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# Syntheses, structures and properties of metal-carboxylate chain-based coordination polymers (CPs) with 1,1′:4′,1″-terphenyl-2′,4,4″,5′-tetracarboxylate

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ABSTRACT

Two coordination polymers (CPs) $\{[Mg_2L(\mu_2\text{-}H_2O)\ (\mu_2\text{-DMA})]\cdot DMA\}_n$ (**1**), and $[Ag_4L(DMF)_2]_n$ (**2**) ($H_4L$ = 1,1′:4′,1″-terphenyl-2′,4,4″,5′-tetracarboxylic acid, DMA = N,N-dimethylacetamine, DMF = N,N-dimethylformamide) have been synthesized and structurally characterized. In **1** and **2**, there exist a series of parallel aligned M—O—C chains, which are linked along two directions by para-terphenyl moieties of $L^{4-}$ ligands to lead to the metal-carboxylate chain-based three-dimensional frameworks. The photoluminescence properties of the compounds **1** and **2** have also been investigated. **1** displays blue-violet light emission with the emission maximum at 380 nm. **2** exhibits a broad emission peak from 300 to 800 nm with an emission maximum at 484 nm and some of the shoulder peaks.

## 1. Introduction

Over the past two decades, a lot of coordination polymers [1] (nonporous CPs and porous CPs also called metal-organic frameworks, MOFs) have been synthesized based on a variety of organic ligands and they exhibit the fascinating functional properties and potential applications in the fields such as luminescence [2–5], magnetism [6,7], gas storage [8–10], sensor [11,12,20], catalysis [13–16], ion exchange [17–19], and so on. Besides the properties, the coordination polymers also show us the charming architectural aesthetics in the microscopic universe, such as the interpenetration, interlocking, self-catenation, helix, metal-carboxylate chain-based structures (also called rod-packing structures), zeolitic imidazolate frameworks featuring four-connected tetrahedral topologies, pillared layered structures and so on.

At present, we are interested in the preparation of the metal-carboxylate chain-based coordination polymers and also have reported a series of metal-carboxylate chain-based coordination polymers [12,22,23]. In general, the multidentate organic ligands are suitable for forming the metal-carboxylate chain-based coordination polymers, such as pyridylbenzote ligands [21], 4,4′-biphenyldicarboxylate acid [24], 2,2′,4,4′-biphenyltetracarboxylic acid [25] and so many other ligands. To our knowledge, few reports studied the coordination polymers based on the [1,1′:4′,1″-terphenyl]-2′,4,4″,5′-tetracarboxylic acid ($H_4L$) so far. Han's group [26] used $H_4L$ to obtain three transition metal coordination polymers exhibiting antiferromegnetic interaction and selective detection for $Al^{3+}$ ion and $Fe^{3+}$ ion in methanol solutions. Wang's group reported a Cd(II)-MOF [27] and a series of solvent-induced Mn(II)-MOFs [28] featuring high selectivity for sensing $Fe^{3+}$ ions and antiferromagnetic interaction, respectively. Huang's group [29] reported a series of transition metal MOFs possessing 3D framework and good catalytic activities for the degradation of methylene blue. Based on the above interesting structures and excellent properties, it is worth researching the formation of coordination frameworks with $H_4L$ further. In recent years, many magnesium [30] and silver [31] based coordination polymers or metal-organic frameworks have been reported. In coordination polymers, magnesium ions tend to form octahedral coordination geometries and don't quench the fluorescence of ligands. Silver ions is apt to form short Ag···Ag contacts and exhibits abundant coordination geometries. Herein, we present the syntheses, structures, and properties of two 3D CPs $\{[Mg_2L(\mu_2\text{-}H_2O)(\mu_2\text{-DMA})]\cdot DMA\}_n$ (**1**), and $[Ag_4L(DMF)_2]_n$ (**2**) (DMA = N,N-dimethylacetamine, DMF = N,N-dimethylformamide).

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## 2. Experimental section

### 2.1. General

The chemicals used in this work are of analytical grade and were purchased from Jinan Henghua Sci. & Tec. Co., Ltd and were used without further purification. The FT-IR spectra were measured with KBr pellets in the range of 4000–400 cm$^{-1}$ on a PerkinElmer FT-IR Spectrometer. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. The thermogravimetric analyses (TGA) were performed in a SHIMADZU DTG-60 simultaneous DTA-TG apparatus instrument, under dynamic $N_2$ atmosphere (20 mL/min) and heating rate of 10 °C/min from room temperature. Powder X-ray diffraction investigation on polycrystalline samples were carried out with a Bruker D8 advanced diffractometer equipped with a diffracted-beamed monochromator set for Cu-*Kα* ($\lambda = 1.5418$ Å) radiation. The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range from 5° to 50° at an angular rate of 0.1 s/step, with a scan step width of 0.02°. Photoluminescent spectra were measured using a PerkinElmer LS55 Fluorescence Spectrometer.

### 2.2. Synthesis of **{[Mg$_2$L(μ$_2$-H$_2$O)(μ$_2$-DMA)]·DMA}$_n$ (1)**

A mixture of $H_4L$ (0.025 mmol, 10.2 mg), $Mg(NO_3)_2 6H_2O$ (0.075 mmol, 19.2 mg), DMF (5 mL), DMA (2 mL) and $H_2O$ (1 mL) was sealed in a 15 mL Teflon-lined bomb and heated at 90 °C for 3 days, and then cooled to room temperature at a rate of 5 °C/h. Colorless hexagonal crystals of **1** suitable for X-ray diffraction analysis were isolated in 72% yield. Elemental analysis calcd. for $C_{30}H_{30}Mg_2N_2O_{11}$: C, 55.97; N, 4.35; H, 4.66%. Found: C, 56.12; N, 4.17; H, 4.82%. IR data (KBr, cm$^{-1}$): 420 w, 509 w, 599 w, 724 w, 786 m, 859 w, 1020 w, 1252 w, 1351 m, 1431 s, 1602 vs, 3428 m.

### 2.3. Synthesis of **[Ag$_4$L(DMF)$_2$]$_n$ (2)**

A mixture of $H_4L$ (0.025 mmol, 10.2 mg), $AgNO_3$ (0.075 mmol, 12.7 mg) and DMF (5 mL) was sealed in a 15 mL Teflon-lined bomb and heated at 85 °C for 2 days, and then cooled to room temperature at a rate of 5 °C/h. Colorless diamond-like crystals of **2** suitable for X-ray diffraction analysis were isolated in 36% yield. Elemental analysis calcd. for $C_{28}H_{24}Ag_4N_2O_{10}$: C, 34.29; N, 2.86; H, 2.45%. Found: C, 34.45; N, 2.78; H, 2.32%. IR data (KBr, cm$^{-1}$): 491 w, 571 w, 652 w, 715w, 786 w, 1020 w, 1342 m, 1378 vs, 1557 s, 1655 w, 3401 s.

### 2.4. Crystal structure determination

X-ray diffraction data of the single crystals of **1**–**2** were collected on a Bruker Smart Apex CCD area detector diffractometer using graphite-monochromated Mo-*Kα* radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined using SAINT [32] on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS [33] supplied by Bruker. Structures were solved by direct methods using the program SHELX-97 [34] program package. The positions of the metal atoms and their first coordination spheres were located from direct-method E maps; other non-hydrogen atoms were found using alternating difference Fourier syntheses and least-squared refinement cycles and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of $U_{iso}$. Crystallographic details for **1**–**2** have been summarized in Table 1. Selected bond lengths and angles for **1**–**2** are listed in Tables S1–S2. CCDC reference numbers for **1**–**2** are 1415281 and 1415287, respectively.

**Table 1**
Crystallographic data for compounds **1**–**2**.

| | 1 | 2 |
|---|---|---|
| formula | $C_{30}H_{30}Mg_2N_2O_{11}$ | $C_{28}H_{24}Ag_4N_2O_{10}$ |
| fw | 643.18 | 979.97 |
| crystal system | Monoclinic | Triclinic |
| space group | *P*2$_1$/*n* | *P*-1 |
| *a*, Å | 12.4956(16) | 9.178(3) |
| *b*, Å | 14.5621(19) | 11.148(3) |
| *c*, Å | 15.818(2) | 14.337(4) |
| α, deg | 90.00 | 88.191(7) |
| β, deg | 97.838(3) | 78.882(7) |
| γ, deg | 90.00 | 77.968(6) |
| *V*, Å$^3$ | 2851.3(7) | 1407.8(7) |
| *Z* | 4 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.498 | 2.312 |
| *T*/K | 293(2) | 293(2) |
| μ, mm$^{-1}$ | 0.153 | 2.805 |
| *F*(000) | 1344 | 948 |
| reflections collected | 17490 | 11961 |
| unique reflections | 4754 | 6845 |
| GOF ($F^2$) | 1.055 | 1.142 |
| $R_1^a, wR_2^b$ (I > 2σ(I)) | 0.0581, 0.1710 | 0.0331, 0.0884 |
| $R_1^a, wR_2^b$ (all data) | 0.0748, 0.1848 | 0.0548, 0.1076 |

$R_1^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

## 3. Results and discussions

Both the compounds **1** and **2** were obtained under the solvothermal conditions and are stable in air. The experimental PXRD patterns of the compounds **1** and **2** are agreed with simulated patterns from their single-crystal structures, which confirm the phase purity of the compounds at room temperature (Fig. S1).

### 3.1. Crystal structure description of **{[Mg$_2$L(μ$_2$-H$_2$O)(μ$_2$-DMA)]·DMA}$_n$ (1)**

Single crystal X-ray crystallographic analysis reveals that the asymmetric unit of **1** contains three crystallographically independent $Mg^{2+}$ ions (Mg2 and Mg3 lie on the special positions with site of fractional (SOF) of 0.5 in the asymmetric unit), one $L^{4-}$ ligand, one coordinated water molecule, one coordinated DMA molecule (DMA is disordered over two symmetrically related sites with 60%:40% split occupancies) and one free DMA molecule (Fig. 1a). The Mg1, Mg2 and Mg3 centers are all six-coordinated and have slight distorted octahedral coordination environments. The Mg1 ion is coordinated by four oxygen atoms (O2, O4$^{i}$, O5$^{ii}$ and O7$^{iii}$) from four $L^{4-}$ ligands, one oxygen atom (O10) from a water molecule and one oxygen atom (O11) from one DMA molecule. The Mg2 ion is coordinated by four oxygen atoms (O3$^{i}$, O3$^{iv}$, O8$^{iii}$ and O8$^{v}$) from four $L^{4-}$ ligands and two oxygen atoms (O11 and O11$^{vi}$) from two DMA molecules. The Mg3 ion is coordinated by four oxygen atoms (O1, O1$^{vii}$, O6$^{ii}$ and O6$^{viii}$) from four $L^{4-}$ ligands and two oxygen atoms (O10 and O10$^{vii}$) from two water molecules. There exist metal–metal bonds between Mg1 and Mg2, Mg1 and Mg3 with the bond lengths of 3.657(1) and 3.652(1) Å, respectively. The M–O bond lengths range from 2.023(2) to 2.228(2) Å for **1.** The $L^{4-}$ ligand bridges eight Mg ions through each carboxylate oxygen atom coordinating to a metal ion (Scheme 1a). The neighboring two Mg ions are tri-bridged by two carboxylate groups and one oxygen atom from the DMA or $H_2O$ to form a series of parallel aligned Mg–O–C chains extending along the *b* axis (Fig. 1b). The Mg–O–C chains are linked along the [301] and [−101] directions by para-