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Original article

# Construction of three novel Co/Zn/Cd(II) coordination polymers based on the same ligands: Different spatial structures, electrocatalysis and photoluminescence properties



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## ABSTRACT

Three new metal coordination polymers with different spatial structure, namely  $\{[Co_2(H_2O)_6(4-PDCA)_2]_2\cdot 3H_2O\}_n$  (SNUT-12),  $\{[Cd(H_2O)_2(4-PDCA)]\cdot 2H_2O\}_n$  (SNUT-13) and  $[Zn_2(4-PDCA)_2]_n$  (SNUT-14), where  $H_2(4-PDCA) = 1-(4-carboxyphenyl)-5$ -methyl-4-oxo-1,4-dihydropyridazine-3-carboxylic acid, were synthesized by changing the central ion with the same ligand under solvothermal and hydrothermal conditions, which were further characterized by single crystal X-ray diffraction, powder XRD, FT-IR and TGA. Single crystal X-ray analysis revealed that SNUT-12 exhibits a 1D infinite zigzag chains which were constructed by Cobalt(II) ion and 4-PDCA<sup>2-</sup> ligand, SNUT-13 features a 2D ladder-like structure. Meanwhile, SNUT-14 displays 2-fold 3D  $\rightarrow$  3D parallel interpenetrating frameworks. In addition, SNUT-12 exhibited high electrocatalytic oxygen evolution reaction, and SNUT-13, SNUT-14 showed strong fluorescence at room temperature.

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# 1. Introduction

At present, industrial production is driven by a myriad of energy-demanding electronic devices owing to the advancements of science and technology. The main energy sources are still based on fossil fuels that have limited reserves (Xu et al., 2017), a series of environmental problems caused by fossil energy seriously affect the survival of human beings, The key to solving the problems is to produce renewable energy in a green and environmental–friendly way (Wang et al., 2021; Zhang et al., 2021). Hydrogen energy has the most potential as a clean energy alternative to fossil energy due to its high heating value and non-polluting combustion product  $H_2O$ . Hydrogen energy on the earth mainly exists in the form of water. The industry mainly uses water electrolysis to produce

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hydrogen. In this process, the oxygen evolution reaction (OER) has been bottlenecked for the sustainable hydrogen production in water electrolysis (Liang et al., 2020; Xiong et al., 2023). OER passes through a four-electron transfer process coupled with the breaking of O–H bond and the formation of O-O bond, which is kinetically sluggish and requires high overpotential to overcome the energy barrier (Lu et al., 2017; Dang et al., 2020).

In order to maximize the efficiency of the reaction and reduce the power consumption on the electrode, it is necessary to select unique composition and structure electrocatalyst which reduce the activation energy of electrocatalytic reactions and provide conduction sites for electrochemical reactions, improving the rate and selectivity of the reactions (Greeley et al., 2006; Zhu et al., 2016). Commercial noble metal catalysts such as RuO<sub>2</sub> and IrO<sub>2</sub> had been generally regarded as the one of highly efficient electrocatalyst for OER (Cheng et al., 2022; Zhang et al., 2020), but the limitations of expensive and scarce resources of precious metals, currently unavailable for practical application (Kumar et al., 2020; Zhang et al., 2021). Therefore, non-noble metal catalysts have become a hot field of electrocatalyst research, such as Co-based (Wang et al., 2019; Liu et al., 2022), Ni-based (Dao et al., 2022; Karuppasamy et al., 2019) and Fe-based (Nivetha et al., 2019; Liang et al., 2022).

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Coordination polymers (CPs), which can be used to prepare highly efficient catalysts, selecting non-noble metals with electrocatalytic activity and coordinating with organic ligands (Wang et al., 2020), due to the bridging ligands, metal agglomeration was effectively avoided, resulting in electrocatalysts with high electron transfer efficiency and stability (Jin, 2018; Qian et al., 2017; Yang et al., 2021). In addition, as a branch of coordination polymers, Metal-Organic Frameworks (MOFs) construct an ordered network structure by coordinating metal ions and organic ligands, which had large surface area, uniform pores, controllable framework materials and other advantages (Kung et al., 2013; Lu et al., 2023; 2022), sensitive detection(Zheng et al., 2021; Han et al., 2023; Wang et al., 2022), molecular probe (Liu et al., 2020; Han et al. 2022) and efficient removal (Lin et al., 2021).

In this paper, three new metal coordination polymers with different spatial structures had been constructed by  $H_2(4-PDCA)$  (the synthetic method of the isomer of this ligand was recently reported by our another paper (Gao et al., 2023)),  $Co^{2+}$ ,  $Cd^{2+}$  and  $Zn^{2+}$  under solvothermal conditions, respectively: { $[Co_2(H_2O)_6(4-PDCA)_2]_2 \cdot 3H_2O\}_n$  (SNUT-12), { $[Cd(H_2O)_2(4-PDCA)] \cdot 2H_2O\}_n$  (SNUT-13) and  $[Zn_2(4-PDCA)_2]_n$  (SNUT-14). OER performance (SNUT-12) and fluorescence emission properties (SNUT-13 and SNUT-14) had been in investigated at room temperature.

# Table 1 Crystal data for the SNUT-12, SNUT-13 and SNUT-14.

Crystal name	SNUT-12	SNUT-13	SNUT-14
Crystal size	$0.32 \times 0.30 \times 0.25$	$0.25\times0.18\times0.12$	$0.23 \times 0.21 \times 0.18$
Formula	C <sub>52</sub> H <sub>66</sub> Co <sub>4</sub> N <sub>8</sub> O <sub>37</sub>	$C_{13}H_{16}CdN_2O_9$	$C_{26}H_{16}Zn_2N_4O_{10}$
Fw	1630.84	456.68	675.17
T/K	293(2)	293(2)	293(2)
Crystal system	orthorhombic	monoclinic	triclinic
Space group	Pccn	$P2_1/n(14)$	P1(2)
a/Å	37.377(4)	14.37834(19)	8.9441(9)
b/Å	7.0812(8)	6.70780(9)	9.1373(10)
c/Å	25.808(3)	16.1461(2)	14.8301(16)
$\alpha / \circ$	90	90	72.3400(10)
β/°	90	98.0104(13)	87.208(2)
$\gamma / ^{\circ}$	90	90	87.383(2)
V/Å <sup>3</sup>	6830.7(13)	1542.05(4)	1152.9(2)
Z	4	4	2
Dc/g⋅cm <sup>-3</sup>	1.586	1.967	1.945
F(000)	3352	912	680
GOF on F <sup>2</sup>	1.176	1.076	1.030
Reflection/unique	5635/4721	2988/2881	4037/3593
$R_1, wR_2 [I > 2\sigma(I)]$	0.1225, 0.3296	0.0476, 0.1269	0.0292/0.0847
$R_1, wR_2$ (all data)	0.1353, 0.3353	0.0476, 0.1282	0.0338/0.0870

 $\mathsf{R}_1 = \Sigma(||F_o| - |F_c||) / \Sigma |F_o|, \ \mathsf{w} \mathsf{R}_2 = [\Sigma(||F_o|^2 - |F_c||^2)_2 / \Sigma \mathsf{w}(F_o^2)]^{1/2}.$ 

Table 2	
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Selected bond lengths (Å) and angles (°) for SNUT-12, SNUT-13 and SNUT-14.

SNUT-12			
Co(1)-O(1)#1	2.033(8)	Co(1)-O(11)#1	2.107(10)
Co(1)-O(1)	2.033(8)	Co(1)-O(12)#1	2.138(11)
Co(1)-O(11)	2.107(10)	Co(1)-O(12)	2.138(11)
O(1)#1-Co(1)-O(1)	180.0	O(1)#1-Co(1)-O(11)#1	87.0(4)
O(1)#1-Co(1)-O(11)	93.0(4)	O(1)-Co(1)-O(11)#1	93.0(4)
O(1)-Co(1)-O(11)	87.0(4)	O(15)#2-Co(3)-O(6)#2	91.0(4)
Symmetry code: #1 $(1/2 + x, -1/2 + y)$	, -z) #2 (1/2-x, -1/2-y, z)		
SNUT-13			
Cd(1)#1-O(3)	2.255(3)	Cd(1)-O(2)	2.296(3)
Cd(1)-O(1)	2.277(3)	Cd(1)-O(6)	2.347(3)
Cd(1)#2-O(4)	2.329(3)	Cd(1)-O(7)	2.310(3)
O(3)#1-Cd(1)-O(1)	172.23(10)	O(3)#1-Cd(1)-O(6)	84.18(12)
O(3)#1-Cd(1)#2-O(4)	86.70(11)	O(3)#1-Cd(1)-O(7)	102.74(12)
O(3)#1-Cd(1)-O(2)	98.50(10)	O(1)-Cd(1)#2-O(4)	90.72(10)
Symmetry code: #1 (1-x, 1-y, 1-z) #2	(3/2-x, -1/2 + y, 1/2-z)		
SNUT-14			
Zn(1)-O(1)	1.9890(19)	O(4)-Zn(3)#1	2.0523(19)
Zn(3)-O(2)	2.176(2)	O(5)-Zn(3)#1	2.0413(19)
O(3)-Zn(1)#1	1.9931(19)	O(6)-Zn(2)#2	2.0960(18)
O(7)#3-Zn(1)-O(3)#4	120.11(8)	O(1)-Zn(1)-O(8)	107.94(8)
O(1)-Zn(1)-O(3)#4	122.48(8)	O(3)#4-Zn(1)-O(8)	99.29(8)
O(7)#3-Zn(1)-O(8)	103.47(8)	O(10)-Zn(2)-O(10)#5	180.00(5)

Symmetry code: #1 (1 + x, -1 + y, z) #2 (1 + x, 1 + y, z) #3 (-1 + x, -1 + y, z) #4 (-1 + x, 1 + y, z) #5 (-1-x, 2-y, 2-z).

# 2. Experimental

## 2.1. Materials and physical measurements

The H<sub>2</sub>(4-PDCA) ligand was synthesized in our laboratory and all used chemical reagents are available from Shanghai Aladdin Biochemical Technology Co., Ltd. Crystal data was obtained on a Rigaku XtaLAB Synergy X-diffractometer. X-ray powder diffraction patterns was obtained on a Bruker D8 ADVANCE. IR spectra were recorded as KBr pellets on a Thermo scientific Nicolet<sup>TM</sup> iS20 FT-IR spectrometer. Electrochemical investigation data was obtained on a Shanghai Chenhua CHI660E workstation. Fluorescence spectra were recorded on EDINBURGH FLS-1000 at room temperature.

## 2.2. Synthesis of $\{[Co_2(H_2O)_6(4-PDCA)_2]_2 \cdot 3H_2O\}_n$ (SNUT-12)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (0.1 mmol), H<sub>2</sub>(4-PDCA) (0.1 mmol) 1,3-BIP (0.1 mmol) in DMF-H<sub>2</sub>O (4 mL) binary solvent was placed in a 25 mL teflon -lined stainless steel container, under heated to 150 °C for 72 h, and then cooled to room temperature over 2d, orange crystals of **SNUT-12** was collected in 79.5 % yield based on Cobalt. Elemental analysis (%): calcd for C<sub>52</sub>H<sub>66</sub>Co<sub>4</sub>N<sub>8</sub>O<sub>37</sub> (Mr = 1630.84): C 38.26, H 4.05, N 6.87; found: C 38.25, H 4.55, N

6.89. IR(v, cm<sup>-1</sup>): 3396(v), 1600(s), 1544(s), 1390(s), 1242(m), 786 (m), 759(m).

## 2.3. Synthesis of $\{[Cd(H_2O)_2(4-PDCA)] \cdot 2H_2O\}_n$ (SNUT-13)

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.2 mmol), H<sub>2</sub>(4-PDCA) (0.05 mmol), 4-Methylimidazole (0.2 mmol) and HNO<sub>3</sub> (30 µL) in DMA-H<sub>2</sub>O (4 mL) binary solvent was placed in a 25 mL teflonlined stainless steel container, under heated to 80 °C for 72 h, and then cooled to room temperature over 2d, light yellow crystals of **SNUT-13** was collected in 74 % yield based on Cadmium. Elemental analysis (%): calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>9</sub>Cd (Mr = 456.68): C 34.16, H 1.31, N 6.13; found: C 34.19, H 1.35, N 6.10. IR(v, cm<sup>-1</sup>): 3433(v), 1639(s), 1611(s), 1451(m), 1395(s), 1255(m), 773(m).

#### 2.4. Synthesis of $[Zn_2(4-PDCA)_2]_n$ (SNUT-14)

A mixture of  $Zn(NO_3)_2$ ·6H<sub>2</sub>O (0.1 mmol), H<sub>2</sub>(4-PDCA) (0.05 mmol) and H<sub>2</sub>O (2 mL) was placed in a 25 mL teflon-lined stainless steel container, under heated to 140 °C for 72 h, and then cooled to room temperature over 2d, colorless crystals of **SNUT-14** was collected in 89.5 % yield based on Zinc. Elemental analysis (%): calcd for C<sub>26</sub>H<sub>16</sub>N<sub>4</sub>O<sub>10</sub>Zn<sub>2</sub> (Mr = 675.17): C 46.17, H 2.37, N 8.29;





Fig. 1. (a) Coordination environment of Co(II) ion in SNUT-12, in which the hydrogen atoms and free water molecules are omitted for clarity; (b) A View of 1D infinite chain of asymmetric unit was connected; (c) A View of 3D structure along the b axis in SNUT-12.



Fig. 1 (continued)

found: C 46.19, H 2.40, N 8.31. IR(v, cm<sup>-1</sup>): 1668(m), 1600(s), 1556 (s), 1384(w), 1288(m), 781(m).

## 2.5. Crystal structure determination

Select suitable crystals of **SNUT-12**, **SNUT-13** and **SNUT-14** were selected, its X-ray diffraction analysis data collection which were performed at 293(2) K with a CCD four-circle diffractometer XtaLAB Synergy, Dualflex, HyPix, with mirror-monochromated Cu Ka radiation ( $\lambda$  = 1.54184 Å). The crystal structure was solved by direct methods with the SHELXT 2014/5 (Sheldrick, 2014) and refined with the SHELXL 2018/3 (Sheldrick, 2015) (Dolomanov et al., 2009; Sheldrick, 2015; Sheldrick, 2015), All non-hydrogen atoms were refined using anisotropic displacement parameters, and all hydrogen atoms were generated geometrically. Crystallographic data and experimental details of structural analyses for molecular was summarized in Table 1. The main bond lengths and angles of **SNUT-12, SNUT-13** and **SNUT-14** are listed in Table 2.

# 2.6. Electrocatalytic properties

(Wang et al., 2022) To mixture of **SNUT-12** (10 mg),  $H_2O$  (500  $\mu$ L), EtOH (490  $\mu$ L) and Nafion (10  $\mu$ L), Ultrasonic dispersion for 20 min, drop the suspension on the surface of the working elec-

trode and air dry, this method will adhere **SNUT-12** on the working electrode. Then, the carbon rod is used as the counter electrode, the saturated calomel electrode (SCE) is used as the reference electrode and KOH (1 mol/L) as electrolyte, Analysis of OER properties of the coordination polymer by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Meanwhile, according to electrochemical impedance spectroscopy (EIS), the ability of the material to transfer electrons can be obtained.

## 3. Results and discussion

# 3.1. Crystal structure of SNUT-12

X-ray single crystal diffraction analysis reveals that **SNUT-12** crystallizes in orthorhombic system, space group *Pccn*. The asymmetric unit of **SNUT-12** consists of two crystallographically independent Co(II) ions, two deprotonated 4-PDCA<sup>2-</sup> ligands, six monodentate coordinated water molecules and three free water molecules (Fig. 1a). Two Co(II) ions exhibit similar but different coordination geometry, Co1 is six-coordinated water molecules and two oxygen atoms from two 4-PDCA<sup>2-</sup> ligands. Meanwhile, Co2 is also six-coordinated with two oxygen atoms from two monodentate coordinated water molecules and six-coordinated with two monodentate coordinated water molecules and two monodentate coordinated water molecules, two carbonyl oxygen atoms



Fig. 1 (continued)

from two 4-PDCA<sup>2-</sup> anions and two carboxyl oxygen atoms from two of the above 4-PDCA<sup>2-</sup> anions. Oxygen atoms from the same source the atoms are in opposite positions. The 4-PDCA<sup>2-</sup> is as a bidentate ligand bridging adjacent above-mentioned two crystallographically independent Co(II) ions to form a 1D zigzag chain (Fig. 1b), the chains are linked by intermolecular hydrogen bonding to form a 3D supermolecules structure (Fig. 1c).

## 3.2. Crystal structure of SNUT-13

**SNUT-13** crystallizes in monoclinic system with space group  $P2_1/n$ . The asymmetric unit of **SNUT-13** consists of one Cd(II) ion, one deprotonated 4-PDCA<sup>2</sup>–ligand, two monodentate coordinated water molecules and two free water molecules. As shown in Fig. 2a, each Cd(II) ion is six-coordinated with two oxygen atoms from two monodentate coordinated water molecules and three carboxyl oxygen atoms from three different 4-PDCA<sup>2–</sup> ligand. Which shows a distorted octahedral geometry. Additionally, two adjacent Cd(II) ions are connected by 4-PDCA<sup>2–</sup> ligands to generate a 2D ladder-like plane (Fig. 2b). Due to the  $\pi$ - $\pi$  stacking interaction between the aromatic rings, the stability of the structure is further enhanced (Fig. 2c). Also, these planes are further linked through

intermolecular hydrogen bonding to form a 3D supermolecule structure (Fig. 2d).

## 3.3. Crystal structure of SNUT-14

SNUT-14 crystallizes in triclinic system with space group P-1. The asymmetric unit of SNUT-14 consists of two crystallographically independent Zn(II) ions and two 4-PDCA<sup>2-</sup> ligands. As shown in Fig. 3a, two Zn(II) ions exhibit different coordination mode, which each Zn1 is four-coordinated with four carboxyl oxygen atoms from four different 4-PDCA<sup>2-</sup> anions (Zn-O = 1.9619(2)-1.9 991(2) Å). Meanwhile, each Zn2 exhibit distorted octahedral coordination geometry, which is six-coordinated with two carbonyl oxygen atoms from two different 4-PDCA<sup>2-</sup> ligands, four carbonyl oxygen atom from four different 4-PDCA<sup>2-</sup> ligands. Additionally, the carboxyl groups of L act as  $\mu_2$ -bridgings to connect adjacent Zn(II) ions to generate a 1D ··· Zn-OCO-Zn-OCO··· zigzag chain along the c-axis direction (Fig. 3b). Then, this chain acts as an inter-connector of countless parallel chains further connects near four neighbors by 4-PDCA<sup>2-</sup> ligands to form a porous 3D architecture (Fig. 3c). As illustrated in Fig. 3d, because there is a large void space, the individual 3D frameworks are interpenetrated into each other, and a 2-fold  $3D \rightarrow 3D$  interpenetrating architecture is thus generated.



**Fig. 2**. (a) Coordination environment of Cd(II) ion in **SNUT-13**, in which the hydrogen atoms are omitted for clarity; (b) A View of 2D infinite layered plane parallel to the b axis; (c) Schematic diagram of π-π stacking in **SNUT-13**; (d) A View of 3D structure along the b axis in **SNUT-13**.

## 3.4. X-ray diffraction(XRD) patterns and FT-IR spectra

The powder XRD patterns of as-synthesized compounds and the simulated patterns on the basis of single-crystal structures of **SNUT-12** (Fig. 4), **SNUT-13** (Fig. 5) and **SNUT-14** (Fig. 6), respectively. The diffraction peaks on patterns correspond well in position, indicating the phase purity of the as-synthesized samples. As shown in Fig. 7, due to same ligand was selected for the three novel coordination polymers reported, so they exhibit the similar IR spectrum. The broad bands at 3430 cm<sup>-1</sup> for **SNUT-12** and **SNUT-13** are the stretching mode of O–H, but **SNUT-14** does not show the band, which indicates there exists coordinated and free water molecules. Furthermore, the C = O vibration peaks of carboxylate groups from titled MOFs can be observed at 1606 and 1400 cm<sup>-1</sup>, respectively.



Fig. 2 (continued)

# 3.5. Thermal properties

Thermogravimetric (TG) measurements were carried out from 25 to 800 °C under N<sub>2</sub> atmosphere flow with a heating rate of 10 °- C·min<sup>-1</sup> (Fig. 8). For **SNUT-12** and **SNUT-13**, the first weight loss at 50~200 °C may be attributed to the removal of free water molecules and monodentate coordinated water molecules, **SNUT-12** exhibits a weight loss of 19.44 % (calcd 20.93 %) and **SNUT-13** exhibits 15.54 % (calcd 15.72 %). Afterwards, the weight loss after 300 °C

corresponds to the collapse of the skeleton. However, for **SNUT-14**, only one weight loss occurred within 425  $\sim$  500 °C, corresponding to the loss of collapse of the skeleton.

# 3.6. Electrochemical performance

To evaluate the OER activity of **SNUT-12**, the linear sweep voltammetry (LSV) polarization plots were first carried out at a



**Fig. 3.** (a) Coordination environment of Zn(II) ion in **SNUT-14**, in which the hydrogen atoms are omitted for clarity; (b) View of a 1D zigzag chain along the c-axis direction; (c) View of 3D structure along the c axis in **SNUT-14**; (d) 2-fold  $3D \rightarrow 3D$  parallel interpenetrating structure of **SNUT-14**.

sweeping rate of 5  $\rm mV \cdot s^{-1}$  in 1.0 M KOH solutions on a three-electrode system.

It was worth noting that an overpotential of 463 mV was required to allow a current density of 20 mA cm<sup>-2</sup>, which was close to that of RuO<sub>2</sub> ( $E_{20}$  mA cm<sup>-2</sup> = 330 mV), as shown in Fig. 9. Also, **SNUT-12** showed a lower Tafel slope of 68 mV dec<sup>-1</sup>, in comparison with RuO<sub>2</sub> (103 mV dec<sup>-1</sup>) (Du et al., 2021; Lyn et al. 2022).

The CV patterns of a series of scan rates were conducted to extract the linear relationship of current density diference  $(\Delta j/2)$  against scan rate (Fig. 10a). Double-layer capacitance ( $C_{dl}$ ) was carried out to estimate the electrochemically active surface area (ECSA) (Li et al., 2023), from Fig. 1, it can be seen that **SNUT-12** exhibit the C<sub>dl</sub> of 61 mF cm<sup>-2</sup> (Fig. 10b), which demonstrate the potential of this material as an available candidate toward OER (Kang et al., 2021).

These data illustrate **SNUT-12** had the smaller overpotential at a current density of 20 mA·cm<sup>-2</sup>, which can effectively reduce the energy consumption required for the electrolytic water reaction. Tafel slope and  $C_{dl}$  can also well characterize the electrocatalytic performance of the catalyst.

As shown in Fig. 11, Electrochemical impedance spectroscopy (EIS) was used to characterize the electrode kinetics of the interface reactions during the OER process, through this method, the size of the charge-transfer resistances  $\left(R_{ct}\right)$  of SNUT-12 will be obtained in EIS.

## 3.7. Fluorescence properties

The solid-state luminescence properties of the H<sub>2</sub>(4-PDCA) ligand as well as coordination polymers SNUT-13 and SNUT-14 were investigated at room temperature. H<sub>2</sub>(4-PDCA) shows emission with a maximum at 448 nm upon excitation at 380 nm in solid state, the maximum emission peaks for SNUT-13 and SNUT-14 are observed at 478 nm and 423 nm upon excitation at 410 nm and 360 nm, shown in Fig. 12, fluorescence intensity was enhanced compared to free H<sub>2</sub>(4-PDCA) ligands. In addition, in order to examine all the possible colors by combining three primary colors. the CIE-1931 (Commission International de L'Elairage 1931) chromaticity coordinates for SNUT-13 and SNUT-14 were determined based on matching their emission spectra and were calculated as (0.22, 0.32) for SNUT-13, and (0.17, 0.12) for SNUT-14 (Fig. 13). At room temperature, the emissions of the two  $d^{10}$  MCPs are located in the blue region, which is consistent with their visible color.

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O Zn



Fig. 3 (continued)

N O Zr



Fig. 3 (continued)



Fig. 3 (continued)



Fig. 4. XRD pattern of SNUT-12.







Fig. 6. XRD pattern of SNUT-14.





Fig. 7. FT-IR spectra of SNUT-12, SNIT-13 and SNUT-14.



Fig. 8. TG curves for SNUT-12, SNUT-13 and SNUT-14.

## 4. Conclusions

In summary, three novel metal coordination polymers had been constructed by 4-PDCA ligand under solvothermal or water conditions. By changing the central ion, three new coordination polymers exhibit different steric configuration. **SNUT-12** features a 1D infinite zigzag chain, **SNUT-13** features an unusual 2D layered structure, and, **SNUT-14** exhibits a porous 2-fold  $3D \rightarrow 3D$  architecture. In addition, **SNUT-12** exhibit excellent catalytic activity for OER in electrochemical performance, **SNUT-13** and **SNUT-14** exhibits different fluorescence properties due to their different coordination structures.

# 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, and CCDC No. 2,232,541 for **SNUT-12**, 2,232,542 for **SNUT-13** and 2,232,543 for **SNUT-14**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44–1223–336033; e-mail: deposit@ccdc.cam.ac.uk or https://www.ccdc.cam.ac.uk).



Fig. 9. OER activity in 1 M KOH electrolyte solution, (a) the Polarization curves and (b) Tafel plots of RuO<sub>2</sub> and SNUT-12.



Fig. 10. Investigation of the electrochemical active surface areas. (a) The cyclic voltammetry (CV) curves of SNUT-12; (b) estimation of C<sub>dl</sub> by plotting the current density variation against scan rate to fit a linear regression.



Fig. 11. Nyquist plots of electrochemical impedance spectra (EIS, 5 mV) for  $\ensuremath{\text{SNUT-12}}$ 

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# CRediT authorship contribution statement

**Jia-Hao Gao:** Conceptualization, Methodology, Software, Investigation, Writing – original draft. **Pei-Pei Huang:** Resources, Writing – review & editing, Supervision, Data curation. **Jie Liu:** Validation, Formal analysis, Visualization, Software. **Nan Zheng:** Software, Data curation. **Dong Wang:** Resources, Writing – review



Fig. 12. Solid-state emission spectra of the H<sub>2</sub>(4-PDCA), SNUT-13 and SNUT-14.



Fig. 13. CIE-1931 chromaticity diagram for  $SNUT\mathchar`-13$  and  $SNUT\mathchar`-14$  at room temperature.

& editing, Supervision, Data curation. **Si-Yu Yue:** Data curation, Formal analysis, Methodology, Investigation. **Er-Nu Liu:** Validation, Formal analysis, Visualization. **Quan Liu:** Writing – review & editing. **Bo Liu:** Validation, Formal analysis, Visualization. **Jiu-Fu Lu:** Writing – review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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