## Accepted Manuscript

Cluster-based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> coordination polymers based on aminofunctionalized tri-phenyl tetra-carboxylate: Bi-functional photo-luminescent sensing for Fe<sup>3+</sup> and antibiotics

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PII: S0143-7208(19)30810-1

DOI: https://doi.org/10.1016/j.dyepig.2019.107631

Article Number: 107631

Reference: DYPI 107631

- To appear in: Dyes and Pigments
- Received Date: 13 April 2019

Revised Date: 30 May 2019

Accepted Date: 6 June 2019

Please cite this article as: Li XS, An JD, Zhang HM, Liu JJ, Li Y, Du GX, Wu XX, Fei L, Lacoste JD, Cai Z, Liu YY, Huo JZ, Ding B, Cluster-based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> coordination polymers based on amino-functionalized tri-phenyl tetra-carboxylate: Bi-functional photo-luminescent sensing for Fe<sup>3+</sup> and antibiotics, *Dyes and Pigments* (2019), doi: https://doi.org/10.1016/j.dyepig.2019.107631.

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## Pictogram



# Cluster-Based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> Coordination Polymers Based

## On Amino-Functionalized Tri-Phenyl Tetra-Carboxylate:

# **Bi-Functional Photo-Luminescent Sensing for Fe<sup>3+</sup> and**

## Antibiotics

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Received Date (automatically inserted by publisher)

Abstract: Excess and deficiency of iron(III) and antibiotics from normal permissible limits will induce serious disorders, so their detection is important but challenging. In this work, the asymmetric amino-functionalized tetra-carboxylate H₄L (2'-amino-1,1':4',1"-terphenyl-3,3",5,5"-tetracarboxylic acid) containing large conjugated ter-phenyl aromatic backbones have been synthesized and employed. Through a one-pot powerful solvo-thermal synthetic strategy, a series of unique tri-nuclear cluster-based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> coordination polymers, namely  $[Ca_{1.5}(\mu_8-HL)(DMF)]_n$ (1),  $\{[Mg_{1.5}(\mu_7-HL)\cdot(H_2O)_2]\cdot 3H_2O\}_n$ (2) and  $\{[Cd_{1.5}(\mu_{10}-L)_{0.75}]_n \cdot H_2O \cdot DMF\}_n$  (3) have been successfully prepared. 1-3 exhibit excellent photo-luminescent properties and good fluorescence stability. Structural

analyses reveal that tri-nuclear Ca<sup>II</sup> secondary building blocks (SBUS) are linked via  $HL^{3-}$ , forming the 2D clustered-based micro-porous coordination polymer 1. As for 2, three carboxylate groups of partly de-pronated HL<sup>3-</sup> also link these neighboring tri-nuclear Mg<sup>II</sup> SBUS, which constructs the 2D Mg<sup>II</sup> coordination framework **2**. As for **3**, fully de-pronated L<sup>4-</sup> also links these neighboring tri-nuclear Cd<sup>II</sup> SBUS, which ultimately constructs the 3D micro-porous coordination framework 3. Experimental powder x-ray diffraction (PXRD) patterns coincide well with the theoretical patterns, which indicate that we have successfully synthesized the pure phase material 1-3. Photo-luminescent experiments demonstrate that coordination polymers 1-3 can be successfully applied towards bi-functional sensing for sensitive detection of  $Fe^{3+}$  and the antibiotics NZF (Nitrofurazone). To the best of our knowledge, this is the first example of the application of amino-functionalized tri-phenyl tetra-carboxylate based MOFs towards bi-functional discrimination of Fe<sup>3+</sup> and NZF antibiotics with high efficiency K<sub>sv</sub> values (For Fe<sup>3+</sup>:  $7.28 \times 10^4$  M<sup>-1</sup> for 1;  $3.38 \times 10^4$  M<sup>-1</sup> for 2 and  $3.29 \times$  $10^4$  M<sup>-1</sup> for **3** and for NZF antibiotics:  $4.47 \times 10^3$  M<sup>-1</sup> for **1**;  $4 \times 10^3$  M<sup>-1</sup> for **2** and 5.6  $\times 10^3 \, \text{M}^{-1}$  for **3**).

*Keywords:* Amino-functionalized; Tetra-Carboxylate; Cluster-Based; Sensing; Fe<sup>3+</sup>; Antibiotics

#### Introduction

With the development of modern industry, iron has been widely utilized; furthermore  $Fe^{3+}$  ions are considered to widely exist in the biological system, playing the crucial roles in many biochemical and physiological processes, such as DNA replication, cellular life cycles, hemoglobin formation, electron transfer and et al. [1-2]. When the amount of  $Fe^{3+}$  exceeds the normal concentrations, or if the amount of  $Fe^{3+}$  drops in the biological systems, the result can give rise to serious diseases such as methemoglobinemia, anemia and Alzheimer's, which also can interfere with metabolism and cellular homeostasis [3-6]. Thus, highly sensitive discrimination of  $Fe^{3+}$  ions in aqueous environments is interesting and crucial for protecting human health.

Since Alexander Fleming discovered penicillin in 1929 [7], antibiotics have been widely applied in the treatment of bacterial infections. Antibiotics have been developed into very important kind of medicines. These antibiotics medications widely exist in various fields such as aquacultures and biological systems, and can be widely utilized for treating bacterial infections in humans and animals bodies. The abuse of these medicines can give rise to an excessive concentration of antibiotics in diverse water environments such as surface water, groundwater, wastewaters, and even drinking water, especially in China [8]. Currently the detection methods for antibiotics are usually limited due to sophisticated devices, high-cost, time consuming, and complicated procedures. Among these methods are capillary electrophoresis, surface enhanced Raman spectroscopy, liquid chromatography tandem mass spectrometry and many more. [9-10]. Thus, the development of fast, cost-effective and convenient detection methods for antibiotics in aqueous environments is interesting and urgently needed.

In the recent thirty years, luminescent metal organic coordination frameworks (MOFs) have been especially interesting [11-12], because they can be utilized for the highly sensitive discrimination of different analytic objects such as environment pollutants, biomarker molecules, volatile organic compounds, enzymes, proteins and more [13-17]. These luminescent MOFs have tunable pore size, excellent structural stability, and large surface areas. These advantages make these fluorescent coordination materials have more competitiveness than other luminescent materials. More analytical objects can effectively interact with the large, tunable, porous surfaces of these fluorescent MOFs, which can enhance luminescent response, decrease the detection limit values and improve the sensitivity [18].

For these luminescent MOFs-based sensors, aromatic poly-carboxylate ligands are appealing and employed as bridging linkers because of their ideal rigid skeleton and good chemical stability [19]. Especially the building blocks of ter-phenyl poly-carboxylate, which have aroused great attention: (1) Ter-phenyl aromatic backbones possess rich conjugated  $\pi$ -electrons, which facilitate good

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photo-luminescent properties of these materials; (2) Introduction of electronic-rich aromatic ligands also has proven to be an efficient strategy to enhance photo-luminescent sensing properties of these coordination materials [20]; (3) -NH<sub>2</sub> functional group is interesting and has received great attention. For example, it is noted that the -NH<sub>2</sub> functional group can be introduced into the coordination material and effectively tune framework properties such as gas absorption/separation and catalytic properties [21]. However, to date, luminescent MOFs-based sensors based on asymmetric amino-functionalized tri-phenyl tetra-carboxylate are not reported [22].

We are interested in the construction of these coordination polymers possessing unique functional applications and beautiful architectures [23]. In this work,  $H_4L$ amino-functionalized tri-phenyl tetra-carboxylate (2'-amino-1,1':4',1"terphenyl-3,3",5,5"-tetracarboxylic acid) containing large conjugated ter-phenyl moieties have been utilized (Scheme 1 and Scheme 2). Based on H<sub>4</sub>L, through one-pot powerful solvo-thermal synthetic strategy, a series of unique tri-nuclear  $Mg^{II}$ Cd<sup>II</sup> coordination Ca<sup>II</sup>, and cluster-based polymers, namely (2)  $[Ca_{1.5}(\mu_8-HL)(DMF)]_n$ (1),  $\{[Mg_{1.5}(\mu_7-HL)\cdot(H_2O)_2]\cdot 3H_2O\}_n$ and  $\{ [Cd_{1.5}(\mu_{10}-L)_{0.75}]_n \cdot H_2O \cdot DMF \}_n$  (3) have been successfully prepared. PXRD patterns have been determined, and clearly indicate pure phases of coordination polymers 1-3. Photo-luminescence investigations suggested that 1-3 can be applied as the first example of bi-functional MOFs-based fluorescent probes for trace amounts of Fe<sup>3+</sup> and antibiotics NZF.

#### **Experiment Section**

**General remarks:** Amino-functionalized tri-phenyl tetra-carboxylate ligand  $H_4L$  can be prepared according to the previous reported procedures [24], which is also listed in the supporting material (Fig. S1). Deionized water has been utilized as the solvent. All the other chemical regents can be commercially purchased and utilized without additional purification. A Perkin-Elmer 240 elemental analyzer is utilized for

elemental microanalyses of C, H and N. A Rigaku D/Max-2500 X-ray diffractometer apparatus equipped with Cu-Ka radiation is utilized for Powder X-ray diffraction characterization of 1-3. An NETZSCH TG 209 apparatus with a 10 °C min<sup>-1</sup> heating rate is utilized for thermogravimetric analysis. PerkinElmer Lambda 35 utilized to recording UV-vis adsorption spectrophotometer was spectra. Photo-luminescent lifetime and quantum yield were performed using a FS5 Spectrometer (Edinburgh). Eclipse Fluorescence Fluorescence А Cary spectrophotometer (Agilent Technologies) is utilized for photo-luminescence sensing experiments, and is equipped with a plotter unit and a quartz cell  $(1 \text{ cm} \times 1 \text{ cm})$  in the phosphorescence mode.

**Preparation of**  $[Ca_{1.5}(\mu_8-HL)(DMF)]_n$  (1): Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (141.6 mg, 0.6 mmol) and H<sub>4</sub>L (42.1 mg, 0.1 mmol) were mixed and stirred for 0.5 h in water (2 mL) and DMF (6 mL), then HNO<sub>3</sub> (5 µL, 0.33 M) was added. Then the mixed solutions were put into a Teflon vessel in a steel autoclave. The temperature of steel autoclave is programmatic controlled to be heated to 90 °C for 0.5 hour and kept at 90 °C for 72 h, then cooled down to ambient temperature during the period of 48 h. The obtained colorless block-shaped crystals were cleansed several times by water and diethyl ether. Yield: 36 % based on H<sub>4</sub>L. Elemental analysis calculations (%) for C<sub>25</sub>H<sub>19</sub>Ca<sub>1.5</sub>N<sub>2</sub>O<sub>9</sub>: C 54.44, H 3.47, N 5.07; found: C 54.89, H 3.76, N 5.67. FT-IR data (cm<sup>-1</sup>): 3347(bm), 1715(m), 1611(w), 1648(w), 1569(w), 1385(s), 1225(m), 1137(w), 1106(m), 779(s), 732(s), 678(s).

**Preparation of {[Mg<sub>1.5</sub>(\mu\_7-HL)·(H<sub>2</sub>O)<sub>2</sub>]·3H<sub>2</sub>O}<sub>n</sub> (2): MgCl<sub>2</sub>·6H<sub>2</sub>O (61.0 mg, 0.3 mmol) and H<sub>4</sub>L (42.1 mg, 0.1 mmol) were mixed and stirred for 0.5 h in water (2 mL) and DMF (6 mL), then HNO<sub>3</sub> (5 \muL, 0.33 M) was added. Then the mixed solutions were put into a Teflon vessel in a steel autoclave. The temperature of steel autoclave is programmatic controlled to be heated to 90 °C for 0.5 hour and kept at 90 °C for 96 h, then cooled down to ambient temperature during the period of 48 h. The obtained colorless block-shaped crystals were cleansed several times by water and diethyl ether. Yield: 49 % based on H<sub>4</sub>L. Elemental analysis calculations (%) for** 

C<sub>22</sub>H<sub>22</sub>Mg<sub>1.5</sub>NO<sub>13</sub>: C 48.50, H 4.07, N 2.57; found: C 49.11, H 3.71, N 2.89. FT-IR data (cm<sup>-1</sup>): 3314(bs), 1715(w), 1630(s), 1540(s), 1480(s), 1251(w), 1104(w), 795(m), 740(m), 725(m), 663(w).

**Preparation of** {[ $Cd_{1.5}(\mu_{10}-L)_{0.75}$ ]<sub>n</sub>·H<sub>2</sub>O·DMF}<sub>n</sub> (3): CdCl<sub>2</sub>·2.5H<sub>2</sub>O (68.5 mg, 0.3 mmol) and H<sub>4</sub>L (42.1 mg, 0.1 mmol) were mixed and stirred for 0.5 h in water (2 mL) and DMF (6 mL), then HNO<sub>3</sub> (5 µL, 0.33 M) was added. Then the mixed solutions were put into a Teflon vessel in a steel autoclave. The temperature of steel autoclave is programmatic controlled to be heated to 90 °C for 0.5 hour and kept at 90 °C for 72 h, then cooled to ambient temperature during the period of 48 h. The obtained colorless block-shaped crystals can be cleansed several times by water and diethyl ether. Yield: 36 % based on H<sub>4</sub>L. Elemental analysis calculations (%) for C<sub>19.5</sub>H<sub>16.5</sub>Cd<sub>1.5</sub>N<sub>1.75</sub>O<sub>8</sub>: C 40.95, H 2.91, N 4.29; found: C 41.17, H 2.67, N 3.71. FT-IR data (cm<sup>-1</sup>): 3408(br), 1660(m), 1615(m), 1612(m), 1578(s), 1446(m), 1369(s), 1252(w), 1101(m), 778(s), 751(m), 725 (s).

**X-ray Crystallography.** Bruker SMART 1000 CCD diffractometer apparatus is equipped with graphite-monochromatic Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å), which is utilized to determine single crystal diffraction intensities for **1-3**. A  $\omega$ - $\varphi$  scanning strategy was utilized adopting Lorentz polarization and absorption corrections. Direct methods are utilized to refine the structures of **1-3**. Full-matrix least-squares techniques utilizing the SHELXL-2014 program are also applied to refine the structure. Aromatic ring hydrogen atoms were allocated geometrically, isotropic thermal parameters of these hydrogen atoms are 1.2 times than those hydrogen atoms attached to carbon atoms. Guest solvent molecules are highly disordered and cannot be precisely allocated utilizing X-ray crystallography, the SQUEEZE strategy has been utilized to remove these guest solvent molecules in the void spaces [25]. Additionally, guest solvent molecules can be further analyzed by elemental analysis and thermal analysis. CCDC-1859883 (**1**), CCDC-1859892 (**2**), CCDC-1870694 (**3**) represent the supplementary crystallographic data for this work. These crystal data can be downloaded free of charge from Cambridge's Crystallographic Data Centre via

the website <u>www.ccdc.cam.ac.uk/data\_request/cif</u>. Crystallographic data and refinement details for **1-3** are summarized in Table 1. Selected bond lengths and angles of **1-3** are listed in Table S1.

#### **Results and Discussion**

**Structural descriptions of coordination polymers 1-3** Crystal X-ray diffraction characterization results reveal that the fundamental structural unit of complex **1** contains a 1.5 Ca<sup>II</sup> center (Ca2 and 0.5 Ca1), one partially de-pronated HL<sup>3-</sup> and one coordinated DMF molecule (Fig. 1). Ca1 is six-coordinated by six O atoms (O1A, O1B, O3A, O3B, O5B, O5A) from HL<sup>3-</sup>, while Ca2 is six-coordinated by five oxygen atom (O1A, O2A, O3A, O4A, O6 and O9) from HL<sup>3-</sup> carboxylate groups and one oxygen atom (O9) from the terminally coordinated DMF. Ca1, Ca2 and Ca2A are inter-linked through oxygen atoms of carboxylate groups generating tri-nuclear Ca<sub>3</sub>O<sub>4</sub> clusters as secondary cluster-based building blocks (SBUS).

Its three carboxylate groups of each  $\text{HL}^{3-}$  ligand also link three neighboring tri-nuclear Ca<sub>3</sub>O<sub>4</sub> SBUS adopting the bridging multi-dentate coordination mode, which ultimately forms the 2D clustered-based micro-porous coordination material **1** (Fig. 2). Neighboring tri-nuclear Ca<sup>II</sup> cluster separations are 9.962(1) Å and 14.843(1) Å (For **1**), which also can be observed through the crystallographic *a*-axis. A one-dimensional channel with dimensionality of 4.978(1) Å × 6.568(6) Å can be observed in the packing architecture of **1** viewed along the crystallographic *a* axis (Fig. S2). The porous percentage in MOF **1** were calculated by Platon program, the calculated results were 1131.8 Å, *ca* 19.0 % free solvent molecules can be accessible to the void in **1** (5957.3Å<sup>3</sup>). On the other hand, coordinated oxygen atoms from HL<sup>3-</sup>, DMF carbon and DMF oxygen atoms were involved into C-H···O hydrogen bonds (C(23)-H(23)···O(3), 3.148(1) Å; C(25)-H(25A)-O(9), 2.785(8) Å). Such hydrogen bonding interactions also play an important role in stabilizing the whole coordination network of **1**.

As for the coordination material 2, structural analysis reveals that the

fundamental structural unit contains a 1.5  $Mg^{II}$  center (Mg1 and 0.5 Mg2), one partially de-pronated  $HL^{3-}$  and two coordinated water molecules (Fig. 3). Mg1 is six-coordinated by four oxygen atoms (O1, O5A, O6A, O7A) from  $HL^{3-}$  and two oxygen atoms (O9, O10) from two coordinated H<sub>2</sub>O molecules. While Mg2 is six-coordinated by six carboxylate oxygen atoms (O2, O2A, O5A, O5B, O8A and O8B) from  $HL^{3-}$ . Mg1, Mg2 and Mg1A are linked via carboxylate oxygen atoms forming tri-nuclear Mg<sub>3</sub>O<sub>4</sub> clusters as secondary cluster-based building blocks (SBUS).

Its three carboxylate groups of each  $HL^{3-}$  ligand also link three neighboring tri-nuclear Mg<sup>II</sup> SBUS adopting a multi-dentate bridging mode, which ultimately forms the 2D clustered-based micro-porous coordination material **2** (Fig. 4). Neighboring tri-nuclear Mg<sup>II</sup> cluster separations are 9.557(1) Å and 14.80(1) Å (For **2**) can be observed through the crystallographic *a* axis. One-dimensional micro-porous channels can be observed in the packing architecture of **2** viewed along the crystallographic *a* axis. The porous percentage in MOF **2** were calculated by the Platon program, the calculated results were 2552.8 Å, *ca* 39.9 % solvent accessible void in **2** (6392.9 Å<sup>3</sup>). On the other hand, coordinated oxygen atoms from  $HL^{3-}$ , coordinated water oxygen atoms were involved into N-H…O and O-H…O hydrogen bonds (N(1)-H(1B)…O(1), 3.052(5) Å; O(9)-H(9B)-O(4), 2.662(7) Å; O(10)-H(10A)-O(4), 2.715(9) Å). Such hydrogen bonding interactions also play an important role in stabilizing the 2D micro-porous network of **2**.

As for coordination material **3**, structural analysis reveals that the fundamental structural unit contains 1.5 Cd<sup>II</sup> center (Cd1 and 0.5 Cd2) and 0.75 full de-pronated  $L^{4-}$  (Fig. 5). Cd1 is seven-coordinated by seven oxygen atoms (O1, O3A, O4A, O5B, O5C, O6B, O6C) from  $L^{4-}$  carboxylate groups, while Cd2 is six-coordinated by six oxygen atoms (O2, O2A, O5B, O5C, O5D, O5E) from carboxylate groups of  $L^{4-}$ . Cd1, Cd2 and Cd1A are linked via carboxylate oxygen atoms forming tri-nuclear Mg<sub>3</sub>O<sub>4</sub> clusters as secondary cluster-based building blocks (SBUS).

Four carboxylate groups of each L<sup>4-</sup> also link these neighboring tri-nuclear Cd<sup>II</sup> SBUS adopting multi-dentate coordination mode, which ultimately forms the 3D clustered-based micro-porous coordination material **3** (Fig. S3). Neighboring tri-nuclear Cd<sup>II</sup> cluster separations are 9.889(1) Å, 10.464(1) Å and 14.90(1) Å (For **3**) can be observed, respectively. One-dimensional micro-porous channels with dimensionality of 6.718(8) Å  $\times$  6.648(6) Å can be observed in the packing architecture of **3** viewed along the crystallographic *b* axis. The porous percentage in MOF **3** were calculated by Platon program, the calculated results were 997.9 Å, *ca* 35.8 %solvent accessible void in **3** (2785.1 Å<sup>3</sup>).

**PXRD, FT-IR, Thermal stabilities and Photo-luminescent properties of coordination polymers 1-3** Powder X-ray diffraction (PXRD) patterns have been determined for the crystalline materials of **1-3**. As shown in Fig. 6, both peaks position and lines sharpness of experiment PXRD patterns are consistent with these simulated theoretical PXRD patterns based on crystal X-ray data. The result also unambiguously reveals that these corresponding as-synthesized samples have the same structures to that that of X-ray crystal data [26-27]. The slight dissimilarities in reflection intensities should be correlated with the crystal orientation difference of powder samples [28]. As for coordination material **3**, varied-temperature powder X-Ray patterns for the highly-dimensional Cd<sup>II</sup> coordination framework also has been made. As exhibited in Fig. 7, structure of **3** can remain stable up to 150 °C indicating the coordination material **3** has good thermal stability.

Thermogravimetric decay analysis (TGA) curves of coordination materials **1-3** also have been determined (Fig. S4). As for **1**, the weight loss varying from 30 °C to 250 °C are 12.6 %, which should be correlated with the weight loss for one coordination DMF. As for **2**, the weight loss varying from 30 °C to 150 °C are 16.3 % (calcd 16.5 %), which should be correlated with the weight loss for two coordination water and three lattice water molecules. As for **3**, the weight loss varying from 30 °C to 250 °C are 15.1 % (calcd 15.9 %), which should be correlated with the weight loss for materials **1** and the water and one free DMF [29]. As for **1**-**3**, the weight loss from 250 °C to 800 °C should correspond for the framework collapse of these coordination polymers. The remaining residue at 800 °C should correspond for the metal oxide.

FT-IR spectra of coordination polymers **1-3** also have been determined, these representative absorption bands for solvent and the building blocks of  $HL^{3-}$  or  $L^{4-}$  can be observed. As for **1-3**, broad and medium bands centered at *ca*. 3400 cm<sup>-1</sup> can be observed, which can be correlated with the typical characteristic band of coordinated and free water or DMF in the coordination network. The absence of strong peaks located at *ca*. 1700 cm<sup>-1</sup> demonstrates complete de-protonated carboxylic groups of  $L^{4-}$  in **3**. For **1-3**, the symmetric and asymmetric stretching vibrations for carboxylate groups are located in the ranges of 1369-1480 and 1540-1662 cm<sup>-1</sup>, respectively, which is consistent with previous literature results [30]. All the FT-IR typical absorption bands and thermogravimetric analyses are well consistent with single crystal X-ray result of coordination polymers **1-3**.

It is well known that coordination polymers can effectively tune their emission wavelengths and strengths through rational incorporation of different conjugated aromatic building blocks. Through introduction of diverse conjugated aromatic organic linkers and metal centers such as 2p, 3d and 4f, the synthetic strategy is efficient for preparing unique photo-luminescent materials [31]. Because H<sub>4</sub>L contains large ter-phenyl rigid backbones, it is anticipated to generate excellent photo-luminescent emissions. Therefore, we are greatly interested to determine photo-luminescent properties of H<sub>4</sub>L and coordination polymers **1-3**, respectively.

As exhibited in Fig. S6, at the room temperature, the amino-functionalized tri-phenyl tetra-carboxylate building block has strong photo-luminescent emissions in water solutions, with a maximum located at 398 nm for free H<sub>4</sub>L ( $\lambda_{ex} = 330$  nm). The strong photo-luminescent band of H<sub>4</sub>L also facilitate that the coordination polymers **1-3** can be applied in the photo-luminescent detection. For H<sub>4</sub>L, the photo-luminescent emissions can be correlated with conjugated ter-phenyl chromospheres, therefore the corresponding bands can be defined as  $\pi$ - $\pi$ \* transition emission. When the crystalline materials of **1-3** were ground into powder samples and suspended into the water solutions, the 2D and 3D metal-organic materials **1-3** also exhibit the strong luminescent emission peaks (maximum peak location: for **1**: 403 nm; for **2**: 402 nm; for **3**: 400 nm upon excitation at 300 nm). In comparison with that

of free H<sub>4</sub>L, these emissions of **1-3** can be ascribed to intra-ligand photo-luminescent emissions because similar photo-luminescent bands can be found for the amino-functionalized tri-phenyl tetra-carboxylate H<sub>4</sub>L in the aqueous solutions [32]. On the other hand, a shoulder emission of **1** at 450 nm also can be observed, which is red-shifted than that of free H<sub>4</sub>L and may be ascribed to ligand to metal charge transfer (MCLT). As illustrated in the previous review literature [33], charge-transfer luminescence are often observed in MOFs, LMCT/MLCT luminescence can also compete with ligand-based luminescence, which can result in both LMCT/MLCT and ligand-based emission bands. Further the completion between LMCT and ligand-based emission bands may make that the intensity of ligand-based band centered at 400 nm is slightly weaker than that of free H<sub>4</sub>L.

Photo-luminescent quantum and the lifetime of cluster-based coordination compounds 1-3 also have been determined. The quantum yield is 12.23 % for 1, 10.89 % for 2 and 8.94 % for 3, which is good and can be correlated with large ter-phenyl conjugated aromatic systems. The result can be compared with the previously reported coordination polymers [34]. On the other, the lifetime of luster-based coordination compounds also has been determined indicating 5.35 ns for 1, 4.75 ns for 2 and 3.16 ns for 3 (Fig. S12 and Table S3). Such result also can be compared with recently reported zinc(II) coordination probes (3.71 ns) [35].

Photo-luminescent sensing for Fe<sup>3+</sup> by Cluster-Based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> Coordination Polymers 1-3. Inorganic-organic hybrid coordination materials have aroused great attention because of their tunable fluorescent emissions and broad application prospects as photo-luminescent materials. Because these materials can deliberately change their emission strengths and wavelengths, the synthesis of coordination materials can be tuned through judiciously selecting diverse organic building blocks and central metal ions/clusters, which is quite important for obtaining these new photo-luminescent coordination materials.

In this work, the fluorescent properties of  $H_4L$  and materials 1-3 based on  $H_4L$  in water solutions have been investigated. Furthermore, the aqueous stability of

coordination polymers **1-3** was also characterized. The solid-state samples of coordination materials **1-3** were suspended into the aqueous solutions for 12 h, then filtered, the resulting solid state samples were then dried by the vacuum oven. These obtained solid state samples were analyzed by PXRD patterns. The PXRD patterns of **1-3** after suspending in the aqueous solutions for 12 hours still are consistent with theoretical PXRD patterns based on single-crystal X-ray data. The result reveals that structures of coordination polymers **1-3** remain unchanged in the aqueous solutions. On the other hand, the photo-luminescent peaks are almost unchanged, indicating coordination polymers **1-3** have good fluorescent stability for at least 12 h. The good photo-luminescent stability may be ascribed to good solvent dispersibility and stability of coordination materials **1-3** in the aqueous solutions. Therefore, coordination materials **1-3** may be considered as good candidates as fluorescent probes in aqueous solutions.

The solid-state samples of coordination polymers 1-3 were then tested for the sensing of diverse metal ions. In order to investigate diverse photo-luminescent responses to metal ions, the crystalline materials of 1-3 were ground into powder samples, these samples are suspended into the water solutions of the same concentration (60 µM) containing diverse metal chloride salt (Na<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>,  $K^+$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Ag^+$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ) in neutral conditions. As shown in Fig. 8 and Fig. 9(a),  $Fe^{3+}$  exhibits a significant fluorescent quenching effect, while other metal ions only have a slight effect. Because Al<sup>3+</sup> can also partially quench the signal, therefore the  $k_{sv}$  value is also compared in 1 (Fig. S11 (a)), the  $K_{sv}[Fe(III)]/K_{sv}[Al(III)]$  comparison value is 6.69, such value can be compared with the comparison value in the recently reported Cd(II)-organic frameworks with chelating NH<sub>2</sub> sites for selective detection of Fe(III) [36]. Further we also compare the emission spectra intensity of 1 dispersed in water suspensions upon addition of Fe(III) ions (30µM), simultaneous addition of Fe(III) ions (30µM) and some other metal cations (150 µM) (Fig. S11(b)), which also indicate selective sensing for Fe(III). PXRD patterns for 1-Fe<sup>3+</sup>, 2-Fe<sup>3+</sup> or 3-Fe<sup>3+</sup> were also characterized and are consistent with theoretical PXRD patterns based on crystal structures, revealing that

coordination structures of micro-porous materials **1-3** remain unchanged. The result demonstrates coordination polymers **1-3** have highly selective discrimination of  $\text{Fe}^{3+}$  in aqueous solutions. Thus, coordination polymers **1-3** should be utilized as the ideal coordination probe materials for selective photo-luminescent detection of  $\text{Fe}^{3+}$  ions.

In order to investigate photo-luminescent detection limit of 1 as a fluorescent probe for Fe<sup>3+</sup>, as shown in Fig. 9(b), a series of suspensions of 1-Fe<sup>3+</sup> (3  $\mu$ M to 286.2 μM) in water solutions have been synthesized by adding diverse concentrations of  $Fe^{3+}$  into the water solutions containing the suspension of coordination material **1**. It is noted that when the concentrations of  $Fe^{3+}$  gradually increase, the photo-luminescent intensity of 1 gradually decreases. As shown in Fig. 9(c), photo-luminescent intensity has a liner correlation with concentration when the concentrations of Fe<sup>3+</sup> changes from 3  $\mu$ M to 286.2  $\mu$ M. The photo-luminescent detection limit of **1** for Fe<sup>3+</sup> can be calculated using the below equation: detection  $\lim_{k \to \infty} 1 = 3\sigma/k$  (where k is the slope between the fluorescent intensity vs. log Fe<sup>3+</sup> at lower concentration;  $\sigma$  is the standard deviation of blank determination) [37]. To characterize the correlation between Fe<sup>3+</sup> concentration and quenching results, the linear fit plot of photo-luminescent intensity vs.  $Fe^{3+}$  concentration was also made (Fig. 9(d)), which can be fitted through the equation  $I_0/I = 1 + K_{sv}[Fe^{3+}]$  ( $I_0$  and I are the photo-luminescent intensities of 1 before and after adding  $Fe^{3+}$ , respectively;  $K_{sv}$  is the photo-luminescent quenching rate constant; and  $[Fe^{3+}]$  is the concentration of  $Fe^{3+}$ ). The K<sub>sv</sub> value is calculated to be  $7.28 \times 10^4$  L·mol<sup>-1</sup> and low detection limit (5.91 × 10<sup>-6</sup> M (S/N = 3)) demonstrating high photo-luminescent quenching efficiency for Fe<sup>3+</sup> based on the emissions of coordination material **1**. Additionally, as listed in Fig. 10 and Table S2, K<sub>sv</sub> values are calculated to be  $3.38 \times 10^4$  L·mol<sup>-1</sup> for **2** and  $3.29 \times 10^4$  L·mol<sup>-1</sup> for **3**, which also indicate high quenching efficiency of Fe<sup>3+</sup> through the photo-luminescent emissions of coordination materials 2-3 (Fig. S9).

To understand the photo-luminescent sensing mechanism of the fluorescence quenching effect of coordination materials 1-3 toward  $Fe^{3+}$ , further experiments were carried out. As for coordination materials 1-3, the investigations were listed as follows: (1) PXRD patterns of samples after photo-luminescent quenching is also compared

and almost identical with that of the as-synthesized powder samples, which indicate coordination materials 1-3 are still stable in the detection process (Fig. S8); (2) The lifetime of fluorescence is an important parameter in judging the mechanism of fluorescence quenching, which can often reflect whether the quenching effect is based on a static or a dynamic mechanism [38]. As shown in Fig. S12 and Table S3, when  $Fe^{3+}$  is added, the luminescence lifetimes of 1-3 gradually decrease, indicating the existence of dynamic quenching mechanism. As described in the recently reported lanthanide chemosensor  $[La(TPT)(DMSO)_2] \cdot H_2O$  (H<sub>3</sub>TPT = p-terphenyl-3,4",5tricarboxylic acid) [39], such dynamic quenching mechanism can be governed by the diffusive collisions between the electron-deficient Fe<sup>3+</sup> and the terphenyl moieties of  $H_4L$ ; (3) on the other hand, as demonstrated in the Stern-Volmer plot of 1 (Fig. 9(d)), there is a non-linear and upward curvature at higher concentrations of  $Fe^{3+}$  ions, suggesting the static quenching mechanism (namely the formation of ground-state non-fluorescent complex between Fe<sup>3+</sup> and coordination frameworks) also exist. Cycle performance for detection of  $Fe^{3+}$  is also explored, however no good cycle performance can be observed, which also behave the existence of the interactions between Fe<sup>3+</sup> and coordination compounds. Generally the NH<sub>2</sub>- group in luminescent materials can be regarded as an electron-donating group and suitable for binding the electron accepting metal ions, which may be important in the interaction with  $Fe^{3+}$ . For example, the luminescent Cd(II)-organic frameworks with chelating NH<sub>2</sub> sites also behave highly sensitive and selective detection of Fe(III) [36]. Overall, the combination of dynamic and static quenching mechanism may be important for fluorescence quenching effect towards Fe(III).

It is also noted that the shoulder peak at about 450 nm increased with increasing the concentration of Fe<sup>3+</sup>. Because the shoulder band centered at 450 nm also is observed in these coordination polymers, which can be assigned as ligand to metal transfer (LMCT). Therefore when LMCT and ligand-based emission bands co-exist and compete in the coordination polymers, if the ligand-based emission bands gradually decrease, the band center at about 450 nm based on LMCT may gradually increase.

In comparison with the heavy metal ions  $Cd^{2+}$  in **3**,  $Fe^{3+}$  is not so toxic, therefore the detection of  $Fe^{3+}$  by the non-toxic alkali  $Ca^{II}$  and  $Mg^{II}$  metal coordination polymers **1** and **2** should be more meaningful and advantageous in the detection process. As far as we know, work on these  $Ca^{II}$  and  $Mg^{II}$  coordination materials as photo-luminescent probes for discriminating and sensitively detecting  $Fe^{3+}$  is still scarcely reported [40-42]. The experiments demonstrated that coordination materials **1-3** represent the scarcely reported example of amino-functionalized tri-phenyl tetra-carboxylate MOFs-based probes for detecting  $Fe^{3+}$  with high selectivity and high sensitivity [43-44].

Chemosensor for antibiotics by Cluster-Based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> Coordination Polymers 1-3. Nowadays antibiotics have been widely utilized for treating bacterial infections in humans and animals bodies. However when these medicines containing antibiotics is overused, they can become a class of organic pollutants in the natural water environments. Thus, rapid discrimination of antibiotics in water environments is of great importance considering that overuse of antibiotics may be harmful to human health and environmental protection. Considering the good photo-luminescence behaviors and high porosities of coordination materials 1-3, it will be interested to utilize them as potential fluorescent sensors for detecting antibiotics such as Nitrofurantoin (NFT), Furazolidone (FZD), Nitrofurazone (NZF), Ornidazole (ORN), Ronidazole (RNZ), Dimetridazole (DMZ), Metronidazole (MDZ), Sulfamethazine (SMZ), Sulfadiazine (SDZ), Thiamphenicol (THI) and Chloramphenicol (CHL). To explore the ability of 1-3 to detect a trace quantity of antibiotics, photo-luminescent experiment were made by gradually adding antibiotics into water suspensions of coordination polymers 1, 2 and 3. During the titration experiments, the samples of coordination polymers 1, 2 or 3 were added into water solutions (2.5 mL), and then a selected antibiotics are subsequently added forming the aqueous solutions containing different antibiotics (180 µM). The fluorescence quenching percentage in terms of a certain amount of different antibiotics at ambient temperature is demonstrated in Fig. 11. Obviously, the sensing experiments show high photo-luminescent quenching of

coordination materials 1-3 occurs upon the addition of different antibiotics, and the order of quenching efficiency is NZF>NFT>MDZ>DMZ>RNZ>SMZ>CHL>ORN>FZD>SDZ>THI for 1. NZF>NFT>MDZ>RNZ>DMZ>SMZ>CHL>ORN>FZD>SDZ>THI for 2. and NZF>NFT>MDZ>DMZ> RNZ>SMZ>CHL>FZD>ORN>SDZ>THI for 3. It is also noted that coordination polymers 1, 2 and 3 have the highest quenching efficiencies toward NZF (Nitrofurazone).

Furthermore, the fluorescence intensity vs. NZF antibiotics plot is also made according to the Stern-Volmer equation. The SV plots for NZF are nearly linear in the concentration ranges varying from 0 to 2.4 mM. Based on the experimental data exhibited in Fig.12 and Fig. S10 in the ESI, the K<sub>sv</sub> of coordination polymers **1-3** are calculated to be  $4.47 \times 10^3$  M<sup>-1</sup> (for **1**),  $4 \times 10^3$  M<sup>-1</sup> (for **2**) and  $5.6 \times 10^3$  M<sup>-1</sup> (for **3**). The detection limits of **1**, **2** and **3** toward NZF were  $9.61 \times 10^{-5}$  M (for **1**),  $1.86 \times 10^{-4}$  M (for **2**) and  $7.67 \times 10^{-5}$  M (for **3**), respectively (Tables S2 in the ESI<sup>†</sup>). Such high K<sub>sv</sub> values and low detection limits are comparable to the value for the reported Zr(IV)-MOFs.

As for the sensing mechanism of NZF, further experiments including PXRD pattern, fluorescence lifetime and UV-visible absorption spectra were carried out. The investigations were listed as follows: (1) PXRD patterns of samples 1-3 after photo-luminescent quenching is also compared and almost identical with that of the as-synthesized powder samples, which indicate cluster-based coordination polymers 1-3 are still stable in the detection process (Fig. S8); (2) The luminescence lifetimes of 1-3 in the absence or presence of NFs are almost the same (Fig. S12 and Table S3), indicating that there is no significant interactions between these coordination polymers 1-3 and the NZF analytes [45-51]; (3) UV-vis absorption spectra of NFs exhibit the overlap with the excitation spectrum of 1-3 between 300 and 450 nm (Fig. S5), there should exist a competitive absorption for the light source energy between 1-3 and NFs; (4) On the other hand, we also examine the cycling performance for detecting NZF antibiotics. As shown in Fig. S7, it can be observed partial photo-luminescent recovery can be accomplished through simple washing these

suspended powders by water, which also indicates there should not strong coordination interactions between coordination polymers **1-3** and NZF; (**5**) It is also noted that the shoulder peak at about 450 nm also increased with increasing the concentration of antibiotics. A possible reason is that when LMCT and ligand-based emission bands co-exist and compete in the coordination polymers, if the ligand-based emission bands gradually decrease, the band center at about 450 nm based on LMCT may gradually increase, which also exhibit the existence of photo-luminescent energy transfer (PET) mechanism.

As a result, the photo-luminescent energy transfer (PET) mechanism enables NZF to have a high photoluminescence quenching effect compared with other studied antibiotics. Similar energy transfer mechanism can be observed in the recently reported sodium(I)–europium(III)-organic sensor for nitrofuran antibiotics detection [52]. However, as far as we know, this represents the first example for photo-luminescent probes for NZF antibiotics utilizing amino-functionalized tri-phenyl tetra-carboxylate based cluster-based coordination polymers **1-3**.

### **Conclusions and Perspectives**

When modern chemical industry is developed in the high-speed model, iron and antibiotics has been widely utilized. Scientists also **gradually realized that**  $Fe^{3+}$ and antibiotics have the important applications in the biochemical processes and medicinal cure. Thus, the development of new sensing materials to detect  $Fe^{3+}$  and antibiotics from the water environment is quite important. In this work amino-functionalized tri-phenyl tetra-carboxylate H<sub>4</sub>L (2'-amino-1,1':4',1''-terphenyl-3,3'',5,5''- tetracarboxylic acid) have been employed. A series of unique tri-nuclear cluster-based  $Ca^{II}$ ,  $Mg^{II}$  and  $Cd^{II}$  coordination polymers, namely { $[Ca_{1.5}(\mu_5-HL)\cdot(DMF)]_n$  (1),  $[Mg_{1.5}(\mu_7-HL)\cdot(H_2O)_2]_n$  (2) and  $[Cd_3(\mu_{10}-L)_{1.5}]_n$ (3) have been isolated under the powerful solvo-thermal methods. Structural analyses reveal that 1 contains tri-nuclear  $Ca^{II}$  secondary building blocks (SBUS), which are further linked via  $HL^{3-}$  forming the 2D clustered-based micro-porous coordination

polymer 1. As for 2, three carboxylate groups of partly de-pronated HL<sup>3-</sup> link these neighboring tri-nuclear Mg<sup>II</sup> SBUS, which constructs the 2D Mg<sup>II</sup> clustered-based coordination material 2. As for 3, four carboxylate groups of fully de-pronated  $L^{4-}$ also link these neighboring tri-nuclear Cd<sup>II</sup> SBUS, which ultimately constructs the 3D clustered-based coordination material 3. PXRD patterns have been characterized confirming coordination polymers 1-3 are pure samples. Photo-luminescent investigations demonstrated that 1-3 can be utilized as bi-functional sensors for Fe<sup>3+</sup> and NZF antibiotics with high efficiency  $K_{sv}$  values (For Fe<sup>3+</sup>:  $7.28 \times 10^4 \text{ M}^{-1}$  for 1;  $3.38 \times 10^4$  M<sup>-1</sup> for **2** and  $3.29 \times 10^4$  M<sup>-1</sup> for **3** and for NZF antibiotics:  $4.47 \times 10^3$  M<sup>-1</sup> for 1;  $4 \times 10^3$  M<sup>-1</sup> for 2 and  $5.6 \times 10^3$  M<sup>-1</sup> for 3). The result also represents these asymmetrical  $\pi$ -electron-rich aromatic polycarboxylate linkers have great applications in the preparation of these unique cluster-based coordination polymers with beautiful structural motifs and ideal photo-luminescent sensing properties. On the basis of this work, further design, synthesis and functional application characterization of coordination materials based on these rigid asymmetrical  $\pi$ -electron-rich ligands are also under way in our laboratory.

**Supporting Information Available:** Listings of Crystallographic data for **1-3** in CIF format, Selected Bond Lengths [Å] and Angles [°] of **1-3**, PXRD patterns of **1-3**, TGA curve of **1-3**, Photo-luminescent spectra of  $H_4L$  and coordination polymers **1-3** dispersed in water solutions..

**Acknowledgments.** This work was supported financially by the Foundation of Development Program of Future Expert in Tianjin Normal University (WLQR201801) , the Open Project of Key Lab Adv Energy Mat Chem (Nankai Univ), 111 project (B12015), Natural Science Foundation of Tianjin (Grant no. 18JCYBJC89700), Young Scientist Fund (Grant no. 21301128) and the Program for Innovative Research Team in University of Tianjin (TD13-5074).

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	1	2	3
empricial formula	$C_{50}H_{38}Ca_3N_4O_{18}$	C <sub>22</sub> H <sub>22</sub> Mg <sub>1.5</sub> NO <sub>13</sub>	$C_{19.5}H_{16.5}Cd_{1.5}N_{1.75}O_8$
Fw	1103.08	544.87	571.96
crystal syst.	Monoclinic	Monoclinic	Monoclinic
Space group	C <sub>2</sub> /c	$I_2/a$	I <sub>2</sub> /m
temperature	173(2)	100.00(10)	135.00(10)
a (Å)	23.2843(19)	24.4785(5)	10.4641(4)
b (Å)	9.9618(8)	9.5570(2)	9.8893(4)
c (Å)	27.309(3)	28.0137(6)	27.0153(10)
α (°)	90	90	90
β (°)	109.873(3)	102.712(2)	94.963(4)
γ (°)	90	90	90
$V(\mathring{A}^{3})$	5957.3(9)	6392.9(2)	2785.15(17)
Z	4	8	4
<i>F(000)</i>	2280	2024.0	1144.0
$\rho (Mg/m^3)$	1.230	1.020	1.147
abs coeff (mm <sup>-1</sup> )	0.345	0.953	9.599
data/restraints/params	5353/1098/480	5665/50/329	2645/11/189
GOF	1.050	1.073	1.060
$R1^{a}(I=2\sigma(I))$	0.0570	0.0502	0.0398
WR2 <sup>a</sup> (I= $2\sigma(I)$ )	0.1136	0.1461	0.1087

### Table 1 Crystal Data and Structure Refinement Information for Compounds 1-3.

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



Scheme 1. Synthesis of amino-functionalized tri-phenyl tetra-carboxylate H<sub>4</sub>L.



Scheme 2. Three different coordination modes of  $H_4L$  in 1-3.



**Fig 1.** The fundamental structural unit of  $\{[Ca_{1.5}(\mu_8-HL)\cdot(DMF)\}_n(1).$ 



**Fig 2**. 2D Cluster-based  $Ca^{II}$  Coordination Framework of **1**.



Fig 3. The fundamental structural unit of  $[Mg_{1.5}(\mu_7-HL)(H_2O)_2]_n$  (2).



**Fig 4**. Trinuclear Mg<sup>II</sup> SBUS are linked via HL<sup>3-</sup> forming the 2D Cluster-based Mg<sup>II</sup> Coordination Framework of **2**.



**Fig 5.** The fundamental structural unit of  $[Cd_{1.5}(\mu_{10}-L)_{0.75}]_n$  (3).



**Fig. 6** Powder X-Ray patterns for (a) the Ca<sup>II</sup> coordination frameworks of **1**; (b) Mg<sup>II</sup> coordination frameworks of **2**; (d) Cd<sup>II</sup> coordination frameworks of **3**.



**Fig.7** Varied-temperature Powder X-Ray patterns for  $Cd^{II}$  coordination framework of **3**.



(a)



<sup>(</sup>b)



Fig 8 Photo-Luminescent intensities of the band centered at (a) 403 nm for 1; (b) 402 nm for 2; (c) 400 nm for 3 in the presence of different metal ions (60  $\mu$ M).



Fig.9 (a) Comparison of the luminescence intensity centered at 403 nm of 1 incorporating various different cations. (b) Liquid luminescence spectra of 1 under different concentrations of Fe<sup>3+</sup>. (c) Comparison of the luminescence intensity centered at 403 nm of 1 under different concentrations of Fe<sup>3+</sup> aqueous solution. (d) The linear luminescence intensity centered at 403 nm vs Fe<sup>3+</sup> concentration plot.



Fig. 10 (a) Comparison of the luminescence intensity centered at 402 nm of 2 incorporating various different cations. (b) The linear luminescence intensity centered at 402 nm vs Fe<sup>3+</sup> concentration plot for 2. (c) Comparison of the luminescence intensity centered at 400 nm of 3 incorporating various different cations. (d) The linear luminescence intensity centered at 400 nm vs Fe<sup>3+</sup> concentration plot for 3.



#### (a)





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Fig. 11 Photo-Luminescent intensities of the band centered at (a) 403 nm for 1; (b) 402 nm for 2; (c) 400 nm for 3 in the presence of different antibiotics (180 μM).



Fig. 12 (a) Comparison of the luminescence intensity of 1 centered at 403 nm incorporating various different antibiotics. (b) Liquid luminescence spectra of 1 under different concentrations of NZF(Nitrofurazone). (c) Comparison of the luminescence intensity of 1 centered at 403 nm under different concentrations of Furacilin aqueous solution. (d) The linear luminescence intensity centered at 403 nm vs NZF concentration plot.

#### **Research Highlights**

- In this work, the asymmetric amino-functionalized tetra-carboxylate H<sub>4</sub>L (2'-amino-1,1':4',1"-terphenyl-3,3",5,5"-tetracarboxylic acid) containing large conjugated ter-phenyl aromatic backbones have been employed.
- A series of unique tri-nuclear cluster-based Ca<sup>II</sup>, Mg<sup>II</sup> and Cd<sup>II</sup> coordination materials, namely [Ca<sub>1.5</sub>(µ<sub>8</sub>-HL)(DMF)]<sub>n</sub> (1), {[Mg<sub>1.5</sub>(µ<sub>7</sub>-HL)·(H<sub>2</sub>O)<sub>2</sub>]·3H<sub>2</sub>O}<sub>n</sub> (2) and {[Cd<sub>1.5</sub>(µ<sub>10</sub>-L)<sub>0.75</sub>]<sub>n</sub>·H<sub>2</sub>O·DMF}<sub>n</sub> (3) have been successfully prepared..
- 3. This is the first example of the application of amino-functionalized tri-phenyl tetra-carboxylate based MOFs as bi-functional discrimination for  $Fe^{3+}$  and NZF antibiotics with high efficiency  $K_{sv}$  values and low detection limit..

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