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Transition-metal-based (Co²⁺, Ni²⁺ and Cd²⁺) coordination polymers constructed by a polytopic ligand integrating both flexible aliphatic and rigid aromatic carboxylate groups: Aqueous detection of nitroaromatics

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ABSTRACT

Three transition-metal-based coordination polymers (1: Co^{2+} ; 2: Ni^{2+} and 3: Cd^{2+}) have been solvothermally synthesized from a newly designed polytopic ligand of 4-(carboxymethoxy)-[1,1'-biphenyl]-3,4'dicarboxylic acid (H_3L_{ws}) that integrates both flexible aliphatic and rigid aromatic carboxylate groups. In 1, each H_3L_{ws} ligand connects two Co^{2+} ions in the partially deprotonated form of HL_{ws}^{2-} , whereas the H_3L_{ws} ligands in 2 and 3 are fully deprotonated (L_{ws}^{3-}), each linking three Ni^{2+} ions and seven Cd^{2+} ions, respectively. Compound 1 shows a one-dimensional chain structure, and compound 2 is composed of a two-dimensional waved sheet based on $Ni_4(\mu_3-OH)_2(\mu_2-O)_4$ cluster. Compound 3 has a three-dimensional network structure that is constructed of two-dimensional Cd/O-based layers pillared by L_{ws}^{3-} spacers. Compounds 1–3 exhibit both thermal stability (>340 °C) and hydrolytic robustness even under the heating condition. In particular, compound 3 displays the strongest luminescence in aqueous solution, which is almost 2.5-fold greater than that in organic solvents. More importantly, it is proved that compound 3 can serve as a highly sensitive luminescent sensor for aqueous detection of those nitro phenolic aromatics.

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1. Introduction

The past years have witnessed a growing surge of interest in design and synthesis of coordination polymers (CPs) or metal-organic frameworks (MOFs) that have found wide applications, such as gas storage and separation, catalysis and chemical sensors [1-5]. However, there are still some unsolved issues that restrict their potential use in practice such as water stability. In fact, those exhibiting both thermal and water stability only take few portions amongst the approximately 20,000 known MOFs [6,7]. As a consequence, researches into water-stable CPs or MOFs have profound significance from both fundamental and application perspectives. Generally, two critical cascade events determine whether the hydrolysis reaction of CPs or MOFs takes place or not. First, the water molecule should interact with metal ion through electron orbitals on the electrophilic metal and nucleophilic water. Second, the energetics of this interaction should overcome the activation energy barrier of the hydrolysis reaction. Guided by the above two principles, several strategies have been explored to improve the hydrolytic stability of CPs or MOFs which essentially relies on proper design of organic ligands and selection of metal ion. From the angle of ligand design, the water-stability might be enhanced by incorporating hydrophobic fluorinated and alkyl functional groups on the ligand, which plays a role in preventing water molecule from either approaching metal ion [8-16] or clustering around the metal center [17,18]. Besides, nitrogen-coordinating ligands, e.g., imidazolate $(pK_a \sim 18.6)$ and pyrazolate $(pK_a \sim 19.8)$, having higher pK_a values than that of water $(pK_a = 15.7)$, are favoured since the high basicity of these ligands renders them not to be easily displaced by less basic water molecules [19,20]. For choice of metal ions, those with high coordination number and oxophilicity, e.g., Zr4+, Ti4+ and Cr3+, are preferred as exemplified by carboxylate-ligand-based MOFs, such as UiO-66(Zr), MIL-125(Ti), PCN-56/59(Zr), DUT-51/67-69, MIL-140(Zr) and MIL-53/101(Cr) [21-23,7,24-27]. Since the pioneering work reported by Li et al. in 2009 [28], luminescent CPs or MOFs have emerged as a promising class of chemical sensors for detection of NACs (nitroaromatics) explosive like TNT, 2,4-DNT, TNP and so on, not only because they are simple, less expensive and easily portable, but also they have short response time with high sensitivity and selectivity [29-35]. By contrast to the vast number of reports on sensing NACs in vapor phase or organic solvent, aqueous detection of NACs based on luminescent CPs or MOFs seems







Flexible ether-linked aliphatic carboxylate group



Rigid aromatic carboxylate group

Scheme 1. Schematic showing of H₃L_{ws} ligand.

still to be less explored probably because of critical demand for hydrolytic stability [36–42]. For practical in-field use in soil and ground water, nonetheless, it urgently calls for the pursuit of water-stable luminescent sensors that can efficiently work in aqueous phase [43].

As a starting point of our program towards water-stable CPs or MOFs, we have designed and synthesized a new biphenyl-based polytopic organic ligand H₃L_{ws} that combines two rigid aromatic carboxylate groups and one flexible ether-linked aliphatic carboxylate moiety (Scheme 1). Prior to our report, the coordination chemistry of few organic ligands carrying both aromatic and aliphatic carboxylate groups have been described in literatures, which highlight the great conformational freedom and the strong inclination to form polynuclear metal clusters [44–51]. We conjectured that the ease of polynuclear cluster formation with such type of ligand might be utilized to access water-stable CPs or MOFs on the basis of two considerations. On the one hand, the polynuclear cluster formation is expected to enforce the metal-ligand coordination interactions. On the other hand, the steric hindrance around the metal ion caused by cluster is anticipated to hamper the water approaching. In this work, solvothermal reactions between H_3L_{ws} ligand and transition metal ions (Co²⁺, Ni²⁺ and Cd²⁺) resulted in three coordination polymers of 1-3. Compound 1 features a onedimensional (1-D) Co(II)-based chain structure, whereas compound 2 is composed of a two-dimensional (2-D) wave-like sheet based on Ni₄O₆ clusters. Compound **3** shows a three-dimensional (3-D) Cd(II)-based coordination network constructed by 2-D Cd/ O-based layers pillared by H₃L_{ws} ligands. Compounds 1-3 demonstrate excellent hydrolytic stabilities even under heating conditions. Particularly, through luminescence quenching compound 3 is capable of detecting those NACs with phenolic group (TNP, 2, 4-DNP and PNP) with higher sensitivity in an aquatic environment.

2. Experimental

2.1. Materials and methods

All reagents and solvents were commercially available and used as received. FT-IR spectra were recorded with a Thermo Scientific Nicolet 5700 FT-IR spectrophotometer with KBr pellets in the 400–3600 cm⁻¹ region. Elemental analyses for C and H were performed on a CHN-O-Rapid analyzer or an Elementar Vario MICRO analyzer. The fluorescent spectra were collected on a Horiba FluoroMax 4 spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Thermogravimetric analyses were carried out on a TA Instruments SDT-Q600 simultaneous DTA-TGA under N₂ atmosphere at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were recorded on XRD diffractometer (Ultima IV, Rigaku Corporation) with Cu-K α radiation (λ = 1.54056 Å).

2.2. Synthesis of H₃L_{ws} ligand

2.2.1. Synthesis of intermediate a

Into a 250 ml round-bottom flask was charged 5-bromosalicylic acid (20 g, 92.16 mmol), methanol (110 ml) and concentrated H_2SO_4 (12 ml). The mixture was stirred under reflux for 22 h. Upon cooled to room temperature, the precipitated white solid, viz. methyl 5-bromosalicylate, was filtered by suction, and washed with cold methanol solvent, which was directly used for the next step without further purification (18.0 g, 84.7%).

Into a 250 ml round-bottom flask was charged methyl 5-bro-30.30 mmol). 4-(Methoxycarbonyl)benmosalicvlate (7 g, zeneboronic Acid (6.54 g, 36.36 mmol), Pd(PPh₃)₂Cl₂ (1.91 g, 0.09 mmol), 20 ml of H₂O and 150 ml of 1,2-Dimethoxyethane in sequence. Under a nitrogen atmosphere the reaction mixture was stirred under reflux for 5 h. After cooled to room temperature, the reaction mixture was filtered to remove insoluble catalyst and inorganic salts, and poured into 200 ml of EtOAc-H₂O (1:1) mixed solvent. The organic phase was separated and washed by saturated NaCl solution. After removal of solvent by rotary evaporation, the key intermediate of a was obtained by flash chromatography. White solid, 4.6 g, yield 53%. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 3.94 (s, 3H), 3.99(s, 3H), 7.09(d, 1H, J = 8.7 Hz), 7.62(d, 2H, J = 7.8 Hz), 7.74(d, 1H, J = 8.4 Hz), 8.10(d, 3H, J = 9.0 Hz), 10.82(s, 1H) (Fig. S1).

2.2.2. Synthesis of intermediate b

Into a 250 ml round-bottom flask equipped with an addition funnel was charged **a** (5.33 g, 18.62 mmol), $K_2CO_3(8.24 g,$ 59.58 mmol) and acetone (120 ml). At room temperature, ethyl bromoacetate (3.11 g, 18.62 mmol) was added dropwise into the above homogeneous solution. After the addition was completed, the reaction was heated to reflux under stirring for 5 h. Upon cooled to room temperature, the reaction was filtered and reduced under vacuum to give a colorless viscous liquid, which solidified into white solid upon treatment with 50 ml of petroleum. The white solid of **b** was collected by filtration and dried at 45 °C under vacuum for 8 h (6.71 g, 96.8% yield).

2.2.3. Synthesis of H₃L_{ws}

Into a 500 ml round-bottom flask was charged **b** (7.15 g, 19.21 mmol), NaOH(7.68 g, 192.1 mmol), THF (200 ml) and H₂O (140 ml) in turn. The resultant turbid solution was heated to reflux for 12 h. After cooled to room temperature, the reaction mixture was partially concentrated by rotary evaporation to remove the THF solvent followed by addition of 2 M HCl solution to adjust pH in the range of 2–3. The precipitated white solid of **H₃L_{ws}** was filtered by suction, and dried at 65 °C under vacuum for 12 h. White solid, 5.77 g, 95.0% yield. ¹H NMR (300 MHz, DMSO-*d*₆, δ , ppm): 4.85 (s, 2H) , 7.14 (d, 1H, *J* = 8.7 Hz) , 7.78(d, 2H, *J* = 8.1 Hz), 7.86(d, 1H, *J* = 8.6 Hz), 7.74(d, 1H, *J* = 8.4 Hz), 8.01(d, 3H, *J* = 8.2 Hz), 12.97(s, 3H) (Fig. S2).

2.3. Synthesis of complexes 1–3

2.3.1. $[Co(HL_{ws})](H_2O)_2]_n$ (1)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (58.2 mg, 0.2 mmol), H_3L_{ws} (31.6 mg, 0.1 mmol) and 1.0 ml of KOH solution (0.2 mol/L) were dissolved in 14 ml of H₂O, and sealed in a Parr Teflon-lined stainless steel vessel (25 ml). The mixture was heated at 160 °C for 3 days. Upon cooled to room temperature at a rate of 5 °C /h, deep

Table 1 Crystal data and structure refinement for 1-3.

Compound	1	2	3
Formula Crystal size Crystal system	$\begin{array}{l} C_{16}H_{14}CoO_9\\ 0.35\times0.30\times0.28\\ orthorhombic \end{array}$	$\begin{array}{l} C_{16}H_{14}Ni_{2}O_{11} \\ 0.30\times 0.28\times 0.25 \\ monoclinic \end{array}$	$\begin{array}{l} C_{16}H_{10}Cd_{2}O_{8} \\ 0.33\times 0.29\times 0.27 \\ monoclinic \end{array}$
Space group	Pbca	$P2_1/c$	C2/c
a (Å)	10.285(2)	16.166(6)	16.8051(6)
b (Å)	7.6940(15)	7.153(3)	6.5211(2)
c (Å)	38.563(8)	15.185(6)	27.9974(10)
α(°)	90	90.00	90
β (°)	90	97.729(11)	95.5580(11)
γ(°)	90	90.00	90
V (Å3)	3051.6(11)	1740.0(12)	3053.75(18)
Ζ	8	4	8
$D_c ({ m g}{ m cm}^{-3})$	1.781	1.907	2.415
F (000)	1672	1016	2128.0
Reflections collected	4522	4261	3821
Unique reflections	4169	3309	3403
Goodness-of- fit (GOF) of	1.037	1.019	1.070
$R_1^a [I > 2\sigma(I)]$	0.0364	0.0532	0.0233
$wR_2^{b} [I > 2\sigma (I)]$	0.1025	0.1624	0.0519

where w = $1/[\sigma^2(F_0^2) + (aP)^2 + bP]$. $P = (F_0^2 + 2F_c^2)/3$.

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

red needle crystals of 1 were collected in 43% yield (based on H₃L_{ws} ligand). IR (KBr, cm⁻¹): 3413(s), 2926(m), 2670(m), 1685(vs), 1676 (vs), 1607(vs), 1561(s), 1486(w), 1421(vs), 1301(m), 1237(m), 1182(s), 1105(m), 1019(m), 858(m), 815(m), 775(m), 751(m), 710(w) 553(w). Anal. Calc. for C₁₆H₁₄CoO₉: C, 46.96; H, 3.45. Found: C, 47.02; H, 3.53%.

2.3.2. $[Ni_2(L_{ws})(OH)(H_2O)_3]_n$ (2)

A mixture of Ni(NO₃)₂·6H₂O (58.2 mg, 0.2 mmol), H₃L_{ws} (13.4 mg, 0.03 mmol) and 0.8 ml of KOH solution (0.2 mol/L) were dissolved in 15 ml of H₂O-CH₃CH₂OH-CH₃CN (in 1:1:1 volume ratio) mixed solvent, and sealed in a Parr Teflon-lined stainless steel vessel (25 ml). The mixture was heated at 160 °C for 3 days. Upon cooled to room temperature at a rate of 5 °C /h, green lamellar crystals of **2** were collected in 38% yield (based on H₃L_{ws} ligand). IR (KBr, cm⁻¹): 3346(s), 3140(w), 1615(vs), 1552(s), 1481(w), 1427

(m), 1381(vs), 1264(w), 1192(m), 1097(w), 1009(m), 836(w), 783 (m), 757(w), 635(w), 470(w). Anal. Calc. for C₁₆H₁₄Ni₂O₁₁: C, 38.46; H, 2.82. Found: C, 38.39; H, 2.86%.

2.3.3. $[Cd_2(L_{ws})(OH)]_n$ (3)

A mixture of Cd(NO₃)₂·6H₂O (61.6 mg, 0.2 mmol), H₃L_{ws} (31.6 mg, 0.1 mmol) and 0.8 ml of KOH solution (0.2 mol/L) were dissolved in 10 ml of CH₃CH₂OH-H₂O (1/4), and sealed in a Parr Teflon-lined stainless steel vessel (25 ml). The mixture was heated at 160 °C for 3 days. Upon cooled to room temperature at a rate of 5 °C /h, pale yellow lamellar crystals of 3 were collected in 56% yield (based on H₃L_{ws} ligand). IR (KBr, cm⁻¹): 3487(m), 2978(w), 1587(vs), 1554(s), 1426(m), 1386(s), 1266(m), 1238(m), 1172(w), 1069(w), 966(w), 815(w),787(w), 716(w). Anal. Calc. for: C₁₆H₁₀-Cd₂O₈: C, 34.62; H, 1.82. Found: C, 34.70; H, 1.88%.

2.4. Crystal structure determinations

X-ray crystallographic data for 1-3 were collected on a Bruker Smart Apex II CCD area-detector diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298(2) K using the ω -scan technique. The diffraction data were integrated using the SAINT program [52], which was also used for the intensity corrections for the Lorentz and polarization effects. A semi-empirical absorption correction was applied using the sadabs program [53]. The structures was solved by direct methods and all the nonhydrogen atoms were refined anisotropically on F^2 by the fullmatrix least-squares technique using the SHELXL-2014 crystallographic software package [54]. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. The details of the crystal parameters, data collection and refinements for 1-3 are summarized in Table 1, and selected bond lengths and angles of 1–3 are listed in Tables S1–S3.

2.5. Fluorescence sensing experiment

The fluorescence properties of **3** in different solvents (C_2H_5OH , CH₃OH, DMF, THF, CH₃CN, CH₂Cl₂. DMAc and H₂O) were investigated in emulsions at 293 K, in which the finely ground powder of **3** (2.77 mg) was dispersed in the respective solvent (10 ml), treated by ultrasonication for 30 min and then aged for 3 days to form a stable emulsion before the fluorescence studies. In a fluorescence titration setup, 13.87 mg of 3 was dispersed in 50 ml of H₂O, treated by ultrasonication for 30 min, then sampling 2.5 ml for the next experiment. The fluorescence was recorded online



Scheme 2. Synthetic route for H₃L_{ws} ligand.





Scheme 3. Coordination modes (i)-(iii) of H₃L_{ws} in 1–3.



Fig. 1. Coordination environment of Co²⁺ ion in 1.

after incremental addition of freshly prepared 1.0 mM aqueous solutions of each analyte (nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), *m*-nitrochlorobenzene (NCB), *p*-nitrophenol (PNP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (TNP)).

3. Results and discussion

Beginning with 5-bromosalicylic acid as the starting material, the target ligand of $H_{3}L_{ws}$ was achieved in four steps wherein the biphenyl backbone was installed through a classic Suzuki–Miyaura coupling reaction (Scheme 2). In order to ensure the hydrolytic stability, hydrothermal reactions between $H_{3}L_{ws}$ ligand and metal ions were conducted in pure H₂O solution or H₂O/organic solvent mixture. Reaction of H_3L_{ws} with Co^{2+} , Ni^{2+} and Cd^{2+} ion resulted in 1-D chain of 1, 2-D sheet of 2 and 3-D network of 3, respectively, all being structurally ascertained by single-crystal X-ray crystallography (vide infra). In 1, H_3L_{ws} ligand is partially deprotonated in form of HL_{ws}^2 with one aromatic carboxylic acid free of metalcoordination. In 2 and 3, H_3L_{ws} is fully deprotonated (L_{ws}^3) with all carboxylate groups participating into metal-coordination. This small difference with H_3L_{ws} ligand amongst 1–3 can be clearly discerned by the IR spectra, wherein the stretching vibration at 1683 cm⁻¹ corresponding to the free carboxylic acid is completely invisible in 2–3 whereas it remains in 1 (Supporting Information: Fig. S3). As a multidentate linker in 1–3, H_3L_{ws} ligand exhibits totally distinct coordination modes (i)-(iii), linking different num-



Fig. 2. (a) 1-D chain structure of 1; (b) alignment of 1-D chains in 1; (c) hydrogen bonds between free carboxylic acid groups; (d) 2-D hydrogen-bonded layers involving coordinated water molecules and carboxylate O atoms.

ber of metal ions (two Co^{2+} ions in **1**, four Ni^{2+} ions in **2**, seven Cd^{2+} ions in **3**) (Scheme **3**) Detailed structures of **1–3** are described below.

3.1. Crystal structure of 1-3

Compound **1** crystallized in the orthorhombic space group *Pbca*, with the asymmetric unit composed of one independent Co^{2+} atom, one HL_{ws}^{2-} ligand and two coordinated water molecules. As depicted in Fig. 1, the Co^{2+} ion adopts an octahedral coordination geometry completed by six O atoms: three chelating O atoms (O2, O3 and O7) from one ligand, one aromatic carboxylate O atom (O6A) from the other ligand, and two O atoms (O8 and O9) from two water molecules. H_3L_{ws} ligand is found to be partially deprotonated having one aromatic carboxylic acid (A-ring) uncoordinated, which connects two Co^{2+} ions in the coordination mode (i) involving one ether-O atom, one aliphatic carboxylate O atom and two aromatic carboxylate O atoms (Scheme 3). Specifically speaking, the ether-O atom coupled with two neighbouring carboxylate O atoms (B-ring) chelates one Co^{2+} ion, and the remaining one aromatic carboxylate O atom (B-ring) is attached to the other Co^{2+}

ion. Compound 1 features a 1-D chain structure that is built from alternate linkage of syn, anti-aromatic carboxylate bridge and Co^{2+} ion (the nearest Co...Co separation: 5.0465(8) Å). Along the chain, the $[Co(CO_2)]_n$ spine is flanked by HL^{2-}_{ws} ligands at the one side and coordinated water molecules at the other side (Fig. 2a). All 1-D chains are aligned in parallel along the b axis, each (green denoted in Fig. 2b) interacting with the other four (blue denoted in Fig. 2b) separately through hydrogen bonding interactions between free aromatic carboxylic acid groups, and between coordinated water molecules. Concretely, uncoordinated aromatic carboxylic acid groups belonging to two chains are paired through a couple of O-H...O hydrogen bonds (O5-H...O4: O5...O4, 2.622 (2)Å, 1 - x, -1 - y, -z) (Fig. 2c). Meanwhile, hydrogen bonding interactions between the carboxylate O atoms and coordinated water molecules lead to a unique 2-D O-H...O hydrogen-bonded layer (08-H...02: 08...02 2.633(2) Å, 1 - x, -1/2 + y, 1/2 - z; 08-H...07: 08...07 3.156(2) Å, 1 - x, 1/2 + y, 1/2 - z; 09-H...01: 09...01 2.715 Å, 1 - x, -1/2 + y, 1/2 - z; 09-H...08: 09...08 2.845(2) Å, 1 - x, 1/2 + y, 1/2 - z) (Fig. 2d).

Compound **2** crystallized in the monoclinic crystal system with space group $P2_1/c$. The asymmetric unit of **2** is composed of two



Fig. 3. Coordination environment of Ni1 and Ni2 ions in 2.



Fig. 4. (a) 2-D waved layer in 2 (pink line represents a simplified uninodal 4-connected network); (b) Ni₄(µ₃-OH)₂(µ₂-O)₄ cluster in 2. (Colour online.)



Fig. 5. (a) Aggregation of 2-D layers through hydrogen bonding interactions; (b) Inter-layer hydrogen bonding interactions involving coordinated water molecules and carboxylate O atoms.



Fig. 6. Coordination environment of Cd1 ion and Cd2 ion in 3.



Fig. 7. (a) 3-D network of 3; (b) 2-D Cd/O-based layer (Polyhedron represents [Cd₃OH] tetrahedral node, only bridging O atoms are shown); (c) Arrangement of L³_{ws} pillars.

independent Ni(II) atoms (Ni1 and Ni2), one L_{ws}^{3} ligand, three coordinated water molecules and one OH ion. As illustrated in Fig. 3 Ni1 atom resides into an octahedral environment bound by one aromatic carboxylate O atom (B-ring) and one aliphatic carboxylate O atom from two L^{3-}_{ws} ligands, one coordinated water molecule and three OH ions, whereas Ni2 atom adopts an octahedral geometry surrounded by one water molecule, one OH ion and two L^{3-}_{ws} ligands wherein one supplies three chelating O atoms from one aliphatic carboxylate group, one aromatic carboxylate group and one ether-O from the same aromatic ring, and the other only provides one aromatic carboxylate O atom (A-ring). Unlike HL^{2–} ligand in 1, L_{ws}^{3} - ligand in 2 links four Ni(II) ions in the coordination mode (ii) that uses one monodentate aromatic carboxylate O atom (A-ring), one μ_2 -aliphalic carboxylate O atom, one monodentate ether-O atom and one μ_2 -aromatic carboxylate O atom (B-ring) (Scheme 3). The overall structure of 2 can be described through interlinkage of central-symmetric $Ni_4(\mu_3-OH)_2(\mu_2-O)_4$ cluster in the way that each $Ni_4(\mu_3-OH)_2(\mu_2-O)_4$ cluster connects four neighbours through four L^{3-}_{ws} ligands, giving rise to a 2-D waved layer (Fig. 4a). The Ni₄(μ_3 -OH)₂(μ_2 -O)₄ cluster has two Ni1 atoms and two Ni2 atoms arranged into a rhombus shape (Ni1-Ni2 edge: 3.09 and 3.10Å), wherein each Ni-Ni edge is spanned by a μ_2 -O atom, and two μ_3 -OH ions are situated above and below the Ni₄ rhombus plane (Fig. 4b). If treating $Ni_4(\mu_3-OH)_2(\mu_2-O)_4$ cluster as four-connected node and L^{3-}_{ws} as linker, the 2-D layer can be simplified as a simple 4-connected uninodal network (pink line denoted Fig. 4a). Eventually, all 2-D layers are aggregated into a 3-D hydrogen-bonded network through inter-layer O-H...O hydrogen bonding interactions (05-H...06: 05...06 2.834(4) Å, 1 – x, 1 – y, 1 - z; 011-H...04: 011...04 2.896(4) Å, x, 1/2 - y, -1/2 + z; 011-H...010: 011...010 3.310(5) Å, 2 - x, 1/2 + y, 3/2 - z) that involves coordinated water molecules and carboxylate O atoms (Fig. 5a and b).

Compound **3** crystallized in the monoclinic space group C2/c, with the asymmetric unit containing two crystallographically independent Cd(II) atoms (Cd1 and Cd2), one L_{ws}^{3-} ligand and one $\mu_3\text{-}OH$ ion. As shown in Fig. 6, both Cd1 and Cd2 atoms are seven-coordinated by an O7 donor set. For Cd1 atom, apart from two O atoms from two $\mu_3\text{-}\text{OH}$ ions, three L^{3-}_{ws} ligands offer two chelating O atoms from the aliphatic carboxylate group, two chelating O atoms from the aromatic carboxylate group (A-ring) and one monodentate O atom of aromatic carboxylate group (Bring), respectively. For Cd2 atom, except one O atom from one μ_3 -OH ion, four \mathbf{L}_{ws}^{3-} ligands in sequence supply one monodentate O atom from the aromatic carboxylate group (B-ring), one monodentate O atom from aliphatic carboxylate, three chelating O atoms combining one aliphatic carboxylate O atom, one aromatic carboxylate O atom with one ether-O atom, and one monodentate O atom from aromatic carboxylate group (A-ring). In **3**, the L_{ws}^{3-} ligand makes full use of all O atoms connecting up to seven Cd atoms in coordination mode (iii) wherein two aromatic carboxylate groups show μ_2 - η^1 : η^2 and μ_3 - η^1 : η^2 coordination fashions, whereas one aliphatic carboxylate group exhibits μ_3 - η^2 : η^2 coordination mode (Scheme 3). As shown in Fig. 7, coordination linkage between Cd(II) and carboxylate O atoms of L^{3-}_{ws} ligand results in the formation of a 2-D Cd/O-based layer. The Cd/O-based layer is composed of flattened $[Cd_3(\mu_3-OH)]$ tetrahedron, wherein $[Cd_3(\mu_3-OH)]$ OH)] tetrahedral nodes are joined together in a vertex-sharing



Fig. 9. (a) Luminescence spectra of 3 in different solvents; (b) Effect of H₂O on luminescence of 3.

fashion to give a 1-D zigzag chain which is further associated mutually through inter-chain μ_2 -O bridges (Fig. 7b). The 2-D layers are finally pillared by \mathbf{L}_{ws}^3 -ligands to create a 3-D coordination network, in which all biphenyl pillars are arrayed in parallel along b direction with no appreciable aromatic interactions.

3.2. Thermal and hydrolytic stability

The thermal stabilities of 1-3 were evaluated by TGA technique as illustrated in Fig. 8a, c and e. For 1, an initial weight loss of 8.4% in the range of 92–150 °C corresponds to the loss of coordinated water molecules (Calcd. 8.8%), and it is stable up to about 360 °C above which decomposition occurs. For 2, the weight loss of 10.8% occurs from 248 °C to 341 °C owing to the loss of coordinated water molecules (Calcd. 10.7%), which is followed by abrupt weight reduction due to network collapse. For 3, TGA curve passes through a flat region from the room temperature to 364 °C, beyond which drastic weight loss takes place due to network decomposition. The hydrolytic robustness of 1-3 was firstly examined under ambient condition. Even after being immersed into water for 5 days, these water-soaked samples of **1–3** show no major change in PXRD pattern compared to those of the pristine samples (Fig. 8b, d and f), indicating their good hydrolytic stability at room temperature. Thereafter, the water stabilities of **1–3** were further evaluated in the heated water. By PXRD comparison with their parent samples, it shows that 1 can remain intact in the 80 °C water for 30 h. but it would lose crystallinity beyond this temperature. By contrast, both **2** and **3** can withstand the boiling water at least for 30 h (Fig. 8b, d and f). According to the above experimental data, we can see that compounds 1-3 exhibit both good thermal stability (>340 °C) and hydrolytic robustness, which might be accounted for by the following factors. First, synergistic cooperation between the ether-linkage O atom and its two neighbouring carboxylate O atoms creates a built-in three-atom chelating compartment in H₃L_{ws} that helps strengthen the metal coordination. Second, H₃L_{ws} tends to form polynuclear cluster with different metal ions, which also strongly enforce the metal-ligand coordination. Finally, it is worth noting that dense hydrogen bonding interactions as found in 1 and 2 might also make a substantial contribution

3.3. Luminescent detection of NACs

For the majority of MOF (or CP)-based chemical sensors in literatures, NACs are typically detected by luminescence signal transduction mechanism, that is, the fluorescence of MOFs (e.g., intensity, wavelength, lifetime) was changed in response to interaction of analyst [30-33]. In this context, solid-state photoluminescence properties of 1-3 were firstly examined at room temperature, amongst which only compound 3 exhibits photoluminescence (λ_{em} = 371 nm, λ_{ex} = 331 nm) that is attributed to ligand-centered transition in comparison to the emission of the free ligand (λ_{em} = 375 nm and 438 nm, λ_{ex} = 355 nm) (Fig. S4). Compared to the d¹⁰Cd²⁺ ion having no unpaired electrons, the unpaired electrons in d⁷ Co²⁺ ion of **1** and d⁸ Ni²⁺ ion of **2** are considered to be responsible for the luminescence quenching albeit with the same H_3L_{ws} ligand. Given that insolubility of MOFs or CPs in common solvents, sensing NACs through MOF (or CP)-based sensor is generally performed in their emulsions, in which finely ground powders of sensor are highly dispersed into suitable solvents by sonication. With this point in mind, the photoluminescence of 3 in different solvents was further examined. As depicted in Fig. 9a, the photoluminescence of 3 shows only small fluctuation in intensity when being dispersed in various organic solvents including CH₃OH, EtOH, CH₃CN, CH₂Cl₂, DMF and DMAc. By sharp contrast, an almost 2.5-fold increase in luminescence intensity of **3** was observed in aqueous solution, concurrent with a small red-shift in emission wavelength. To accentuate the remarkable solvent effect of water on photoluminescence properties of 3, the emission spectra of 3 were collected in different



Fig. 10. The fluorescence titration plots of 3 towards different NACs.

volume ratios of CH_3OH-H_2O mixtures. As shown in Fig. 9b, It can be clearly seen that the luminescence intensity of **3** is significantly enhanced with the wavelength being gradually red-shifted as the volume percentage of H_2O is increased. The observed photoluminescence phenomena of **3** is reminiscent of AIE (Aggregation Induced Emission) behaviour proposed by Tang and co-authors in 2001 [55], and in our case it is probably caused by the fact that intramolecular rotations of two phenyl rings within the biphenyl skeleton are restricted in the presence of water, which blocks nonradiative relaxation pathways of the excited species, and thus enhances luminescent intensity with red shifts [56,57].

The strong fluorescence of **3** in water coupled with its excellent hydrolytic stability encourages us to explore its NACs sensing capability in aqueous solution. The NACs sensing ability of 3 was assessed through fluorescence titration in aqueous solution. As shown in Fig. 10, the luminescence intensity of **3** decreases with the increasing addition of NACs including NB. 2.4-DNT, NCB. PNP. 2,4-DNP and TNP. Apart from NB and NCB with the linear SV plots, the SV plots of the other NACs shows almost the same feature, that is, they are almost linear at low concentrations followed by bending upwards at higher concentrations (Figs. S5-S10). The deviation from the linearity at higher concentrations might be attributed to self-absorption or energy transfer process [41,58–61]. The quenching constants for NB, 2,4-DNT and NCB are in the range from 386.88 to 601.98, whereas those for PNP, 2,4-DNP and TNP falls into the range between 1.27X10⁴ and 2.23X10⁴ (Table S4). Clearly, compound **3** exhibits higher sensitivity for those nitro phenolic aromatics, viz. PNP, 2,4-DNP and TNP. The limit of detection (LOD) of **3** for those nitro phenolic aromatics reaches the ppm level (2,4-DNP: 4.72 ppm; PNP: 2.90 ppm; TNP: 2.69 ppm) (Table S4) [62].

Generally, two mechanisms account for luminescence quenching, viz. photo-induced electron transfer (PET) and fluorescenceresonance energy transfer (FRET). To better understand the high sensibility of **3** towards those nitro phenolic aromatics, we firstly calculated the orbital energies of HOMO and LUMO for selected NACs and sensor of **3** based on the density functional theory at the B3LYP/6-31G* level, and in this case **3** is treated as a giant "molecule" with the valence-band (VB) and conduction-band (CB) energy levels calculated in a manner similar to that applied for molecular orbitals (MOs) [63]. As shown in Fig. S11, the LUMO energy level of **3** lies above all tested NACs, which favours the PET mechanism. However, the order of observed quenching efficiency is not fully in accordance with the order of LUMO energies, implicating that the fluorescence quenching is not operative solely via PET mechanism. Afterward, we compare the emission spectra of 3 and the absorption spectra of all NACs (Fig. S12). Apparently, there is a negligible spectral overlap for those NACs without phenolic hydroxyl group. On the contrary, a considerable spectral overlap is observed for those nitro phenolic aromatics (TNP, 2,4-DNP and PNP). Taken together, it can be reasonably concluded that the luminescence quenching of 3 towards those NACs without phenolic group is dominated by PET mechanism whereas for those NACs with phenolic group it is likely governed by synergistic work of both PET and FRET mechanisms, which may also account for the higher quenching efficiency for those NACs with phenolic group.

4. Conclusions

Three thermo and water-stable transition-metal-based coordination polymers of **1–3** have been solvothermally synthesized with a biphenyl-based polytopic ligand of H_3L_{ws} comprising both aliphatic and aromatic carboxylate groups. The excellent hydrolytic robustness of **1–3** might stem from the unique characteristic of the designed H_3L_{ws} ligand that favours the formation of polynu-

clear cluster. Moreover, dense hydrogen-bonding interactions found in these coordination polymers are assumed to be another important factor contributing to both thermal and water stabilities. In addition, luminescent coordination polymer of **3** shows high sensibility for aqueous detection of those nitro phenolic aromatics. Current work provides another option to ligand design for constructing hydrolytically stable functional coordination polymers or metal–organic frameworks, which can be practically applied in an aquatic environment.

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Appendix A. Supplementary data

CCDC 1496439–1496441 contains the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.poly.2017.02.041.

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