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Five 8-hydroxyquinolate-based coordination polymers with tunable structures and photoluminescent properties for sensing nitroaromatics†

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Using two 8-hydroxyquinolate ligands (L_1 -MOM and L_2 -MOM) containing 3-pyridyl or 4-pyridyl groups, five novel coordination polymers, namely, $[Zn_3(L_1)_6]$ (**1**), $[Zn(L_1)_2] \cdot 2\text{MeOH}$ (**2**), $[Zn(L_2)_2]$ (**3**), $[Cd(L_2)_2]$ (**4**), and $[Cd_4(L_1)_6] \cdot 13H_2O$ (**5**), were synthesized and characterized by a variety of techniques. Single-crystal X-ray structures have revealed that these coordination polymers exhibit a structural diversification due to the different choices of metal salts and the effect of pyridyl nitrogen position. Compounds **1–5** exhibited different fluorescence emissions and lifetimes upon excitation in the solid state. The sensing behavior of these polymers was also investigated upon exposure to vapors of various nitroaromatic molecules (analytes). The results show that all five polymers are capable of sensing these nitroaromatic molecules in the vapor phase through fluorescence quenching. Interestingly, **3** exhibits superior sensitivity to the analytes in comparison with other polymers. 2-Nitrotoluene quenches the emission of **3** by as much as 96%.

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Introduction

Coordination polymers (CPs), known as a fascinating organic-inorganic hybrid material class, are certainly very promising as a multifunctional luminescent material, because both the inorganic metal cations (or metal clusters) and the organic linkers can provide the platforms to generate luminescence.^{1,2} The variety of metal ions, organic ligands, and structural motifs affords an essentially infinite number of combinations.³ Furthermore, both postsynthetic modification and guest molecules can also emit and/or induce luminescence.⁴ These features enable the electronic nature of luminescent CPs to be tailored for a particular application by varying the lumophore type, secondary building units, and their relative spatial arrangements.^{5,6} These merits also make them promising candidates for chemical sensing applications.⁷ Recently, fluorescence active CPs have been applied in the detection of hazardous substances,^{8,9} which is an important area of current research for homeland security, environmental safety, and human health. The development of sensitive and efficient explosive detection methods has become especially urgent in

recent years due to the continuing rise of terrorist activities around the globe. In comparison with well-trained canines¹⁰ and sophisticated instrumental methods,¹¹ optical sensing based on fluorescent materials has the advantages of cost effectiveness and portability.¹² To tailor MOFs for chemical sensing, some CPs with a specific structure and functionality were constructed by the deliberate design and selection of organic linkers and metal-containing units,¹³ such as the introduction of guest accessible functional organic groups,¹⁴ and the reservation of open metal sites.¹⁵ The tuned geometry and functionalization of pores may lead to selective adsorption and molecular sensing.⁷

Motivated by the success of tris(8-hydroxyquinolinato)-aluminum (Alq_3) in vacuum-deposited LEDs, the photoluminescent materials based on 8-hydroxyquinoline complexes have, in particular, attracted a lot of attention.^{16,17} 8-Hydroxyquinolate (in its deprotonated form) can bridge the gaps between the neutral bipyridine and the dianionic catecholate, because it contains one pyridine donor of bipy and one phenolate unit of catecholate. In addition, the geometry and chelating size of 8-hydroxyquinolate are the same as found for bipy and catecholate, which are very often used as appropriate building blocks for organic ligands. It has been demonstrated that the 8-hydroxyquinoline unit is an ideal building block in metallosupramolecular chemistry.^{16,17} With few notable exceptions, 8-hydroxyquinolate-based coordination polymers with desirable structures and functionalities have not yet been developed.¹⁸

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In recent years, our research group has reported a series of photoluminescent complexes involving 2-substituted 8-quinalinolate ligands with NO donor set.¹⁹ Herein, we have synthesized two bispyridyl-based quinoline ligands from the commercially available 8-hydroxyquininaldine to form five new Zn(II) and Cd(II) coordination polymers, and characterized the five polymers by a variety of techniques, including microanalysis, IR, and powder and single-crystal X-ray diffraction. The polymeric skeletons exhibit a structural diversification, which can be attributed to the different choices of metal salts and the effect of pyridyl nitrogen position. The investigation of their fluorescent properties shows disparate emission wavelengths and lifetimes in the solid state. In addition, we have also studied the applicability of polymers **1–5** for sensing nitroaromatic molecules at room temperature. The results further suggest that both the electronic properties and supramolecular structures of coordination polymers may play a key role in the observed fluorescence quenching behavior.

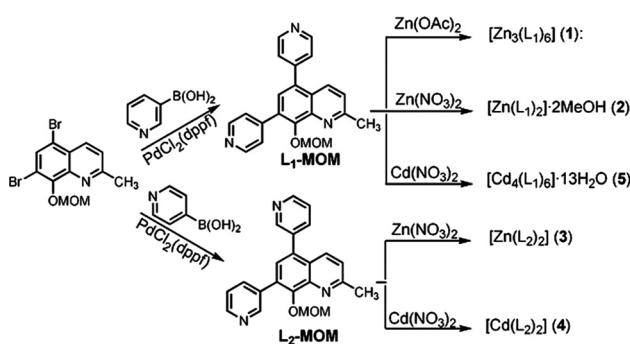
Results and discussion

Synthetic chemistry

The two ligands L₁-MOM and L₂-MOM (MOM: methoxy-methoxy) were synthesized in more than 80% yield by Suzuki coupling reaction between 3- or 4-pyridylboronic acid and 5,7-dibromo-2-methyl-8-methoxymethoxyquinoline. The L₂-MOM ligand was fully characterized by ¹H and ¹³C NMR, ESI-MS, and microanalysis. Single crystals of [Zn₃(L₁)₆] (**1**), [Zn(L₁)₂]·2MeOH (**2**), [Zn(L₂)₂] (**3**), [Cd(L₂)₂] (**4**), and [Cd₄(L₁)₆]·13H₂O (**5**) were readily obtained in good yield by heating the corresponding Zn(II) or Cd(II) salts and L-MOM in the mixture of MeOH-DMF-H₂O (Scheme 1). It is notable that an anion-dependent self-assembly behavior was observed in **1** and **2**. The -MOM group was completely removed from the starting ligands upon reactions with the metal ions. Coordination polymers **1–5** are stable in air and insoluble in water and common organic solvents, and were formulated on the basis of microanalysis, IR, and single-crystal X-ray diffraction.

Structural description

Single crystals of complex **1** were readily obtained in good yields by heating Zn(OAc)₂ and L₁-MOM in a mixture of



Scheme 1 Synthesis of ligands L₁-MOM, L₂-MOM and polymers **1–5**.

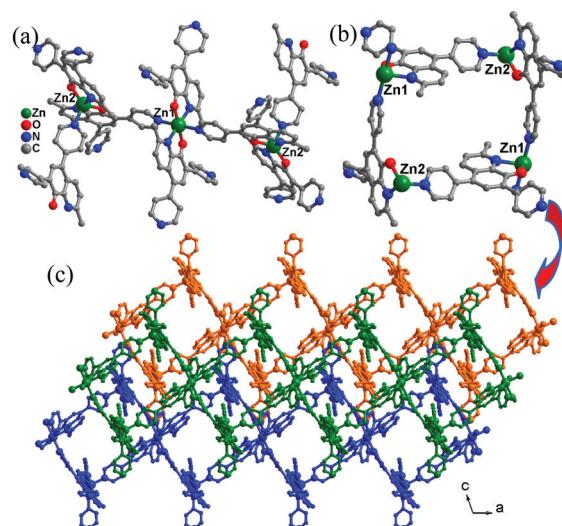


Fig. 1 (a) Views of the coordination geometries of Zn(II) atoms in **1**; (b) view of a cyclic tetramer Zn₄L₆ in **1**; (c) 3-fold interpenetrated architecture in **1**.

MeOH-DMF. Complex **1** crystallizes in the space group *P*2₁/*n*, with one Zn(II) ion and three L₁ ligands in the asymmetric unit. The MOM groups were completely removed from the starting ligands upon complexation with the metal ions. The Zn1 centre is coordinated by two nitrogen atoms from pyridyl groups, two nitrogen atoms and two oxygen atoms from quinoline rings, forming a ZnN₄O₂ slightly distorted octahedral coordination geometry (Fig. 1a). The bond lengths around Zn1 are 2.0338(3) Å for Zn–O, 2.2213(4) Å and 2.2495(4) Å for Zn–N, respectively. The Zn2 centre is five-coordinated by one nitrogen atom of a pyridyl group, two oxygen and two nitrogen atoms from two quinoline rings to result in a distorted trigonal bipyramidal coordination geometry (Fig. 1a). The distances of Zn–N and Zn–O bonds around Zn2 are 2.0887(4)–2.2599(3) Å and 1.9336(2)–1.9612(2) Å, respectively.

In **1**, six L₁ ligands with eight uncoordinated pyridyl groups connect four Zn cations (two Zn1 and two Zn2 atoms) to form a cyclic tetramer Zn₄(L₁)₆ (Fig. 1b), which is further linked into a 1D infinite chain along the crystallographic *a*-axis. The spacious nature of one single chain allows another two independent identical chains to penetrate it in a normal mode, thus giving a 3-fold interpenetrated architecture (Fig. 1c and S3†). The interdigitation of uncoordinated pyridyl rings from adjacent square grids has efficiently filled all the void space; No solvent molecule is encapsulated in **1**. In addition, two intertwined helical chains (one is left-handed, the other is right-handed) are constructed via non-classical C–H···N hydrogen bonds between the C–H group of methyl and the nitrogen atom of pyridine (Fig. 2b, C–H···N: 3.5275(5) Å and 3.7871(6) Å) along the *b*-axis with a pitch of 23.6412(43) Å, which is equal to the *b* axis length (Fig. 2a). PLATON calculations indicate that complex **1** contains 6.7% void space (341.4 Å³ per unit cell) that is accessible to solvent molecules.

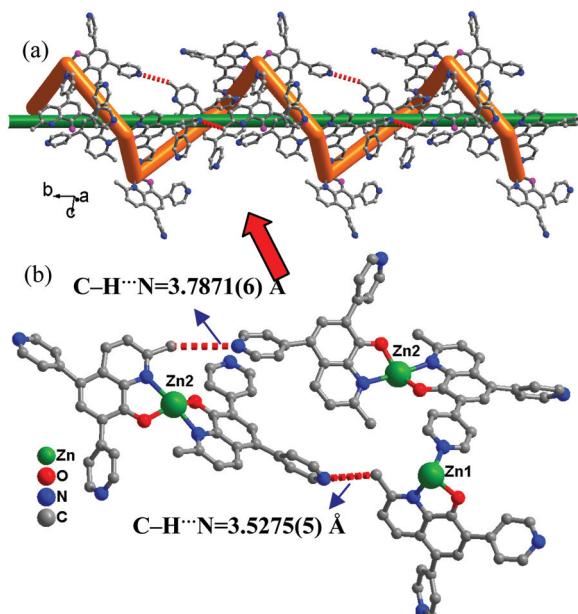


Fig. 2 (a) View of 1D helical chains fabricated via C-H...N interactions in **1** along the *b*-axis; (b) perspective view of intermolecular C-H...N interactions in **1**.

When ZnCl₂ was used instead of Zn(NO₃)₂ under the same synthesis condition of **1**, the coordination polymer **2** was obtained as yellow block-like crystals. A single-crystal X-ray diffraction study shows that compound **2** is a 2D network, with one crystallographically independent Zn(II) ion, one L₁ ligand and one uncoordinated CH₃OH molecule in the asymmetric unit. It crystallizes in the monoclinic system, space group *P2₁/c*. Similar to **1**, the MOM groups were also removed. The metal center Zinc is six-coordinated by two nitrogen atoms from pyridyl groups, two oxygen atoms and two nitrogen atoms from quinoline rings, showing a slightly distorted octahedral coordination geometry (Fig. 3a). The bond lengths around the Zn centre are 2.0199(2) Å for Zn–O, 2.2221(2) Å and 2.2428(2) Å for Zn–N, respectively. The Zn(II) metal centers are bridged by L₁ ligands to form a 2D square grid in the *bc* plane (Fig. 3b). It is notable that a kind of *meso*-helical chains (*P* + *M*) constructed via the metal-ligand coordination interactions is observed in the solid state of this compound (Fig. 4a). These *meso*-helical chains with a pitch of 10.2951(14) Å are alternately arranged along *b* axis, which is identical to the *b* axis length. The 2D layers are further stacked into a 3D supramolecular structure (Fig. 4b) via non-classical C–H...N hydrogen bonds (C–H...N: 3.3489(4) Å) between the C–H group and nitrogen atom from the pyridyl group (Fig. S4†). There is significant void space formed between the lamellae, and a space-filling model of **2** viewed along the *a* axis clearly indicates the presence of large channels with the largest dimension of 5.3 Å (Fig. S5†). PLATON calculations indicate that complex **2** contains 12.8% void space (222.0 Å³ per unit cell) that is accessible to solvent molecules.

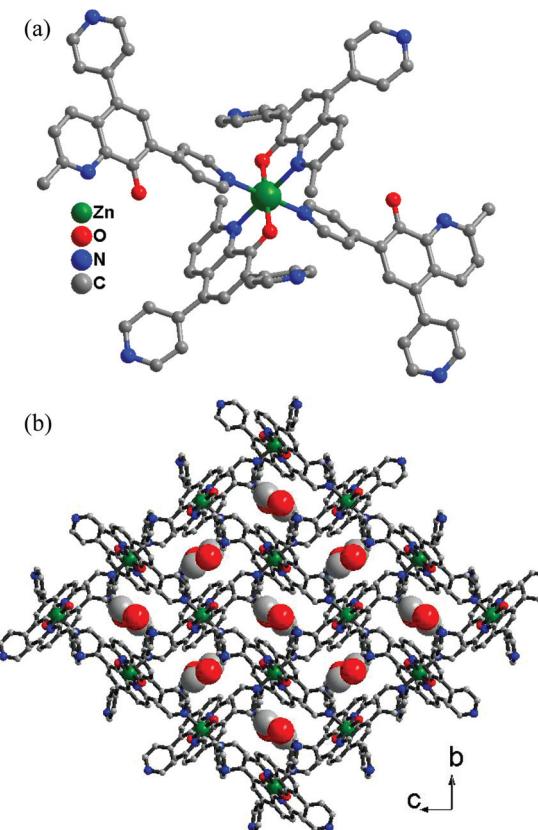


Fig. 3 (a) View of the coordination geometries of Zn(II) atoms in **2**; (b) 2D square grid of **2** in the *bc* plane (MeOH molecules are indicated by space-filling mode).

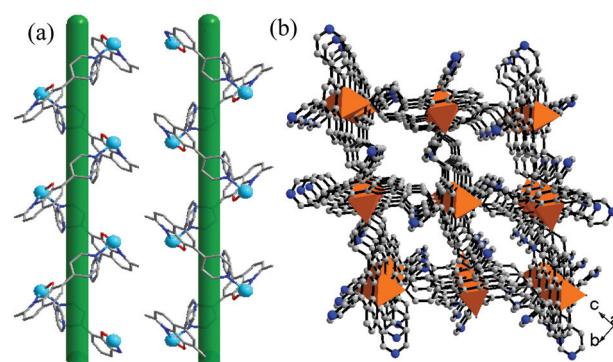


Fig. 4 (a) The *meso*-helical chains (*P* + *M*) constructed via the metal–ligand coordination interactions in **2**; (b) view of 3D supramolecular structure in **2**.

When the ligand L₂-MOM reacted with Cd(NO₃)₂ under the same reaction conditions, the complex **4** was obtained as yellow block-like crystals. Coordination polymer **4** was crystallized in a orthorhombic system and *Pbca* space group. Each asymmetric unit contains one half of a crystallographically distinct Cd(II) ion and one L₂ ligand. The coordination environment of Cd²⁺ ions in complex **4** is shown in Fig. 5a, and it can

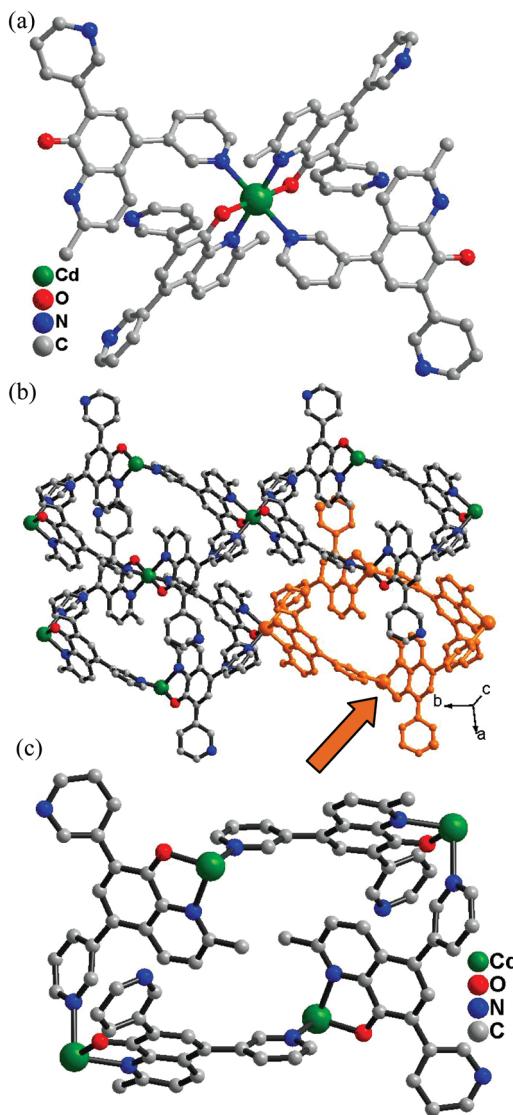


Fig. 5 (a) View of the coordination geometries of $\text{Cd}^{(II)}$ atoms in 4; (b) 2D square grid of 4 in the bc plane; (c) View of the Cd_4L_4 building unit in 4.

be seen that $\text{Cd}^{(II)}$ is six-coordinated to two phenolate oxygen atoms and four nitrogen atoms from four ligands L_2 . The $\text{Cd}^{(II)}$ center adopts an octahedral geometry with the equatorial plane occupied by two chelating NO donor sets from two ligands L_2 and the apical position by two pyridyl nitrogen atoms of two other ligands. In the ab plane, each Cd atom is linked to four adjacent Cd atoms through the chelating NO donors and pyridyl nitrogen atoms of ligands L_2 to form a 2D grid structure (Fig. 5b). However, no obvious void space for solvent molecules was observed due to the difference of pyridyl nitrogen position compared with that of 2 (Fig. S8†). The coordination polymer 3 is isostructural to 4. The main distinction is that the metal centre was replaced by $\text{Zn}^{(II)}$ ion such that there are subtle differences between them.

X-ray single-crystal diffraction analysis reveals that complex 5 is a 3D network. It crystallizes in the trigonal crystal system

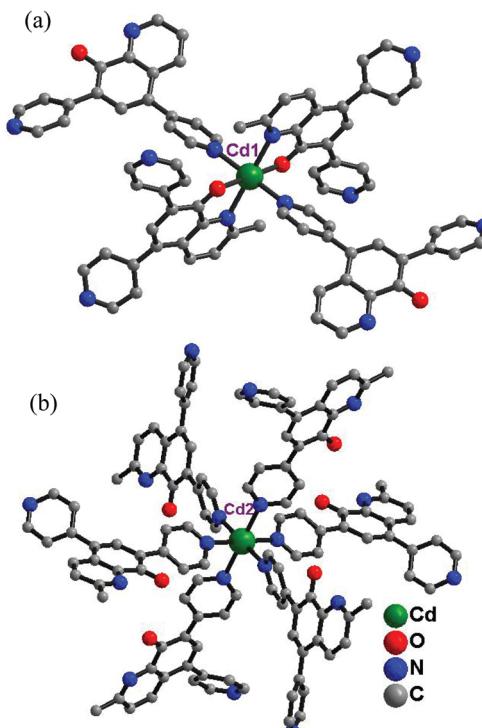


Fig. 6 Views of the coordination geometries of $\text{Cd}1$ (a) and $\text{Cd}2$ (b) in 5.

with space group of $R\bar{3}$. The asymmetric unit contains two crystallographically independent $\text{Cd}^{(II)}$ ions. $\text{Cd}1$ is six-coordinated to two nitrogen atoms of pyridyl groups, two oxygen atoms and two nitrogen atoms from quinoline rings, forming a slightly distorted octahedral geometry (Fig. 6a). The bond lengths around $\text{Cd}1$ centre are 2.2104(1) Å for $\text{Cd}-\text{O}$, 2.3734(2) Å and 2.3788(1) Å for $\text{Cd}-\text{N}$. The $\text{Cd}2$ centre is coordinated to six nitrogen atoms from pyridyl groups, showing an octahedral coordination geometry (Fig. 6b). The bond distance of $\text{Cd}-\text{N}$ around $\text{Cd}2$ is 2.3849(1) Å. Two $\text{Cd}1$ ions and one $\text{Cd}2$ ion are held together by one L_1 ligand to yield a complicated 3D network (Fig. 7b). The most fascinating structural feature of 5 is that six $\text{Cd}1$ centers are arranged around one $\text{Cd}2$ centre to form a chair conformation metallocycle (Fig. 7a). The six $\text{Cd}1$ centers occupy the edge of the chair, $\text{Cd}2$ centre is in the core of the seat. The distance between $\text{Cd}1$ and $\text{Cd}2$ is 9.1051 Å. One hexagonal channel, which is separated into six sections evenly by the pyridyl groups, was observed along the c axis. PLATON calculations indicate that complex 1 contains 34.5% void space (3420.3 Å³ per unit cell) that is accessible to solvent molecules.

Photophysical properties

To confirm that the crystal structures of coordination polymers 1–5 are truly representative of their bulk materials tested in photophysical studies, powder X-ray diffraction (PXRD) experiments were carried out on the as-synthesized samples. As we can see from Fig. 8, the peak positions of the experimental

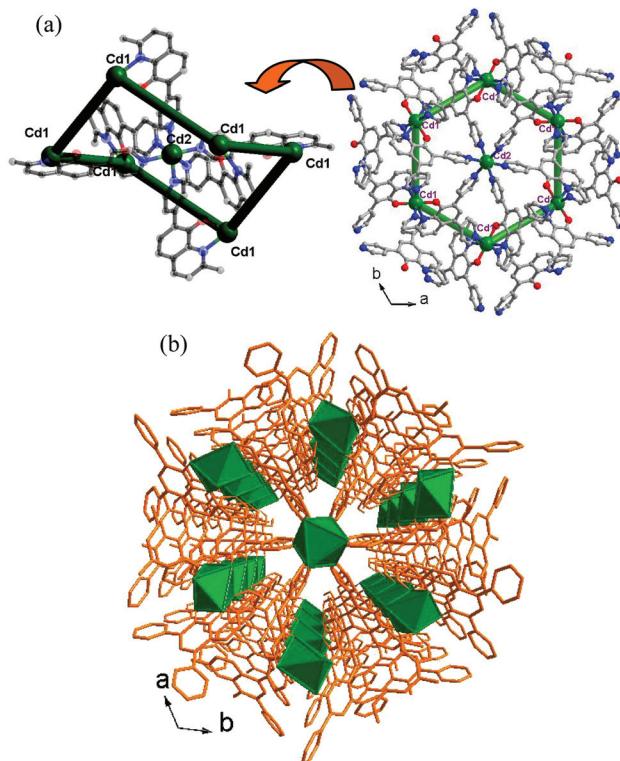


Fig. 7 (a) View of a chair conformation metallocycle fabricated by six Cd1 atoms around one Cd2 center in 5; (b) the 3D framework of 5.

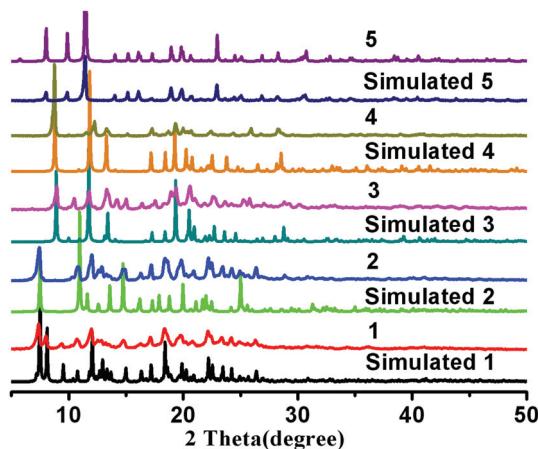


Fig. 8 PXRD patterns of coordination polymers 1–5.

and simulated PXRD patterns are in good agreement with each other. The differences in intensity may be owing to the preferred orientation of the crystal samples.

The luminescent behaviors of five complexes and their corresponding free ligands L₁-MOM and L₂-MOM were investigated in the solid state at room temperature. When excited with 300 nm light, the free ligands L₁-MOM and L₂-MOM display maximum emission wavelengths at 404 and 415 nm, respectively (Fig. 9), which originated from charge transfer of

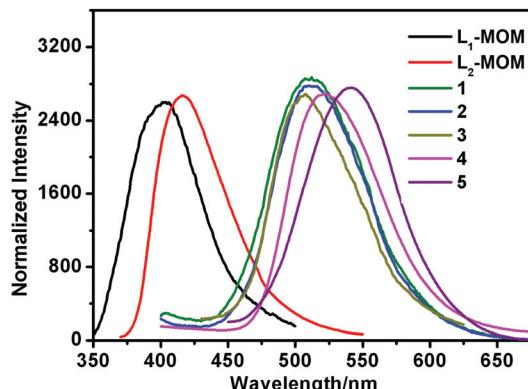


Fig. 9 Emission spectra of ligands L₁-MOM and L₂-MOM, and coordination polymers 1–5 in the solid state.

the internal ligand. Coordination polymers 1–5 exhibit intense photoluminescences with the emission maximum at 511, 511, 506, 523, and 543 nm, respectively, upon excitation at 340 nm (Fig. 9). Compared with the emission spectra of the corresponding ligands L₁-MOM and L₂-MOM, varying degrees of red shifts of 107 nm in 1 and 2, 102 nm in 3, 108 nm in 4, and 128 nm in 5 have been observed, which are considered to mainly arise from the coordination of metal centers to the ligands L₁-MOM and L₂-MOM. The incorporation of metal ions effectively increases the conformational rigidity of the ligand and reduces the loss of energy *via* vibrational motions.²⁰ In addition, the coordination of the ligand with Zn(II) or Cd(II) ions forms additional five-membered rings, which increases the π - π^* conjugation length and the conformational coplanarity, and accordingly reduces the energy gap between the π and π^* molecular orbital of the ligand.²¹ From Fig. 9, the emission wavelengths of polymers 4 and 5 are red-shifted in comparison with those of the other three complexes, which may be attributed to their Cd(II) centers and close-packed supramolecular structures.

To further understand the fluorescent properties of coordination polymers 1–5, their fluorescence lifetimes were investigated at room temperature in the solid state (Fig. S12†). The average lifetime was determined by allowing α_i and τ_i to vary, and then convoluting eqn (1) with the instrument response function. The data was successfully modeled using double exponentials, and the average lifetime was determined using

Table 1 Detailed parameters extracted from photoluminescent properties of 1–5^a

Complex	λ_{ex} (nm)	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
1	511	4.39(54%)	10.53(46%)	8.51
2	511	5.62(73%)	17.43(27%)	11.93
3	506	5.45(39%)	14.32(61%)	12.58
4	523	3.78(70%)	11.42(30%)	8.09
5	543	3.53(69%)	7.94(31%)	5.75

^a τ_{avg} : average fluorescence lifetimes; λ_{em} : emission wavelength.

eqn (2). In both equations t is time, τ is lifetime, and α is a pre-exponential factor.¹⁹ The results are summarized in Table 1. The shortest fluorescence lifetime of coordination polymer 5 (5.75 ns), in comparison with polymers 1–4, may arise from a combined contribution from a competitive non-radiative decay process in the metal complex (such as the incompletely hindered electron transfer), and distinct supramolecular structures.

$$I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

$$\tau_{\text{avg}} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \quad (2)$$

Sensing of nitroaromatics

Li and coworkers recently explored that many Zn(II) coordination polymers exhibit unique selectivity for the detection of high explosives and other environmentally deleterious aromatics *via* a fluorescence quenching and enhancement mechanism.⁸ This stimulates us to probe the applicability of polymers 1–5 for the sensing of electron-deficient nitroaromatics (NACs). Fluorescent spectra were recorded on powder samples of 1–5 in thin-layer form, and it was found that all nitroaromatics act as fluorescence quenchers for 1–5 (Fig. S13–17†). The quenching efficiency (%) was estimated using the formula $(I_0 - I)/I_0 \times 100\%$, where I_0 is the maximum fluorescence intensity of the polymers before exposure to the analyte, I is the maximum intensity after exposure to the analyte. Among these NACs used in this study, the most effective quencher is 2-nitrotoluene (2-NT) compared with nitrobenzene (NB) and 3-nitrotoluene (3-NT) (Fig. 11). 2-NT quenches the emission by 61%, 72%, 96%, 44%, 51%, respectively, for polymer 1–5. For 1, 2 and 5, the order of quenching efficiency for the selected nitroaromatics is 2-NT > NB > 3-NT; for 3 and 4, the quenching efficiency of NACs was found to decrease in the order 2-NT > 3-NT > NB. Notably, this order is not in accordance with the trend of electron-withdrawing groups, which also cannot be explained when the vapor pressure of each analyte is also taken into consideration. The observed fluorescence attenuation can be explained by the donor–acceptor electron-transfer mechanism.⁸ 2-NT exhibits the strongest quenching effect, which may be attributed to its strongest polymer-analyte π-stacking, compared with NB and 3-NT.^{9,22} As shown in Fig. 10, the rates of quenching of Zn(II) polymers 1–3 were faster with NACs than that of Cd(II) polymers 4 and 5. In addition, a higher quenching effect was observed for 3 than isostructural 4 due to their different metal centers. From these data, fluorescence quenching is undergoing a mixed quenching pathway for polymers 1–5. The observed quenching trend is not controlled by a single factor but by a number of properties such as the nature of the analyte molecules, metal centers and supramolecular structures of the coordination polymers, relative orbital energies and interactions between coordination polymers and analyte molecules.^{8,9}

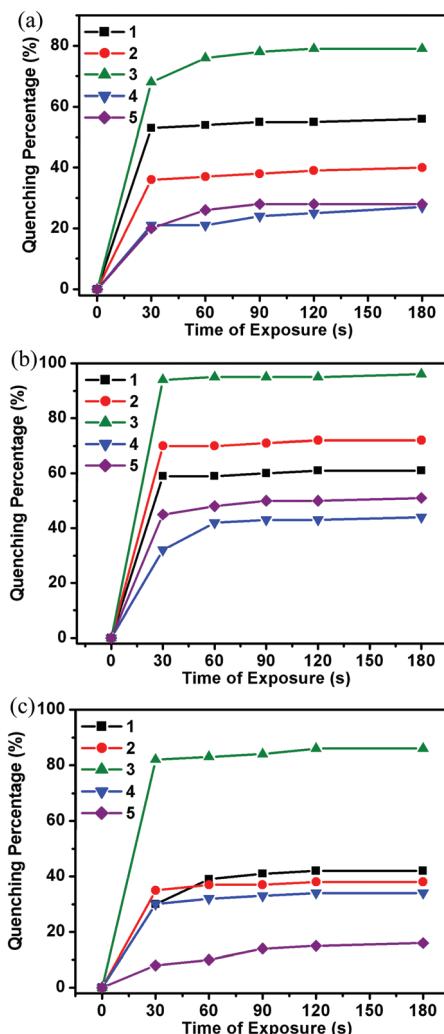


Fig. 10 Fluorescence quenching response of 1–5 upon exposure to saturated vapour of NB (a), 2-NT (b), and 3-NT (c) at room temperature for the specified times.

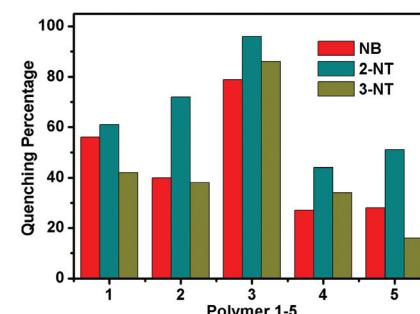


Fig. 11 Percentage of fluorescence quenching after 3 min by five different analytes for coordination polymers 1–5 at room temperature.

Experimental section

Chemicals, reagents, and analyses

All of the chemicals are commercially available, and were used without further purification. Elemental analyses were

performed with an EA1110 CHNS-O CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400–4000 cm⁻¹ region) on a Nicolet Magna 750 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu K α radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. All fluorescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). The room-temperature (RT) lifetime measurements were determined on a FLS920 time-resolved and steady-state fluorescence spectrometer (Edinburgh Instruments). ¹H and ¹³C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 400 MHz. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as the mobile phase.

Synthesis

5,7-Dibromo-2-methyl-8-methoxymethoxyquinoline and ligand L₁-MOM were synthesized according to our previous report.^{18b}

Ligand L₂-MOM. 5,7-Dibromo-2-methyl-8-methoxymethoxyquinoline (3.6 g, 10.0 mmol), 3-pyridylboronic acid (3.7 g, 30.0 mmol), Na₂CO₃ (8.0 g, 75.5 mmol) and PdCl₂(dpf)-CH₂Cl₂ (0.41 g, 0.80 mmol) were weighed into a 100 mL Schlenk flask, which was then pump-purged with N₂ three times. DME (40 mL) and H₂O (20 mL) were added under a dry N₂ atmosphere. The mixture was stirred at 95 °C overnight. The reaction mixture was cooled to room temperature and extracted with CH₂Cl₂. The organic layers were dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (8 : 3 : 1 AcOEt-hexane-Et₃N) to afford ligand L₂-MOM as a white solid. Yield: 3.0 g, 84%. ¹H NMR (400 MHz, CDCl₃) δ : 8.96 (d, *J* = 2 Hz, 1H), 8.74 (d, *J* = 2 Hz, 1H), 8.69 (dd, *J* = 6.4 Hz, 1H), 8.61 (dd, *J* = 6.4 Hz, 1H), 8.06–8.01 (m, 2H), 7.80–7.77 (m, 1H), 7.46–7.39 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 1H), 5.43 (s, 2H), 3.03 (s, 3H), 2.76 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) δ : 159.2, 150.9, 150.7, 150.1, 149.2, 148.7, 142.6, 137.5, 135.0, 134.3, 132.6, 131.0, 128.6, 126.3, 123.6, 123.3, 123.0, 100.4, 57.5, 25.8; ESI-MS: *m/z* 358.1 ([M + 1]⁺), 359.0 ([M + 2]⁺). Elemental analysis (%): calcd for (C₂₂H₁₉N₃O₂) C: 73.93, H: 5.36, N: 11.76; found C: 73.75, H: 5.27, N: 11.88.

Synthesis of compounds 1–5. A mixture of ZnX₂ (X = OAc⁻, NO₃⁻, 0.08 mmol) or Cd(NO₃)₂ (0.08 mmol), L₁-MOM or L₂-MOM (0.04 mmol), H₂O (0.2 mL), DMF (0.2 mL) and MeOH (2 mL) in a capped vial was heated at 80 °C for one day. Yellow blocklike crystals of 1–5 suitable for single-crystal X-ray diffraction were collected, washed with ether and dried in air. Yield: 1, 11.3 mg, 82%; 2, 12.1 mg, 80%; 3, 11.5 mg, 85%; 4, 11.6 mg, 79%; 5, 13.6 mg, 80%.

Compound 1: 1 was prepared by solvothermal reactions of Zn(OAc)₂ with ligand L₁-MOM according to the abovementioned general procedure. Elemental analysis data and IR of [Zn₃(L₁)₆] (1): Anal (%). Calcd for C₁₂₀H₈₄N₁₈O₆Zn₃: C, 69.62; H, 4.09; N, 12.18. Found: C, 69.13; H, 4.16; N, 12.03. FTIR (KBr

pellet): 3748(w), 3449(s), 3425(s), 1598(s), 1548(w), 1514(w), 1419(s), 1363(w), 1271(m), 1224(w), 1104(w), 1065(w), 1020(w), 834(m), 750(m), 656(w), 580(m), 557(w), 509(w).

Compound 2: 2 was prepared by solvothermal reactions of Zn(NO₃)₂ with ligand L₁-MOM according to the abovementioned general procedure. Elemental analysis data and IR of [Zn(L₁)₂]-2MeOH (2): Anal (%). Calcd for C₄₂H₃₆N₆O₄Zn: C, 66.89; H, 4.81; N, 11.14. Found: C, 66.65; H, 4.90; N, 11.34. FTIR (KBr pellet): 3446(s), 3025(w), 1598(s), 1548(m), 1513(m), 1435(s), 1409(s), 1364(m), 1318(w), 1272(m), 1216(w), 1104(w), 1065(w), 1017(w), 832(m), 749(w), 695(w), 684(w), 656(w), 584(m), 522(w).

Compound 3: 3 was prepared by solvothermal reactions of Zn(NO₃)₂ with ligand L₂-MOM according to the abovementioned general procedure. Elemental analysis data and IR of [Zn(L₂)₂] (3): Anal (%). Calcd for C₄₀H₂₈N₆O₂Zn: C, 69.62; H, 4.09; N, 12.18. Found: C, 69.46; H, 4.36; N, 12.01. FTIR (KBr pellet): 3867(w), 3785(w), 3449(s), 3058(w), 1624(w), 1516(m), 1420(s), 1364(m), 1326(w), 1272(m), 1186(m), 1107(m), 1029(w), 950(w), 901(w), 823(m), 754(m), 710(m), 655(w), 630(w), 578(w).

Compound 4: 4 was prepared by solvothermal reactions of Cd(NO₃)₂ with ligand L₂-MOM according to the abovementioned general procedure. Elemental analysis data and IR of [Cd(L₂)₂] (4): Anal (%). Calcd for C₄₀H₂₈N₆O₂Cd: C, 65.18; H, 3.83; N, 11.40. Found: C, 65.02; H, 3.98; N, 11.24. FTIR (KBr pellet): 3423(w), 3273(w), 3082(w), 2854(w), 2805(w), 2575(w), 2160(w), 1888(m), 1752(m), 1674(m), 1566(m), 1520(m), 1427(s), 1357(s), 1263(m), 1179(w), 1143(w), 1101(w), 1049(m), 974(w), 948(s), 897(w), 801(w), 750(w), 707(w), 628(w), 566(w), 538(s).

Compound 5: 5 was prepared by solvothermal reactions of Cd(NO₃)₂ with ligand L₁-MOM according to the abovementioned general procedure. Elemental analysis data and IR of [Cd₄(L₁)₆]-13H₂O (5): Anal (%). Calcd for C₁₂₀H₁₁₀N₁₈O₁₉Cd₄: C, 56.35; H, 4.33; N, 9.86. Found: C, 56.77; H, 4.28; N, 9.95. FTIR (KBr pellet): 3750(m), 3673(m), 3540(m), 3463(m), 3419(m), 3261(w), 3189(w), 2834(w), 2805(w), 2595(w), 2563(w), 1885(w), 1841(w), 1748(w), 1655(m), 1604(s), 1547(m), 1514(m), 1385(s), 1260(w), 1216(w), 1171(w), 1062(m), 1006(m), 949(m), 832(m), 740(w), 655(m), 581(m).

Preparation of thin layers for photoluminescence study. For photoluminescence (PL) studies, samples were prepared in the form of thin layers on glass slides. Quartz slides of dimension 1 × 2 cm were first rinsed with de-ionized water and methanol, and then dried in the oven. Double sided tape was then applied to the upper half of the slide. For making the thin layers of the sample, the tape was peeled off from the slide after 5 minutes, such that the glue from the tape is stuck in the glass slide. well-ground powder of the as-made sample was then sprinkled evenly onto the glued surface of the slide. The extra samples were removed by gentle tapping and putting the face of the slide down. By this process a very thin continuous layer of sample was formed on the glass surface. This glass was then used for the PL study of the sample. New slides with a thin layer were used for each of the quenching experiments. The original fluorescence spectra of each layer were collected before placing the particular glass slides onto each of the

analytes. The fluorescence response of the thin layers to the vapors of NACs was ascertained by inserting the prepared thin layers into quartz cuvettes at RT containing the analytes and cotton gauze, which prevents the direct contact of the thin layers with the analyte and helps to maintain a constant saturated vapor pressure. Thin layers were placed in the quartz cuvette and fluorescence spectra were measured after exposing the thin layers for a specific interval time.

X-ray crystallography

Single-crystal XRD data for compounds **1–5** were all collected on a Bruker APEX area-detector X-ray diffractometer with Mo_{Kα} radiation ($\lambda = 0.71073 \text{ \AA}$). The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). In coordination polymers **1** and **5**, the solvent-masking procedure (aka SQUEEZE) has been applied to the entire contents of the voids. Crystal data and details of the data collection are given in Table S1,[†] whereas the selected bond distances and angles are presented in Table S2–6.[†] The CCDC numbers of **1–5** are 1016361–1016365, respectively.

Conclusion

In summary, five coordination polymers with different structures are prepared under solvothermal conditions, using Zn(II) or Cd(II) salts and two bispyridyl-based quinolinate ligands synthesized from the cheap commercially available 8-hydroxy-quininaline. These polymers exhibited disparate fluorescence emissions and lifetimes upon excitation in the solid state due to their different metal centers and supramolecular structures. We have also evaluated the fluorescence-based sensing properties of **1–5** at room temperature. Fluorescence quenching was observed when the coordination polymers were exposed to the vapor of aromatic compounds. However, compound **3** shows superior sensitivity to the analytes in comparison with other polymers. The rate of quenching of polymers **1–5** was higher with 2-NT compared to those with NB and 3-NT. This work shows that fluorescence quenching undergoes a mixed quenching pathway, and is governed by a number of factors such as the nature of the analyte molecules, metal centers and supramolecular structures of the coordination polymers, relative orbital energies and interactions between the coordination polymers and analyte molecules.

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