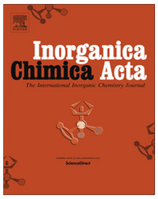
Inorganica Chimica Acta 469 (2018) 11–19

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Research paper

Structural diversity, single-crystal to single-crystal transformation and photocatalytic properties of Cu(II)-metal-organic frameworks based on 1,4-phenylenedipropionic acid

Surapoj Sanram, Jaursup Boonmak *, Sujittra Youngme

Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

A R T I C L E I N F O

Article history:
Received 28 October 2016
Received in revised form 26 January 2017
Accepted 28 August 2017
Available online 31 August 2017

Keywords:
Metal-organic frameworks
Copper(II)
1,4-Phenylenedipropionic acid
Photocatalytic properties
Solvothermal syntheses
Single-crystal to single-crystal transformation

A B S T R A C T

A series of four new copper(II) based metal-organic frameworks containing 1,4-phenylenedipropionic acid and different *N,N′*-donor coligands, namely, $[Cu(ppa)(bpy)]_n$ (**1**), $\{[Cu(ppa)(azp)(H_2O)](H_2O)\}_n$ (**2**), $\{[Cu(ppa)(tdp)(H_2O)](H_2O)_2\}_n$ (**3**), and $\{[Cu(ppa)(tdp)](H_2O)\}_n$ (**4**), (H_2ppa = 1,4-phenylenedipropionic acid, bpy = 4,4′-bipyridine, azp = 4,4′-azobipyridine, tdp = 4,4′-thiodipyridine) have been successfully synthesized and structurally characterized by elemental analysis, IR, UV–vis, TGA, XRPD and single-crystal X-ray diffraction. Compound **1** containing a short and rigid bpy coligand displays a 2D square lattice (*sql*) topology while **2** and **3** which contain more flexible and longer azp and tdp coligands possess two-fold interpenetrating diamond-like (***dia***) 3D framework. Finally, the thermal-induced compound **4** is transformed from compound **3** by heating, through single-crystal-to-single-crystal transformation, adopting a $CdSO_4$-like (***cds***) 3D framework. Additionally, the solid stated compounds **1**–**4** exhibit the energy band gaps of 3.50, 3.16, 3.53 and 3.31 eV, respectively. Thus, the photocatalytic properties of **1**–**4** have been investigated. Approximately 84.9% for **1**, 93.3% for **2**, 82.0% for **3** and 85.4% for **4** of methylene blue were decomposed within 105 min.

1. Introduction

Metal-organic frameworks (MOFs) made by linking inorganic and organic units have great flexibility with the constituents' geometry, size, and functionality, and are considered as candidates for catalysis, adsorption, separation, magnetism, and luminescence [1–5]. Most recently, many researchers have also been focused on exploiting new photocatalytic materials based on MOFs because this material usually exhibits absorption bands in the ultraviolet region, which indicates that MOFs may undergo photochemical processes and exhibit responses upon UV-light excitation [6–14].

The structural diversity of the crystalline MOFs is dependent on many factors, such as a ligand, pH, solvents, temperature, and metal atom [15–24]. Among the strategies, it is well-known that the MOFs containing carboxylates show various dimensional networks with interesting properties [25–27]. This diversity results from the fact that the carboxylate groups can coordinate metal centers in various ways [28–32]. In this study, 1,4-phenylenedipropionate (ppa) ligand is an interesting building block, mainly because of the possibility of variety coordination sites, as well as its flexibility. Furthermore, the geometric inclination of both of the opposing aliphatic carboxylate groups freely adjusts their conformations (*trans-trans, trans-cis,* and *cis-cis*) to get various coordination requirements of the metal ion [33–35]. The different geometry of ligands will provide a different pathway for ligand-to-metal-charge-transfer (LMCT) resulting in different energy band gap (E_g) in the use as a photocatalyst [6–14]. However, the chemistry of MOFs containing ppa ligand has been rarely explored to date and its application as photocatalyst are few [33–35]. Besides from carboxylate ligands, *N,N′*-donor coligands are also of great importance in the formation of the compounds. Rigid *N,N′*-donor coligands result in certain geometrical shapes of MOFs while flexible *N,N′*-donor coligands produce different coordination modes of MOFs which would affect their final topology [36–39].

Apart from mixing bridging ligands, the structural dynamic behaviors, such as single-crystal-to-single-crystal (SC-SC) transformations also play an important role in the structural architectures, dimensionalities, and topologies upon the driving forces of transformations of MOFs including light, heat, guest removal, uptake or exchange and chemical oxidation however the SC-SC structural transformation in MOFs are not often observed [40–55].

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* Corresponding author.
E-mail address: Jaursup@kku.ac.th (J. Boonmak).

http://dx.doi.org/10.1016/j.ica.2017.08.055

Based on all above consideration, four new MOFs from the combination of Cu(II) salt, 1,4-phenylenedipropionic acid (H_2ppa) and diverse *N,N′*-donor coligands, 4,4′-bipyridyl (bpy), 4,4′-azobipyridyl (azp) and 4,4′-thiobipyridyl (tbd), namely $[Cu(ppa)(bpy)]_n$ (**1**), $\{[Cu(ppa)(azp)(H_2O)](H_2O)\}_n$ (**2**), $\{[Cu(ppa)(tdp)(H_2O)](H_2O)_2\}_n$ (**3**) and $\{[Cu(ppa)(tdp)](H_2O)\}_n$ (**4**), were chemically and structurally characterized (Scheme 1). We found that ppa ligand in each compound adopts a *cis*-conformation. The variation of topologies observed in the resulting coordination networks is discussed, based on the length and flexibility of the building blocks and diverse coordination environment of Cu(II) ion. The irreversible thermal-induced structural transformation through single-crystal-to-single-crystal from **3** to **4** is investigated. Furthermore, the photocatalytic performances of all compounds in decomposing methylene blue (MB) in water under ultraviolet (UV) light are also examined.

2. Experimental section

2.1. Materials and general methods

All reagents and solvents were obtained from commercial suppliers and used without further purification. Elemental analyses were carried out on a PerkinElmer PE 2400CHNS analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a PerkinElmer Spectrum One FTIR spectrophotometer. XRPD patterns of the samples were collected on a Bruker D8 ADVANCE diffractometer using monochromatic CuKα radiation, and the recording speed was 0.5 s/step over the 2θ range of 5–50° at room temperature. Thermogravimetric (TG) analyses were performed on a TG-DTA 2010S MAC analyzer heated from 45 to 800 °C under nitrogen gas. Diffuse reflectance spectra were collected on finely ground samples with a UV-3101pc UV–VIS-NIR scanning spectrophotometer Shimadzu, which was measured from 400 to 1100 nm using barium sulfate as a standard with 100% reflectance.

2.2. Synthesis of $[Cu(ppa)(bpy)]_n$ (1)

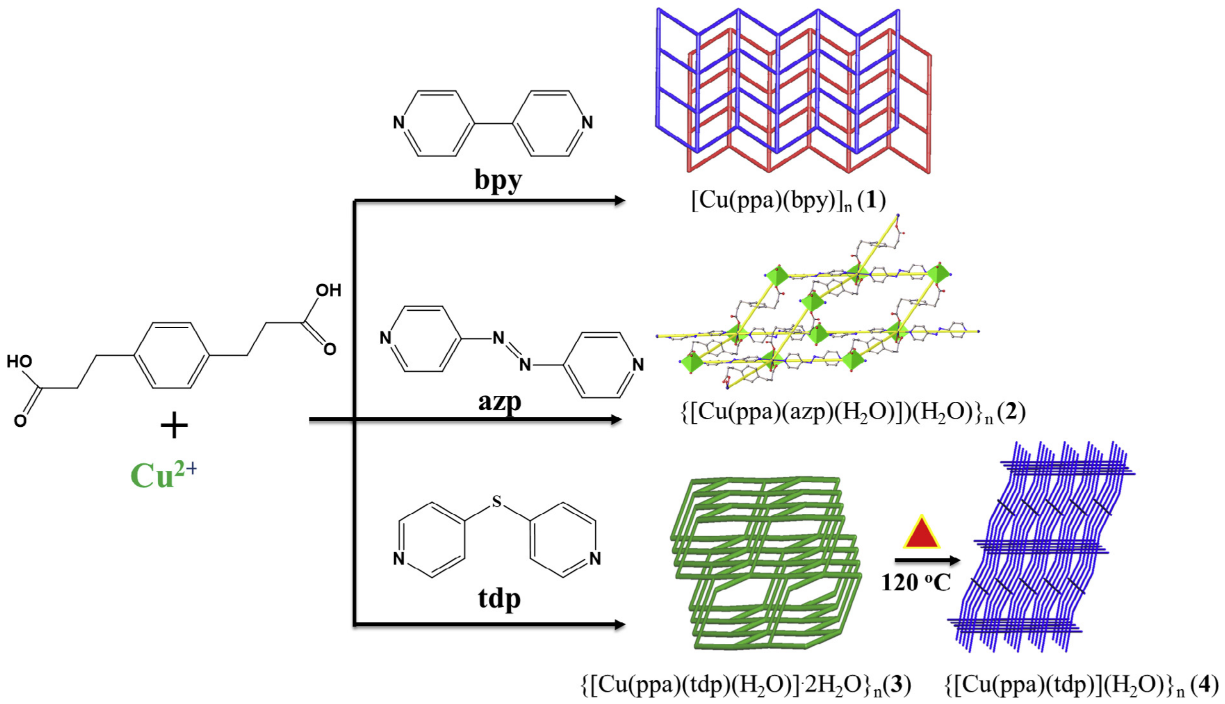
Compound **1** was synthesized by hydrothermal technique at 60 °C. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (150 mg, 0.5 mmol), 1,4-phenylenedipropionic acid (220 mg, 1 mmol), 4,4-bipyridyl (180 mg, 1 mmol) and H_2O/DMF (6 ml; 1:1 v/v) was placed in a 20 ml Teflon-lined stainless steel reactor, and then the vessel was sealed and heated at 60 °C for 12 hours. After the mixture was slowly cooled to room temperature, violet block-shaped crystal of **1** were obtained. Yield: 117 mg (43%) based on metal. Anal. Calcd for $C_{18}H_{17}CuNO_4$: C, 60.06; H, 4.58; N, 6.37%. Found: C, 59.98; H, 4.45; N, 6.32%. IR (KBr, cm^{-1}): 3430(s), 3054(w), 2928 (w), 2857(w), 1616(s), 1508(w), 1429(w), 1385(s), 1275(m), 1220 (w), 1163(w), 1105(w), 1067(w), 1031(m), 817(m), 521(m).

2.3. Synthesis of $\{[Cu(ppa)(azp)(H_2O)](H_2O)\}_n$ (2)

Compound **2** was synthesized by solvent diffusion method at room temperature. A dimethylformamide solution (3 ml) of 1,4-phenylenedipropionic acid (220 mg, 1 mmol) was layered on the solution (3 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (150 mg, 0.5 mmol). Then a methanol solution (3 ml) of 4, 4-azobipyridyl (180 mg, 1 mmol) was layered on the mixture layer. Then, the vial was sealed and allowed to stand undisturbed at room temperature. After 3 days, greenish-brown block-shaped crystals were obtained. The crystals were separated, washed with water and dried in air. Yield: 125 mg (41%) based on copper salt. Anal. Calcd for $C_{22}H_{24}CuN_4O_6$: C, 52.43; H, 4.80; N, 11.12%. Found: C, 52.47; H, 4.67; N, 11.10%. IR (KBr, cm^{-1}): 1656(w), 1562(s), 1512(w), 1443(w), 1403(s), 1330(s), 1309(w), 1289(s), 1225(s), 1152(w), 1108(w), 1065(s), 873(w), 843(s), 823(w).

2.4. Synthesis of $\{[Cu(ppa)(tdp)(H_2O)](H_2O)_2\}_n$ (3)

Compound **3** was synthesized in the same way as **2**, except that 4,4-thiodipyridine (180 mg, 1 mmol) was used instead of 4,4-azodipyridine. Blue block-shaped crystals of **3** suitable for X-ray



Scheme 1. Synthetic scheme of compounds **1–4**.