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วิศวกรรมเชิงผลึกของโคออดิเนชันพอลิเมอร์โครงข่ายสามมิติของโคบอลต์(II) และคอปเปอร์(II)ร่วมกับลิแกนด์เอโซพิริดีนและกรดฟีนิลีนไดอะซิติก

Crystal engineering of three-dimensional frameworks of cobalt(II) and copper(II) coordination polymers constructing from azopyridine and phenylenediacetic acid ligands

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บทคัดย่อ

งานวิจัยนี้เกี่ยวข้องกับการสังเคราะห์สารประกอบโคออดิเนชันพอลิเมอร์ของโคบอลต์(II) และคอปเปอร์(II)ที่ประกอบด้วยลิแกนด์เอโซพิริดีนและกรดฟีนิลีนไดอะซิติกได้แก่$[Co_2(ppda)_2(azp)_2]_n$ (**1**) และ $[Cu(ppda)(azp)]_n$ (**2**)เมื่อ azp= 4,4'-azobis(pyridine) และ ppda=1,4-phenylenediacetate พิสูจน์เอกลักษณ์และศึกษาโครงสร้างโดยเทคนิค CHN, IR, PXRD, TGA และการเลี้ยวเบนของรังสีเอกซ์ผ่านผลึกเดี่ยว สารประกอบ**1**มีโครงสร้างเป็นโครงข่าย 3 มิติที่มีหน่วยโครงสร้างทุติยภูมิเป็น dinuclear $[Co_2(COO)_2]$ ขณะที่สารประกอบ **2** มีโครงสร้างเป็นโครงข่ายสามมิติแบบสองโครงข่ายประสานกันและมีหน่วยโครงสร้างทุติยภูมิเป็น paddle-wheel dinuclear $[Cu_2(COO)_4]$ ซึ่งสารประกอบทั้งสองมีสถาปัตยกรรมของโครงสร้างที่ต่างกัน

ABSTRACT

The cobalt(II)and copper(II) coordination polymers constructed fromazopyridine and phenylenediacetic acid as ligands, $[Co_2(ppda)_2(azp)_2]_n$ (**1**), and $[Cu(ppda)(azp)]_n$ (**2**)when azp=4,4'-azobis(pyridine),ppda=1,4-phenylenediacetate,are successfully synthesized and characterized by CHN analysis, IR, PXRD, TGA and single crystal X-ray diffraction. Compound **1** exhibits a 3D framework with dinuclear $[Co_2(COO)_2]$ secondary building unitswhile **2** is a 2-fold interpenetrated

3D coordination polymer with paddle-wheel dinuclear $[Cu_2(COO)_4]$ secondary building units, both are different in structural architecture.

คำสำคัญ:โคออดิเนชันพอลิเมอร์โครงข่ายสามมิติเอโซพิริดีนกรดฟีนิลีนไดอะซิติก

Keywords: Coordination polymer, Three-dimensional frameworks, 4,4'-azobis-(pyridine), 1,4-phenylenediacetate

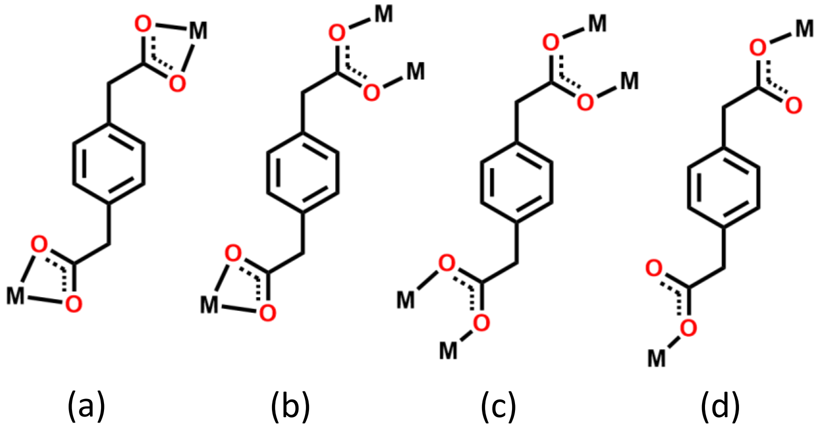
INTRODUCTION

Nowadays, coordination polymers (CPs) continue to be reported with a great variety of new materials due to the exchange of ligands and metal ions, the method of synthesis, the substitution of guest molecules, and heat-induced structural transformation. Moreover, the CPs reported have received great attention due to structural diversity and potential applications in areas such as gas separation and adsorption, energy conversion(Suckert et al., 2016), sensing(Khatri et al., 2016), magnetism(Mistri et al., 2014), drug delivery, and medicine (Elsaidi et al., 2016). Therefore, by carefully choosing these metal ions, organic linkers, synthesis methods or crystal to crystal transformation, one-, two-, and three-dimensional structures can be exhibited, so the structural design can be rationalized with the secondary building unit (SBU) (Mistrl et al., 2014).

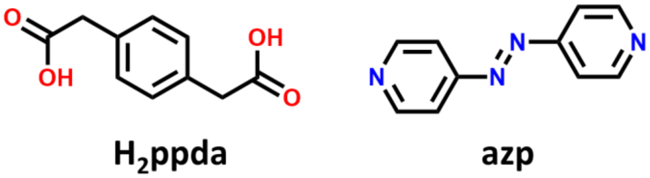
Along these lines, exchange metal and/or ligand can be a key factor in obtaining new materials. It is also necessary to develop new and/or alternative synthetic technologies that will enrich the diversity and complexity of coordination polymers to prepare.Metal replacement and fine-turning synthetic methods can achieve new structures and new properties in existing structures. However, it is difficult to control a coordination number of metal central ions with tailored structure and desired functional properties, since it is difficult to predict the influence of all the variables involved in the self-assembly and crystallization process (Mistrl et al., 2014). To this end, the clever selection of metal node, co-ligand and organic ligand plays an important role in controlling the dimensionality of the resulting coordination polymers and topology (Elsaidi et al., 2016). In addition,the various coordination modes of the ligand by changing temperatures can generate several types of secondary building units and structural architectures of the frameworks. Moreover, thecombined various functional groups of ligands have an influence to contributea high-dimensional framework with desired properties.

Although coordination polymers which based on bipyridine ligands such as 4,4’-bis(pyridine)ethane (bpa), 4,4’-bis(pyridine) ethane (bpe), and 4,4′-azobis(pyridine) (azp)have been intensively studied (Ren et al., 2011), intentional synthesis and implications for their controls are attractive since the resulting material can be applied in fields such as molecular switching, synthesized method (Zhu et al., 2003). Moreover, the ligand 1,4-phenylenediacetic acid (H_2ppda) can adopt a variety of coordination modes depending on the coordination habits of the metal ions (Scheme 1) (Hsu et al., 2012).Consequently, the ppda^{2-} is very structurally flexible and can form different types of entangled structures (Chen et al., 2010).

Herein we present the synthesis and characterization of two coordination polymers that are stabilized by the same ligands, 4,4'-azobis(pyridine) (azp) and 1,4-phenylenediacetate (ppda) with different metal centersnamely,$[Co_2(ppda)_2(azp)_2]_n$ (**1**), and $[Cu(ppda)(azp)]_n$(**2**)(Scheme 2). Compound **1** is a 3D metal coordination polymer while **2** shows 2-fold interpenetrated 3D framework, both are different in structural architecture(Scheme 3).



Scheme 1 The ppda ligand and its common coordination modes: (a) tetradentate bis-chelating, (b) tetradentate chelating-bridging, (c) tetradentate bis-bridging and (d) bidentate bis-bridging mode.



Scheme 2 Structures of H_2ppda (1,4-phenylenediacetic acid) andazp (4,4'-azobis(pyridine))

EXPERIMENT

Materials and physical methods: High-purity of4,4'-azobis(pyridine) (azp) (98%), and1,4-phenylenediacetic acid (H_2ppda) (97%), were purchased from the Aldrich Chemical Co. Inc. and were used. All other chemicals were of AR grade. FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the region 450-4000 cm^{-1}. CHN analyses were carried out on a PerkinElmer PE 2400CHNS analyzer. Thermogravimetric analysis (TGA) measurements were determined on TG-DTA 2010S MAC apparatus under N_2 atmosphere in the temperature range 40–800 °C with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE diffractometer with monochromatic Cu Kα radiation, and the 2θ range of 5–50°.

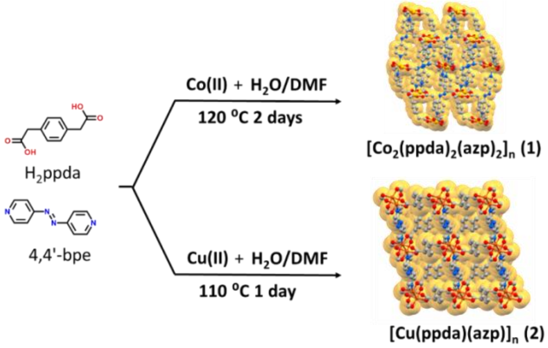
X-ray Crystallography: Structural and refinement parameters are presented in Table 1. The single-crystal X-ray data of **1** and **2** were collected at 298 Kby using a Bruker D8 Quest PHOTON100 with graphite-mono chromated Mo-Kα radiation using the APEX2 program. Data integration was done by SAINT and absorption correction was perfomed by SADABS. The diffraction data were solved using OLEX2 and refined by fullmatrix least squares procedures using OLEX. All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were assigned to the calculated positions and isotropically refined. The selected bond lengths, and angles for compounds **1** and **2** are shown in Table 2 and 3.

Synthesis of $[Co_2(ppda)_2(apz)_2]_n$ (1): Compound **1** was prepared from a mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.029 g, 0.1 mmol), H_2ppda (0.019 g, 0.1 mmol), azp (0.018 g, 0.1 mmol), ultrapure water (6.0 mL) and DMF (2.0 mL). The mixture was loaded into a 25 mL Teflon-lined stainless steel bomb and kept at 120°C under autogenous pressure for 2 days. The reaction system was cooled to room temperature during 12 hours. The resulting block dark red crystals of **1** were obtained and washed several times by DMF then dried under desiccation overnight. Yield: 25% (based on Co). Anal. Calc. for $C_{40}H_{32}N_8O_8Co_2$: C, 55.18%; H, 3.67%; N, 12.87%. Found: C, 56.24; H, 3.58; N, 12.95 (%). IR (cm^{-1}): 3060(vw), 3008(vw), 2931(vw), 1598(s), 1547(s), 1410(vs), 1274(m), 1254(m), 1102(m), 1015(m), 980(s), 875(w), 831(s), 709(m), 693(m) and 662(m).

Synthesis of $[Cu(ppda)(apz)]_n$ (2): Compound **2** was prepared from a mixture of $Cu(NO_3)_2{\cdot}6H_2O$ (0.029 g, 0.1 mmol), H_2ppda (0.019 g, 0.1 mmol), azp (0.018 g, 0.1 mmol), ultrapure water (6.0 mL) and DMF (2.0 mL). The mixture was loaded into a 25 mL Teflon-lined stainless steel bomb and kept at 110°C under autogenous pressure for 1 day. The reaction system was cooled to room temperature during 12 hours. The resulting block dark green crystals of **1** can be obtained and washed several times by DMF then dried under desiccation overnight. Yield: 34% (based on Cu). Anal. Calc. for $C_{15}H_{12}N_2O_4Cu$: C, 51.79%; H, 3.45%; N, 8.05%. Found: C, 52.24; H, 3.98; N, 7.53 (%). IR (cm^{-1}): 3377(m) 3060(vw), 3008(vw), 1614(s), 1514(m), 1387(vs), 1297 (m), 1270(m), 1254(m), 1102(m), 1068(w), 1017(m), 978(s), 965(s), 880(w), 829(s), 717(m) and 692(m).

RESULTS AND DISCUSSION

Structural description of $[Co_2(ppda)_2(azp)_2]_n$ (1). Single crystal X-ray diffraction revealed that compound **1** crystallizes in the triclinic crystal system of$P\bar{1}$. Asymmetric unit comprises two cobalt ions, two azp ligands and two ppda ligands (Figure 1(a)). As depicted in Figure 1(a), both cobalt centers show the distorted octa-hedral, being hexacoordinated by two nitrogen (N1, N4 for Co1 and N5, N8 for Co2) atoms from azp ligands at the axial positions, and four oxygen (O1, O2, O5, O6 for Co1 and O3, O4, O7, O8 for Co2) atoms from three ppda ligands at equatorial positions. The detail of bond lengths and angles are given in Table 2.The ppda ligandshows tetradentate chelating-bridging with three different Co^{2+} ions. The structure contains a Co_2 dinuclear secondary building unit (SBU) within the eight-membered non-coplanar ring $[Co_2(COO)_2]$ (Figure 1(b)) which has been commonly reported. Such SBUs are further extended into a three-dimensional (3D) coordination framework by the carboxylic groups of ppda ligands at the equatorial positions approving chelating-bidentate mode and azp ligands at the axial positions approving bridging mode as tilted pillar, resulting in the formation of a single 3D network (Figure 1(c)). From a topological perspective, considering each metal as a node by ToposPro program, this program indicates a 4,5-c net (sqc65) and 6-connected pcu topology with the point symbol of $\{4^{12}.6^3\}$(Figure 1(d)).



Scheme 3 The synthetic representation of compounds **1** and **2**

Table 1 Crystallographic data for compounds **1** and **2**

Crystal data	**1**	**2**
Empirical Formula	$C_{40}H_{32}N_8O_8Co_2$	$C_{15}H_{12}N_2O_4Cu$
Formula weight	870.59	347.81
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.6952(8)	8.4688(8)
b (Å)	13.3504(9)	9.3673(9)
c (Å)	13.5586(10)	9.8394(9)
α (°)	92.310(2)	67.724(3)
β (°)	92.202(2)	81.354(3)
γ (°)	101.764(2)	75.583(3)
V ($Å^3$)	1891.6(2)	698.19(11)
Z	2	2
ρ_{caled} ($g\ cm^{-3}$)	1.592	1.597
μ (Mo K_α) (mm^{-1})	0.947	1.582
data collected	6612	2558
Unique data (R_{int})	4915(0.0485)	2248(0.0306)
$^aR_1$ / $^bwR_2$[$I > 2\sigma(I)$]	0.0765/ 0.1694	0.0599/0.1835
$^aR_1$ / $^bwR_2$[all data]	0.1067/ 0.1802	0.0679/0.1758
GOF	1.182	1.098
max/min electron density (e $Å^{-3}$)	0.903/-0.538	2.118/-0.766

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$

Structural description of [Cu(ppda)(azp)]$_n$ (2). Single crystal X-ray diffraction revealed that compound **2** crystallizes in the triclinic crystal system of $P\bar{1}$. Asymmetric unit comprises one copper ion, half azp ligand and two half-size of ppda ligands. As depicted in Figure 2(a), the framework is composed of paddle-wheel dinuclear $[Cu_2(COO)_4]$ units, which are coordinated by four oxygen atoms (O1, O3, O2' and O4') from ppda ligands to form paddle-wheel and coordinated with nitrogen (N1) atom from azp ligand to further pillared and finally the framework form a 3D two interpenetrated framework which can be classified as type Class Ia, Z = 2 (Z_t =2; Z_n = 1). The detail of bond lengths and angles are given in Table 3.The ppda ligandexhibitstetradentate bis-bridging with four different Cu^{2+} ions. Because of an interpenetration of the two inderpenedent 3D frameworks, compound **2** do not obtain pores (Figure 2(b)). From a topological perspective, considering each metal as a node by program ToposPro, this program indicates a 4,5-c net (sqc65) and 6-connected pcu topology with the point symbol of {$4^{12}.6^{3}$} (Figure2(c)).

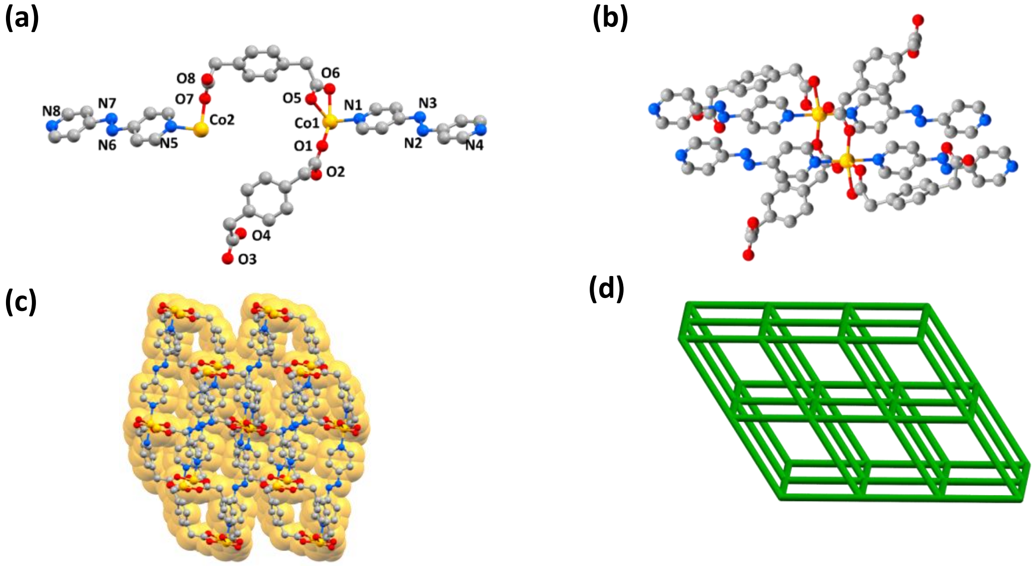


Figure 1 (a) Asymmetric unit of compound **1** (b) Illustration of compound **1** as SBU and its extension through ligands (c) A 3D structure in compound **1** (d) Topological representation of the 3D framework in compound **1**

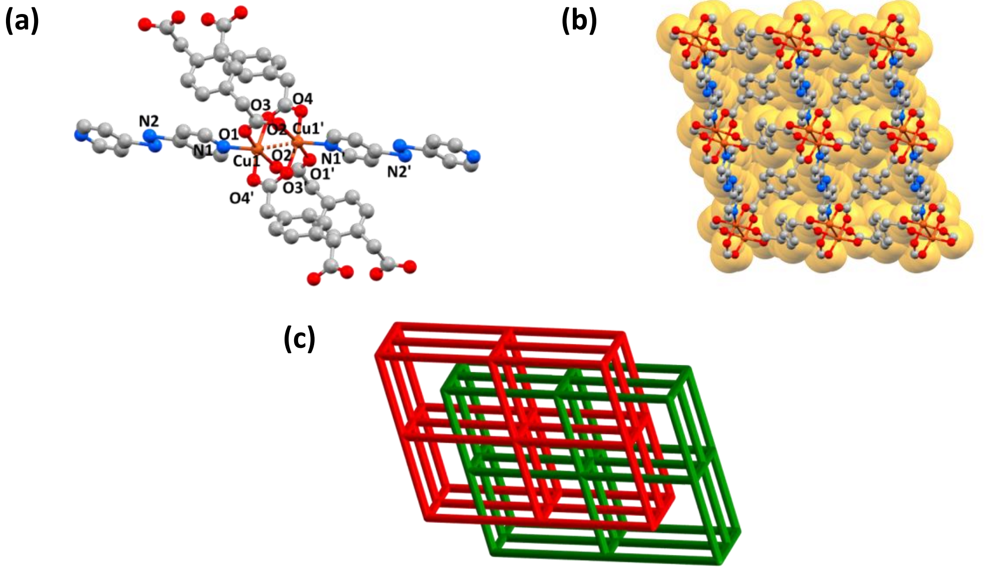


Figure 2 (a) Coordination geometry of Cu(II)center in compound **2** (b) A 3D structure in compound **2** (c) Topological representation of the 2-fold interpenetrated 3D framework in compound **2** (two different 3D structures are shown in two different colors)

Table 2 Bond distances (Å) and angles (°) for **1**

Compound **1**			
Co1-O1	2.013(5)	Co2-O3^{iii}	2.189(5)
Co1-O2^{i}	2.000(5)	Co2-O4^{iii}	2.181(5)
Co1-O5	2.228(5)	Co2-O7	2.015(5)
Co1-O6	2.155(5)	Co2-O8^{iv}	2.010(5)
Co1-N1	2.177(5)	Co1-N5	2.172(5)
Co1-N4^{ii}	2.195(6)	Co1-N8^{v}	2.177(6)
O1-Co1-O2^{i}	117.1(2)	O3^{iii}-Co2-O4	59.79(19)
O1-Co1-O5	92.1(2)	O3^{iii}-Co2-O7	91.0(2)
O1-Co1-O6	151.7(2)	O3^{iii}-Co2-O8	151.4(2)
O1-Co1-N1	93.2(2)	O3^{iii}-Co2-N5	88.0(2)
O1-Co1-N4^{ii}	88.2(2)	O3^{iii}-Co2-N8	93.2(2)
O2^{i}-Co1-O5	150.7(2)	O4-Co2-O7	150.5(2)
O2^{i}-Co1-O6	91.2(2)	O4-Co2-O8^{iv}	91.7(2)
O2^{i}-Co1-O1	85.4(2)	O4-Co2-N5	87.9(2)
O2^{i}-Co1-O4	91.6(2)	O4-Co2-N8^{v}	95.4(2)
O5-Co1-O6	59.6(2)	O7-Co2-O8^{iv}	117.1(3)
O5-Co1-N1	97.9(2)	O7-Co2-N5	86.9(2)
O5-Co1-N4^{ii}	84.7(2)	O7-Co2-N8^{v}	89.9(2)
O6-Co1-N1	93.2(2)	O8^{iv}-Co2-N5	88.3(2)
O6-Co1-N4^{ii}	86.8(2)	O8^{iv}-Co2-N8^{v}	92.2(2)
N1-Co1-N4^{ii}	177.0(2)	N5-Co2-N8^{v}	176.6(2)

symmetry codes:(i) 2-x, 2-y, 1-z; (ii) x, -1+y, z; (iii) 1-x, 1-y, 1-z; (iv) 1-x, 1-y, -z; (v) x, 1+y, z.

Table 3 Bond distances (Å) and angles (°) for **2**

Compound **2**			
Cu1-O1	1.974(4)	O2^{i}-Cu1-O3	90.60(16)
Cu1-O2^{i}	1.968(4)	O2^{i}-Cu1-O4^{i}	86.97(16)
Cu1-O3	1.985(3)	O2^{i}-Cu1-N1	99.19(15)
Cu1-O4^{i}	1.971(3)	O2^{i}-Cu1-Cu1^{i}	88.59(11)
Cu1-N1	2.171(4)	O3-Cu1-O4^{i}	167.26(14)
Cu1-Cu1^{i}	2.6634(10)	O3-Cu1-N1	90.48(14)
O1-Cu1-O2^{i}	167.08(14)	O3-Cu1-Cu1^{i}	79.6(1)
O1-Cu1-O3	88.68(17)	O4^{i}-Cu1-N1	102.25(15)
O1-Cu1-O4^{i}	90.90(17)	O4^{i}-Cu1-Cu1^{i}	87.84(10)
O1-Cu1-N1	93.72(15)	N1-Cu1-Cu1^{i}	167.50(11)
O1-Cu1-Cu1^{i}	78.59(11)	O1-Cu1-Cu1^{i}	78.59(11)

symmetry codes:(i) 1-x, 1-y, 1-z; (ii) -x, 2-y, 1-z

Other characterizations: Metal-organic frameworks **1** and **2** were inspected via infrared spectroscopy (IR), thermogravimetric analyses (TGA), and powder X-ray diffraction (PXRD).

FT-IR analyses: As shown in Figure 3, the IR spectra of**1** and **2** are very similar. Only the differences in characteristic peaks of the asymmetric COO and symmetric COO stretching are observed, due to different coordination mode of the ppda ligand for both compounds. In **1** with chelating-bridging coordination mode, the asymmetric COO stretching clearly splits into 1605 and 1550cm^{-1} with a symmetric COO stretching at 1413 cm^{-1} while in **2** with bis-bridging coordination mode, the absorption of asymmetric COO stretching shows a broad peak at 1612 cm^{-1} and asymmetric COO stretching at 1390 cm^{-1}.

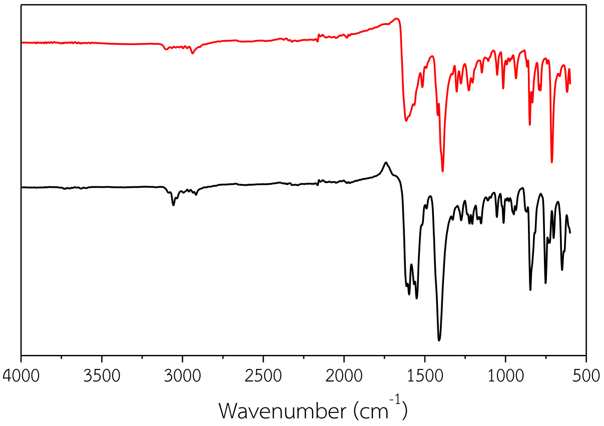


Figure 3 FT-IR spectra of as-synthesized compounds**1** and **2**

Thermal analyses: The TG studies of compounds**1** and **2** have been performed under nitrogen environment on the as-synthesized products. These TG curves are shown inFigure 4. A thermogravimetric analysis of compound **1**showsno weight loss until around 320°C. The decomposition of compound **1** starts above 340°C to show one-step weight loss. While in **2**, TGA curve indicates thermal stability of the frameworkup to 270°C and then the decomposition of compound **2** starts.

Powder X-ray diffraction analyses: The phase-purity of the bulk materials was analyzed by powder X-ray diffraction (PXRD). The PXRD profiles of as-synthesized compounds **1** and **2** and the simulated patterns are presented in Figure 5. These experiments, combined with elemental analyses and IR spectra confirm the identity of the crystalline materials.

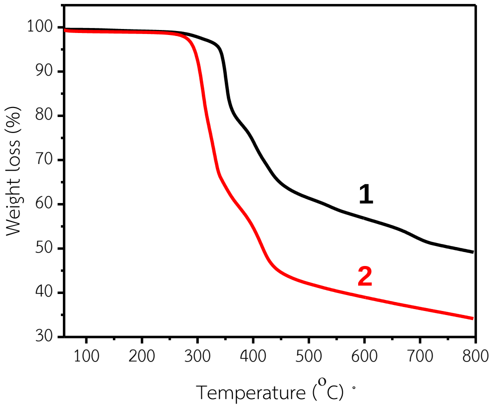


Figure 4 TGA plots of as-synthesized compound **1**(black line) and compound **2** (red line)

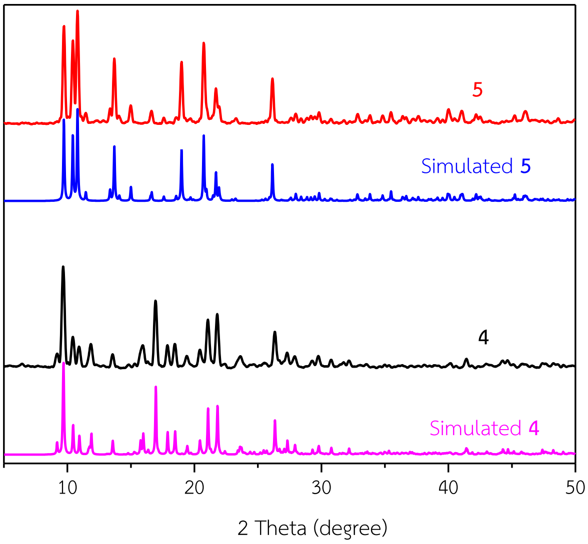


Figure 5 PXRD patterns of compound **1**and compound **2**

CONCLUSION

In summary, under hydrothermal method, we have successfully combined the metal ions (Co^{2+} or Cu^{2+}), azopyridine, and phenylenediacetate ligands and synthesized two novel coordination polymers to show 3D framework $[Co_2(ppda)_2(azp)_2]_n$(**1**) and two-fold interpenetrating 3D framework $[Cu(ppda)\text{-}(azp)]_n$(**2**). The ppda ligands adopt different coordination modes which generates different secondary building units and structural architectures of the frameworks. Changing temperature and using different components of framework open the path to get desired materials with potential functions. If such transition metal ions with fine-tuned reaction conditions and synthetic methods are introduced into such systems, a more elaborate structure can be realized. The follow-up research with functional property studies is underway in our group.

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