

Article

Fabrication, Crystal Structures, Catalytic, and Anti-Wear Performance of 3D Zinc(II) and Cadmium(II) Coordination Polymers Based on an Ether-Bridged Tetracarboxylate Ligand

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Abstract: Two 3D Zn(II) and Cd(II) coordination polymers, $[Zn_2(\mu_4\text{-dppa})(\mu\text{-dpe})(\mu\text{-H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**1**) and $[Cd_2(\mu_4\text{-dppa})(\mu\text{-dpe})(\text{H}_2\text{O})]_n$ (**2**), have been constructed hydrothermally using 4-(3,5-dicarboxyphenoxy)phthalic acid (H_4dppa), 1,2-di(4-pyridyl)ethylene (dpe), and zinc or cadmium chlorides. Both compounds feature 3D network structures. Their structure and topology, thermal stability, catalytic, and anti-wear properties were investigated. Particularly, excellent catalytic performance was displayed by zinc(II)-polymer **1** in the Knoevenagel condensation reaction at room temperature.

Keywords: coordination polymer; carboxylic acids; hydrothermal generation; topological analysis; catalysis; Knoevenagel condensation



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1. Introduction

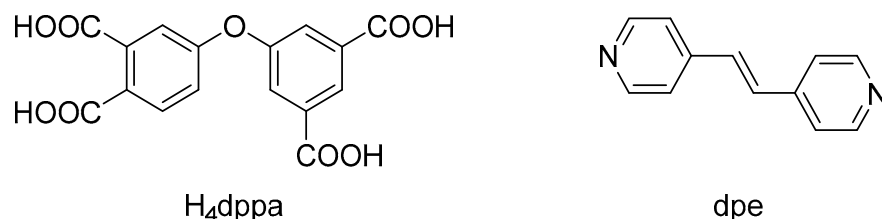
The design and preparation of transition metal coordination polymers have become the topics of material study because of their interesting structures and functional properties, namely in gas separation, heterogeneous catalysis, molecular sensing, luminescence, and magnetism [1–10]. The synthesis of functional coordination polymers depends largely on metal centers, organic ligands, and reaction conditions, including solvents, temperatures, and pH values [11–20].

In this context, semi-rigid polycarboxylate ligands have been widely employed to generate various functional coordination polymers because of their good coordination effects in meeting the geometric requirement of the metal centers [8,15,18,19].

Since 2018, our group has been working on the preparation of transition metal coordination polymers based on multi-carboxylic acids and developing their catalytic activities in organic reactions [8,18,21]. The Knoevenagel condensation reaction is an important organic synthetic reaction involving the formation of active carbon–carbon double bonds that can be further added by nucleophiles, which are widely employed in the production of fine chemicals [22–25]. It is reported that some transition metal coordination compounds have good catalytic performance in the Knoevenagel condensation reaction [26–29]. Coordination compound catalysts present a higher efficiency and recyclability than traditional catalysts (NaOH, pyridine, and amine).

In this study, we selected 4-(3,5-dicarboxyphenoxy)phthalic acid (H_4dppa) as an organic linker (Scheme 1) owing to the following characteristics: (1) it may twist and rotate to produce different angles between the two benzene planes through the $\text{C}-\text{O}_{\text{ether}}-\text{C}$ bond to meet the coordination requirements of metal ions; (2) it bears nine potential coordination sites (eight carboxyl O donors and one O_{ether} atom), which is useful in forming coordination polymers with high dimensionalities; (3) in 2015–2022, several Cu(II), Mn(II), Co(II), Zn(II),

Ni(II), and Cd(II) coordination compounds bearing the ligand were reported [30–36], and their luminescence and magnetism were studied (Table S1). However, only three Cu-dppa networks with catalytic properties in dye degradation have been reported [31]. Therefore, the present work provides us with a good chance to research this field.



Scheme 1. Structure formulae of H_4dppa and dpe.

2. Experimental Section

2.1. Materials and Measurements

All solvents and chemicals were of A.R. grade and used directly. H_4dppa was acquired from Yanshen Tec. Co., Ltd. (Changchun, China). C, H, and N were analyzed using an Elementar Vario EL elemental analyzer. IR spectra were collected using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) curves were obtained using a LINSEIS STA PT1600 thermal analyzer with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The ^1H NMR spectra were obtained using a JNM ECS 400M spectrometer (JEOL, Tokyo, Japan). PXRD data were collected using a PANalytical X-ray diffractometer at room temperature (Cu- $\text{K}\alpha$ radiation, $\lambda = 1.54060\text{ \AA}$); the X-ray tube was operated at 40 kV and 40 mA. Quartz glass plates were used for loading samples. The data collection range was between 5 and 45° . The step was 0.02° .

2.2. Synthesis of $[\text{Zn}_2(\mu_4\text{-dppa})(\mu\text{-dpe})(\mu\text{-H}_2\text{O})]_n\cdot n\text{H}_2\text{O}$ (**1**)

To a stirred mixture containing ZnCl_2 (0.027 g, 0.20 mmol), H_4dppa (0.035 g, 0.10 mmol) and dpe (0.036 g, 0.20 mmol) in H_2O (10 mL) was added NaOH (0.016 g, 0.40 mmol). The mixture was stirred for another 15 min at room temperature, then sealed in a 25 mL Teflon-lined cup and heated at $160\text{ }^\circ\text{C}$ for 3 days. After the mixture cooled to indoor temperature, colorless block-shaped crystals of $[\text{Zn}_2(\mu_4\text{-dppa})(\mu\text{-dpe})(\mu\text{-H}_2\text{O})]_n\cdot n\text{H}_2\text{O}$ (**1**) were collected manually, then washed with distilled water. Yield: 53% (based on H_4dppa). Anal. Calcd. for $\text{C}_{28}\text{H}_{20}\text{Zn}_2\text{N}_2\text{O}_{11}$ (%): C 48.65, H 2.92, N 4.05; found: C 48.33, H 2.93, N 4.07. IR (KBr, cm^{-1}): 3529 w, 3066 w, 1616 s, 1567 s, 1426 m, 1386 s, 1369 s, 1294 w, 1263 w, 1214 w, 1144 w, 1095 w, 1069 w, 1025 w, 980 w, 906 w, 831 m, 782 w, 730 w, 690 w, 553 w. ν_{OH} : 3529 and 3066; $\nu_{\text{as}}(\text{CO}_2)$: 1616 and 1567; $\nu_{\text{s}}(\text{CO}_2)$: 1426, 1386, and 1369.

2.3. Synthesis of $[\text{Cd}_2(\mu_8\text{-dppa})(\mu\text{-dpe})(\text{H}_2\text{O})]_n$ (**2**)

The preparation of **2** was similar to that of **1**, except $\text{CdCl}_2\cdot\text{H}_2\text{O}$ was used instead of ZnCl_2 . After cooling the reaction mixture to room temperature, colorless block-shaped crystals of **2** were collected manually, then washed with distilled water and dried in desiccator. Yield: 48% (based on H_4dppa). Anal. Calcd. for $\text{C}_{28}\text{H}_{18}\text{Cd}_2\text{N}_2\text{O}_{10}$ (%): C 43.83, H 2.36, N 3.65; found: C 43.57, H 2.38, N 3.61. IR (KBr, cm^{-1}): 3401 w, 3045 w, 1630 s, 1612 s, 1576 s, 1497 w, 1439 w, 1399 m, 1347 m, 1303 w, 1268 w, 1223 w, 1148 w, 1077 w, 1007 w, 972 w, 906 w, 831 w, 782 w, 707 w, 658 w, 618 w, 548 w. ν_{OH} : 3401 and 3045; $\nu_{\text{as}}(\text{CO}_2)$: 1630, 1612 and 1576; $\nu_{\text{s}}(\text{CO}_2)$: 1399 and 1347. Both compounds are insoluble in water, methanol, ethanol, acetone, and DMF.

2.4. Structural Determination (Single-Crystals)

Two single crystals (size: $0.06\text{ mm} \times 0.04\text{ mm} \times 0.03\text{ mm}$ for **1** and $0.07\text{ mm} \times 0.04\text{ mm} \times 0.03\text{ mm}$ for **2**) were analyzed at 286(2) K on a Bruker SMART APEX II CCD diffractometer with Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54184\text{ \AA}$). The structures were solved through direct methods and refined using a full matrix least-square on F^2 using the SHELXTL-2014

program [37]. C, N, and O atoms were refined anisotropically. All the H atoms were positioned geometrically and refined using a riding model. There is one disordered solvent molecule in **1**. The number of solvent water molecules was obtained on the basis of the difference electron map (using the SQUEEZE routine in PLATON) [38] and elemental and thermogravimetric analyses. The crystallography data of **1** and **2** are summarized in Table 1. The relevant bond lengths and angles of **1** and **2** are listed in Table S2 (Supplementary Materials). The H bond parameters for compound **2** are listed in Table S3. Analysis of topologies for **1** and **2** was performed using an underlying network concept [39,40]. Simplified networks were generated upon the removal of dpe and H₂O ligands, along with producing a reduction of the dppa^{4−} ligands to their centroids. CCDC-2295640 and 2295641 contain the structural parameters.

Table 1. Summary of crystal data of compounds **1** and **2**.

Compound	1	2
Chemical formula	C ₂₈ H ₂₀ Zn ₂ N ₂ O ₁₁	C ₂₈ H ₁₈ Cd ₂ N ₂ O ₁₀
Molecular weight	691.18	767.24
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.5941(2)	11.33826(10)
<i>b</i> /Å	23.0545(4)	20.23587(17)
<i>c</i> /Å	17.5393(4)	11.39034(10)
α /(°)	90	90
β /(°)	101.943(2)	93.9031(8)
γ /(°)	90	90
<i>V</i> /Å ³	3399.89(13)	2607.33(4)
<i>Z</i>	4	4
<i>F</i> (000)	1360	1504
Crystal size/mm	0.06 × 0.04 × 0.03	0.07 × 0.04 × 0.03
θ range for data collection	3.211–64.997	4.370–76.380
Limiting indices	−8 ≤ <i>h</i> ≤ 10, −27 ≤ <i>k</i> ≤ 26, −20 ≤ <i>l</i> ≤ 20	−14 ≤ <i>h</i> ≤ 12, −25 ≤ <i>k</i> ≤ 25, −14 ≤ <i>l</i> ≤ 11
Reflections collected/unique (<i>R</i> _{int})	21,562/5754 (0.1006)	23,647/5188 (0.0800)
<i>D</i> _c /(g·cm ^{−3})	1.315	1.955
μ /mm ^{−1}	2.176	13.641
Data/restraints/parameters	5754/2/387	5188/0/380
Goodness-of-fit on <i>F</i> ²	1.003	1.024
Final <i>R</i> [(<i>I</i> ≥ 2σ(<i>I</i>))] <i>R</i> ₁ , <i>wR</i> ₂	0.0675, 0.1804	0.0416, 0.1124
<i>R</i> (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.0806, 0.1895	0.0434, 0.1139
Largest diff. peak and hole/(e·Å ^{−3})	0.814 and −0.511	1.201 and −1.253

2.5. Catalytic Knoevenagel Reaction

To a stirred solution of aromatic aldehyde (0.50 mmol, benzaldehyde as a model substrate), propanedinitrile (1.0 mmol) in solvent (1.0 mL, typically CH₃OH) was added as a catalyst (typically 2 mol%), then the mixture was stirred for an expected reaction time at indoor temperature. Then, the catalyst was wiped off by centrifugation. The remaining filtrate was concentrated under reduced pressure to produce a crude solid product. The quantification of the product was analyzed by ¹H NMR spectroscopy (in CDCl₃) (Figure S5). So as to run recycling experiments, the used catalyst was collected again by centrifugation, then washed with CH₃OH, dried at 25 °C, and reused in subsequent tests as discussed above.

2.6. Friction Test

The wear performances and the friction of oils were determined by High Frequency Oscillating Tribometer (UMT-TRIBOLAB) under simulated operating conditions. In the testing configuration, the static upper specimen was a GCr15 steel ball (diameter of 10 mm), and a GCr15 steel block with thickness of 8 mm and diameter of 25 mm was used as the

reciprocating lower specimen. Before tests, the balls and blocks were washed in acetone in ultrasonic cleaner for 10 min. The sample oil (0.1 mL) was dropped on the steel block using a micro-syringe and made to cover its entire surface before each friction test. The testing temperatures were tested by a thermocouple fitted below the holder and set at 25 °C by the tribometer control program. All the friction tests were performed at a reciprocating stroke of 2 mm with a frequency of 25 Hz for 30 min under a consistent load of 200 N (the Hertzian contact pressure of ~1602 MPa). Each test was repeated 3 times under the same condition for the verification of the repeatability of the measured values.

3. Discussion of Results

3.1. Crystal Structure of 1

An asymmetric unit of **1** has two Zn centers (Zn1 and Zn2), one μ_4 -dppa^{4−} block, one μ -dpe moiety, one μ -H₂O ligand, and one lattice water molecule (Figure 1a). The Zn1 and Zn2 centers are four-coordinate and reveal tetrahedral {ZnNO₃} environments, which are completed by two O atoms from two individual μ_4 -dppa^{4−} blocks, one O atom of the μ -H₂O ligand, and a N_{dpe} donor. The lengths of the Zn–O and Zn–N bonds are 1.907(4)–1.991(4) and 2.032(4)–2.067(4) Å, respectively; these values are similar to those of other zinc compounds [15,41]. The dppa^{4−} ligand is employed as a μ_4 -block (mode I, Scheme 2 and Figure S3), wherein all four deprotonated carboxyl groups adopt monodentate modes. In the μ_4 -dppa^{4−} block, the dihedral angle of two benzene rings as well as the C–O_{ether}–C angle are 82.91 and 117.38°. The dpe auxiliary ligand adopts a bridging coordination mode. The μ_4 -dppa^{4−} blocks, μ -dpe moieties, and μ -H₂O ligands link adjacent Zn(II) centers to give a 3D network (Figure 1b). It features channels (11.78 × 10.79 Å measured by atom-to-atom distances) (Figure 1b), which are filled with water molecules of crystallization. Upon the removal of the water molecules of crystallization, we computed, using PLATON, an effective free volume that is 30.4% of the crystal volume [38]. This 3D network structure is composed of the 4-linked Zn nodes, 4-linked μ_4 -dppa^{4−} nodes, 2-connected μ -dpe, and μ -H₂O linkers (Figure 1c). This is a 2,2,4,4-connected framework with a new topology and a point symbol of (6².8.7.8.7)(6².8.7³)(6)(8².6².8.7).

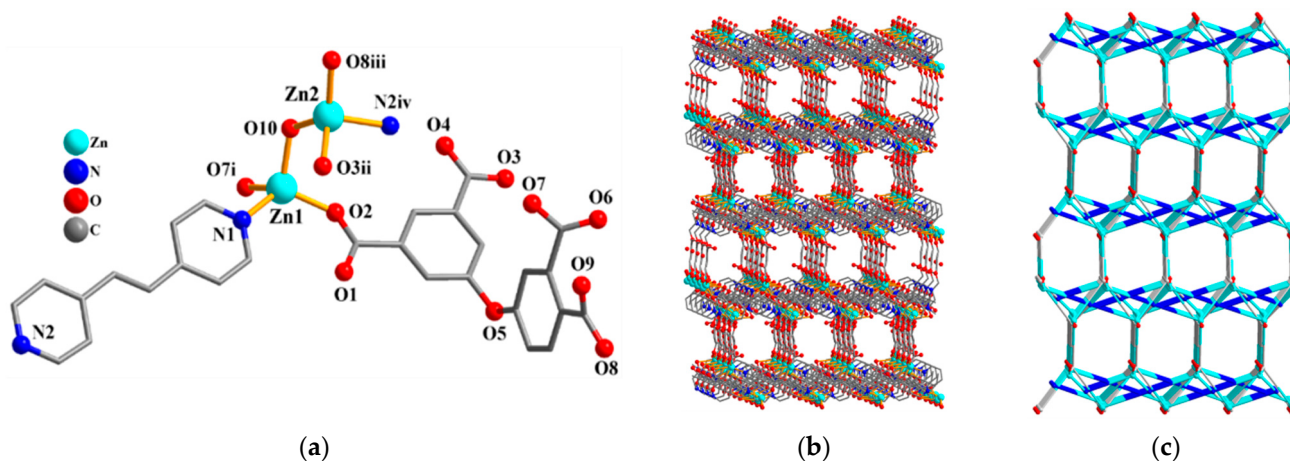
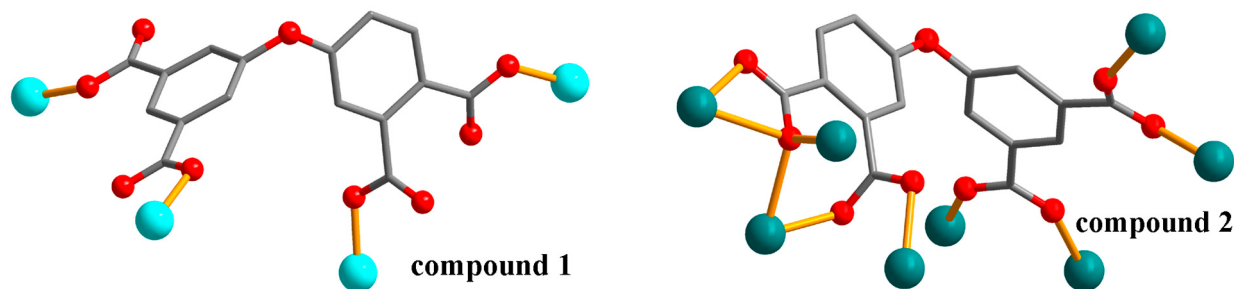


Figure 1. Structure of **1**. (a) Coordination environment around Zn(II) atoms (H atoms and lattice water molecules are ignored, symmetry codes: i: $x - 1/2, -y + 3/2, z - 1/2$; ii: $x - 1, y, z$; iii: $-x + 3/2, y + 1/2, -z + 3/2$; iv: $x + 3/2, -y + 3/2, z + 1/2$). (b) View of a 3D network along the *c* axis. (c) Topological representation of a 2,2,4,4-connected framework with a new topology, perspective view along the *c* axis; Zn nodes (blue), centroids of μ_4 -dppa^{4−} nodes (gray), centroids of 2-connected μ -dpe (dark blue), and μ -H₂O (red) linkers.



Scheme 2. The coordination modes of dppa^{4-} linkers in compounds **1** and **2**.

3.2. Crystal Structure of **2**

This compound also reveals a 3D network. An asymmetric unit has two Cd(II) centers (Cd1 and Cd2), one $\mu_8\text{-dppa}^{4-}$ block, one dpe moiety, and one H_2O ligand (Figure 2a). The Cd1 center is six-coordinate and reveals a distorted octahedral $\{\text{CdNO}_5\}$ geometry. It is defined by five O donors from four individual $\mu_8\text{-dppa}^{4-}$ blocks and one N_{dpe} donor. The Cd2 atom is also six-coordinate and adopts a distorted octahedral $\{\text{CdO}_6\}$ environment comprising five O atoms of four different $\mu_8\text{-dppa}^{4-}$ moieties and one O atom of the H_2O ligand. The Cd–O [2.215(3)–2.650(2) Å] and Cd–N [2.294(3) Å] bonds are within standard values [42,43]. The dppa^{4-} block is employed as a μ_8 -linker with its carboxylate groups adopting a μ -bridging bidentate or tridentate mode (mode II, Scheme 2 and Figure S3). Within the $\mu_8\text{-dppa}^{4-}$ block, the dihedral angle between two benzene rings is 82.83° , whereas the $\text{C–O}_{\text{ether}}\text{–C}$ angle is 117.22° . The dpe auxiliary ligand adopts a terminal coordination mode. The $\mu_8\text{-dppa}^{4-}$ blocks and μ -dpe moieties connect adjacent Cd(II) centers to give a 3D network (Figure 2b). It also features channels (7.90×6.97 Å measured by atom-to-atom distances) (Figure 2b). We computed, using PLATON, an effective free volume that is 1.80% of the crystal volume [38]. The 3D network in this compound features an intricate binodal 4,8-connected net composed of the 4-linked Cd nodes and 8-linked $\mu_8\text{-dppa}^{4-}$ nodes (Figure 2c). It adopts a new topology with a point symbol of $(4^{12}.6^{12}.8^4)(4^5.6)_2$.

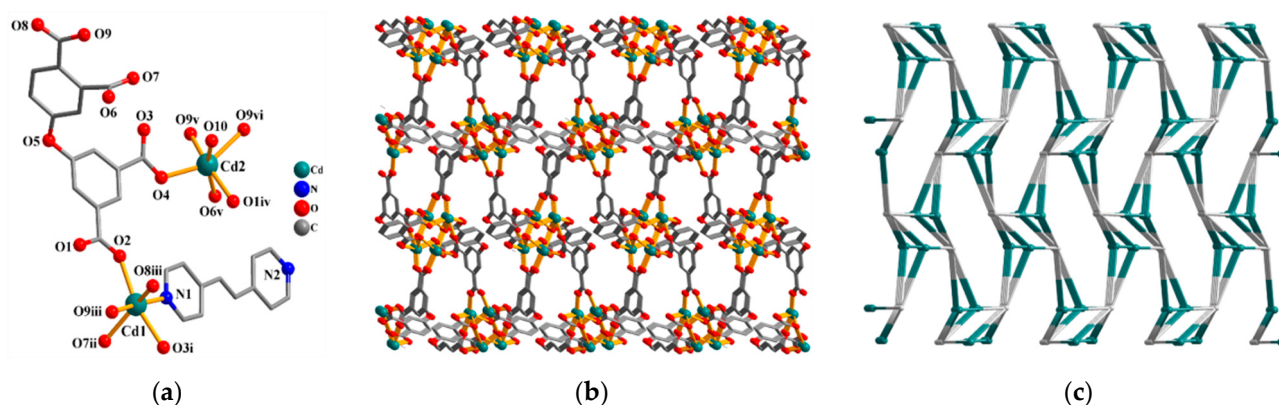


Figure 2. Structure of **2**. (a) Coordination environment of Cd(II) atoms (H atoms and lattice water molecules are ignored, symmetry codes: i: $-x + 1/2, y + 1/2, -z + 1/2$; ii: $x - 1/2, -y + 3/2, z + 1/2$; iii: $-x + 1/2, y + 1/2, -z - 1/2$; iv: $x + 1/2, -y + 3/2, z + 1/2$; v: $x, y, z + 1$; vi: $-x + 1, -y + 1, -z$). (b) View of a 3D framework along the c axis. (c) Topological representation of a binodal 4,8-connected framework with a new topology; perspective view along the c axis; Cd nodes (turquoise balls), centroids of $\mu_8\text{-dppa}^{4-}$ nodes (gray).

3.3. TGA and PXRD Data

To study the thermal stability of polymers **1** and **2**, thermogravimetric analysis (TGA) was carried out. As shown in Figure 3, the TGA curve of **1** shows that there is a loss of one free water molecule and one H_2O ligand between 55 and 192°C (exptl, 4.9%; calcd,

5.2%); further heating above 277 °C leads to a decomposition of the dehydrated framework. Compound **2** loses its one lattice water molecule and one H₂O ligand at 134–198 °C (exptl, 2.5%; calcd, 2.3%), followed by decomposition at 341 °C. The corresponding metal oxides (ZnO and CdO) are expected to be the final product of polymers **1** and **2**. Although polymers **1** and **2** have similar compositions, their TGA curves differ greatly. The difference may be attributed to the different coordination modes of the dppa^{4−} ligands in both polymers (μ_4 -linker in **1** and μ_8 -linker in **2**).

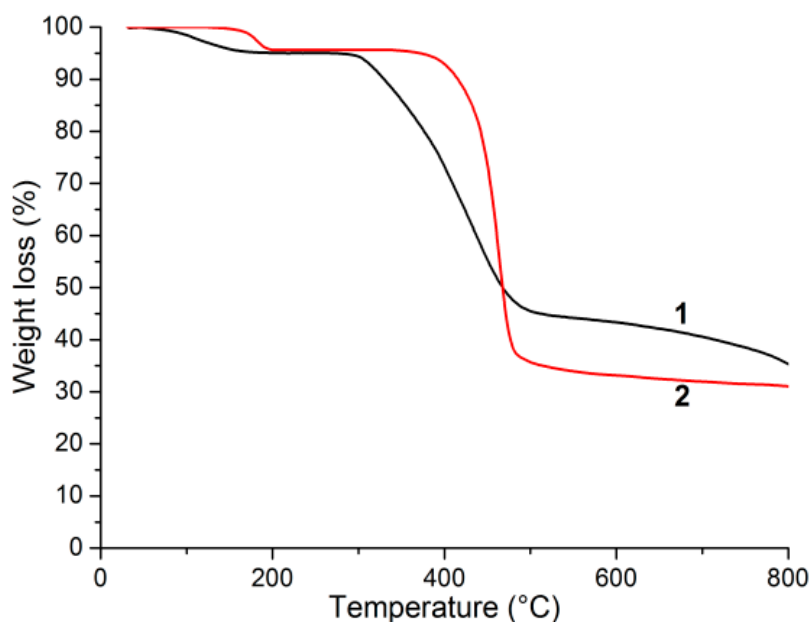
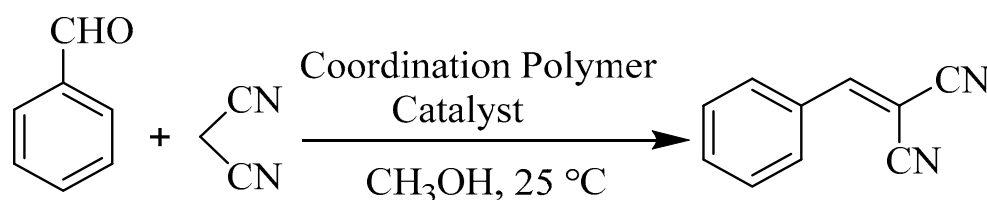


Figure 3. TGA curves of polymers **1** and **2**.

Crystalline samples of polymers **1** and **2** were researched using the PXRD method. Experimental and simulated PXRD patterns are provided in Figure S2. Their peak position and intensity are similar. Their comparison demonstrates a good match and determines the formation of phase purity for the obtained compounds.

3.4. Catalytic Knoevenagel Reaction

Considering the potential ability of some metal (II) coordination polymers to serve as catalysts in a Knoevenagel reaction [8,43,44], we probed compounds **1** and **2** as heterogeneous catalysts in the reaction of some aldehydes with malononitrile. Benzaldehyde and malononitrile, as the model substrates, reacted at 25 °C in a methanol medium to produce 2-benzylidenemalononitrile (Scheme 3, Table 2). The influence of important parameters (including reaction time, solvent, catalyst loading, and recycling) on the reaction was explored.



Scheme 3. Zn-catalyzed Knoevenagel reaction of benzaldehyde with malononitrile.

Table 2. Knoevenagel reaction of benzaldehyde with propanedinitrile ^a.

Entry	Catalyst	T (°C)	Time (min)	Catalyst Loading, mol%	Solvent	Yield ^b , %
1	1	25	10	2.0	CH ₃ OH	45
2	1	25	20	2.0	CH ₃ OH	62
3	1	25	30	2.0	CH ₃ OH	74
4	1	25	40	2.0	CH ₃ OH	85
5	1	25	50	2.0	CH ₃ OH	94
6	1	25	60	2.0	CH ₃ OH	100
7	1	25	60	1.0	CH ₃ OH	95
8	1	25	60	2.0	H ₂ O	99
9	1	25	60	2.0	C ₂ H ₅ OH	96
10	1	25	60	2.0	CH ₃ CN	87
11	1	25	60	2.0	CHCl ₃	63
12	2	25	60	2.0	CH ₃ OH	81
13	Blank	25	60	—	CH ₃ OH	20
14	ZnCl ₂	25	60	2.0	CH ₃ OH	32
15	H ₄ dppa	25	60	2.0	CH ₃ OH	26

^a Reaction conditions: benzaldehyde (0.5 mmol) and malononitrile (1 mmol) in solvent (10 mL). ^b Calculated by ¹H NMR spectroscopy: mol (product)/mol (aldehyde + product) × 100 (Figure S5).

When compound **1** was used as a heterogeneous catalyst, the 2-benzylidenemalononitrile product was obtained smoothly (Table 2 and Figure S4). When benzaldehyde and malononitrile were treated in CH₃OH catalyzed by **1** (2 mol%), the yields of 2-benzylidenemalononitrile accumulated, with a yield increase from 45 to 100% by extending the reaction time from 10 to 60 min (Table 2, entries 1–6; Figure S6). The effect on the catalyst amount was also researched, showing a product yield growth from 95 to 100% upon increasing the amount of catalyst from 1 to 2 mol% (entries 6 and 7). Besides CH₃OH, other solvents were employed. Ethanol, water, chloroform, and acetonitrile were less suitable for the reaction (63–99% product yields).

In comparison with **1**, compound **2** was less active, giving a maximum product yield of 81% (entry 12, Table 2). Significantly, under similar reaction conditions, the Knoevenagel reaction of benzaldehyde with malononitrile was significantly less efficient in the absence of the above catalyst (only 20% product yield). And, when using H₄dppa (26% yield) or ZnCl₂ (32% yield) as catalysts (entries 13–15, Table 2), the yields were near those seen in the absence of a catalyst.

Some substituted benzaldehyde substrates were employed to research the substrate scope of the Knoevenagel reaction of benzaldehyde with malononitrile. These reactions were performed under optimized conditions (2.0 mol% **1**, CH₃OH, 25 °C, 60 min). The yields of the related products were in the range of 37–100% (Table S4). Benzaldehydes bearing a strong electron-withdrawing group (including NO₂ and Cl substituent in the ring) showed better efficiency (entries 2–5, Table 2), which can be attributed to an improved electrophilicity of aldehyde groups. The benzaldehydes with electron-donating groups (e.g., hydroxyl, methyl, and methoxy groups) led to low product yields (entries 6–8, Table S4).

Finally, to address the reusability properties of catalyst **1**, the cycle reactions were carried out under the reaction conditions of entry 7 in Table 2. The catalyst was separated via centrifugation after each reaction cycle, then washed with methanol, dried in air at indoor temperature, and used in the next cycle. The gained results prove that compound **1** preserved the activity for at least five reaction cycles (the yields are 94, 92, 90, and 87% for the second to the fifth cycle, respectively, Figure S7). Additionally, the PXRD patterns confirm that the structure of **1** is maintained (Figure S8).

In order to determine whether polymer **1** is a heterogeneous catalyst in Knoevenagel condensation, we carried out a catalyst-leaching experiment [45,46]. Hence, a control test with catalyst **1** was performed until an intermediate product yield (~45% in 10 min) was obtained. After 10 min, the coordination polymer catalyst **1** was isolated by centrifugation and the reaction mixture was kept for an additional 50 min. As depicted in Figure S6 (blue dotted line), there was no significant increase in the yield of the reaction after removing the

catalyst. These experimental results fully show that the catalyst is a heterogeneous catalyst. In another test, after removing the catalyst, the filtrate was dried in vacuo, followed by the determination of the amount of zinc. The obtained analysis showed only traces of zinc (0.047%). This result proves that there is no significant leakage of zinc in the catalyst.

According to the literature, the catalytic activities of coordination polymer catalyst **1** are generally better than other coordination polymer catalysts in the Knoevenagel reaction of aldehydes (Table S5) [26–28,44,47–53].

Based on the literature [54,55], we put forward a possible mechanism for this reaction catalyzed by **1** (Figure S9). The unsaturated Zn(II) center in catalyst **1** is eventually employed as the Lewis acidic site and interacts with the H–C=O group of benzaldehyde, giving the group polarization and an enhanced electrophilicity of the corresponding carbon atom. The polarization can promote the nucleophilic attack of this site by malononitrile, which acts as a nucleophile precursor. Instead, the interaction between the –CN group of malononitrile and the Lewis acid site increases the acidic character of the methylene functionality and enhances its deprotonation. The basic sites that exist in **1** (O-carboxylate sites) can easily take the proton from the –CH₂– group to give the resultant nucleophilic species, which react with the H–C=O group of benzaldehyde to form a carbon–carbon bond, followed by dehydration to produce the product 2-benzylidenemalononitrile.

3.5. Anti-Wear Property of **1**

The use of inorganic additives is a novel method for improving the lubrication performance of lubricating oil to increase the operational efficiency of engines. Lubricating additives can rapidly infiltrate the friction area to prevent direct contact between the friction pair's surfaces [56]. On a damaged friction surface, they are more likely to precipitate or form a protective coating. Inspired by the fact that zinc dialkyl dithiophosphate (ZDDP) is commonly used in engine oils as a superb anti-wear additive, zinc(II) coordination polymer **1** was used as an additive in polyalphaolefin synthetic lubricant (PAO10), whose viscosity at 100 °C is 10.1 mm²/s, to evaluate its anti-wear performance.

Compound **1** (10 mg), which was ground into powder with a mortar, was added to PAO10 (10 mL). The mixture was stirred at 85 °C for 24 h and ultrasonically dispersed for 1 h to obtain the oil sample (**1**/PAO10). Although TGA measurements for crystal **1** suggested a loss of water molecules starting from 55 °C, compound **1** was present in a solid state in sample **1**/PAO10. As shown in the fluorescence microscope images (Figure S10), the particle size of **1** in **1**/PAO10 was in the micron to nanometer scale, which was similar to the size and fluorescence of the powder of **1**. In order to confirm the preservation of the nature of compound **1** in sample **1**/PAO10, sample **1**/PAO10 was diluted with petroleum ether, and the precipitate was collected and washed with petroleum ether by centrifugation. The PXRD experiments of the sediment were carried out (Figure S11). The PXRD patterns confirm that the structure of **1** is retained despite the observation of several novel signals or widening of some parent peaks. These alterations can be associated with a decrease in crystallinity and the presence of impurities.

The friction coefficient curves versus sliding time for PAO10 and **1**/PAO10 samples at 25 °C are shown in Figure 4. The friction coefficient of PAO10 increased sharply at 300 s, stabilizing at approximately 0.12. For **1**/PAO10, the friction coefficient curve was steady. The friction coefficient was close to that of PAO10 in the beginning and not over 0.9 during the entire test time. This indicates that the addition of compound **1** improved the wear resistance of lubricating oil, which will have potential applications as an additive in lubricating oil. This significant improvement was due to the nanobearing and deposition exerted by solid **1** on the surface of the friction pair, which contributed to a decline in the contact area and surface roughness and effectively repaired the friction pair.

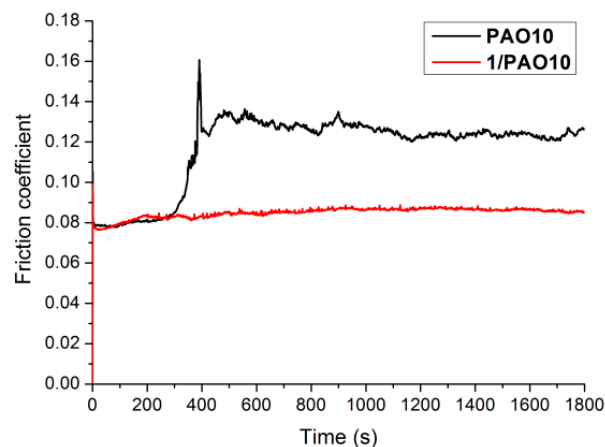


Figure 4. Friction curves versus sliding time for PAO10 and 1/PAO10.

4. Concluding Remarks

In summary, two new zinc and cadmium coordination polymers were assembled and characterized by using one ether-bridged tetracarboxylic acid as a main ligand under hydrothermal conditions. Both polymers show a 3D network structure. Additionally, the anti-wear and catalytic performances were also researched and discussed. The results show that coordination polymer **1** is a potential multifunctional crystal material with excellent fluorescence, catalytic, and anti-friction properties. The present work demonstrates that such ether-bridged tetracarboxylic acids can serve as useful building blocks in the preparation of new coordination polymers. We hope this study can stimulate other research on the preparation of coordination polymers with better catalytic performance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13121681/s1>. Figures S1 and S2: FT-IR spectra and PXRD patterns of **1** and **2**; Figure S3: the coordination modes of dppa^{4-} linkers in this work and previously reported works; Figures S4–S8 and Table S4: catalysis data for the catalytic reactions of **1**; Figure S9: plausible mechanism for the Knoevenagel condensation reaction catalyzed by **1**; Figure S10: fluorescence images of the powder of **1** and **1/PAO10**; Figure S11: PXRD patterns for **1** [simulated (red), powder (black), and powder from **1/PAO10** (blue)]; Table S1: reported coordination polymers with dppa^{4-} ligand; Tables S2 and S3: selected structural parameters for **1** and **2**; Table S4: substrate scope for Zn-catalyzed Knoevenagel reaction; Table S5: comparison of various catalysts for the Knoevenagel reaction between benzaldehyde and propanedinitrile.

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