Four Novel d¹⁰ Metal-Organic Frameworks Incorporating Amino-Functionalized Carboxylate Ligands: Synthesis, Structures, and Fluorescence Properties

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By employment of amino-functionalized dicarboxylate ligands to react with d¹⁰ metal ions, four novel metal-organic frameworks (MOFs) were obtained with the formula of {[Cd(BCPAB)(μ₂-H₂O)]ₙ} (1), {[Cd(BDAB)·2H₂O·DMF]ₙ} (2), {[Zn(BDAB)(BPD)₀.₅(H₂O)]·2H₂O}ₙ (3) and {[Zn(BDAB)(DBPB)₀.₅(H₂O)]·2H₂O}ₙ (4) (H₂BCPAB = 2,5-bis(p-carbonylphenyl)-1-aminobenzene; H₂BDAB = 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene); BPD = (4,4′-bipyridine); DBPB = (E,E-2,5-dimethoxy-1,4-bis-[2-pyridin-vinyl]-benzene; DMF = N,N-dimethylformamide). Complex 1 is a three-dimensional (3D) framework bearing seh-3,5-Pbca nets with point symbol of {4.6²}{4.6⁷.8²}. Complex 2 exhibits a 4,4-connected new topology that has never been reported before with point symbol of {4².8⁴}. Complex 3 and 4 are quite similar in structure and both have 3D supramolecular frameworks formed by 6-fold and 8-fold interpenetrated 2D coordination layers. The structures of these complexes were characterized by single crystal X-ray diffraction (SC-XRD), thermal gravimetric analysis (TGA) and powder X-ray diffraction (PXRD) measurements. In addition, the fluorescence properties and the sensing capability of 2–4 were investigated as well and the results indicated that complex 2 could function as sensor for Cu²⁺ and complex 3 could detect Cu²⁺ and Ag⁺ via quenching effect.

Keywords: metal-organic frameworks, d¹⁰ -metal ions, amino groups, fluorescence, detection

INTRODUCTION

Metal-organic frameworks (MOFs), which are formed by coordination bonds between metal nodes and organic linkers (Tranchemontagne et al., 2009), have been one of the most rapidly developing areas of material science, not only because of the tunable porosity, controlled structure, and readily chemical functionalization of these materials, but also because of their wide potential applications such as heterogeneous catalysis, gas adsorption and storage, chemical sensing and explosive detection, drug delivery, and optoelectronics. (Barea et al., 2014; Canivet et al., 2014; Dhakshinamoorthy and García, 2014; He et al., 2014; Hu et al., 2014; Liu et al., 2014; Van de Voorde et al., 2014; Silva et al., 2015; Zhu et al., 2015; Sheberla et al., 2017; Li et al., 2018; Park et al., 2018; Prasad et al., 2018; Wang et al., 2018; Cao et al., 2019; Mallick et al., 2019) For example, as a kind of
new absorbent materials, quantities of MOFs have been widely investigated in the capture and separation of various gases, such as CO₂, SO₂, H₂S, NH₃, hydrocarbons and so on. (Li et al., 2009; Peng et al., 2013; Zhang et al., 2014; Trickett et al., 2017; Zárate et al., 2019a; Zárate et al., 2019b; Tchalala et al., 2019; Wang et al., 2020; Han et al., 2021) Varieties of MOFs have also been explored as luminescent materials in different fields, for example, sensing, nonlinear optical materials, OLED, and so forth. (Lastig et al., 2017; Medishetty et al., 2017; Gutiérrez et al., 2018) Although many MOFs have exhibited relatively superior performance, the majority of them do not meet the requirements of practical applications. In order to further improve the properties of MOFs, some strategies have been proposed in previous reports and the introduction of substituent groups into the organic ligands has been proved one of the most effective manners. Among various substituent groups, the influence of amino groups on the structures and properties of MOFs has been intensively studied because amino groups could coordinate with metal ions and form hydrogen bonds with guest molecules, which thus may strengthen some performance or even endow MOFs more functionalities. For instance, Hu et al. demonstrated that the supramolecular interactions of C-H···O, C-O, and O···O could distinctly enhance the adsorption capacity for CO₂. (Hu et al., 2015) Dong and co-workers found that the introduction of amino groups to UiO-66 could provide sensing capability towards lysine and arginine via fluorescence turn-on effect. (Dong et al., 2020)

In consideration of the positive effect of amino groups on the properties of MOFs, we employed amino-functionalized dicarboxylate ligands to construct MOFs in this work. For this purpose, ligands 2,5-bis(p-carbonylphenyl)-1-aminobenzene (H₂BCPAB) and 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene (H₂BDAB) were synthesized to react with d¹⁰ metal ions Zn²⁺ and Cd²⁺ in the absence and presence of auxiliary ligands and four novel MOFs with the formula of \[[\text{Cd}(\text{BCPAB})](\mu₁,\text{H}_2\text{O})\]₂₄, \[[\text{Cd}(\text{BDAB})].\text{2H}_2\text{O}·\text{DMF}\]₆₈, \[[\text{Zn}(\text{BDAB})(\text{BPD})_{0.5}(\text{H}_2\text{O})·\text{2H}_2\text{O}\]₂₈ and \[[\text{Zn}(\text{BDAB})(\text{DBPB})_{0.5}(\text{H}_2\text{O})·\text{2H}_2\text{O}\]₄ were synthesized with N₂ for more than 10 min and stirred at 50°C for 12 h. After removing THF in vacuum, the residue was added with water and then acidiﬁed with diluted HCl (1 M) until no precipitate formed. The atrovirens powder was collected by ﬁltration as target product (1.35 g, yield: 67.3%).

**MATERIALS AND METHODS**

All chemicals and solvents except the organic ligands H₂BCPAB, H₂BDAB, and DBPB were of reagent-grade quality from commercial sources and were used without further puriﬁcation. The as-synthesized complexes were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 500°C using a heating rate of 10°C min⁻¹ under a N₂ atmosphere. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation (1.5418 Å), and the X-ray tube was operated at 40 kV and 40 mA. The gas sorption isotherms were measured by using a Micromeritics ASAP 2020M + C surface area analyzer. Fluorescence spectra were recorded on a PerkinElmer LS-55 fluorescence spectrophotometer. Organic ligands H₂BCPAB (Scheme 1), H₂BDAB (Scheme 2) and DBPB (Scheme 3) were synthesized by previously reported procedures. (Nagarkar et al., 2015; Shen et al., 2016; Dutta et al., 2018)

**Synthesis of 2,5-bis(p-ethoxycarbonylphenyl)-1-aminobenzene (C)**

2,5-bis(p-ethoxycarbonylphenyl)-1-aminobenzene (C) was synthesized by previously reported procedures. To a 1,000 ml round-bottom flask was added with 2, 5-dibromoaniline (1.2 g, 5 mmol), p-ethoxycarbonylphenyboronoc acid (2.9 g, 15 mmol), Pd(PPh₃)₄ (0.58 g, 0.5 mmol), CsF (3.6 g, 24 mmol) and tetrahydrofuran (75 ml). The mixture solution was bubbled with N₂ for more than 10 min and reﬂuxed for 3 days. TLC (hexane : ethyl acetate = 6 : 1) showed that the reaction has ﬁnished. After cooling to room temperature, water was added onto the reaction mixture and then extracted with ethyl acetate (30 ml × 3). The combined organic solution was dried with anhydrous MgSO₄ and concentrated in vacuum. The crude residues were puriﬁed by column chromatography with the eluant (hexanecthyl acetate = 30 : 1) to give a light yellow solid as target product (1.35 g, yield: 67.3%).

**Synthesis of 2,5-Bis (p-carbonylphenyl)-1-Aminobenzene (H₂BCPAB).**

Compound C (1.35 g, 3.4 mmol), KOH (6.24 g, 111 mmol), tetrahydrofuran (THF, 40 ml) and water (100 ml) were added to a 1 L round-bottom flask. The mixture solution was bubbled with N₂ for more than 10 min and stirred at 50°C for 12 h. After removing THF in vacuum, the residue was added with water and then acidified with diluted HCl (1 M) until no precipitate formed. The atrovirens powder was collected by ﬁltration as target product (0.88 g, yield: 72%). LC-MS (M + H)¹Œ = 334.12.

**Synthesis of 4,7-Dibromobenzo[c]Thiadiazole (F)**

2,1,3-Benzothiadiazole (D) (0.5 g, 3.68 mmol), N-bromosuccinimide (NBS, 1.35 g, 7.61 mmol) and H₂SO₄ (98%, 5 ml) were added to a 25 ml round bottom-ﬂask. The reaction mixture was stirred at 60°C for 3 h. After cooling to room temperature, the solution was added with distilled water (25 ml) dropwise in an ice bath. The white desired solid was collected by ﬁltration (1.06 g, yield: 97%).

**Synthesis of 4,7-bis(p-ethoxycarbonylphenyl)-2,1,3-benzothiadiazole (H)**

Compound F (2.49 g, 10 mmol), p-ethoxycarbonylphenyboronoc acid (5.82 g, 30 mmol), Pd(PPh₃)₄ (1.16 g, 1 mmol), Cs₂CO₃ (8.15 g, 25 mmol), N,N-dimethylformamide (DMF, 100 ml), and
SCHEME 1 | Synthesis and structures of ligand H$_2$BCPAB. (A) Pd(PPh$_3$)$_4$, CsF, THF, N$_2$; (B) KOH, THF/H$_2$O.

SCHEME 2 | Synthesis and structures of ligand H$_2$BDAB. (A) H$_2$SO$_4$ 98%; (B) Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, DMF/Toluen, N$_2$; (C) NaBH$_4$, CoCl$_2$·H$_2$O; (D) KOH, THF/H$_2$O.

SCHEME 3 | (A) Br$_5$, AcOH; (B) K$_2$CO$_3$, acetone, CH$_3$Br/(CH$_3$)$_2$SO$_4$; (C) 4-vinylpyridine, Pd(PPh$_3$)$_4$, tris(2-methylphenyl)phosphine, Et$_3$N, CH$_3$CN.
FIGURE 1 | Coordination environment of Cd(II) cation in 1 with ellipsoids drawn at 50% probability level. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 1-x, -1/2 + y, 3/2-z; #2 x, 3/2-y, -1/2 + z; #3 1/2-x, -1/2 + y, z.

FIGURE 2 | (A) The 1D Cd²⁺-[BOPAB]− chain. Amino groups were omitted for clarity. (B) The 2D coordination layers constructed from the Cd²⁺-[BOPAB]− chains via the bonds between amino groups and Cd²⁺ cations. (C) The 3D frameworks formed by the coordination between the bridged μ₂-H₂O molecules (green) with Cd²⁺ cations from different 2D Cd²⁺-[BOPAB]− layers and the 1D chains formed by Cd²⁺ cations and μ₂-H₂O molecules. Description of the crystal structure of [Cd(BDAB)]·2H₂O·DMF)n (2).
Toluene (100 ml) were added to a 500 ml round-bottom flask. The reaction solution was bubbled with N2 for more than 10 min and refluxed at 110°C for 24 h. TLC (hexane:ethyl acetate/8:1) showed that the reaction has finished. The reaction solution was added with water and extracted with ethyl acetate (20 ml × 3). The combined organic solution was dried with anhydrous MgSO4 and concentrated in vacuum. The crude product was purified by column flash chromatography with the eluant (hexane:ethyl acetate/40:1) to give an orange solid as the target product (2.25 g, yield: 49%).

**Synthesis of 3,6-bis(p-ethoxycarbonylphenyl)-1,2-diaminobenzene (I)**

To a solution of H (1.296 mg, 3 mmol) in EtOH/THF (3:1, EtOH = ethyl alcohol) was added sodium borohydride (0.46 g, 12 mmol) and CoCl2·6H2O (29 mg, 0.12 mmol). The reaction solution was bubbled with N2 for more than 10 min and refluxed for 3 h. After removal of EtOH and THF, the residues were added with water and extracted with ethyl acetate (20 ml × 3). The combined organic phase was dried with anhydrous MgSO4 and concentrated in vacuum. The obtained solid was purified by column flash chromatography with the eluant (hexane:ethyl acetate/20:1) to give a grey solid as the target product (0.92 mg, yield: 74.3%). LC-MS (M + H)+ found 405.30.

**Synthesis of 3,6-bis(p-carbonylphenyl)-1,2-Diaminobenzene**

Compound I (0.90 g, 2.22 mmol), KOH (4.09 g, 73 mmol), THF (20 ml), and water (60 ml) were added to a 500 ml round-bottom flask. The reaction solution was bubbled with N2 for more than 10 min and stirred at 60°C for 24 h. After removing THF in vacuum, the mixture was added with water and then acidified with diluted HCl (1 M) until no precipitate formed. The yellow powder was collected by filtration as the target product (0.63 mg, 82% yield). LC-MS (M + H)+ found 349.23.

**FIGURE 3** | Coordination environment of Cd(II) cation in 2 with ellipsoids drawn at 50% probability level. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 1/2-x, 1/2-y, -1/2-z; #2 -1/2 + x, 1/2 + y, -1/2 + z; #3 1-x, -y, -z.
Synthesis of [{Cd(BCPAB) (μ$_2$-H$_2$O)}]$_n$ (1)
A mixture of H$_2$BCPAB (6.7 mg, 0.02 mmol), Cd(NO$_3$)$_2$·4H$_2$O (31 mg, 0.1 mmol), DMA (3.5 ml), H$_2$O (3 ml) was placed in a 25 ml glass vial and heated at 95°C for 4 days. The resultant plate crystals were washed with fresh DMA and collected. Yield: 72% (based on H$_2$BCPAB).

Synthesis of [Cd(BDAB)]$_2$H$_2$O·DMF$_n$ (2)
A mixture of H$_2$BDAB (7 mg, 0.02 mmol), Cd(NO$_3$)$_2$·4H$_2$O (31 mg, 0.1 mmol), DMF (2 ml), H$_2$O (4 ml) was placed in a 25 ml glass vial and heated at 95°C for 4 days. The resultant plate crystals were washed with fresh DMA and collected. Yield: 93% (based on H$_2$BDAB).
**Synthesis of \([\text{Zn(BDAB)}(\text{BPD})_{0.5}(\text{H}_2\text{O})]\)·2\text{H}_2\text{O}}_n\) (3)**
A mixture of H$_2$BDAB (7 mg, 0.02 mmol), BPD (1.5 mg, 0.01 mmol), Zn(NO$_3$)$_2$·6H$_2$O (30 mg, 0.1 mmol), DMF (3.5 ml), H$_2$O (2.5 ml) was placed in a 25 ml glass vial and heated at 100°C for 3 days. The resultant red featheriness crystals were washed with fresh DMF and collected. Yield: 36% (based on H$_2$BDAB).

**Synthesis of \([\text{Zn(BDAB)}(\text{DBPB})_{0.5}(\text{H}_2\text{O})]\)·2\text{H}_2\text{O}}_n\) (4)**
A mixture of H$_2$BDAB (7 mg, 0.02 mmol), DBPB (3.5 mg, 0.01 mmol), Zn(NO$_3$)$_2$·6H$_2$O (30 mg, 0.1 mmol), DMF (3.5 ml), and H$_2$O (1.5 ml) was placed in a 25 ml glass vial and heated at 105°C for 3 days. The resultant red featheriness crystals were washed with fresh DMF and collected. Yield: 59% (based on H$_2$BDAB).

**FIGURE 6**
(A) The 1D BDAB$^2$-Zn$^{2+}$ chains in 3. (B) The 2D BDAB$^2$-Zn$^{2+}$-BPD coordination networks. (C) The interlaced mode of the adjacent BDAB$^2$-Zn$^{2+}$-BPD networks. (D) The 2D interpenetrated BDAB$^2$-Zn$^{2+}$-BPD layers. (E) The final 3D supramolecular architecture of 3.
RESULTS AND DISCUSSION

Description of the Crystal Structure of \{[\text{Cd}(\text{BCPAB})(\mu_2-\text{H}_2\text{O})]_n \} (1)

SC-XRD analysis revealed that complex 1 was crystallized in the orthorhombic system with a space group of \text{Pbca} and each asymmetric unit consisted of one Cd(II) metal center, one BCPAB$^{2-}$ ligand and one water molecule. As shown in Figure 1, atom Cd1 adopted a distorted pentagonal bipyramid coordination geometry to coordinate with four carboxylate oxygen atoms (O1, O2, O3#2, O4#2) from two neighboring BCPAB$^{2-}$ ligands, two coordinated water molecules (O5, O5#3) and one nitrogen atom (N1#1) from the amino group of BCPAB$^{2-}$ ligand. The Cd-O bond lengths were in the range of 2.281–2.448 Å and the Cd-N bond length was 2.425 Å, which are comparable to the previous Cd-based
coordination complexes. (Spek, 1998) Further structural analysis revealed that each carboxylate group of BCPAB$^{2-}$ was bound to one Cd$^{2+}$ ion and each Cd$^{2+}$ ion coordinated with two carboxylate groups from two adjacent BCPAB$^{2-}$ ligands, which thus resulted in the formation of one-dimensional (1D) coordination chains (Figure 2A). Furthermore, the coordination bonds between amino groups of the BCPAB$^{2-}$ ligands and Cd$^{2+}$ ions joined the 1D Cd$^{2+}$-BCPAB$^{2-}$ chains together to afford two-dimensional (2D) coordination layers (Figure 2B). On the other hand, each water molecule linked two Cd$^{2+}$ ions to give 1D Cd-O coordination and thus the 2D Cd$^{2+}$-BCPAB$^{2-}$ layers were connected by the $\mu_2$-H$_2$O molecules into the final 3D frameworks (Figure 2C; Supplementary Figure S1A). From the viewpoint of topology, the seven coordination secondary building unit and the BCPAB$^{2-}$ ligand can be regarded as a 5-connected and 3-connected node, respectively, and the structure of 1 could be represented as seh-3, 5-Pbca nets with point symbol of $\{4.6^2\{4.6^2\}}$ (Supplementary Figure. S1B).

According to SC-XRD measurements, complex 2 was crystallized in the tetragonal $P4/nnc$ space group and each asymmetric unit contained half one Cd$^{2+}$ and half one BDAB$^{2-}$ ligand. As depicted in Figure 3, atom Cd1 was six-coordinated in a disordered octahedral coordination geometry with four carboxylate oxygen atoms (O1, O2, O1#1, O2#1) from two neighboring BDAB$^{2-}$ ligands and two amino groups (N1#2, N1#3) from another two adjacent BDAB$^{2-}$ ligands. Each Cd$^{2+}$ ion connected two carboxylate groups from different BDAB$^{2-}$ ligands to form 1D helical coordination chains (Figure 4A). Further inspection into the structure found that every four helical chains could assemble into a coordination nanotubular structure with the help of the
binding between Cd\(^{2+}\) atoms and amino groups of BDAB\(^{2-}\)
ligands on the chains (Figure 4B). The Cd\(^{2+}\) ions in the
structure of nanotube were only coordinated with carboxylate groups or amino groups and thus they could
bind to the amino groups or carboxylate groups from
neighboring nanotubes, which then resulted in the
formation of the final 3D coordination frameworks with 1D
channels running along c-axis. From the point of topological
view, because one Cd\(^{2+}\) cation connects four BDAB\(^{2-}\) ligands
and one BDAB\(^{2-}\) ligand links four Cd\(^{2+}\) cations, the central
Cd\(^{2+}\) cation and BDAB\(^{2-}\) ligand can both be treated as 4-
connected nodes. Thence, the network of 2 can be represented
with the point symbol is \(4^{2}7\) \({}\) calculated by TOPOS software
(Supplementary Figure S2). The total solvent cavity volume
of 2 is 35.0% per unit cell calculated by PLATON. (Zou et al.,
2010)

Description of the Crystal Structure of
\(\{[\text{Zn}(\text{BDAB})(\text{BPD})_{0.5}(\text{H}_{2}\text{O})]_{n}\} \times 2\text{H}_{2}\text{O}\) \(n\) (3) and
\(\{[\text{Zn}(\text{BDAB})(\text{DBPB})_{0.5}(\text{H}_{2}\text{O})]_{n}\} \times 2\text{H}_{2}\text{O}\) \(n\) (4)
According to the results of SC-XRD measurements,
complexes 3 and 4 were both crystallized in the
monoclinic C2/c space group and shared a similar
framework structure. Each asymmetric unit of 3 consisted
of one Zn\(^{2+}\) cation, one BDAB\(^{2-}\) ligand, half of one BPD
molecule, and one coordinated water molecule. As illustrated
in Figure 5, atom Zn1 in 3 adopted a slightly disordered
tetrahedral coordination geometry surrounded by two
carboxylic oxygen atoms (O2, O4#1) from two adjacent
BDAB\(^{2-}\) ligands, one nitrogen atom (N3) from the BPD
ligand and one coordinated water molecule (O5). The
connection between Zn\(^{2+}\) cations and the carboxylate
groups of BDAB\(^{2-}\) ligands afforded 1D coordination
chains (Figure 6A), which were further assembled by the
coordination between Zn\(^{2+}\) cations and the nitrogen atoms of
BPD ligands to give 2D coordination networks (Figure 6B).
On closer inspection, due to the existence of the large pores in
the 2D networks, it could be found that six adjacent 2D
networks could interlace with each other to give 6-fold
interpenetrated 2D supramolecular layers via the p...p,
C-H...p interactions (Figures 6C,D; Supplementary
Figure S3A). Furthermore, the interpenetrated layers were
joined together to generate the final 3D supramolecular
architecture by the noncovalent interactions including
hydrogen bonds, p...p and C-H...p interactions
(Figure 6E; Supplementary Figure S3B).

Although a more complicated pyridine ligand DBPB
was used instead of BPD to prepare complex 4, the structure of 4
was almost identical to that of 3 and shared the same
topological structure with complex 3 (Supplementary
Figure S4). Each asymmetric unit of 4 also consisted of one
Zn\(^{2+}\) cation, one BDAB\(^{2-}\) ligand, half of one DBPB molecule,
and one coordinated water molecule. Similar to that of 3, the
central Zn\(^{2+}\) cations in 4 also adopted a distorted tetrahedral
geometry (Figure 7A) and connected the organic ligands
BDAB\(^{2-}\) and DBPB to generate 2D coordination networks
(Figure 7B). But differently, due to the much larger size, the
pyridine ligand DBPB could allow more 2D BDAB\(^{2-}\)-Zn\(^{2+}\)-
DBPB coordination networks to interpenetrate with each other
to give an 8-fold interpenetrated 2D supramolecular layers
(Figures 7C,D; Supplementary Figure S4A). These
supramolecular layers further interact with each other to
give the final 3D supramolecular frameworks (Figure 7E;
Supplementary Figure S4B) via various noncovalent
interactions including C-H...p interactions and hydrogen
bonds (Supplementary Figure S4C). Furthermore, one
more difference between the structure of 3 and 4 was that
1D channels along b-axis could be observed in the framework
of 4 (Figure 7E) and the total solvent cavity volume is 22.5%
per unit cell calculated by PLATON. (Zou et al., 2010).

Powder X-ray Diffraction Results and
Thermogravimetric Analyses
The PXRD experiments were carried out to confirm whether
the crystal structures are truly representative of the bulk
materials. The PXRD experimental and computer-simulated
patterns of the corresponding complexes are shown in the ESI
(Supplementary Figures S5–S8). The experimental data
shows that the bulk synthesized materials are the same as
the measured single crystals, suggesting the bulk-phase purity
of the obtained MOFs. Furthermore, TGA experiments were
also carried out in the N\(_2\) atmosphere from 30 to 500°C to
examine the thermal stability of 1–4 and the results were
depicted in Supplementary Figures S9–S12. Complex 1
showed a weight loss of 3.6 % from 30 to 260°C, suggesting
the release of the coordinated water molecules (calcld 3.92 %)
and their structure began to collapse at 400 °C. Complex 2
shows a weight loss of 19 % before 250°C, which corresponds
to the release of free water and DMF molecules (calcld 19 %),
and further weight loss was observed at about 380°C owing to
the collapse of the framework of 2. The TGA curve of complex
3 showed that the framework structure began to decomposing
at 350°C. Complex 4 displayed a weight loss of 5.4 % before
110°C corresponding to the release of free water molecules
(calcld 5.6 %) and then a weight loss of 2.7 % between 110 and
180°C corresponding to the release of coordinated water
molecules (calcld 2.8%). Further quick weight losses were
observed at 360°C owing to the decomposition of the
frameworks of 4.

Fluorescence Properties and Sensing
Capacity
Previous studies have demonstrated that MOFs containing
d\(^{10}\)-metal ions usually exhibit outstanding fluorescence
properties and could function as sensing materials for
various substances. On the other hand, in consideration of
the existence of channels or uncoordinated amino groups in
the structure of complexes 2–4, their fluorescence properties
and sensing capability were checked. Hence, the solid-state
fluorescence properties of 2–4 were firstly examined at room
temperature. As illustrated in Figure 8, the free ligand
Cu²⁺ could cause obvious reduction in the fluorescence emission bands with maxima at 571 nm upon excitation at 356 nm, while the fluorescence emission maxima of 2–4 were observed at 401, 396, and 473 nm upon excitation at 330, 330, and 380 nm, respectively. Compared to the free ligand, apparent blue-shift emissions were observed for 2–4, which may be attributed to the coordination of multi-aromatic ligands to the metal centers. (Nagarkar et al., 2015) Then, the sensing capacities of 2–4 towards common metal ions were checked as well. Before the sensing experiments, the powder samples of 2–4 were fully ground and immersed in DMF to prepare stable suspension (1.0 mg ml⁻¹), respectively. Then, the DMF solutions (50 µl, 100 mM) containing different metal ions, including K⁺, Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, Pb²⁺, and Ag⁺, were added into the DMF suspension of 2–4. The changes in the fluorescence emission intensities were recorded (Supplementary Figures S13–S15) and the results were described in Figure 9. It could be found that the existence of Cu²⁺ could cause obvious reduction in the fluorescence intensity of 2 while there was no significant change for other metal ions. As for 3, the addition of Cu²⁺ and Ag⁺ both lead to the quenching of the fluorescence quenching and the addition of other metal ions only caused slight or moderate change in the emission intensities of 3. The fluorescence emissions of 4 were either almost unchanged or enhanced and no specific response was observed for metal ions. Therefore, complex 2 may function as a fluorescent sensor for Cu²⁺ and complex 3 could detect Cu²⁺ and Ag⁺ via fluorescence quenching effect.

**Carbon Dioxide Adsorption Properties**

Coordination polymers 3 and 4 can maintain the stability of the frameworks after 10 h heating and activation. We used CO₂ as the adsorpive gas to measure the sorption properties of these two complexes. The CO₂ sorption isotherms of these two complexes measured at 298 K are shown in Figure 7. The gas sorption isotherms indicated a CO₂ uptake of 2.4 cm³/g for 3, 15.9 cm³/g for 4. Complex 4 exhibits much more adsorption than complex 3 due to its high porosity: 1,455.9 Å³ and the accessible volumes 22.5% for 3, 24.4% for 4. The changes in the fluorescence intensities of 3. The fluorescence quenching and emissions of 4 were either almost unchanged or enhanced and no specific response was observed for metal ions. Therefore, complex 2 may function as a fluorescent sensor for Cu²⁺ and complex 3 could detect Cu²⁺ and Ag⁺ via fluorescence quenching effect.

**CONCLUSION**

In summary, amino-functionalized dicarboxylate ligands H₂BCPAB and H₂BDAB were employed to react with d¹⁰ metal ions Cd²⁺ and Zn²⁺ to generate four novel MOFs with the formula of [[Cd(BCPAB)(H₂O)]ₙ (1), [[Cd(BDAB)]₂(H₂O)]ₙ (2), [[Zn(BDAB)(BDP)]ₙ(H₂O)]₂·H₂O (3) and [[Zn(BDAB)(BDPB)]ₙ(H₂O)]₂·2H₂O (4) in the absence and presence of auxiliary pyridyl ligands. Complexes 1 and 2 are 3D frameworks with point symbol of {4.6².8₂} and {4².8₄}, respectively. Complexes 3 and 4 are generally isosstructural and have the similar 3D supramolecular frameworks constructed from 6-fold to 8-fold 2D interpenetrated coordination layers. The fluorescence properties of 2–4 were studied and their capacity as fluorescent sensors for metal ions were explored as well. In addition, the adsorption properties of 3 and 4 for CO₂ were investigated. The sensing experiments suggested that complex 2 could detect Cu²⁺ and complex 3 could act as a sensor for Cu²⁺ and Ag⁺ via quenching effect.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

**AUTHOR CONTRIBUTIONS**

KS and ZW designed experiments; WX and JW carried out experiments; XH and HZ analyzed experimental results; KS wrote the manuscript.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2021.708314/full#supplementary-material

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