Volume 27 Number 5 7 February 2025 Pages 571-704

# CrystEngComm

rsc.li/crystengcomm



ISSN 1466-8033



#### PAPER

Shih-Miao Liu, Jhy-Der Chen *et al.* Coordination polymers constructed from bis-pyridyl-bis-amides and 1,4,5,8-naphthalenetetracarboxylic acid: ligand transformation and metal ion sensing

# CrystEngComm



**View Article Online** 

## PAPER



Cite this: CrystEngComm, 2025, 27, 606

Received 4th November 2024, Accepted 19th December 2024

DOI: 10.1039/d4ce01119h

rsc.li/crystengcomm

## Introduction

Coordination polymers (CPs) have been widely researched by scientists in recent years due to their intriguing structural diversity and various applicable functions.<sup>1,2</sup> By careful evaluation of the factors that govern the structural diversity of CPs, including metal types, the softness, length, coordination ability and coordination direction of organic ligands, and reaction conditions such as solvent, temperature and reaction

# Coordination polymers constructed from bispyridyl-bis-amides and 1,4,5,8naphthalenetetracarboxylic acid: ligand transformation and metal ion sensing<sup>†</sup>

Wei-Hao Chen,<sup>a</sup> Yen-Hsin Chen,<sup>a</sup> Kedar Bahadur Thapa,<sup>b</sup> Shih-Miao Liu<sup>\*c</sup> and Jhy-Der Chen <sup>1</sup>/<sub>2</sub>\*<sup>a</sup>

Hydrothermal reactions of 1,4,5,8-naphthalenetetracarboxylic acid (1,4,5,8-H<sub>4</sub>NTC) with various bis-pyridyl-bisamides, N,N'-di(pyridin-3-yl)adipamide (L<sup>1</sup>), N,N'-di(pyridin-3-yl)succinamide (L<sup>2</sup>), N,N'-di(pyridin-3-yl)oxalamide  $(L^3)$  or N,N'-bis(pyridin-3-ylmethyl)oxalamide (L<sup>4</sup>) and transition metal salt afforded seven coordination polymers (CPs) and one dinuclear complex, including  $[Cd(L^1)_{0.5}(1,4,5,8-NTC')(H_2O)_2]_n$  (1,4,5,8-H<sub>2</sub>NTC' = 1,4,5,8naphthalenetetracarboxylic acid 1,8-monoanhydride), 1,  $\{[Zn(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_{7}], H_2O\}_{n}$ 2  $\{[Cd(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_2], H_2O\}_{n}, 3, \{[Zn(L^5)(1,4,5,8-NTC')(H_2O)], 0.5OA\}_{n}, \{L^5 = 2,7-di(pyridin-3-yl), (L^5), (L^5),$ benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone}, **4**, [Cd(L<sup>5</sup>)(1,4,5,8-NTC')(H<sub>2</sub>O)]<sub>n</sub>, **5a**, {[Cd(L<sup>5</sup>)(1,4,5,8-NTC')(H<sub>2</sub>O)]<sub>n</sub>, **5a**, {[Cd(L<sup>5</sup>)(1,4,5,8-NTC')(H<sub>2</sub>O)]<sub>n</sub>, **5b**, {[ NTC')(H<sub>2</sub>O)]·2H<sub>2</sub>O}<sub>n</sub>, **5b**, [Zn<sub>2</sub>(L<sup>4</sup>)(1,4,5,8-NTC')<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>], **6**, and {[Cd(L<sup>4</sup>)(1,4,5,8-NTC)<sub>0.5</sub>(H<sub>2</sub>O)]·0.5H<sub>2</sub>O)<sub>n</sub> (1,4,5,8-NTC)<sub>0.5</sub>(H<sub>2</sub>O)]·0.5H<sub>2</sub>O)<sub>n</sub> (1,4,5,8-NTC)<sub>0.5</sub>(H<sub>2</sub>O)]·0.5H<sub>2</sub>O)]·0.5H<sub>2</sub>O)]·0.5H<sub>2</sub>O)  $H_4$ NTC = 1,4,5,8-naphthalenetetracarboxylic acid), 7. These CPs and the dinuclear complex were structurally characterized by using X-ray single-crystal diffraction. CPs 1, 2, and 3 exhibit one-dimensional (1D) structures with the 2,3C2 topology and 4 and 5 display two-dimensional (2D) structures with the 2,4L1 topology, whereas 6 is a dinuclear complex and 7 shows a three-dimensional (3D) framework with the mog topology. Ligand transformations from 1,4,5,8-H<sub>4</sub>NTC to 1,4,5,8-NTC<sup>2-</sup> and L<sup>3</sup> to L<sup>5</sup> are observed. The evaluation of the metal ion sensing properties of 1, 2, 3, 6, and 7 shows that 7 has the highest potential for detecting  $Fe^{3+}$  ions in aqueous solution with 1.06  $\times$  10<sup>3</sup> M<sup>-1</sup> and 1.99  $\times$  10<sup>-4</sup> M for the Stern–Volmer constant ( $K_{SV}$ ) and the limit of detection (LOD), respectively,

> time, CPs with different characteristics can be designed.<sup>3,4</sup> Through metal-ligand bonds, CPs form infinitely extending one- (1D), two- (2D) or three-dimensional (3D) structures.<sup>5–8</sup> CPs are applicable in various fields such as gas storage and separation, sensors, magnetism, conductive material, catalysis, degradation of dyes or pollutants, drug delivery, *etc.*<sup>9–19</sup>

> Di-, tri- and tetracarboxylate ligands have been used frequently to prepare CPs with interesting structural topologies. The bis-pyridyl-bis-amide (bpba)-based CPs constructed from 1,2,4,5-benzenetetracarboxylic acid (1,2,4,5-H<sub>4</sub>BETC) have been extensively investigated.<sup>8,20–22</sup> Structural comparisons of the  $Co(\pi)$ ,<sup>20,21</sup>  $Zn(\pi)^{22}$  and  $Cu(\pi)^8$  CPs thus prepared indicate that their structural diversity is manipulated by the flexibility of the bpba ligands, which is also subject to the coordination and co-crystallization of the solvent molecules. The structural diversity of these CPs demonstrates that the combination of the flexible bpba and 1,2,4,5-H<sub>4</sub>BETC under suitable conditions may form diverse and interesting structures.

> To further investigate the role of the tetracarboxylate ligand in determining the structural diversity of bpba-based CPs,

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taiwan, R. O.C.. E-mail: jdchen@cycu.edu.tw

<sup>&</sup>lt;sup>b</sup> Makawanpur Multiple Campus, affiliated to Tribhuvan University, Municipality Rd, Hetauda, Nepal

<sup>&</sup>lt;sup>c</sup> Center for General Education, Hsin Sheng Junior College of Medical Care and Management, Longtan, Taiwan, R.O.C., E-mail: lsm0301@hsc.edu.tw

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: PXRD patterns (Fig. S1– S8, S17–S21 and S32). TGA curves (Fig. S9–S16). Emission spectra (Fig. S22–S31 and S38). UV-vis absorption spectrum (Fig. S33). EDX data (Fig. S34). IR spectra (Fig. S35). XPS spectra (Fig. S36 and S37). Nitrogen adsorption-desorption isotherm (Fig. S39–S48). CCDC no. 2395512–2395519 contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4ce01119h

#### CrystEngComm

1,4,5,8-naphthalenetetracarboxylic acid (1,4,5,8-H<sub>4</sub>NTC) was invoked to react with the bpba ligand, N,N'-di(pyridin-3-yl) adipamide  $(L^1)$ , N,N'-di(pyridin-3-yl)succinamide  $(L^2)$ , N,N'di(pyridin-3-yl)oxalamide  $(L^3)$  or N,N'-bis(pyridin-3-ylmethyl) oxalamide  $(L^4)$ , and  $Zn(\pi)$  or  $Cd(\pi)$  salt to synthesize new CPs. Fig. 1 shows the structures of the bpba ligands and 1,4,5,8-H<sub>4</sub>NTC used in this investigation. Herein, the syntheses and structures of  $[Cd(L^{1})_{0.5}(1,4,5,8-NTC')(H_2O)_2]_n$  (1,4,5,8-H<sub>2</sub>NTC' = 1,4,5,8-naphthalenetetracarboxylic acid 1,8-monoanhydride), 1,  ${[Zn(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_2]}\cdot H_2O_n$ , 2,  ${[Cd(L^2)_{0.5}(1,4,5,8-NTC')]}$  $(H_2O)_2$ ]· $H_2O$ ]<sub>n</sub>, 3, {[Zn(L<sup>5</sup>)(1,4,5,8-NTC')(H<sub>2</sub>O)]·0.5OA]<sub>n</sub>, (L<sup>5</sup> = 2,7-di(pyridin-3-yl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)tetraone), 4,  $[Cd(L^5)(1,4,5,8-NTC')(H_2O)]_n$ , 5a,  $\{[Cd(L^5)(1,4,5,8-NTC')(H_2O)]_n$ , 5a,  $\{[Cd(L^5)(H_2O)]_n$ , 5a,  $\{[Cd(L^5)(H_2O)]_n$ , 5a,  $\{[Cd(L^5)(H_2O)]_n$ , 5a,  $\{[Cd(H_2O)]_n$ , 5a,  $\{[C$ NTC')(H<sub>2</sub>O)]·2H<sub>2</sub>O $_{n}$ , **5b**, [Zn<sub>2</sub>(L<sup>4</sup>)(1,4,5,8-NTC')<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>], **6**, and  $\{ [Cd(L^4)(1,4,5,8-NTC)_{0.5}(H_2O)] \cdot 0.5H_2O \}_n$ , 7, form the subject of this report. The structural diversity and ligand transformation of these CPs and the complex are discussed and their metal ion sensing capabilities evaluated.

## Experimental details

#### General procedures

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Open Access Article. Published on 27 December 2024. Downloaded on 7/26/2025 2:45:07 PM.

IR spectra (KBr disk) were obtained with a Thermo Nicolet IS5 FT-IR spectrometer. Elemental analyses were performed on an Elementar Vario EL III or an Elementar Vario EL cube type analyzer. Thermal gravimetric analyses (TGA) measurements were carried out on a SII Nano Technology Inc. TG/DTA 6200 over the temperature range of 30 to 900 °C at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. Powder X-ray diffraction measurements were performed on a Bruker D2 PHASER diffractometer with CuK<sub>α</sub> ( $\lambda_{\alpha} = 1.54$  Å) radiation. X-ray photoelectron spectroscopy (XPS) was on performed on a ULVAC-PHI (Quantes) spectrometer. Emission spectra were collected by using a Hitachi F-7000 spectrometer and the setting of PMT voltage was 250 V. Gas sorption measurements were conducted on a Micromeritics ASAP 2020 system.

#### Materials



The reagent  $Cd(OAc)_2 \cdot 2H_2O$  and  $Zn(OAc)_2 \cdot 2H_2O$  was purchased from Fisher Scientific Co. and 1,4,5,8-

Fig. 1 Structures of (a)  $L^1,$  (b)  $L^2,$  (c)  $L^3,$  (d)  $L^4,$  (e)  $L^5$  and (f) 1,4,5,8-H\_4NTC.

naphthalenetetracarboxylic acid was purchased from Nova Materials Co., Ltd. The ligands  $L^1$ ,  $L^2$ ,  $L^3$ ,  $L^4$ , and  $L^5$  was prepared according to published procedures.<sup>12,23</sup>

**Preparation of**  $[Cd(L^1)_{0.5}(1,4,5,8-NTC')(H_2O)_2]_n$ , 1. A mixture of  $Cd(OAc)_2 \cdot 2H_2O$  (0.053 g, 0.20 mmol),  $L^1$  (0.030 g, 0.10 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O was sealed in a 23 mL Teflon-lined stainless steel autoclave, which was heated under autogenous pressure to 120 °C for two days and then the reaction system was cooled down to room temperature over 48 hours. The colorless crystals suitable for single-crystal X-ray diffraction were obtained. Yield: 0.030 g (26%). Anal. calcd for  $C_{22}H_{17}N_2O_{10}Cd$  (MW = 581.79): C, 45.42; H, 2.95; N, 4.82%. Found: C, 45.88; H, 2.62; N, 5.32% FT-IR (cm<sup>-1</sup>): 3554(w), 3297(m), 3062(w), 1772(m), 1721(m), 1658(s), 1582(s), 1511(s), 1427(s), 1345(s), 1222(m), 1024(m), 766(m), 698(m).

Preparation of { $[[Zn(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_2] \cdot H_2O\}_n$ , 2. CP 2 was prepared by following similar procedures for 1, except that a mixture of  $Zn(OAc)_2 \cdot 2H_2O$  (0.022 g, 0.10 mmol),  $L^2$  (0.027 g, 0.10 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O at 100 °C was used. Colorless crystals were obtained. Yield: 0.017 g (32%). Anal. calcd for  $C_{21}H_{17}N_2O_{11}Zn-0.5H_2O$  (MW = 529.76): C, 47.61; H, 3.04; N, 5.29%. Found: C, 47.52; H, 2.84; N, 6.03%. FT-IR (cm<sup>-1</sup>): 3559(w), 3273(m), 3051(w), 1771(m), 1720(m), 1666(s), 1580(s), 1516(s), 1428(s), 1384(s), 1217(m), 1018(m), 769(m), 706(m).

**Preparation of** {[ $Cd(L^2)_{0.5}(1,4,5,8$ -NTC')( $H_2O$ )<sub>2</sub>]· $H_2O$ }<sub>n</sub>, 3. CP 3 was prepared by following similar procedures for 1, except that a mixture of  $Cd(OAc)_2 \cdot 2H_2O$  (0.053 g, 0.20 mmol),  $L^2$  (0.027 g, 0.10 mmol) and 1,4,5,8- $H_4$ NTC (0.030 g, 0.10 mmol) in 10 mL of  $H_2O$  at 80 °C was used. Colorless crystals were obtained. Yield: 0.052 g (44%). Anal. calcd for  $C_{21}H_{17}N_2O_{11}Cd$ -0.5 $H_2O$  (MW = 576.78): C, 43.73; H, 2.80; N, 4.86%. Found: C, 43.72; H, 2.80; N, 5.32% FT-IR (cm<sup>-1</sup>): 3560(w), 3375(w), 2937(w), 1778(m), 1725(m), 1579(s), 1425(s), 1384(s), 1339(s), 1290(m), 1214(m), 1158(m), 1030(m), 771(m).

**Preparation of {**[**Zn**(**L**<sup>5</sup>)(**1**,**4**,**5**,**8**-**NTC**')(**H**<sub>2</sub>**O**]**·0.5OA***}<sub><i>n*</sub>,**4**. CP**4**was prepared by following similar procedures for**1**, except that a mixture of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.022 g, 0.10 mmol),**L**<sup>3</sup> (0.024 g, 0.10 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O was used. Colorless crystals were obtained. Yield: 0.012 g (15%). Anal. calcd for C<sub>39</sub>H<sub>19</sub>N<sub>4</sub>O<sub>14</sub>Zn (MW = 832.98): C, 56.23; H, 2.30; N, 6.73%. Anal. calcd for C<sub>39</sub>H<sub>19</sub>N<sub>4</sub>O<sub>14</sub>Zn-0.5EDA (MW = 787.96): C, 57.92; H, 2.30; N, 7.11%. Found: C, 57.46; H, 2.19; N, 8.29% FT-IR (cm<sup>-1</sup>): 3538(w), 3382(w), 3114(w), 1771(m), 1721(s), 1668(s), 1629(s), 1587(m), 1479(m), 1436(s), 1379(m), 1334(s), 1237(s), 1190(m), 1037(m), 869(m), 769(m).

**Preparation of**  $[Cd(L^5)(1,4,5,8-NTC')(H_2O)]_n$ , 5a. CP 5a was prepared by following similar procedures for 1, except that a mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.053 g, 0.20 mmol), L<sup>3</sup> (0.024 g, 0.10 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O was used. Colorless crystals were obtained. Yield: 0.012 g (7%). Anal. calcd for C<sub>38</sub>H<sub>20</sub>N<sub>4</sub>O<sub>13</sub>Cd (MW = 853.02):

#### Paper

C, 53.51; H, 2.36; N, 6.57%. Found: C, 54.23; H, 2.01; N, 8.69% FT-IR (cm<sup>-1</sup>): 3585(m), 3167(w), 2926(w), 1754(m), 1691(s), 1617(s), 1527(s), 1428(m), 1312(s), 1245(w), 1202(w), 1044(w), 872(w), 782(s), 508(s).

Preparation of { $[Cd(L^5)(1,4,5,8-NTC')(H_2O)] \cdot 2H_2O$ }<sub>n</sub>, 5b. CP 5b was prepared by following similar procedures for 1, except that a mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.053 g, 0.20 mmol), L<sup>5</sup> (0.021 g, 0.050 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O at 100 °C was used. Colorless crystals were obtained. Yield: 0.020 g (12%). Anal. calcd for C<sub>38</sub>H<sub>22</sub>N<sub>4</sub>O<sub>14</sub>Cd (MW = 852.98): C, 52.46; H, 2.55; N, 6.43%. Found: C, 52.48; H, 2.53; N, 6.26% FT-IR (cm<sup>-1</sup>): 3561(m), 3190(w), 3064(m), 1776(m), 1720(s), 1675(s), 1579(s), 1432(s), 1387(s), 1339(s), 1244(m), 1209(m), 1020(s), 765(m).

Preparation of  $[Zn_2(L^4)(1,4,5,8\text{-NTC})_2(H_2O)_6]$ , 6. Complex 6 was prepared by following similar procedures for 1, except that a mixture of Zn(OAc)\_2·2H\_2O (0.022 g, 0.10 mmol), L<sup>4</sup> (0.027 g, 0.10 mmol) and 1,4,5,8-H\_4NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O at 80 °C was used. Colorless crystals were obtained. Yield: 0.059 g (55%). Anal. calcd for C<sub>42</sub>H<sub>34</sub>N<sub>4</sub>O<sub>22</sub>Zn<sub>2</sub> (MW = 1077.51): C, 46.82; H, 3.18; N, 5.20%. Found: C, 47.82; H, 3.13; N, 4.84%. FT-IR (cm<sup>-1</sup>): 3552(w), 3292(s), 3062(m), 1773(s), 1719(s), 1665(s), 1592(s), 1509(s), 1429(s), 1385(s), 1330(s), 1277(s), 1217(s), 1019(s), 768(s).

Preparation of {[Cd(L<sup>4</sup>)(1,4,5,8-NTC)<sub>0.5</sub>[H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub>, 7. CP 7 was prepared by following similar procedures for 1, except that a mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.053 g, 0.20 mmol), L<sup>4</sup> (0.027 g, 0.10 mmol) and 1,4,5,8-H<sub>4</sub>NTC (0.030 g, 0.10 mmol) in 10 mL of H<sub>2</sub>O at 80 °C was used. Colorless crystals were obtained. Yield: 0.044 g (39%). Anal. calcd for C<sub>21</sub>H<sub>19</sub>N<sub>4</sub>O<sub>7.5</sub>Cd + 0.25H<sub>2</sub>O (MW = 541.81): C, 45.79; H, 3.29; N, 10.17%. Found: C, 45.59; H, 3.10; N, 10.25%. FT-IR (cm<sup>-1</sup>): 3561(m), 3201(m), 3064(m), 1772(s), 1721(s), 1585(s), 1546(s), 1528(s), 1385(s), 1328(s), 1158(m), 1019(s), 765(m).

#### X-ray crystallography

The diffraction data for the CPs and dinuclear complex were collected on a Bruker AXS SMART APEX II CCD diffractometer, which was equipped with a graphitemonochromated Mo  $K_{\alpha}$  ( $\lambda_{\alpha} = 0.71073$  Å) radiation. Data reduction was carried out by standard methods with use of well-established computational procedures.<sup>24</sup> The structure factors were obtained after Lorentz and polarization corrections. An empirical absorption correction based on "multi-scan" was applied to the data. The position of some of the heavier atoms were located by the direct or Patterson method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements, while the hydrogen atoms except those of the water molecules were added by using the HADD command in SHELXTL 6.1012.25 The solvent molecules of 5a were seriously disordered and were squeezed.<sup>26</sup> The calculated structure factors of 5a were thus reported without solvent contribution. Table 1 lists the crystal data for 1-7.

## Results and discussion

#### Syntheses and ligand transformation

Seven CPs,  $[Cd(L^1)_{0.5}(1,4,5,8-NTC')(H_2O)_2]_n$ , 1,  $\{[Zn(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_2]\cdot H_2O\}_n$ , 2,  $\{[Cd(L^2)_{0.5}(1,4,5,8-NTC')(H_2O)_2]\cdot H_2O\}_n$ , 3,  $\{[Zn(L^5)(1,4,5,8-NTC')(H_2O)]\cdot 0.5OA\}_n$ , 4,  $[Cd(L^5)(1,4,5,8-NTC')(H_2O)]\cdot 0.5A\}_n$ , 5b, and  $\{[Cd(L^4)(1,4,5,8-NTC')(H_2O)]\cdot 2H_2O\}_n$ , 5b, and  $\{[Cd(L^4)(1,4,5,8-NTC')(H_2O)]\cdot 2H_2O\}_n$ , 7, and one dinuclear complex,  $[Zn_2(L^4)(1,4,5,8-NTC')_2(H_2O)_6]$ , 6, have been synthesized. A distinctive feature showing the transformation from 1,4,5,8-H\_4NTC to 1,4,5,8-NTC'^{2-} can be observed in 1–6, presumably due the condensation of the carboxylate groups of 1,4,5,8-H\_4NTC under the influence of the metal ion, as shown in Fig. 2. Such a transformation has been observed in  $\{[Cd_2(H_2Me_4bpz)(ntcaa)_2(H_2O)]H_2O\}_n$  (ntcaa = 1,4,5,8-NTC'^{2-}).^{27} In a marked contrast, in 7, the metal ion is coordinated with the unmodified 1,4,5,8-NTC<sup>4-</sup>.

On the other hand, in CPs 4 and 5a, the starting  $L^3$  has been transformed to  $L^5$ , indicating the hydrolysis of  $L^3$  to form oxalic acid and 3-aminopyridine, as shown in Fig. 3, followed by the reaction of 3-aminopyridine with 1,4,5,8naphthalenetetracarboxylic dianhydride (1,4,5,8-NTC") to establish  $L^5$ . Oxalic acid was found co-crystallizing in the crystal structure of 4. To confirm the formation of  $L^5$  and 5a,  $L^5$  was synthesized by the reaction of 3-aminopyridine and NTC",<sup>23</sup> which was then reacted with 1,4,5,8-H<sub>4</sub>NTC and Cd( $\pi$ ) salt to afford 5b.

Structures  $[Cd(L^{1})_{0.5}(1,4,5,8-NTC')(H_{2}O)_{2}]_{n}$ of 1, NTC') $(H_2O)_2$  $|H_2O|_n$ , 3. Single-crystal X-ray diffraction analyses show that CPs 1–3 crystallize in the triclinic space group  $P\overline{1}$ , with each asymmetric unit consisting of one M(II) (M = Cd, 1; Zn, 2; Cd, 3) cation, a half of a bpba ligand (bpba =  $L^1$ , 1;  $L^2$ , 2 and 3), one 1,4,5,8-NTC'2- ligand and two coordinated water molecules, as well as one co-crystallized water molecule in each of 2 and 3. Fig. 4(a)-(c) depict drawings showing the coordination environments about the metal ions of 1-3. Both the Cd(II) ion of 1 and Zn(II) ion of 2 adopt the distorted square pyramidal geometry ( $\tau_5 = 0.30$ , **1**; 0.05, **2**).<sup>28</sup> The Cd(II) ion of **1** is coordinated by two oxygen atoms from two different 1,4,5,8-NTC'<sup>2-</sup> ligands [Cd-O = 2.1876(19)-2.1933(18) Å], two oxygen atoms from two coordinated water molecules [Cd-O = 2.230(3)-2.368(8) Å] and one pyridyl nitrogen atoms from the  $L^1$  ligand [Cd-N = 2.271(2) Å], whereas the  $Zn(\pi)$  center of 2 is coordinated by two oxygen atoms from two different 1,4,5,8-NTC<sup>2-</sup> ligands [Zn-O = 2.049(3)-2.060(3) Å], two oxygen atoms from two coordinated water molecules [Zn-O = 2.026(3)-2.114(3) Å] and one pyridyl nitrogen atoms from the  $L^2$  ligand [Cd–N = 2.069(4) Å]. On the other hand, the  $Cd(\pi)$  ion of 3 is coordinated by three oxygen atoms from two different 1,4,5,8-NTC'<sup>2-</sup> ligands [Cd-O =2.226(4)-2.534(4) Å], two oxygen atoms from two coordinated water molecules [Cd-O = 2.250(4)-2.336(4) Å] and one pyridyl nitrogen atoms from the  $L^2$  ligand [Cd–N = 2.253(5) Å], resulting in a distorted octahedral geometry.

The metal ions are further linked together by 1,4,5,8- $\rm NTC'^{2-}$  and bpba ligands to afford 1D decorated zigzag

: Article. Published on 27 December 2024. Downloaded on 7/26/2025 2:45:07 PM.	This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.
Open Acces	(cc)) BY-NC

Table 1 Crystallographic data for 1–7

CP/complex	1	2	3	4	5a	5 <b>b</b>	9	7
Formula Formula weight Temperature, K Crystal system Space group $a, \stackrel{\circ}{A}$ $b, \stackrel{\circ}{A}$ $c, \stackrel{\circ}{A}$ c,	$\begin{array}{c} C_{22}H_{17}CdN_{2}O_{10}\\ 581.77\\ 581.77\\ 296(2)\\ Triclinic\\ Pi\\ 7.5267(6)\\ 11.4086(9)\\ 11.4086(9)\\ 11.4086(9)\\ 11.4086(9)\\ 11.48797(16)\\ 91.182(2)\\ 94.865(2)\\ 1037.85(14)\\ 2\\ 1.862\\ $	$\begin{array}{c} C_{21}H_{17}ZnN_2O_{11}\\ 538.73\\ 538.73\\ 538.73\\ 296(2)\\ Triclinic\\ \vec{P1}\\ 8.103(4)\\ 10.232(5)\\ 12.720(6)\\ 97.593(12)\\ 99.913(11)\\ 91.322(13)\\ 1028.7(8)\\ 2\\ 1.739\\ 1.739\\ \end{array}$	$\begin{array}{c} C_{21}H_{17}CdN_{2}O_{11}\\ \\ 585.77\\ \\ 585.77\\ \\ 296(2)\\ \\ Triclinic\\ Pi\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	$\begin{array}{c} C_{39}H_{19}ZnN_4O_{14}\\ 832.95\\ 293(2)\\ Triclinic\\ Pi\\ 10.256(3)\\ 12.694(4)\\ 13.590(5)\\ 97.295(9)\\ 97.295(9)\\ 99.972(10)\\ 105.313(8)\\ 1652.6(9)\\ 2\\ 2\\ 1.674\end{array}$	$\begin{array}{c} C_{38}H_{18}CdN_4O_{12}\\ 834.96\\ 296(2)\\ 71\\ 71\\ 10.4465(6)\\ 10.4465(6)\\ 10.4465(6)\\ 12.6964(7)\\ 13.5740(8)\\ 97.2892(13)\\ 97.2892(13)\\ 97.2832(13)\\ 13.57654(13)\\ 105.7654(13)\\ 105.7654(13)\\ 1681.83(17)\\ 2\\ 2\end{array}$	$\begin{array}{c} C_{38}H_{22}CdN_4O_{14}\\ 870.99\\ 293(2)\\ Triclinic\\ \vec{P1}\\ 10.24(3)\\ 10.24(3)\\ 112.29(4)\\ 113.58(5)\\ 97.39(9)\\ 97.39(9)\\ 99.45(13)\\ 104.61(11)\\ 1604(10)\\ 1604(10)\\ 2\\ \end{array}$	$\begin{array}{c} C_{42}H_{34}Zn_2N_4O_{22}\\ 1077.47\\ 296(2)\\ Triclinic\\ \vec{PI}\\ 6.546(4)\\ 12.633(7)\\ 12.865(7)\\ 97.026(19)\\ 97.026(19)\\ 97.026(19)\\ 97.026(2)\\ 10.41.9(10)\\ 1\\ 1\end{array}$	$\begin{array}{c} C_{2,1}H_{1,9}CdN_{4}O_{7,5}\\ 559,80\\ 299(2)\\ Triclinic\\ \dot{P}\bar{1}\\ 10.1088(13)\\ 10.4401(13)\\ 11.9209(14)\\ 11.9209(14)\\ 11.92209(14)\\ 11.92209(13)\\ 11.2.725(3)\\ 112.725$
F(000) $\mu(Mo K_{cl}), mm^{-1}$ Range (2 $\theta$ ) for data collection, °	$582 \\ 1.119 \\ 3.36 \le 2\theta \le 56.30 \\ 5049 [R(int) = 0.0363]$	$550 \\ 1.265 \\ 3.28 \le 2\theta \le 52.00 \\ 3990 [R(int) = 0.1255]$	$586 \\ 1.089 \\ 3.29 \le 2\theta \le 51.99 \\ 4203 [R(int) = 0.0418]$	$846 \\ 0.829 \\ 3.09 \le 2\theta \le 50.14 \\ 5836 [R(int) = 0.1137]$	$836 \\ 0.725 \\ 3.09 \le 2\theta \le 52.00 \\ 6620 [R(int) = 0.0640] $	$\begin{array}{l} 876 \\ 0.769 \\ 3.48 \leq 2\theta \leq 51.99 \\ 6249 \left[ R(\mathrm{int}) = 0.0430 \right] \end{array}$	550 1.249 $3.20 \le 2\theta \le 52.00$ 4092 [R(int) =	562 1.054 4.46 $\leq 2\theta \leq 52.00$ 4276 [R(int) = 0.0847]
Data/restraints/parameters Quality-of-fit indicator <sup><math>\varepsilon</math></sup> Final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$ <i>R</i> indices (all data)	$\begin{array}{c} 5049003\\ 504900332\\ 1.034\\ R_1=0.0332, WR_2=\\ 0.0607\\ R_1=0.0517, WR_2=\\ 0.0663\end{array}$	$\begin{array}{c} 3990/0/316\\ 3990/0/316\\ 1.064\\ R_1=0.0742, wR_2=\\ 0.0917\\ R_1=0.1386, wR_2=\\ 0.1055\end{array}$	$\begin{array}{c} 4203/0/316\\ 4203/0/316\\ 1.123\\ R_1=0.0493, \ WR_2=\\ 0.1295\\ R_1=0.0565, \ WR_2=\\ 0.1334\end{array}$	$\begin{array}{c} 5836/2/508\\ 1.048\\ R_1=0.0838, WR_2=\\ 0.2025\\ R_1=0.1468, WR_2=\\ 0.2372\end{array}$	$\begin{array}{c} 0.002.0 \\ 0.002.0 \\ 1.005 \\ R_1 = 0.0438, \ WR_2 = \\ 0.0852 \\ R_1 = 0.0675, \ WR_2 = \\ 0.0926 \end{array}$	$\begin{array}{c} 6249/1/519\\ 1.015\\ R_1=0.0467, wR_2=\\ 0.1104\\ R_1=0.0716, wR_2=\\ 0.1226\\ 0.1226\end{array}$	$\begin{array}{c} 0.002.\\ 0.027\\ 1.027\\ R_1 = 0.0463, WR_2 = \\ 0.0899\\ R_1 = 0.0857, WR_2 = \\ 0.1029\end{array}$	$\begin{array}{l} 4276/0/302 \\ 4.276/0/302 \\ 1.012 \\ R_1 = 0.0378, \ WR_2 = \\ 0.0598 \\ R_1 = 0.0636, \ WR_2 = \\ 0.0655 \end{array}$
${}^{a}R_{1} = \sum   F_{o}  -  F_{c}  /\sum  F_{o}  \\ 0.0749, b = 2.0348 \text{ for } 3; a \\  \sum w( F_{o}^{2}  -  F_{c}^{2} )^{2}/(N_{\text{observed}})$	$\left  \begin{array}{c} ^{b} \text{ wR}_{2} = \left[ \sum \text{w}(F_{0}^{2} - 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0$	$-F_{c}^{2}^{2}^{2}/\sum w(F_{o}^{2})^{2}]^{1/2}. w$ ) for 4; $a = 0.0596, b$ :	v = $1/[\sigma^2(F_0^2) + (ap)^2]$ = 2.4584 for 5a; $a = 1$	+ $(bp)$ ], $p = [\max(F_0^2 0.0666, b = 0.0000 \text{ fc})$	or 0) + $2(F_c^2)]/3$ . $a =$ or 5 <b>b</b> ; $a = 0.0426$ , $b =$	= 0.0482, b = 0.4052 $= 0.1291 $ for 6; $a = 0.0$	for 1; $a = 0.0229$ , $b$ 0210, $b = 0.0000$ for	= 0.5143 for 2; <i>a</i> = .7. <sup><i>c</i></sup> Quality-of-fit =

### CrystEngComm



Fig. 2 Condensation pathways from 1,4,5,8-H<sub>4</sub>NTC to 1,4,5,8-H<sub>2</sub>NTC' and NTC".



chains, Fig. 5(a)–(c). If the metal ions are defined as 3-connected nodes, the 1,4,5,8-NTC'<sup>2–</sup> ligands as 2-connected nodes, while the bpba ligands as linkers, the structures of CPs **1–3** can be regarded as 1D looped chains with the (4)-2,3C2 topology, as shown in Fig. 5(d), as determined using ToposPro.<sup>29</sup> The structural types of **1–3** are thus subject to the formation of 1,4,5,8-NTC'<sup>2–</sup>, regardless of the identities of the metal ions and the bpba ligands.

Structures of  $\{[Zn(L^5)(1,4,5,8-NTC')(H_2O)] \cdot 0.5OA\}_n$ ,  $[Cd(L^{5})(1,4,5,8-NTC')(H_{2}O)]_{n}$ , 5a, and  $\{[Cd(L^{5})(1,4,5,8-NTC')$ (H2O)]·2H2O}n, 5b. The crystal structures of CPs 4, 5a and 5b were in the triclinic space group P1. Each of the asymmetric units consists of one M(II) cation (M = Zn, 4; Cd, 5a; Cd, 5b), two halves of an  $L^5$  ligand, one 1,4,5,8-NTC'2- ligand and one coordinated water molecule. In addition, there are a half of a co-crystallized oxalic acid in 4 and two cocrystallized water molecule in 5b, respectively. Fig. 6(a) depicts a representative drawing showing the coordination environment about the metal ion, which is five-coordinated by two oxygen atoms from two 1,4,5,8- $NTC'^{2-}$  ligands [Zn-O = 2.063(5)-2.084(6) Å for 4; Cd-O = 2.234(3)-2.246(3) Å for 5a; Cd-O = 2.234(3)-2.246(3) Å for 5b], one oxygen atom from the coordinated water molecule [Zn–O = 2.029 (5) Å for 4; Cd–O = 2.231(2) Å for 5a; Cd–O = 2.231(2) Å for **5b**] and two pyridyl nitrogen atoms from two different  $L^5$  ligands [Cd-N = 2.084(6)-2.119(6) Å for 4; Cd-N = 2.292(3)-2.279(3) Å for 5a; Cd-N = 2.292(3)-2.279(3) Å for **5b**], resulting in a distorted square pyramidal geometry ( $\tau_5 =$ 0.03 for 4; 0.06 for 5a; 0.03 for 5b). The M(II) ions are further linked by 1,4,5,8-NTC'<sup>2-</sup> and  $L^5$  ligands to afford a 2D structure. If the M(II) ions are defined as 4-connected nodes and 1,4,5,8-NTC'2- ligands as 2-connected nodes, while L<sup>5</sup> as linkers, the structures of these CPs can be regarded as 2D nets with the  $\{4\cdot8^5\}$  $\{4\}$ -2,4L1 topology,



**Fig. 4** (a) Coordination environment about the Cd(II) ion of **1**. Symmetry transformations used to generate equivalent atoms: (A) -x, -y + 2, -z + 2. (b) Coordination environment about the Zn(II) ion of **2**. Symmetry transformations used to generate equivalent atoms: (A) -x - 1, -y + 2, -z + 1. (c) Coordination environment about the Cd(II) ion of **3**. Symmetry transformations used to generate equivalent atoms: (A) -x + 1, -y + 1, -z.

Fig. 6(b). Similar to 1–3, the structural types of 4–5 are subject to the formation of 1,4,5,8-NTC<sup> $2^-$ </sup>.

Structure of  $[Zn_2(L^4)(1,4,5,8-NTC)_2(H_2O)_6]$ , 6. Crystals of complex 6 conform to the triclinic space group  $P\overline{1}$  and the asymmetric unit comprises one Zn(II) cation, a half of an L<sup>4</sup> ligand, one 1,4,5,8-NTC'<sup>2-</sup> ligand and three coordinated water molecules. Fig. 7(a) depicts a drawing showing the dinuclear structure of 6, in which the two Zn(II) ions are bridged by the L<sup>4</sup> ligand. Each of the two Zn(II) ions is six-coordinated by two oxygen atoms from the 1,4,5,8-NTC'<sup>2-</sup> ligand [Zn-O = 2.203(3)–2.230(3) Å], three oxygen atoms from three coordinated water molecules [Zn-O = 2.039(3)–2.154(3) Å] and one pyridyl nitrogen atoms from the L<sup>4</sup> ligand [Zn-N = 2.061(3) Å], resulting in a distorted octahedral geometry.



Fig. 5 Drawings showing the 1D decorated zigzag chains of (a) 1, (b) 2 and (c) 3. (d) A representative topological structure showing a 1D looped chain with the (4)-2,3C2 topology.

Moreover, the dinuclear molecules are interlinked extensively through O-H-O [O-H···O = 2.1010-2.2237 Å] hydrogen bonds. Considering molecules of 6 as nodes that are linked by the hydrogen bonds, a topological  $(4^{12} \cdot 6^3)$ -pcu supramolecular structure can be obtained, as shown in Fig. 7(b).

Structure of  $\{ [Cd(L^4)(1,4,5,8-NTC)_{0.5}(H_2O)] \cdot 0.5H_2O \}_n$ , 7. CP 7 crystallizes in the triclinic space group  $P\bar{1}$  and the asymmetric unit consists of one Cd(II) cation, two halves of an L<sup>4</sup> ligand, a half of a 1,4,5,8-NTC<sup>4-</sup> ligand, one coordinated water molecule, and a half of a cocrystallized water molecule. Fig. 8(a) depicts a drawing showing the coordination environment about of Cd(II) ion of 7, which is five-coordinated by two oxygen atoms from two 1,4,5,8- $NTC^{4-}$  ligands [Cd-O = 2.227(2)-2.229(2) Å], one oxygen atom from the coordinated water molecule [Cd-O = 2.279(2) Å] and two pyridyl nitrogen atoms from two  $L^4$ ligands [Cd-N = 2.271(2) Å], resulting in a distorted square pyramidal geometry ( $\tau_5 = 0.21$ ). The Cd(II) ions are further linked together by 1,4,5,8-NTC<sup>4-</sup> and L<sup>4</sup> ligands to afford a 3D structure. If the Cd(II) atoms are defined as 4-connected nodes, 1,4,5,8-NTC<sup>4-</sup> as 4-connected nodes, while  $L^4$  as linkers, the structure of CP 7 can be simplified as a 3D net with the  $\{4\cdot 6^4\cdot 8\}_2\{4^2\cdot 6^2\cdot 8^2\}$ -mog topology, Fig. 8(b). A structural comparison of 6 and 7



Fig. 6 (a) A representative drawing for the coordination environment about the metal ion of 4 (M = Zn), 5a (M = Cd) and 5b (M = Cd). Symmetry transformations used to generate equivalent atoms: (A) -x +2, -y + 2, -z + 1 for 4, (A) -x + 1, -y, -z - 2 for 5a and (A) -x, -y + 1, -z+ 2 for 5b. (b) A representative topological structure showing a 2D net with the 2,4L1 topology.

indicates that the metal identity governs the structural diversity.



Fig. 7 (a) A drawing showing the dinuclear structure of 6. Symmetry transformations used to generate equivalent atoms: (A) -x + 1, -y + 1, -z + 2. (b) A drawing showing the supramolecular structure of 6 with the pcu topology.



**Fig. 8** Coordination environment about the Cd( $\mu$ ) ion of 7. Symmetry transformations used to generate equivalent atoms: (A) x - 1, y - 1, z. (b) A drawing showing the 3D net with the **mog** topology.

#### Ligand conformations and bonding modes

The  $L^1$  and  $L^2$  can be arranged in A and G conformations when the C-C-C-C torsion angle ( $\theta$ ) is 180  $\geq \theta > 90^{\circ}$ and  $0 \le \theta \le 90^\circ$ , respectively, and based on the relative orientation of the C=O groups, each conformation can adopt a *cis* or *trans* arrangement.<sup>12</sup> Due to the difference in the orientations of the pyridyl nitrogen atom positions, three more orientations, anti-anti, syn-anti and syn-syn, are possible for the ligands  $L^1$ ,  $L^2$  and  $L^4$ . By determining the orientation of the nitrogen on the pyridine, the conformation of  $L^5$  can be classified into *cis* or *trans*. Accordingly, the ligand conformations of 1-7 are assigned and listed in Table 2. On the other hand, the polycarboxylate ligands show various coordination modes in 1-7. While the 1,4,5,8-NTC'2- ligands in 1, 2, 4, 5a, and 5b bridge two metal ions through two of the carboxylate oxygen atoms, that in 3 bridges two metal ions through a chelation mode. In complex 6, the 1,4,5,8-NTC<sup>2-</sup> ligand chelates a metal ion through the two oxygen atoms of one carboxylate group, and the 1,4,5,8-NTC<sup>4-</sup> ligand in 7 bridges four metal ions through four oxygen atoms from four carboxylate groups.

#### Powder X-ray analysis

In order to check the bulk purities of the products, powder X-ray diffraction (PXRD) patterns have been measured for 1–7. As shown in Fig. S1–S8,† the peak positions of the experimental and simulated PXRD patterns are in agreement with each other, which demonstrate that the crystal structures are representative of the bulk materials. The

differences in intensity may be owing to the preferred orientation of the powder samples.

#### Thermal properties

Thermal gravimetric analysis (TGA) was carried out to examine the thermal decomposition of 1–7. The samples were recorded from about 30 to 800 °C at 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere, as shown in Fig. S9–S16† and Table 3. Two-step decompositions involving losses of solvents and organic ligands are observed.

#### Chemical stability

To select the solvent for subsequent metal ion sensing experiments, 10 mg of each of **1–3**, **6**, and 7 was immersed in 10 ml of 10 different solvents for seven days. Afterward, the samples were vacuum-dried and PXRD patterns measured. As shown in Fig. S17–S21,† **1** and 7 maintain their crystal structures in all of the 10 different solvents, whereas **2** undergoes complete structural changes in DMF and dissolves completely in DMA, whereas **3** experiences complete collapse of its crystal structure in MeOH, DMA and DMF and **6** shows structural changes in DMA, DMF and ether. The results indicate that these **1–7** are stable in water for seven days.

#### Luminescent properties

The excitation and emission spectra of  $L^1$ ,  $L^2$ , and  $L^4$  and 1–3, 6, and 7 in the solid state are shown in Fig. S22–S26.† Table 4 lists their corresponding parameters. The spectra of  $L^1$ ,  $L^2$ ,  $L^4$  and 1,4,5,8-H<sub>4</sub>NTC show emissions in the range of 459–496 nm, which may be ascribed to the intraligand (IL) n to  $\pi^*$  or  $\pi$  to  $\pi^*$  transitions. Since Zn(II) and Cd(II) ions are not easily oxidized or reduced, the emissions of 1–3, 6, and 7, which are in the range 404–510 nm, are not due to ligand-to-metal charge transfer (LMCT) or metal-to-ligand charge transfer (MLCT), but most probably ligand-to-ligand charge transfer (LLCT) or intra-ligand charge transfer.<sup>30,31</sup>

#### Metal cation detection

For each experiment, 30 mg of the sample was immersed in 10 mL of  $10^{-2}$  M aqueous solutions of different metal ions, involving  $Fe(NO_3)_3$  and  $M(OAc)_2$  (M =  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ) at room temperature for 24 hours. The sample was filtered, washed with water and dried under vacuum, and then its solid-state emission spectrum measured. Fig. S27–S31† display the emission spectra and the bar charts showing the percentages of quenching of 1–3, 6, and 7. Fig. 9 depicts the bar charts showing the average quenching percentages of three experiments. The percentages of quenching of 1–3, 6, and 7 toward  $Fe^{3+}$  are 66, 71, 64, 80 and 90%, respectively, indicating that 7 affords the best quenching efficiency.

Electron transfer, structure collapse, competitive absorption, and cation exchange are the main causes of fluorescence quenching.<sup>32</sup> The PXRD patterns of 7 before and after immersion in  $Fe^{3+}$  solution are thus compared. Fig.

Paper

Table 2 Ligand conformations and bonding modes of 1-7



S32† indicates that no significant change of the PXRD patterns can be observed, revealing that the quenching is not due to the structural collapse. Fig. S33† shows that the absorption spectrum of the Fe<sup>3+</sup> solution partially overlaps with the excitation spectrum of 7, therefore, the fluorescence quenching can be ascribed to competitive absorption. SEM-EDX spectra, as shown in Fig. S34,† demonstrate that Fe<sup>3+</sup> ions are indeed adsorbed by 7.

FT-IR and XPS spectroscopy are applied for the investigation of the interactions between the Fe<sup>3+</sup> ion and 7. As shown in Fig. S35,† the amide C=O stretching frequency shifted slightly from v = 1676 cm<sup>-1</sup> to v = 1659 cm<sup>-1</sup>, indicating a red shift due to the weak interaction between Fe<sup>3+</sup> and the amide oxygen atom. Fig. S36† shows the XPS spectra of 7 before and after immersing in Fe<sup>3+</sup>. The fitting analysis reveals four signals at 531.0, 531.8, 532.5 and 533.8 eV, Fig. S37,† assignable to O\*=C-N, O\*=C-O, O=C-O\* and H<sub>2</sub>O\*, respectively.<sup>33,34</sup> There is no significant change in the

binding energy of O 1s electrons before and after the sensing experiments, therefore, the changes in the intensities are evaluated. The intensity of the peak at 531.0 eV decreased from 19 to 11%, while that at 531.8 eV increased from 39 to 45%, indicating the possible interaction between the oxygen atom of  $O^*=C-N$  and  $Fe^{3+}$ , which further verifies the result from the investigation of the IR spectra.

#### Quenching efficiency

To understand the dependence of the quenching efficiency of 7 on the concentration of Fe<sup>3+</sup> ions in aqueous solution, the sample of 7 was immersed in solutions of different concentrations (0.25–6 mM) of Fe<sup>3+</sup> for 24 hours, followed by the measurement of the emission spectrum after immersion. The quenching efficiency of Fe<sup>3+</sup> ions by 7 was analyzed by using the Stern–Volmer (SV) equation:  $(I_0/I) = 1$ +  $K_{\rm SV}[M]$ ,<sup>35</sup> where  $I_0$  is the emission intensity of the intact

 Table 3
 Weight loss of 1–7

CP/complex	Solvent, <i>T</i> , °C (found/calc), %	Ligand, <i>T</i> , °C (found/calc), %
1	2H <sub>2</sub> O	$L^1$ + 1,4,5,8-NTC' <sup>2-</sup>
	30-190 (6.19/5.62)	230-800 (74.49/79.39)
2	3H <sub>2</sub> O	$L^2 + 1,4,5,8-NTC'^{2-}$
	30-190 (3.18/4.25)	235-800 (74.60/79.15)
3	2.5H <sub>2</sub> O	$L^2 + 1,4,5,8-NTC'^{2-}$
	30-153 (9.04/9.22)	240-800 (72.41/71.58)
4	$1H_2O + 0.5EDA$	$L^5 + 1,4,5,8-NTC'^{2-}$
	30-143 (9.33/7.57)	320-800 (76.16/84.13)
5a	1H <sub>2</sub> O	$L^5$ + 1,4,5,8-NTC <sup>2-</sup>
	30-88 (4.67/2.11)	192-800 (79.48/82.61)
5b	2H <sub>2</sub> O	$L^5 + 1,4,5,8-NTC'^{2-}$
	30-100 (7.06/4.14)	147-800 (78.90/82.63)
6	2H <sub>2</sub> O	$L^4 + 1, 4, 5, 8-NTC'^{2-}$
	30-100 (10.30/10.03)	180-800 (77.64/77.83)
7	1.75H <sub>2</sub> O	$L^4 + 1,4,5,8-NTC^{4-}$
	30–173 (3.33/4.05)	200-900 (75.61/75.84)



Fig. 9 Bar charts showing the average quenching percentages of the 1–3, 6, and 7 in the various cations.

sample, *I* is the emission intensity after immersion,  $K_{SV}$  is the quenching constant and [M] is the molar concentration of Fe<sup>3+</sup> ion. Fig. S38<sup>†</sup> shows the dependence of emission intensity of 7 on the concentration of Fe<sup>3+</sup> ions, which decreases as the concentration of Fe<sup>3+</sup> ions increases. Fig. 10 displays the Stern–Volmer (SV) plot of Fe<sup>3+</sup> ions, indicating that at low concentrations (6–0.25 mM), the variation of ( $I_0/I$ ) is linear, giving 1.06 × 10<sup>3</sup> M<sup>-1</sup> and 1.99 × 10<sup>-4</sup> M for the Stern–Volmer constant ( $K_{SV}$ ) and the limit of detection (LOD), respectively.

#### **Recycling capability**

To evaluate the recycling capability, CP 7 was immersed in  $Fe^{3+}$  solution for one day, filtered, washed with water and then subjected to the measurement of PXRD patterns. As shown in Fig. S39,† the structure of 7 may probably remain stable for five cycles.

#### Gas adsorption

 $N_2$  adsorption measurements of  $1,\ 2,\ 3,\ 6,\ \text{and}\ 7$  were conducted at 77 K, with the results shown in Fig. S40–

Table 4 The excitation and emission wavelengths of 1-3, 6, and 7 in solid state

	·ex ()	$\lambda_{\rm em}$ (IIII)	Compound	$\lambda_{\rm ex} ({\rm nm})$	$\lambda_{\rm em} ({\rm nm})$
$ \begin{array}{cccc} \mathbf{L}^{1} & 4 \\ \mathbf{L}^{2} & 3 \\ 1 & 2 \end{array} $	411 368	459 496	L <sup>4</sup> 1,4,5,8-H <sub>4</sub> NTC	347 400	473 472
1 3 2 3 3 4	338 367 410	404 510 443	6 7	405 442	445 500

S49.† The BET surface areas of **1**, **2**, **3**, **6** and **7** are 273.32, 180.59, 266.25, 418.44 and 102.61 m<sup>2</sup> g<sup>-1</sup>, respectively. Additionally, the pore-size distribution curves show that the pore sizes of **1**, **2**, **3**, **6** and **7** are 6.22, 7.77, 8.26, 7.02 and 5.99 nm, respectively. While 7 gives the best quenching efficiency, its BET surface area and pore size are not the largest among **1**, **2**, **3**, **6** and **7**, indicating the stable 3D framework of **7** may enhance the quenching efficiency.

## Conclusions

Seven new CPs and one dinuclear complex ranging from 0D to 1D, 2D and 3D CPs have been successfully synthesized through hydrothermal reactions by using bpba, 1,4,5,8-H<sub>4</sub>NTC and metal salt. Ligand transformations from 1,4,5,8- $H_4NTC$  to 1,4,5,8- $H_2NTC'^2$  and  $L^3$  to  $L^5$  are observed in 1-6, whereas in 7, the 1,4,5,8-NTC<sup>4-</sup> anion retains its structure. CPs 1, 2, and 3 exhibit 1D chains with the 2,3C2 topology and 4, 5a, and 5b show 2D layers with the 2,4L2 topology, whereas 6 is dinuclear, exhibiting a 3D supramolecular structure with the pcu topology, and 7 has a 3D structure with the mog topology. The structural diversities of 1-7 are subject to the formation of 1,4,5,8-NTC' and the identities of the bpba ligands. CPs 1, 2, 3 and 7 and the dinuclear complex 6 exhibit fluorescence properties, giving the 3D 7 the highest potential for detecting Fe<sup>3+</sup> ions in aqueous solution with  $1.06 \times 10^3$  M<sup>-1</sup> and  $1.99 \times 10^{-4}$  M for K<sub>sv</sub> and LOD, respectively.



Fig. 10 The SV plot of 7.

# Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for complexes 1–7 has been deposited at the CCDC with no. 2395512–2395519.

## Author contributions

Investigation, W.-H. C.; data curation, Y.-H. C.; review and supervision, K. B. T., S.-M. L. and J.-D. C. All authors have read and agreed to the published version of the manuscript.

# Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We are grateful to National Science and Technology Council of the Republic of China for support.

## References

- 1 S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem.*, 2013, **85**, 1715–1724.
- 2 E. R. T. Tiekink and J. J. Vittal, *Frontiers in Crystal Engineering*, John Wiley & Sons, Ltd., England, 2006.
- 3 C.-Yi. Lee, M. Usman, S.-W. Wang, K. B. Thapa, T.-R. Chen and J.-D. Chen, *CrystEngComm*, 2024, **26**, 5099–5107.
- 4 C.-Yi. Lee, Y.-H. Ye, S.-W. Wang and J.-D. Chen, *Molecules*, 2024, **29**, 1748.
- 5 X.-K. Yang, W.-T. Lee, J.-H. Hu and J.-D. Chen, *CrystEngComm*, 2021, 23, 4486–4493.
- 6 C.-J. Chen, C.-L. Chen, T.-H. Liu, W.-T. Lee, J.-H. Hu, P. M. Chhetri and J.-D. Chen, *Chemistry*, 2021, 3, 1–12.
- 7 K. B. Thapa and J.-D. Chen, *CrystEngComm*, 2015, 17, 4611–4626.
- 8 T.-T. Liao, M. Usman, Y.-H. Ye, K. B. Thapa and J.-D. Chen, *Inorg. Chim. Acta*, 2023, **574**, 122368.
- 9 X. Yan, J. Lei, Y.-P. Li, P. Zhang and Y. Wang, *CrystEngComm*, 2022, **24**, 2264–2269.
- 10 S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, Royal Society of Chemistry, Cambridge, UK, 2009.
- 11 S. Li, B. Wang, G. Liu, X. Li, C. Sun, Z. Zhang and X. Wang, *Inorg. Chem. Front.*, 2024, **11**, 1561–1572.
- 12 M. Govindaraj, S.-Y. Zhong, C.-H. Lin and J.-D. Chen, *Molecules*, 2023, **28**, 2226.
- 13 F. Nie and D. Yan, Angew. Chem., Int. Ed., 2023, 62, e202302751.

- 14 X.-Y. Ren, F.-Y. Chen, C.-H. Zhang, Z.-G. Liang, X.-Y. Yu, S.-D. Han and G.-M. Wang, *Chem. Eur. J.*, 2024, **30**, e202402581.
- 15 X.-G. Yang, Y.-J. Chen, P.-P. Yin, Y. Li, S.-Y. Yang, Y.-M. Li and L.-F. Ma, *Chem. Sci.*, 2024, **15**, 14202–14208.
- 16 X.-G. Yang, J.-H. Qin, Y.-D. Huang, Z.-M. Zhai, L.-F. Ma and D. Yan, *J. Mater. Chem. C*, 2020, 8, 17169–17175.
- 17 Y. Chen, A.-G. Liu, P.-D. Liu, Z.-T. Chen, S.-Y. Liu and B. Li, J. Mater. Chem. A, 2023, 11, 18236–18246.
- 18 G. C. Liu, Y. Li, J. Chi, N. Xu, X. L. Wang, H. Y. Lin and Y. Q. Chen, *Dyes Pigm.*, 2020, **174**, 108064.
- 19 B. Fu, J. Chen, Y. Cao, H. Li, F. Gao, D.-Y. Guo, F. Wang and Q. Pan, Sens. Actuators, B, 2022, 369, 132261.
- 20 Y.-F. Liu, J.-H. Hu, W.-T. Lee, X.-K. Yang and J.-D. Chen, *Cryst. Growth Des.*, 2020, **20**, 7211–7218.
- 21 T.-T. Liao, S.-Y. Lin and J.-D. Chen, *CrystEngComm*, 2023, 25, 1723–1730.
- 22 Y.-H. Liu, T.-T. Liao, S.-Y. Lin, S.-Y. Zhong, T.-R. Chen and J.-D. Chen, *Inorg. Chim. Acta*, 2023, **556**, 121641.
- 23 S. Fang, E. Li, D. Zhu, G. Wu, Q. Zhang, C. Lin, F. Huang and H. Li, *Chem. Commun.*, 2021, 57, 6074–6077.
- Bruker AXS, APEX2, V2008.6; SAD ABS V2008/1; SAINT +V7.60A; SHELXTL V6.14, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
- 25 G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3–8.
- A. L. Spek, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 9–18.
- 27 Y.-Q. Sun, S. Deng, S.-Z. Ge, Q. Liu and Y.-P. Chen, J. Cluster Sci., 2013, 24, 605–617.
- 28 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
- 29 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, 14, 3576–3586.
- 30 D. Sun, Z.-H. Yan, V. A. Blatov, L. Wang and D.-F. Sun, *Cryst. Growth Des.*, 2013, 13, 1277–1289.
- 31 J.-X. Yang, Z. Xin, Y.-Y. Qin and Y.-G. Yao, *Cryst. Growth Des.*, 2020, **20**, 6366–6381.
- 32 M. Pamei and A. Puzari, *Nano-Struct. Nano-Objects*, 2019, **19**, 100364.
- 33 NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg, M. D., 2000.
- 34 G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, Wiley, New York, NY, 1992.
- 35 S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem.*, *Int. Ed.*, 2013, 52, 2881–2885.