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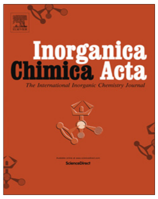

Controllable assembly of three copper(II/I) metal–organic frameworks based on *N,N′*-bis(4-pyridinecarboxamide)-1,2-cyclohexane and 4,4′-oxydibenzoic acid: From three-dimensional interpenetrating framework to one-dimensional infinite chain

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By adjusting molar ratio of the reactants (metal salt and two types of ligands), three new $Cu^{II/I}$ metal–organic frameworks, $[Cu^{II}_2(4,4'\text{-oba})_2(H_2O)_2]\cdot H_2O$ (**1**) and $[Cu^{I}_2(4\text{-bpah})_2(\mu_2\text{-OH})(\mu_3\text{-Cl})]\cdot{\sim}H_2O$ (**2**) and $[Cu^{II}(4\text{-bpah})_2(4,4'\text{-oba})(H_2O)]$ (**3**) (4,4′-H_2oba = 4,4′-oxydibenzoic acid and 4-bpah = *N,N′*-bis(4-pyridinecarboxamide)-1,2-cyclohexane), have been prepared and structurally characterized by single-crystal X-ray diffraction analyses. When Cu:4-bpah:4,4′-H_2oba ratio is 4:1:2, complex **1** is a 5-fold interpenetrated three-dimensional (3D) framework with 4-connected *PtS* topology, which contains 4,4′-oba ligand. Complex **2** exhibits a 2D network with Cu:4-bpah:4,4′-H_2oba ratio of 4:2:1, which contains 1D $[Cu^{I}_2(\mu_2\text{-OH})(\mu_3\text{-Cl})]_n$ chains and 4-bpah ligand. Complex **3** is a 1D infinite chain based on 4-bpah and 4,4′-oba mixed ligands with Cu:4-bpah:4,4′-H_2oba ratio of 4:2:3. The results reveal that **1**–**3** are particularly sensitive to the molar ratio of the reactant metal salts and organic ligands in this system. The fluorescent, electrochemical, and photocatalytic properties of **3** were investigated.

1. Introduction

Metal–organic frameworks (MOFs) have received much attention owing to their novel multi-dimensional architectures, unique functionalities and potential applications in photoluminescence, magnetism, catalysis, gas storage and separation [1–8]. It is well known that the construction of MOFs mainly depends on the nature of metal ions and organic ligands [9]. In order to obtain novel structures and expected functionalities, many researchers have focused on the design and synthesis of new organic ligands and their corresponding MOFs, including multidentate imidazoyl- or pyridyl-based derivatives, and polycarboxylates, etc. [10–15]. However, other factors, such as solvent [16], pH [17], temperature [18] and the molar ratio of reactants [19] also can induce the formation of diverse MOFs, which are rarely subjected to systematic investigation. Especially, reports on the effect of molar ratios of reactants on the self-assembly process are very limited [20–22]. Different reactant ratios may perturb the delicate coordination equilibrium preventing the crystal formation or resulting in different MOFs with respect to the original or expected structure [20–22]. For example, Wang and co-workers have fabricated three entangled Cd(II) MOFs by adjusting the molar ratio of the metal salt and ligands (Cd/tib/H_2tbta) of 1:1:1, 1:1:2 and 1:1:3, which exhibit a rare 2-fold interpenetrated 3D *hex* framework, a 2D → 3D interdigitated network and a 3D self-penetrated framework, respectively [22]. Zhou's group have synthesized two porous coordination networks by solvothermal reactions of Zn(II) nitrate with anthrancene-9,10-dicarboxylic acid through tuning the molar ratio of metal salt and ligand from 5:1 to 1:1 [21]. The results suggest that judiciously tuning the metal–ligand molar ratio could be an effective way to form different structures.

On the other hand, the bis-pyridyl-bis-amide ligands or dicarboxylic acids are frequently introduced as secondary ligands to build the intriguing networks with multi-dimensional structures [23–29]. Firstly, bis-pyridyl-bis-amide ligands exhibit the following structural characters: (i) it possesses two pyridine moieties and two amide groups, which can provide more potential coordination sites to meet the requirements of the coordination geometries of metal ions; (ii) the amide groups can provide potential supramolecular recognition sites for hydrogen bonding interactions [23,24,27–29]. Secondly, dicarboxylic acids have been extensively used to construct novel MOFs owing to their versatile coordination modes and high structural stability [25,26]. On the basis of the aforementioned points and our previous work, in this study, we

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want to investigate the influence of reactant ratios on the architectures based on bis-pyridyl-bis-amide, dicarboxylic acid and Cu(II) ions. The fine distinctions of reactant ratio led to three entirely different Cu(II) metal–organic frameworks: $[Cu^{II}_2(4,4'\text{-oba})_2(H_2O)_2]\cdot H_2O$ (**1**) and $[Cu^{I}_2(4\text{-bpah})_2(\mu_2\text{-OH})(\mu_3\text{-Cl})]\cdot{\sim}H_2O$ (**2**) and $[Cu^{II}(4\text{-bpah})_2(4,4'\text{-oba})(H_2O)]$ (**3**) (4,4′-H$_2$oba = 4,4′-oxydibenzoic acid and 4-bpah = *N,N*′-bis(4-pyridinecarboxamide)-1,2-cyclohexane). In addition, the fluorescent, electrochemical, and photocatalytic properties of **3** were investigated.

2. Experimental

2.1. Materials and general methods

All reagents were obtained from commercial sources without further purification. The N-donor ligand 4-bpah (R,R-/S,S-racemic mixture) was prepared according to the literature [27].

The elemental analyses (C, H and N) were determined on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra (KBr pellets) were taken on a Varian FT-IR 640 spectrometer in the range of 500–4000 cm^{-1}. Thermogravimetric data for the complexes **1**–**3** were carried out on a Pyris Diamond thermal analyzer. Fluorescent spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. A CHI 440 electrochemical workstation was used for control of the electrochemical measurements and for data collection. A conventional three-electrode cell was used at room temperature. The carbon paste electrode bulk-modified with complex **3** (**3**-CPE) was used as the working electrode. An SCE (saturated calomel electrode) and a platinum wire were used as reference and auxiliary electrodes, respectively. The UV–Vis absorption spectra were obtained using a SP-1901 UV–Vis spectrophotometer.

2.2. Preparation of the title complexes

2.2.1. Synthesis of $[Cu^{II}_2(4,4'\text{-oba})_2(H_2O)_2]\cdot H_2O$ (1)

A mixture of CuCl$_2$·2H$_2$O (0.034 g, 0.20 mmol), 4-bpah (0.016 g, 0.05 mmol), 4,4′-H$_2$oba (0.026 g, 0.10 mmol) and NaOH (0.016 g, 0.40 mmol) in 12 mL water was stirred for 30 min at room temperature, and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slowly cooling to room temperature, green block-shape crystals of **1** suitable for single crystal X-ray diffraction were manually isolated, and washed off the green precipitate with distilled water (yield: 8% based on Cu). *Anal.* Calc. for $C_{28}H_{22}Cu_2O_{13}$: C, 48.49; H, 3.20. Found: C, 48.52; H, 3.24%. ν_{max} (KBr)/cm^{-1}: 3388 (s), 1617 (s), 1317 (s), 804 (m), 659 (m), 520 (m).

2.2.2. Synthesis of $[Cu^{I}_2(4\text{-bpah})_2(\mu_2\text{-OH})(\mu_3\text{-Cl})]\cdot{\sim}H_2O$ (2)

A mixture of CuCl$_2$·2H$_2$O (0.034 g, 0.20 mmol), 4-bpah (0.032 g, 0.10 mmol), 4,4′-H$_2$oba (0.013 g, 0.05 mmol) and NaOH (0.016 g, 0.40 mmol) in 12 mL water was stirred for 30 min at room temperature, and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slowly cooling to room temperature, red block-shape crystals of **2** suitable for single crystal X-ray diffraction were manually isolated, and washed off the white precipitate with distilled water (yield: 9% based on Cu). *Anal.* Calc. for $C_{36}H_{42}ClCu_2N_8O_6$: C, 51.15; H, 5.02; N, 13.25. Found: C, 51.12; H, 5.04; N, 13.29%. ν_{max} (KBr)/cm^{-1}: 3363 (s), 3211 (s), 1664 (s), 1386 (s), 1054 (m), 900 (m), 786 (w), 580 (w), 549 (m).

2.2.3. Synthesis of $[Cu^{II}(4\text{-bpah})_2(4,4'\text{-oba})(H_2O)]$ (3)

A mixture of CuCl$_2$·2H$_2$O (0.034 g, 0.20 mmol), 4-bpah (0.032 g, 0.10 mmol), 4,4′-H$_2$oba (0.039 g, 0.15 mmol) and NaOH (0.016 g, 0.40 mmol) in 12 mL water was stirred for 30 min at room temperature, and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slowly cooling to room temperature, blue block-shape crystals of **3** suitable for single crystal X-ray diffraction were manually isolated, and washed off the blue precipitate with distilled water (yield: 46% based on Cu). *Anal.* Calc. for $C_{50}H_{50}CuN_8O_{10}$: C, 60.87; H, 5.12; N, 11.35. Found: C, 60.83; H, 5.15; N, 11.37%. ν_{max} (KBr)/cm^{-1}: 3336 (s), 3247 (s), 1645 (s), 1610 (s), 1390 (s), 1319 (s), 1035 (m), 744 (m), 719 (m), 646 (w), 578 (w).

2.3. Preparation of complex 3 bulk-modified carbon paste electrode (3-CPE)

The complex **3** bulk-modified carbon paste electrode (**3**-CPE) was fabricated by the following steps [30]. Graphite powder 0.22 g and complex **3** 0.02 g were mixed together with an agate mortar for about 30 min to achieve uniform mixture; then 0.05 mL paraffin oil was added and stirred with a glass rod. The homogenized mixture was packed into a 3 mm inner diameter glass tube, and a copper stick was used as the electrical contact. The surfaces of the modified electrodes were polished on a piece of weighing paper to achieve a mirror finish before use. The same procedure was used for preparation of bare CPE without copper complex.

2.4. X-ray crystallography

X-ray diffraction data for complexes **1**–**3** were collected on a Bruker SMART APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα (λ = 0.71073 Å) by ω and θ scan mode. All of the structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXS program of the SHELXTL package [31]. For complexes **1**–**3**, the crystal parameters, data collection, and refinement results are summarized in Table 1. Selected bond distances and bond angles are listed in Tables S1–S3.

3. Results and discussion

3.1. Synthesis

Complexes **1**–**3** were synthesized by using a mixture of CuCl$_2$·2H$_2$O, 4-bpah and 4,4′-H$_2$oba with different molar ratios. The

Table 1
Crystal and refinement data for complexes **1**–**3**.

Empirical formula	$C_{28}H_{22}Cu_2O_{13}$	$C_{36}H_{42}ClCu_2N_8O_6$	$C_{50}H_{50}CuN_8O_{10}$
Formula weight	693.54	845.31	986.52
Crystal system	tetragonal	monoclinic	triclinic
Space group	$I4_1/a$	$C2/m$	$P1$
a (Å)	17.8699(6)	16.5382(14)	5.2170(12)
b (Å)	17.8699(6)	29.639(3)	15.759(4)
c (Å)	17.0343(12)	10.0978(9)	15.870(4)
α (°)	90	90	118.034(4)
β (°)	90	125.1430(10)	95.106(4)
γ (°)	90	90	90.313(4)
V (Å^3)	5439.6(5)	4047.4(6)	1145.5(5)
Z	8	4	1
T (K)	296(2)	296(2)	296(2)
D_{calc} (g cm^{-3})	1.694	1.358	1.430
F(000)	2816	1708	515
Goodness-of-fit on F^2	1.026	1.002	1.017
Reflections collected	13804	10360	5825
Unique data	2432	3647	4786
R_{int}	0.0362	0.0324	0.0335
θ Range (°)	1.65–25.13	1.37–25.00	1.47–25.00
R_1[a] ($I > 2\sigma(I)$)	0.1493	0.0547	0.0471
wR_2[b] (all data)	0.3321	0.1858	0.1200

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.