), adjacent Cu₄L₄ clusters with the approximate size of 12.12 Å and the shortest distance between

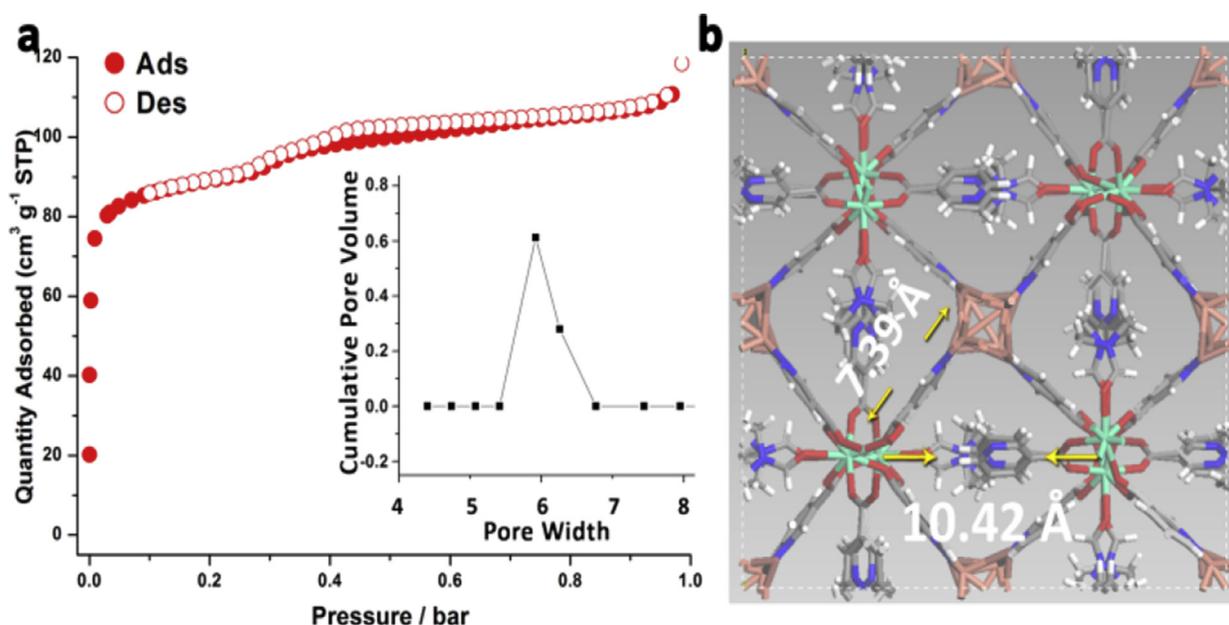


Fig. 2. (a) Experimental nitrogen adsorption-desorption isotherms at 77 K for FJI-7; Inset shows the pore size distribution (PSD) calculated by DFT method; (b) the coordinated and disordered DMF molecules and ina⁻ligands within the ball-and-stick FJI-7 model viewed long the c axis.

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