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Central-metal Exchange, Improved Catalytic Activity, Photoluminescence Properties of A New Family of d¹⁰ Coordination Polymers Based on 5, 5'-(1H-2, 3, 5-triazole-1, 4diyl)diisophthalic Acid Ligand

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The rigid and planar tetracarboxylic acid 5,5'-(1H-2,3,5-triazole-1,4-diyl)diisophthalic acid (H₄L), incorporating a triazole group, has been used with no or different pyridine-based linkers to construct a family of d¹⁰ coordination polymers, namely, {[H₂N(CH₃)₂]₃[Cd₃(L)₂(HCOO)]]_n (1), {[Cd₂(L)(py)₆]·H₂O)_n (2), {[H₂N(CH₃)₂] [Cd₂(L)(HCOO)(H₂O)_A] _n (3), {[Zn(H₂L)]·H₂O)_n (4), {[Zn(H₂L)(4,4'-bipy)_{0:5}]·C₂H₅OH·H₂O]_n (5) (py = pyridine, 4,4'-bipy = 4,4'-bipyridine). 1 constructs a 3D porous network containing two kinds of channels: one are filled with coordinated HCOO⁻ anions, and the other with [H₂N(CH₃)₂]⁺ cations. The framework of 1 can be described as a rare (5,6,7)-connected net with the Schläfli symbol of (4¹².5.⁶)(4⁵.5³.6²)₂(4⁸.5³.6⁸.8²)₂. The Cd(II) ions in 2 are connected through the carboxylate ligands to form a 2D layer, with aperture dimensions of ~15.1 Å × 16.2 Å. The network of 3 features a 3D (3,4)-connected (6.8.10)₂(6.8³.10²) topology. 3D network with (4².6³.8)(4².6) topology. The fluorescence lifetime τ values of 1-5 are on the nanosecond timescale at room temperature. In particular, central-metal exchange in 2 leads to a series of isostructural M(II)-Cd frameworks [M = Cu (2a), Co (2b), Ni (2c)] showing improved catalytic activity for the synthesis of 1,4,5,6-tetrahedropyrimidine derivatives. Based on that, a plausible mechanism for the catalytic reaction has been proposed and the reactivity-structure relationship has been further

Introduction

Coordination polymers (CPs) have been suggested for potential applications in different fields, especially catalysis,¹⁻³ gas storage and separation,⁴⁻⁶ metal sensing and sequestration.^{7,8} The effective approach to the design of these CPs is usually the fabrication of metal ion as nodes and multidentate ligands as bridges or terminal groups. Normally, metal ions possess variational coordination geometries in different coordination cases and organic ligands such as carboxylic species possess a variety of coordination modes under different reaction/coordination conditions.⁹ Furthermore, the coordination or combination of given metal ions and organic ligands can also be affected by some other factors, including reaction temperature, reactant concentration, solvents used, template, and so on.¹⁰⁻¹⁶ Explorations on the factors that contribute to a given structure are important to prepare the desired CPs.

On the other hand, the functionalization of target architectures with specific properties and applications has become one of the hottest topics in CPs research. In principle, specific potential applications are tightly linked to the ability to present a

performance of CPs for catalysis by adding functionality that could (1) dock substrates by molecular recognition,¹⁷ (2) act as acid/base catalytic sites,^{18,19} or (3) bind transition metals for tandem catalysis with the metal core.²⁰ With respect to catalytic applications CPs possessing highly accessible, redox active metal centers are particularly interesting.²¹ Central-metal exchange offers an attractive strategy for the incorporation of catalytically active metal centers in CPs. For instance, after replacing the inactive Cd^{II} ions in porph@MOM-10 with Mn["] or Cu["], the product could catalyze the epoxidation of trans-stilbene with 75% conversion (compared to only 7% conversion provided by the original Cd^{II} containing porph@MOM-10).²² Improving catalytic activity through centralmetal exchange is only just emerging. Because of excluding the effect of ligands and geometries, the research of isostructural CPs before and after central-metal exchange is beneficial to find out the relationship between the central-metal ions and corresponding catalytic property of CPs.

corresponding functionality within CPs. As a way to produce coordination polymer materials with more sophisticated properties,

postsynthetic modification (PSM) has the potential to enhance the

The emergence of central-metal exchange synthetic pathway in CPs has been relatively recent, with around thirty reports of successful cases. The complete exchange cases are relatively few.²³ Most of exchange examples in CPs take place between the transition metal ions, such as Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} ions. Based on previous studies from our group, as well as work of others, we believe that the central-metal exchange would be a favorable

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process in porous coordination polymers (PCPs), because exchange process must occur in the CPs pores. The process is therefore likely influenced by diffusion and pore size effects.²³

Taking the aforementioned idea into consideration, we choose rigid and planar tetracarboxylic acid 5,5'-(1H-2,3,5-triazole-1,4diyl)diisophthalic acid (H₄L, Scheme 1) as the ligand. H₄L is an excellent candidate for the preparation of porous CPs, with three obvious characteristics: first, H₄L has four carboxylate groups at two ends of the ligand and a triazole group in the middle, which is difficult to bind with metal ions during the de novo synthesis of CPs. This is conducive to construct PCPs; second, the C-C bonds between the rigid benzene rings and the triazole ring can rotate to some degree to accommodate various coordination environments; and third, it can be partially or completely deprotonated, allowing its different coordination models to the metal ion connectors. Then, reactions of Zn(II) or Cd(II) salts and H₄L with no or different pyridine-based linkers were carried out under hydrothermal condition. In this work, we present the syntheses, structures of five new CPs, crystal namely, ${[H_2N(CH_3)_2]_3[Cd_3(L)_2(HCO_2)]}_n$ (1), $\{[Cd_2(L)(py)_6] \cdot H_2O\}_n$ (2), $\{[H_2N(CH_3)_2][Cd_2(L)(HCO_2)(H_2O)_4]\}_n$ (3), $\{[Zn(H_2L)] \cdot H_2O\}_n$ (4), $\{[Zn(H_2L)(4,4'-bipy)_{0.5}]\cdot C_2H_5OH\cdot H_2O\}_n$ (5). The thermal stability and solid-state photoluminescence of the complexes 1-5 were also reported. The fluorescence lifetime τ values of 1-5 are on the nanosecond timescale at room temperature. Moreover, the metalion exchange behavior for 2 was studied. Heating up a 2 suspension/M(NO₃)₂ (M = Cu^{II}, Co^{II}, Ni^{II}) solution in N,Ndimethylformamide (DMF) leads to isostructural replacement of cadmium by M(II) centres. The exchange products showed improved catalytic activity for the synthesis of 1,4,5,6tetrahedropyrimidine derivatives. Furthermore, the reactivitystructure relationship has also been illuminated.

Experimental

Materials and physical measurements

All reagents and solvents were commercially available except for $H_{4}L$, which was prepared according to the literature procedure.² FT-IR spectra were recorded on a Bruker-ALPHA spectrophotometer with KBr pellets in 400–4000 cm⁻¹ region. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using Cu $K\alpha_1$ radiation on a PANalytical X'Pert PRO diffractometer. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from room temperature at a heating rate of 10 $^{\rm Q}{\rm C}$ min $^{\rm 1}$ in air. The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi 850 fluorescence spectrophotometer. The excitation slit and emission slit were both 2.5 nm. Fluorescence lifetimes were obtained on Edinburgh FIS-980 fluorescence spectrometer. The amounts of metal ions exchanged were determined by inductively coupled plasma spectroscopy (ICP). performed on a Thermo ICAP 6500 DUO ICP was

spectrometer



Preparation of complexes

Synthesis of { $[H_2N(CH_3)_2]_3[Cd_3(L)_2(HCO_2)]$, (1). H₄L (19.8 mg, 0.05 mmol) and Cd(NO₃)₂·4H₂O (23.6 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then H₂O (1 mL) and 0.1 mL HNO₃ were added into the mixture solution. The mixture was placed in a capped 10 mL vial and heated at 100 °C for 3 d. Colorless block crystals suitable for X-ray diffraction were obtained with a yield of 78% (based on H₄L). Anal. calcd for C₄₃H₃₉N₉O₁₈Cd₃ (%): C, 39.52; H, 3.01; N, 9.65. Found: C, 39.81; H, 3.03; N, 9.43. IR (KBr, cm⁻¹): 3156(w), 3076(w), 1614(m), 1539(s), 1405(m), 1356(s),1107(w),1021(w),918(w), 728(s), 669(w).

Synthesis of {[Cd₂(L)(py)₆]·H₂O}_n (2). H₄L (19.8 mg, 0.05 mmol) and Cd(NO₃)₂·4H₂O (23.6 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then pyridine (1 mL) and 0.05 mL HNO₃ were added into the mixture solution. The mixture was placed in a capped 10 mL vial and heated at 100 °C for 4 d. The crystal products of **2** were obtained with a yield of 65% (based on H₄L). Anal. calcd for C₄₈H₃₈N₉O₉Cd₂ (%): C, 51.95; H, 3.45; N, 11.36. Found: C, 51.81; H, 3.57; N, 11.21. IR (KBr, cm⁻¹): 3423(w), 3072(w), 1602(s), 1448(m), 1363(s), 1038(m), 723(s), 696(s), 630(m).

Synthesis of {[$Cd_{0.78}Cu_{1.22}(L)(py)_6$]· H_2O }_n (2a). Compound 2a was prepared by immersing crystals of 2 in an DMF solution of Cu(NO₃)₂ (0.05 M) and heating to 50 °C for 48 h. The exchange products were proved by ICP atomic emission spectrometric analysis, which showed that 61% replacement of Cd^{II} ions by Cu^{II} ions. Anal. calcd for C₄₈H₃₈N₉O₉Cd_{0.78}Cu_{1.22} (%): C, 54.90; H, 3.65; N, 12.01. Found: C, 54.62; H, 3.85; N, 11.83. IR (KBr, cm⁻¹): 3418(w), 2927(w), 1652(s), 1544(m), 1435(m), 1373(s), 1105(m), 783(m), 759(m), 735(m).

Synthesis of {[$Cd_{0.9}Co_{1.1}(L)(py)_6$]· H_2O }_n (2b). Compound 2b was prepared by immersing crystals of 2 in an DMF solution of Co(NO₃)₂ (0.05M) and heating to 50 °C for 48 h. The exchange products were proved by ICP atomic emission spectrometric analysis, which showed that 55% replacement of Cd^{II} ions by Co^{II} ions. Anal. calcd for C₄₈H₃₈N₉O₉Cd_{0.9}CO_{1.1} (%): C, 54.86; H, 3.64; N, 12.00. Found: C, 54.74; H, 3.81; N, 11.88. IR (KBr, cm⁻¹): 3202(w), 2979(w), 1651(s), 1609(w), 1562(s), 1411(s), 1105(m), 787(m), 758(s), 735(s).

Synthesis of {[Cd_{1.84}Ni_{0.16}(L)(py)₆]·H₂O}_n (2c). Compound 2c was prepared by immersing crystals of 2 in an DMF solution of Ni(NO₃)₂ (0.05M) and heating to 50 °C for 48 h. The exchange products were proved by ICP atomic emission spectrometric analysis, which showed that 8% replacement of Cd^{II} ions by Ni^{II} ions. Anal. calcd for C₄₈H₃₈N₉O₉Cd_{1.84}Ni_{0.16} (%): C, 52.36; H, 3.48; N, 11.45. Found: C, 52.14; H, 3.61; N, 11.33. IR (KBr, cm⁻¹): 3427(m), 3019(w), 1652(m), 1541(s), 1411(s), 1371(s), 1309(m), 1037(m), 765(m), 729(m).

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Synthesis of {[$H_2N(CH_3)_2$][$Cd_2(L)(HCO_2)(H_2O)_4$]}_n (3). H₄L (19.8 mg, 0.05 mmol), malonic acid (5.2 mg, 0.05 mmol) and Cd(NO₃)₂·4H₂O (23.6 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then H₂O (1 mL) and 0.1 mL HNO₃ were added into the mixture solution. The mixture was placed in a capped 10 mL vial and heated at 100 °C for 3 d. The crystal products of **3** were obtained with a yield of 23% (based on H₄L). Anal. calcd for C₂₁H₁₆N₄O₁₄Cd₂ (%): C, 32.62; H, 2.09; N, 7.25. Found: C, 32.31; H, 2.23; N, 7.13. IR (KBr, cm⁻¹): 3346(w), 3176(w), 2810(w), 1616(m), 1540(s), 1409(m), 1362(s), 1280(m), 1020(w), 916(w), 766(w), 727(s).

Synthesis of {[Zn(H₂L)]·H₂O}_n **(4).** H₄L (19.8 mg, 0.05 mmol) and Zn(NO₃)₂·4H₂O (18.9 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then H₂O (1 mL), CH₃CH₂OH (1 mL) and 0.1 mL HNO₃ were added into the mixture solution. The mixture was placed in a capped 10 mL vial and heated at 85 °C for 4 d. The crystal products of **4** were obtained with a yield of 72% (based on H₄L). Anal. calcd for C₁₈H₁₁N₃O₉Zn (%): C, 45.17; H, 2.32; N, 8.78. Found: C,44.86; H, 2.41; N, 8.90. IR (KBr, cm⁻¹): 3068(w), 2800(w), 1710(w), 1618(m), 1574(m), 1470(w), 1334(s), 1270(m), 1021(w), 783(w), 755(m), 725(s).

Synthesis of {[Zn(H₂L)(4,4'-bipy)_{0.5}]·C₂H₅OH·H₂O}_n (5). H₄L (19.8 mg, 0.05 mmol), 4,4'-bipy (7.8 mg, 0.05 mmol) and Zn(NO₃)₂·4H₂O (18.9 mg, 0.1 mmol) were dissolved in DMF (5 mL) in a capped vial, then H₂O (1 mL), CH₃CH₂OH (1 mL) and 0.1 mL HNO₃ were added into the mixture solution. The mixture was placed in a capped 10 mL vial and heated at 100 °C for 3 d. The crystal products of **5** were obtained with a yield of 86% (based on H₄L). Anal. calcd for C₂₅H₂₁N₄O₁₀Zn (%): C, 49.81; H, 3.51; N, 9.29. Found: C, 48.87; H, 3.63; N, 9.53. IR (KBr, cm⁻¹): 3053(w), 2800(w), 1720(w), 1615(m), 1549(m), 1426(w), 1359(s), 1228(m), 1021(w), 780(w), 729(s), 682(m).

Typical procedure of the synthesis of 1,4,5,6-tetrahydropyrimidine derivatives (7a-7b) with catalysts 2 and 2a-2c

Aromatic nitrile (1.0 mmol, 1.0 equiv), 1,3-diaminopropane (0.5 mL) and catalyst (0.1 mmol, 0.1 equiv based on M(II) ions, **2** and **2a-2c**) were mixed with toluene reflux. After 4 h, the bulk of the cool solvent was filtrated and evaporated in vacuo and then the residue was partitioned between chloroform (25 mL) and H₂O (25 mL). The organic phase was washed by saturated aqueous NaCl, dried by Na₂SO₄, filtered and evaporated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc–MeOH, 3:1). Column chromatography was performed with silica gel (200–300 mesh). ¹H NMR spectra were recorded on 300 MHz instrument.

Single crystal X-ray crystallography

The data of the 1 and 3-5, were collected on a Rigaku Saturn 724 CCD diffractomer (Mo-K α , λ = 0.71073 Å) at temperature of 20 ± 1 °C. The data of the 2 was collected on a SuperNova diffractometer with graphite monochromated Cu K α radiation (λ = 1.54178 Å) at 160(2) K. The empirical absorption corrections were applied by using multi-scan program. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package.²⁵ The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. There is a large solvent accessible void volume in 4 which is occupied by highly disordered free solvent molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove its electron densities.²⁶ Crystallographic crystal data and structure processing parameters for 1-5 are summarized in Table 1. Selected bond lengths and bond angles for 1-5 are listed in Table S1 (Supporting Information).

Compound	1	2	3	4	5
Formula	C43H39N9O18Cd3	$C_{48}H_{38}O_9N_9Cd_2$	$C_{21}H_{16}N_4O_{14}Cd_2$	C18H11N3O9Zn	C25H21N4O10Zn
Fw	1307.03	1109.67	773.18	478.67	602.83
Temp(K)	293(2)	160(10)	293(2)	293(2)	293(2)
Wavelength(Å)	0.71073	1.54178	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	$P2_{1}/c$	$P2_1/c$	$P\overline{1}$
a (Å)	18.944(4)	25.1439(5)	7.7476(15)	8.0098(16)	8.2275(16)
<i>b</i> (Å)	23.156(5)	18.3001(3)	18.393(4)	13.813(3)	11.413(2)
<i>c</i> (Å)	14.411(3)	16.0070(3)	18.753(4)	22.126(4)	14.634(3)
a(deg)	90	104.32(3)	90	90	72.56(3)
β (deg)	126.63(3)	126.410(2)	101.72(3)	98.25	86.08(3)
y(deg)	90	109.51(3)	90	90	74.18(3)
$V(\text{\AA}^3)$	5073.0(18)	5927.59(19)	2616.6(9)	2422.6(8)	1261.1(4)
Ζ	4	4	4	4	2
D_c (g·cm ⁻³)	1.711	1.243	1.963	1.312	1.587
μ (mm ⁻¹)	1.330	6.183	1.704	1.061	1.041
F(000)	2592	2228	1512	968	618
GOF on F ²	1.168	1.043	1.159	1.078	1.134
eflections collected /	17262 / 4682	11990 / 5087	20639 / 4882	4508 / 4508	12853 / 4670
R_1 , $wR_2[I>2\sigma(I)]^a$	0.0723,0.2001	0.0929, 0.2481	0.0829, 0.2028	0.0781, 0.1888	0.0567, 0.1581
R_1 , wR_2 (all data) ^b	0.0817,0.2151	0.1016, 0.2631	0.1167, 0.2353	0.1069, 0.2050	0.0613, 0.1655
$f = \sum F_0 - F_0 / \sum F_0 ^{-b} w l$	$R_2 = [\sum w (F_0^2 - F_c^2)^2 / \sum w (F_0^2)^2 / \sum w (F_0^2) / \sum w (F_0^2) / \sum w (F_0^2) / \sum w$	211/2			

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Results and discussion

Synthesis. The addition of nitric acid is important for the synthesis of complex 1-5 while its absence will lead to a large amount of precipitate and are not preferred for X-ray crystallographic study, although it did not appear in their final frameworks. The formate anions and $[H_2N(CH_3)_2]^+$ in **1** are generated by the in situ hydrolysis of DMF under acid conditions and incorporated into the compound.²⁷ In consideration of the bridging capability of formic ligand in the structure of 1, attempts to replace the formic ligand by other aliphatic groups, flexible carboxylic ligands such as acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid and succinic acid were conducted by addition of the corresponding acid to the reaction system under the same reaction conditions. The result showed that the formic ligand could not be replaced and 1 always generated except for the case of malonic acid. However, the malonic acid ligand was not coordinated to metal ions but only adjusted the pH value of the system, which resulted in structural transformation from 1 to 3. It should be noted that there does not exist $[H_2N(CH_3)_2]^+$ counter cations in the structure of **2** and **4-5**. For 2. $[H_2N(CH_2)_2]^+$ cations can't generate with no water involed. For 4-5. this phenomenon may be ascribed to the addition of ethanol, which restrains the hydrolysis of DMF. The free $[H_2N(CH_3)_2]^+$ cations could be assigned by crystallographic analysis in spite of their disorder, which were corroborated by thermogravimetric analyses (TGA) and elemental analysis (EA).

Crystal structures

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Structural description of {[H₂N(CH₃)₂]₃[Cd₃(L)₂(HCO₂)]}_n (1). Single crystal X-ray diffraction analysis reveals that complex 1 crystallizes in the monoclinic space group $P2_1/c$ and exhibits a 3D porous network. There are two crystallographically independent Cd(II) centers in 1, as shown in Fig. 1a, Cd1 ion is seven-coordinated by six oxygen atoms from four L⁴⁻ ligands, and one oxygen atom from one HCOO⁻ anion. Cd2 ion has a slightly distorted octahedral coordination geometry, formed by six carboxylate oxygen atoms from six different L⁴⁻ ligands. All the Cd–O [2.163(2)–2.592(4) Å] bond distances as well as the bond angles around each Cd(II) atom



In the structure of 1, the L⁴⁻ ligands are completely deprotonated, exhibiting one kind of coordination mode: coordination mode (Mode I of Scheme 2). In this mode, four carboxylic groups act as μ_1 - $\eta^1:\eta^1, \mu_2-\eta^1:\eta^1$, and $\mu_2-\eta^1:\eta^2$ modes, respectively, to bridge seven Cd(II) ions together. On the basis of these connection modes, all the Cd(II) ions are linked together to generate the 3D network of 1. The solvent is one of the most important parameters in the synthesis of CPs, where they act as counterions for charge balance, as spacefilling molecules, or as "true" templates, in the case of well-defined host-guest interactions.^{28,29} The $[H_2N(CH_3)_2]^+$ cations and HCOO⁻ anions generated via decomposition of the DMF solvent, act not only as charge balance ions, but also as templates to construct the 3D porous network. A view along the crystallographic [101] axis (Fig. 1b) shows two kinds of channels: one are filled with coordinated HCOO⁻ anions, and the other with $[H_2N(CH_3)_2]^+$ cations. The effective free volume of ${\bf 1}$ was calculated by ${\rm PLATON}^{30}$ analysis as 34.3 % of the crystal volume (1739.3 out of the 5073.0 Å³ unit cell volume). To fully understand the structure of 1, the topological approach is applied to simplify such a 3D coordination framework. From the viewpoint of topology, Cd1, Cd2 and L⁴⁻ ligand can be considered as five-, six- and seven-connected nodes, respectively, thus, the framework of 1 can be described as a rare (5,6,7)connected net with the Schläfli symbol of $(4^{12}.5.6^2)(4^5.5^3.6^2)_2(4^8.5^3.6^8.8^2)_2$ (Fig.

complex 1.



Structural description of $\{ [Cd_2(L)(py)_6] \cdot H_2O \}_n$ (2). When pyridine was added, a structurally different 2 was isolated. Complex 2 crystallizes in the monoclinic space group C2/c. The coordination geometry of Cd can be described as a distorted pentagonal bipyramid containing (N_3O_4) from two chelating L⁴⁻ and three pyridine ligands. Two oxygen atoms from the chelating L4asymmetrically coordinate to the Cd atoms (Cd-O 2.281(6)-2.389(5) and 2.512(8)-2.529(6) Å), and this distortion of chelation may be attributed to the seven-coordination in **2**.³¹ Two nitrogen atoms from two different pyridine ligands occupy axial positions, while one nitrogen atom from the third pyridine ligand occupies a horizontal position. The Cd-N bond distances range from 2.362(6) to 2.383(4) Å, which are similar to those in the related complexes.³² Each L⁴⁻ ligand is completely deprotonated and coordinates to four Cd(II) ions through its terminal carboxylate groups in chelating mode (Mode II of Scheme 2). These Cd(II) ions are bridged by the long aromatic backbone of the carboxylate ligands to generate 2D layer, with aperture dimensions of ~15.1 Å × 16.2 Å. However, the pyridine ligands which reside in the horizontal position diminish the void of the layer significantly (Fig. 2b). In addition, the extended 3D supramolecular network is formed through C-H-O hydrogen bonds interactions (C13-O5^a: 3.452 Å, C1-H13···O5^a angle 163 °. Symmetry codes a = x, 1-y, -1/2+z) between pyridine rings and carboxylic groups (Fig. 2c).



Fig. 2 (a) Coordination environments of the Cd(II) ions in **2**. Symmetry code: #1 = -x+1/2, y+1/2, -z+1/2. (b) Ball-and-stick view of the 2D network of **2** along *a* direction. (c) Ball-and-stick view of the 3D superamolecular network of **2** along [110] direction.

Structural description of {[H₂N(CH₃)] [Cd₂(L)(HCO₂)(H₂O)₄]}_n (3). The results of crystallographic analysis revealed that the asymmetric unit of complex **3** consists of two Cd(II) atoms, one L⁴⁻ anion, one HCOO⁻ anion, four coordinated water molecules as well as [H₂N(CH₃)₂]⁺ cations as charge balance ions. As shown in Fig. 3a, Cd1 center adopts a distorted pentagonal bipyramidal coordination environment and is coordinated with four carboxylic oxygen atoms from two L⁴⁻ ligands, one oxygen atom from one HCOO⁻ anion and two coordinated water molecules. Cd2 center is coordinated by three carboxylic oxygen atoms from two L⁴⁻ ligands, one oxygen atom from one HCOO⁻ anion and two coordinated water molecules, showing a distorted octahedral geometry. All the Cd–O [2.230(7)–2.502(7) Å] bond distances as well as the bond angles around each Cd(II) atom [54.0(2)–163.6(3) °] are in the normal range.

Four carboxylate groups of L⁴⁻ are deprotonated and adopt $\mu_1 - \eta^1 : \eta^1$ and $\mu_1 - \eta^1 : \eta^1$ coordination modes, respectively (Mode III of Scheme 2). The Cd(II) atoms are bridged by L⁴⁻ and HCOO⁻ ligands to form a complicated 3D framwork (Fig. 3b). The $[H_2N(CH_3)_2]^+$ cations act as charger balance ions filling in the voids of these channels. From the topological perspective, each L⁴⁻ Ligand coordinates to four Cd(II) ions and therefore the ligand can be considered as 4-connected node. Both of Cd1 and Cd2 can be considered as 3-connected node. The network of **3** features a (3,4)-connected (6.8.10)₂(6.8³.10²) topology (Fig. 3c).

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Structural description of $\{[Zn(H_2L)] \cdot H_2O\}_n$ (4). When Cd(II) salt was replaced by Zn(II) salt, two new Zn complexes 4 and 5 were isolated. The fundamental building unit of 4 consists of one crystallographically unique Zn(II) ions, one $H_2L^{2\text{-}}$ ligand, and one guest water molecule. As illustrated in Fig. 4a, each Zn(II) ion is four-coordinated with a distorted square pyramidal geometry by four carboxylic oxygen atoms from two different H_2L^{2-} ligands. All carboxylic groups of $H_2L^{2^-}$ ligand exhibits $\mu_1 - \eta^1 : \eta^0$ modes to bridge four Zn(II) ions giving ride to a 3D network (Fig. 4b). View along a direction, 3D network possesses open 1D channel with the free volume of 29.2 % (707.6 out of the 2422.7 Å³ unit cell volume). To better understand the nature of this intricate framework, topology analysis is provided: both of the H_2L^{2-} anions and Zn(II) ions can be regarded as 4-connected nodes. Thus, the whole 3D framework can be represented as a 4-connected net with $(4^2.6.8^3)$ topology (Fig. 4c).



code: #1 = x+1, y+1, z, #2 = -x+2, y+1/2, -z+1/2, #3 = -x+2, -y+2, -z. Hydrogen atoms are omitted for clarity. (b) Ball-and-stick view of the 3D network of **4** along *a* direction. (c) Schematic representation of the 3D 4-connected ($4^2.6.8^3$) topology in complex **4**.

Structural description of $\{[Zn(H_2L)(4,4'-bipy)_{0.5}]\cdot C_2H_5OH\cdot H_2O\}_n$ (5). The results of crystallographic analysis revealed that complex 5 crystallizes in the triclinic space group Pī and the asymmetric unit of which consists of one Zn(II) atom, one H₂L²⁻ anion, one of a half 4,4'bipy ligand, one guest water as well as one alcohol molecule. As shown in Fig. 5a, each Zn(II) atom is coordinated by three carboxylate oxygen atoms from three different H_2L^{2-} ligands (Zn–O = 1.940(3), 1.961(3), and 2.001(3) Å) and one nitrogen atom from one 4,4'-bipy ligand (Zn-N = 2.018(3) Å) to constitute a (ZnO_3N) tetrahedral geometry. In the structure of 5, each partly deprotonated H_2L^{2-} ligand utilizes its three carboxylic groups, with monodentate coordination mode, to bridge three Zn(II) atoms, generating a 1D polymer chain and then a 2D layer extended by 4,4'-bipy ligands (Fig. 5b). Owing to the long H_2L^{2-} ligand, the 2D layer of 5 shows big window with the Zn…Zn separation through 4,4'-bipy is 11.083 Å, which is shorter than the one through the $H_2L^{2^-}$ ligand (17.272 Å). The 2D layer structure of 5 topologically possesses a (3,4)-connected network with the Schläfli symbol of $(4^2.6^3.8)(4^2.6)$, as illustrated in Fig. 5c. Analysis of the crystal packing of complex 5 reveals that the 2D layer are further linked together to generate an overall 3D network (Fig. 5d) by the co-effects of the inter-layer $\pi \cdots \pi$ stacking between completely parallel triazole and phenyl rings (triazole ring: N1-C9-N2-N3-C10; phenyl ring: C2-C3-C4-C5-C6-C7) of H_2L^{2-} ligands in an off-set fashion with the centroidcentroid separations of 3.401-3.688 Å and O-H…O hydrogenbonding interactions (O1···O5^a: 2.576 Å, O1-H1···O5^a angle 154 °. Symmetry codes a = 1-x, 3-y, 1-z) between carboxylic groups of two H₂L²⁻ ligands.

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Fig. 5 (a) Coordination environments of the Zn(II) ions in **5**. Symmetry code: #1 = x+1, *y*, z+1, #2 = -x+2, -y+2, -z+2. (b) Ball-and-stick view of the 2D network of **5**. (c) Schematic illustrating the 2D (3,4)-connected ($4^2.6^3.8$)($4^2.6$) topology in complex **5**. (d) View of 3D superamolecular network of **5**.

Thermal properties and PXRD

Powder X-ray diffraction (PXRD) has been conducted to confirm the phase purity of these compounds. For complexes **1–5**, the measured PXRD patterns were well comparable to the corresponding simulated one based on the single-crystal X-ray data, indicative of a pure phase of each product (Fig. S1).

To evaluate the stability of the coordination architectures with entangled structures, TGA was carried out to examine the thermal stability of compounds 1-5 in the temperature range of 30-800 °C as shown in Fig. S2 (Supporting Information). For 1, the first weight loss of 10.85% is close to the calculated value (10.33%) corresponding to the loss of the dimethylamine in the range of 100 and 200 °C. It should be noted that $[H_2NMe_2]^{\dagger}$ cations is removed but the proton is needed for charge balance. The second weight loss of 3.51% between 280 °C and 310 °C is attributed to the loss of formic ligands composite (calculated: 3.67%), there is a sudden weight loss of L⁴⁻ ligand above 350 °C, giving final metal oxides. 2 is stable up to 120°C and then loses weight to 490 °C, corresponding to the release of coordinated pyridine molecules and decomposition of organic ligands. For 3, the first weight loss of 15.02% is close to the calculated value (15.14%) corresponding to the loss of the dimethylamine and the coordinated H₂O molecule in the range of 100 and 280 °C, and the second weight loss of 54.19% between 300 °C and 500 °C is attributed to the loss of ligand composite (calculated: 53.49%). Compound 4 loses the weight of 3.65% ranging from 100 to 260 °C, which can be attributed to the removal of lattice water molecules (calc. 3.75%). Then it has undergone a sudden weight loss above 350 °C, giving final metal oxides. For 5, the first weight loss of 10.27% ranging from 90 to 340 °C, which can be ascribed to the removal of lattice water and ethanol molecules (calc. 10.61%). With temperature increasing, there is a sudden weight loss of 4,4'-bipy and H_2L^{2-} ligands above 350 °C, giving final metal oxides.

Photoluminescence Properties of 1-5

The solid-state photoluminescent spectra of Zn(II)/Cd(II) complexes 1–5, the free H₄L ligand were investigated at ambient temperature, as depicted in Fig. 6. The free ligand H₄L displays a relatively weak emission band at 425 nm (λ_{ex} = 359 nm). Complexes 1–5 exhibit the emission maxima at 439 nm (λ_{ex} = 359 nm) for 1, 423 nm (λ_{ex} = 359 nm) for **2**, 441 nm (λ_{ex} = 359 nm) for **3**, 442 nm (λ_{ex} = 359 nm) for **4**, 448 nm (λ_{ex} = 359 nm) for **5**, respectively. Since the Zn(II)/Cd(II) ions are difficult to oxidize or to reduce because of the d¹⁰ configuration, the emission of these complexes are mainly based on the luminescence of ligands.³³ For 1 and 3-5, the emission bands are red-shifted compared with that of the free ligand H₄L, which may be assigned to the intraligand emission of carboxylate ligand. It is possible that the coordination of the carboxylate groups to the Zn(II)/Cd(II) ion decreases the $\pi^* \rightarrow$ n gap of the carboxylate ligand, leading to the red-shift of the emission peak. $^{\rm 34\text{--}36}$ The emission spectra of $\mathbf{2}$ is parallel to that of the H₄L ligand, which could be mainly ascribed the intraligand to emission of

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The fluorescence lifetime τ values of complexes **1-5** and the free ligand are on the nanosecond timescale at room temperature, as shown in Table 2 and Fig. S3-S8 (Supporting Information). The τ values of these complexes are fitted to two components by a biexponential decay curve except that of **3**, which is fitted to three components triexponentially. The fluorescence lifetime of **1-5** is similar. This reveals that different crystal structures and coordination models in **1-5** have no significant effect on the fluorescence lifetime. The nanosecond timescale of lifetime shows that the emission is fluorescent in nature.

gand/complex	$\lambda_{em}(nm)$	τ, ns; (weight)	χ^2
H ₄ L	426	$\begin{aligned} \tau_1 &= 0.9507 \; (0.52) \\ \tau_2 &= 3.9482 \; (0.48) \end{aligned}$	0.926
1	439	$\tau_1 = 1.8121 (0.40)$ $\tau_2 = 5.2321 (0.60)$	1.086
2	423	$\tau_1 = 1.7702 (0.43)$ $\tau_2 = 4.9348 (0.57)$	1.180
3	441	$\begin{aligned} \tau_1 &= 0.9725 \ (0.20) \\ \tau_2 &= 3.3635 \ (0.65) \\ \tau_3 &= 8.3612 \ (0.15) \end{aligned}$	0.962
4	442	$\tau_1 = 2.1979 (0.68)$ $\tau_2 = 4.7857 (0.32)$	1.162
5	448	$\tau_1 = 2.4945 \ (0.67)$ $\tau_2 = 5.6240 \ (0.33)$	1.066

Central-metal exchange of 2

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After 1-5 were synthesized, a further investigation was performed to determine which types of metal cations can generate CPs with similar structures. Under the similar conditions, divalent Cu(II), Co(II), and Ni(II) cations were selected to synthesize CPs, but all attempts failed. In view of its ability to prepare CPs featuring metals that are difficult to obtain for specific compounds through direct syntheses,⁴⁰⁻⁴⁵ we explored the possibility of replacing the Zn(II), Cd(II) cations in CPs 1-5 with Cu(II), Co(II), and Ni(II) cations by central-metal exchange method. Fortunately, colorless crystals of 2 turned green in a few hours when they were immersed in a 0.05 $mol \cdot L^{-1}$ solution of Cu(NO₃)₂ in DMF and heated in a 10 mL capped vial at 50 °C. Similar phenomenon were also observed when crystals of **2** were immersed in a 0.05 mol·L⁻¹ solution of $Co(NO_3)_2$ or $Ni(NO_3)_2$ in DMF and heated at 50 °C. The exchange products were proved by ICP atomic emission spectrometric analysis, which showed that 61% replacement of Cd^{II} ions by Cu^{II} ions (the incomplete exchange product labeled as 2a) after 72 h, 55% Cd¹ ions were replaced by Co" ions (the incomplete exchange product labeled as **2b**) and only 8% Cd^{II} ions were replaced in Ni^{II} case (the incomplete exchange product labeled as 2c). Obviously, relative stabilities of the 2 analogues were deduced to be in the order of Cu¹ > Co'' >> Ni''. Cu'' typically inserts to the greatest extent. The high electronegativity of Cu^{II} would enable it to form bonds that are more covalent and thermodynamically stable. PXRD study (Fig. S9 of the Supporting Information) indicated that the incompletely exchanged products 2a-2c had the same framework as 2.

The catalytic capacity of 2 and 2a-2c

Although large amounts of CPs have been reported, their huge potential in heterogeneous catalysis is still not fully appreciated and far less explored. In recent work of our group,⁴⁶ from the study of three heterogeneous catalysts synthesized by Co^{II} and pdpa⁴⁻ (H₄pdpa = 5,5'-(pentane-1,2-diyl)-bis(oxy)diisophthalic acid) for the synthesis of 2-imidazoline derivatives, we have gained some understanding of the relationship between their structural features and catalytic capacities. For instance, accessible catalytic sites and suitable channel size and shape have positive effect on the catalytic ability for heterogeneous catalysts. As well as the use of versatile connectors during construction, central-metal ions undoubtedly Page 8 of 11

play crucial roles in determining the properties of CPs. Excluding the effects of ligands and geometries, research into isostructural CPs is beneficial for determining the relationships between metal ions and the corresponding properties of CPs.^{47–52} As to isostructural **2** and **2a-2c**, they consist of same secondary building units with different proportions of Cd^{II} and Cu^{II}, Co^{II}, Ni^{II} ions, respectively. To determine the relationships between metal ions and the corresponding catalytic properties of isostructural **2** and **2a-2c**, the catalyzed reactions of aromatic nitriles with 1,3-diaminopropane were performed.

As shown in Table 3, **2a** and **2b** are effective catalysts for the cascade cyclozation of 4-pyridyl nitriles with 1,3-diaminopropane to generate 2-(pyridin-4-yl)-1,4,5,6-tetrahydropyrimidine. **2a** was higher active than **2b**, giving a conversion of 57 % and 43 %, respectively. By contrast, **2** exhibits poor yield, which may originate from the inactive Cd^{il} central-metal ions. Meanwhile, **2c** indicates lower catalytic capacity than **2a-2b**, which can be attributed to the low degree of exchange extent. Similarly, **2a** and **2b** are relative effective, while **2** and **2c** give poor conversions, towards the synthesis of 2-phenyl-1,4,5,6-tetrahydropyrimidine.

Table 3 Synthesis of 1,4,5,6-tetrahydropyrimidine										
derivatives with Different Catalysts.										
Ar-CN +	Ar $\stackrel{N}{\longrightarrow}$									
6a: Ar = Ph 7a-7b 6b: Ar = 4-pyridyl										
Entry	Ar	Product	Catalyst	Yield (%)						
1			2	trace						
2	Ph	79	2a	36						
3	111	74	2b	15						
4			2c	trace						

7b

4-pyridyl

5

6

7

8

2

2a

2b

2c

trace

57

43

12

As observed in the structure of **2**, all Cd^{II} ions are seven-coordinated and are coordinated with not only carboxylic groups but also pyridine molecules. Since pyridine molecules are good leaving groups, they may departure during catalytic process, leaving unsaturated metal sites to be exposed to aromatic nitriles. Centralmetal ions can be used as unsaturated metal centers providing vacant coordination sites/Lewis acid sites. The catalytic capacity of **2** and **2a-2c** increases in the order of **2** < **2c**< **2b** < **2a**, consistent with the expansion of their Lewis acid strength. This trend indicates that the electron accepting ability of central-metal ions can be a crucial factor in determining the reaction rate for this catalyzed reaction. The catalytic activity of a metal ion is largely governed by its Lewis acidity. The stronger the Lewis acidity, the larger the effect





Based upon the above results and the mechanisms of synthesis of 2-imidazolines catalyzed by the Co"/Cu"-based CPs suggested in the literature,^{46,54} a potential reaction pathway for the synthesis of 1.4.5.6-tetrahedropyrimidines catalyzed by the M^{II} -based CPs is proposed (Scheme 3). The nitrile is first activated by the catalyst to give I. 1,3-diaminopropane attacks I to afford II. Cyclization of II gives the final product. An increase in the Lewis acidity of a metal ion in turn results in a decrease of the nucleophilicity of a metalbound cyanide ion. In this work we demonstrate that the stronger the Lewis acidity of the metal ion, the larger the propensity of the metal ion to catalyze synthesis of 1,4,5,6-tetrahedropyrimidine derivatives. Moreover, the PXRD of the $\mathbf{2a}$ recovered from the reation closely matched that of the pristine solid of 2a, strongly proving that 2a is stable under the catalytic condition (Fig. S10). In addition, 2a recovered from the catalytic reaction via centrifugation could be recycled and reused at least four times (Fig. S11). Next, we carried out a filtration experiment. At the 20 % conversion of the 4pyridyl nitriles (6b) in the presence of 2a for 1h, the reaction mixture was passed through a sand core funnel to remove the catalyst, and the supernatant was allowed to stand for 10 h. It was found that the conversion of the supernatant remained almost unchanged during the time.

Conclusions

In this work, using a polycarboxylic acid H₄L as ligand, we have synthesized and characterized five d¹⁰ CPs 1-5. The thermal stability and solid-state photoluminescence of the complexes 1-5 were also reported. Specially, central-metal exchange in 2 leads to a series of isostructural M(II)-Cd containing framework [M = Cu (2a), Co (2b), Ni (2c)]. In an attempt to evaluate the effect of metal ions, i.e. which metal ion is likely to be more efficient in activating the model substrate aromatic nitriles, detailed catalytic experiments were carried out under the same conditions. Results revealed that the Cu exchange product 2a is the most efficient in activating aromatic nitriles, followed by 2b, thirdly 2c, 2 fourthly. This fact indicates that the higher the Lewis acidity of the M^{II} ion, the faster the rate of activation. Because of excluding the effect of ligands and geometries, the research of isostructural CPs before and after central-metal exchange is beneficial to find out the relationship between the centralmetal ions and corresponding catalytic property of CPs. Thus, the effect of active metal centers as Lewis acid can be clarified in the catalytic reaction process. However, improving catalytic activity through central-metal exchange is a very young field. More practices should be done to find out how the new central metal activates the substrate more effectively compare with the parent central metal for a given catalytic reaction.

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Central-metal Exchange, Improved Catalytic Activity, Photoluminescence Properties of A New Family of d¹⁰ Coordination Polymers Based on 5, 5'-(1H-2, 3, 5-triazole-1, 4-diyl)diisophthalic Acid Ligand

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Five d^{10} coordination polymers (CPs) have been successfully isolated under hydrothermal conditions by the reaction of polycarboxylate ligand H₄L together with Zn(II)/Cd(II) salts in the presence of no or different pyridine-based linkers. Central-metal exchange in CP **2** leads to a series of isostructural M(II)-Cd CPs (M = Cu, Co, Ni) showing improved catalytic activity for the synthesis of 1,4,5,6-tetrahedropyrimidine derivatives.

