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## Introduction

Photoluminescent materials have been extensively explored and realized for their diverse functionalities and applications in lighting, display, sensing, and optical devices.<sup>1</sup> Motivated by the success of tris(8-hydroxyquinolinato)aluminum (Alq<sub>3</sub>) in vacuum-deposited LEDs, organic chelate metal complexes based on 8-hydroxygunoline derivatives have, in particular, attracted a lot of attention.<sup>2-4</sup> Significantly, recent reports have suggested that the fluorescent properties of the metal derivatives of 8-hydroxyquionoline (q-H) in the solid state are dependent on the character of the metal ion, the degree of aggregation, the molecular and crystal structure, as well as the intermolecular noncovalent interactions involved.<sup>5</sup> Therefore, the development of new synthetic methods and strategies for the construction of well-defined heteroleptic molecular complexes or multinuclear clusters supported by 8-hydroxyquinoline ligands, with unique self-assembly structures and properties and with enhanced and tunable photoluminescence features, is a big challenge for chemists. Recently, zinc(II) has been explored as a metal center to construct analogues of Alq3, bis(8-hydroxyquinoline)zinc(II) (Znq<sub>2</sub>) complexes, which have been demonstrated to be potential candidates to enhance the

## Anion-controlled structures and luminescent properties of three Cd(II) complexes assembled by a 2-substituted 8-hydroxyquinoline ligand<sup>†</sup>

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This work reports the self-assembly of three cadmium complexes **1–3** from one 2-substituted 8-hydroxyquinoline ligand (HL). The skeleton exhibits an unprecedented structural diversification and fabricates one mononuclear and two different tetranuclear Cd(II) building units in response to the counteranions NO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup> and I<sup>-</sup>, respectively. The self-assembly behavior of the cadmium salts and the HL in MeOH was subsequently investigated using UV-vis spectroscopy. In the solid state, the supramolecular structures of **1–3** feature unique helical chains or a 3D network *via* non-covalent interactions, such as  $\pi \cdots \pi$  stacking, C–H $\cdots \pi$ , hydrogen bonding and halogen-related interactions. As a result, the three Cd(II) complexes exhibit disparate photophysical properties. This unique capability may provide a useful strategy to tune the optical properties of multinuclear materials, which could be exploited as important components for optoelectronic devices.

electron-transporting properties for organic light-emitting devices (OLEDs).<sup>6</sup> Similar to zinc(II), cadmium(II) also has a spectroscopically silent  $d^{10}$  electronic configuration. Therefore, owing to the amiability to form bonds with different donors simultaneously, the larger radius, and the wide variety of coordination modes and coordination numbers of the Cd(II) ions, much attention has been given to the functional complexes involving Cd(II) ions in search of molecular-based materials with interesting physical properties.<sup>7</sup> With few notable exceptions, oligomeric (multinuclear) Cd(II) 8-hydroxyquinolinate-based complexes with high luminous efficiencies have not yet been developed.<sup>8</sup>

Over the past decades, zero-, one-, two-, or three-dimensional (0D, 1D, 2D, or 3D) coordination assemblies have been studied extensively owing to their structural versatility and distinctive properties, as well as their potential applications in different fields of science.<sup>9-11</sup> The observed properties are very much influenced by subtle changes in the supramolecular structure of the building entities, and the development of synthetic strategies to achieve the desired product with predefined properties is a long-term challenge. Numerous routes have been investigated in recent times to predict and control the supramolecular assembly. Some are controlled by the structure-directing factors such as the inbeing of the metal ions, the predesigned organic ligands,12 the solvent,13 the pH value of the solution,<sup>14</sup> the temperature,<sup>15</sup> the counterion with a different bulk or coordination ability,16 the template and metal-to-ligand stoichiometry,17 while others are controlled by the inter- and intramolecular noncovalent forces such as hydrogen bonding,  $\pi \cdots \pi$  stacking, metal...metal, metal... $\pi$ , C-

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<sup>†</sup> Electronic supplementary information (ESI) available. CCDC numbers 923976– 923978 contain the supplementary crystallographic data for **1–3**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce40348c

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H<sup>...</sup> $\pi$ , anion<sup>...</sup> $\pi$  and halogen-related interactions that also determine the supramolecular topology and dimensionality in the solid state.<sup>18</sup>

Of particular interest to us are works on the elegant design and synthesis of novel crystalline photoluminescent materials whose core (or supramolecular) structures can be tuned.<sup>19</sup> Our goal is to achieve control over the molecular or supramolecular structures and thereby the physical properties of the new materials. The HL ligand ((E)-2-[2-(2,6-dichlorophenyl)ethenyl]-8-hydroxyquinoline) is chosen for the following reasons: (1) in the quinolinolate ligands, the HOMO-orbitals are mainly located on the phenoxide side of the ligand, while the LUMO-orbitals are mainly located on the pyridyl side.<sup>20</sup> This implies that the band gap of the 8-hydroxyquinoline-based coordination complexes could be delicately tuned by the introduction of electron withdrawing groups onto the 2-position of the pyridine ring, thus modulating the emission property; (2) the chlorine group on the HL ligand can facilitate the formation of diverse halogen bonds (such as C-Cl···H-C, C-Cl<sup> $\dots$ </sup> $\pi$ , and C-Cl<sup> $\dots$ </sup>Cl-C interactions), which may affect the supramolecular structure of the coordination complexes by extending the multinuclear discrete subunits or low dimensional entities into high-dimensional supramolecular networks, hence generating fascinating properties in the solid state.<sup>19a,21</sup> Herein, we report the self-assembly of three cadmium complexes 1-3 from the 2-substituted 8-hydroxyquinoline HL ligand (Scheme 1). The skeleton exhibits an unprecedented structural diversification and fabricates one mononuclear and two different tetranuclear Cd(II) core structures in response to the counteranions NO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup> and I<sup>-</sup>, respectively. In the solid state, the supramolecular structures of 1-3 feature unique helical chains or a 3D network *via* non-covalent interactions, such as  $\pi^{...}\pi$  stacking, C-H··· $\pi$ , hydrogen bonding and halogen-related interactions. As a result, the three Cd(II) complexes exhibit disparate



Scheme 1 Synthesis of Cd(II) complexes 1-3 from ligand HL.

fluorescent properties due to their different core and supramolecular structures.

## **Experimental section**

### Materials and characterization methods

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 cm<sup>-1</sup> region) on a Nicolet Magna 750 FT-IR spectrometer. The powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Ka 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). All UV-vis absorption spectrum were recorded on a Lambda 20 UV-vis Spectrometer (Perkin Elmer, Inc., USA).

#### Synthesis of compounds 1-3

A mixture of  $CdX_2$  (X =  $NO_3^-$ ,  $OAc^-$ ,  $I^-$ , 0.02 mmol), HL (0.01 mmol), H<sub>2</sub>O (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 1–3 suitable for single-crystal X-ray diffraction were collected, washed with ether and dried in air. The products were not significantly affected by a change in the molar ratio of Cd(II) and HL (1 : 1, 2 : 1 or 1 : 2). Yield: 1, 3.0 mg, 75%; 2, 3.4 mg, 80%; 3, 3.5 mg, 78%.

Elemental analysis data and IR of 1. Anal (%). calcd for  $C_{35}H_{28}Cl_4N_2O_5Cd: C, 51.84; H, 3.48; N, 3.45.$  Found: C, 51.95; H, 3.62; N, 3.56. FTIR (KBr pellet): 3720.2(s), 3649.2(s), 3545.6(s), 3467.3(s), 3418.1(s), 3271.1(m), 2841.1(w), 2599.6(w), 2164.2(w), 2012.9(w), 1886.2(w), 1743.6(w), 1639.5(m), 1620.7(m), 1548.4(m), 1434.4(m), 1365.7(m), 1340.7(m), 1280.7(m), 1176.8(w), 1144.4(w), 1096.7(m), 971.1(m), 948.5(m), 828.4(w), 770.82(m), 740.7(m), 607.6(s), 571.6(s).

Elemental analysis data and IR of 2. Anal (%). calcd for  $C_{108}H_{74}Cl_{12}N_6O_{12}Cd_4$ : C, 51.42; H, 2.96; N, 3.33. Found: C, 51.32; H, 2.93; N, 3.26. FTIR (KBr pellet): 3856.5(s), 3805.1(s), 3747.0(s), 3671.9(s), 3626.2(s), 3569.5(s), 3514.1(s), 3449.7(s), 3418.0(s), 3381.2(s), 2600.8(w), 1670.5(m), 1602.3(m), 1553.0(m), 1503.1(w), 1437.2(s), 1369.9(m), 1333.1(m), 1268.4(m), 1099.5(m), 966.8(w), 878.2(w), 829.2(w), 774.7(m), 746.4(m), 610.8(w), 576.5(w).

Elemental analysis data and IR of 3. Anal (%). calcd for  $C_{104}H_{68}Cl_{12}I_2N_6O_8Cd_4$ : C, 46.98; H, 2.58; N, 3.16. Found: C, 46.80; H, 2.55; N, 3.13. FTIR (KBr pellet): 3858.2(m), 3801.9(m), 3748.3(s), 3714.1(s), 3635.0(s), 3556.6(s), 3451.3(s), 3416.7(s), 2600.2(w), 1634.7(s), 1617.8(s), 1551.8(s), 1503.9(w), 1435.6(s), 1369.2(m), 1332.3(s), 1274.2(m), 1148.4(w), 1100.4(s), 1065.5(m), 968.8(m), 948.6(m), 828.7(w), 773.3(m), 7443.5(m), 595.9(s), 5571.1(s).

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

Paper

Identification code	1	2	3
Empirical formula	$C_{35}H_{28}Cl_4N_2O_5Cd$	C <sub>108</sub> H <sub>74</sub> Cl <sub>12</sub> N <sub>6</sub> O <sub>12</sub> Cd <sub>4</sub>	C104H68Cl12I2N6O8Cd4
Formula weight	809.98	2522.78	2658.58
Temperature (K)	296(2)	296(2)	58(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c
Unit cell dimensions	a = 9.090(3) Å	a = 14.7666(10) Å	a = 15.880(2) Å
	b = 26.329(8) Å	b = 24.2437(17) Å	b = 24.478(3) Å
	c = 14.854(5) Å	c = 14.9700(10) Å	c = 26.637(7) Å
	$alpha = 90^{\circ}$	$alpha = 90^{\circ}$	$alpha = 90^{\circ}$
	beta = $95.5^{\circ}$	beta = $112^{\circ}$	beta = $106.3^{\circ}$
	gamma = $90^{\circ}$	gamma = $90^{\circ}$	gamma = $90^{\circ}$
Volume (Å <sup>3</sup> ), Z	3538.5(19), 4	4968.1(6), 2	9940(2), 4
Density (calculated) (Mg $m^{-3}$ )	1.507	1.686	1.734
Absorption coefficient $(mm^{-1})$	0.962	1.234	1.845
F(000)	1600	2512	5056
$\theta$ range for data collection (°)	2.38 to 27.48	2.36 to 27.48	1.57 to 27.55
Reflections collected	21 813	30 702	22 554
Independent reflections	$8039 [R_{int} = 0.0293]$	11 286 $[R_{int} = 0.0387]$	11 258 $[R_{int} = 0.0420]$
Completeness to theta	27.48/98.9%	27.48/99.0%	27.55/98.2%
Data/restraints/parameters	8039/0/414	11 286/710/671	11 258/582/603
Goodness-of-fit on $F^2$	1.033	1.049	1.111
Final <i>R</i> indices $[I > 2 \operatorname{sigma}(I)]$	$R_1 = 0.0448, wR_2 = 0.1212$	$R_1 = 0.0504, wR_2 = 0.1256$	$R_1 = 0.0538, wR_2 = 0.1432$
<i>R</i> indices (all data)	$R_1 = 0.0648, wR_2 = 0.1341$	$R_1 = 0.0916, wR_2 = 0.1464$	$R_1 = 0.1071, wR_2 = 0.2035$
Largest diff. peak and hole (e $Å^{-3}$ )	1.158 and −0.609	1.060 and -0.692	1.715 and -0.901

#### X-ray crystallography

The single-crystal XRD data for compounds 1–3 were all collected on a Bruker APEX area-detector X-ray diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). 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 the 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). The crystal data and the details of the data collection are given in Table 1, whereas the selected bond distances and angles are presented in Tables S1–S3, ESI.† The CCDC numbers of 1–3 are 923976, 923977 and 923978, respectively.

## **Results and discussion**

### Coordination studies in solution

In order to further investigate the interaction mode of the HL ligand with the  $Cd^{2+}$  ion, the coordination reaction of HL with the  $Cd^{2+}$  ion was monitored through a UV-vis spectroscopic titration. The absorption bands of HL in MeOH dramatically change upon the addition of the  $Cd^{2+}$  ions. As depicted in Fig. 1a, the band of 1 showed a significant bathochromism shift from 283 to 297 nm. The peak at 329 nm was found to become weak and disappeared in the end in the presence of increasing amounts of the  $Cd^{2+}$  ion. The new band at 420 nm is attributed to the charge transfer from the metal to ligand

band. No differences were observed in the absorption spectra after the 1 : 2 ratio of  $Cd^{2+}/HL$ , so this experiment clearly indicates the formation of  $(CdL_2)_n$ . By following the same procedure, the formation of  $(Cd_2L_3)_n$  for 2 and 3 was also determined by UV-vis spectroscopic titrations (Fig. 1a and 1b).

### Structural description

[CdL<sub>2</sub>]·2H<sub>2</sub>O·2MeOH (1). Single-crystals of complex 1 were readily obtained in good yields by heating Cd(NO<sub>3</sub>)<sub>2</sub> and HL in a mixture of DMF, MeOH and water. Complex 1 crystallizes in the monoclinic space group  $P2_1/c$  with Z = 4. The asymmetric unit contains one formula unit, that is, one unique Cd(II) center, two L ligands, two coordinated H2O, and one methanol molecule. The Cd(II) center adopts an octahedral geometry with the equatorial plane occupied by the NO3 donors of two L ligands and one H<sub>2</sub>O molecule, and the apical position is occupied by one quinoline nitrogen atom and one H<sub>2</sub>O molecule (Fig. S1, ESI<sup>†</sup>). The bond lengths around Cd(II) are 2.359(4)-2.365(3) Å for Cd-O, and 2. 397(3) and 2.438(3) Å for Cd-N, respectively. The two crystallographically unique ligands have dihedral angles (ca.  $58.6^{\circ}$  and  $66.8^{\circ}$  for 1) between the quinoline and 2,6-dichlorophenyl moieties which indicate that the ligands are non-coplanar in 1. There are weak nonclassical C-H-O and C-H-Cl intramolecular hydrogen bonds in 1 between the phenolato oxygen (or 2,6-dichlorophenyl chlorine) atoms and the C-H group of ethenyl (C···O = 3.226(4) and 3.357(5) Å, C-H···O = 148 and 156°; C···Cl = 3.165(4) Å, C-H···Cl =  $109^{\circ}$ ), which play a significant role in the construction of the mononuclear Cd(II) unit (Fig. S2, ESI<sup>†</sup>).

Interestingly, a kind of *meso*-helical chain (P + M) along the *b* axis constructed *via* a C-H···Cl interaction between the -Cl atom of dichlorophenyl and the C-H group of the adjacent



Fig. 1 UV-vis titrations of HL (10  $\mu$ M) in methanol with Cd(NO<sub>3</sub>)<sub>2</sub> (a), Cd(OAc)<sub>2</sub> (b) and CdI<sub>2</sub> (c), respectively. Each spectrum was acquired 5 min after the Cd<sup>2+</sup> addition.

ligand (3.744 Å) is observed in the solid state of this compound. As shown in Fig. 2a, the two 2<sub>1</sub> helices have an identical pitch of 26.329(8) Å (equal to the *b* axis length). To the best of our knowledge, such helical chains constructed by C-H···Cl interactions are very rare. Additionally, it is notable that each cluster of **1** involves abundant intermolecular C-H···π (between the C-H group of the quinoline units and the pyridine ring of the adjacent ligand, 3.402(4) Å) and C-Cl···π (between the C-Cl group of dichlorophenyl and the pyridine ring of the adjacent ligand, 3.716(2) and 3.382(2) Å) interactions in the *ac* plane (Fig. 2b). By the coactions of the three kinds of noncovalent interactions, the structure extends into a 3D network (Fig. 2c).

 $[Cd_4(L)_6(OAc)_2]$ ·2MeOH (2). When the 8-hydroxyquinoline HL ligand was reacted with  $Cd(OAc)_2$  under the same reaction conditions, one double cubane tetranuclear compound, namely,  $[Cd_4(L)_6(OAc)_2]$ ·2MeOH (2), was obtained. The single-crystal structure analysis reveals that 2 crystallizes in the



**Fig. 2** a) A view of the 1D intertwined supramolecular helical chains in **1** along the *b* axis; b) the 2D supramolecular structure of **1** mediated by C–H··· $\pi$  and C–Cl··· $\pi$  interactions; c) the 3D network of **1**.

monoclinic space group  $P2_1/n$ , with one half of a formula unit in the asymmetric unit, that is, two Cd(II) atoms, three L ligands, one coordinated acetate anion and one methanol molecule. The coordination environment of the Cd<sup>2+</sup> ions in complex 2 is shown in Fig. 3, and it can be seen that there are two crystallographically independent Cd(II). Cd1 is six-coordinated to four phenolato oxygen atoms (one O1, one O2, and two O3) and two nitrogen atoms (N1 and N2) from four L ligands displaying a distorted octahedron geometry. Cd2 is also six-coordinated with a distorted octahedron geometry. In addition to O1, O2, O3 and N3 from three L ligands, the other two coordination atoms for Cd2 are O4 and O5 from one acetate anion. The bond lengths and angles around Cd(II) are 2.324(4)-2.392(4) Å for Cd-N, 2.200(3)-2.435(3) Å for Cd-O, 78.18(11)-169.28(12)° for O-Cd-O, 71.92(11)-150.99(13)° for O-Cd-N and 103.55° for N-Cd-N, respectively. However, the bridging of the six oxygen atoms of the six L ligands makes 2Cd1 and 2Cd2 involved in a double-open cubane-like unit  $(Cd_4O_6)$  (Fig. 3). To the best of our knowledge, the double-open cubane-type Cd<sub>4</sub>O<sub>6</sub> cluster of 2 reported here is the first example of a tetranuclear Cd(II) oxygen cluster, although a



Fig. 3 Views of the coordination geometries of Cd(11) atoms in  ${\bf 2}$  (H atoms omitted for clarity).



**Fig. 4** A view of the 1D helical chains fabricated *via* the C–Cl···Cl–C intermolecular interaction in **2** along the *b* axis.

number of face-sharing double cubane structures of other metal complexes have been reported.<sup>22</sup>

There are intramolecular C-H···Cl (between the 2,6-dichlorophenyl chlorine atoms and the C-H group of ethenyl, 2.993(5)-3.205(7) Å) and  $\pi^{...}\pi$  interactions (face-to-face distance: 3.550(5) Å) in 2, which play a significant role in the construction of the tetranuclear Cd(II) units (Fig. S8, ESI<sup>†</sup>). Through the C-Cl···Cl-C intermolecular interaction (Cl1···Cl6 = 3.215(2) Å), the tetranuclear Cd(II) units are further linked into a helical chain along the *b* axis. The helical chain is thus generated around the crystallographic 2(1) axis with a pitch of 16.712(4) Å, which is equal to the b axis length (Fig. 4). Additionally, halogen bonds involving Cl2 and Cl3 from different tetranuclear units (Cl2…Cl3 = 3.810(2) Å) link the tetranuclear Cd(II) units into a supramolecular chain along the c axis. Based on the two kinds of C-Cl···Cl-C intermolecular interactions, the tetranuclear Cd(II) units are connected into a 2D network (Fig. 5).

 $[Cd_4(L)_6I_2]$ ·2MeOH (3). In order to further investigate the influence of the counterions on the formation and structures of the complexes, the 8-hydroxyquinoline HL ligand was reacted with  $CdI_2$  under the same conditions, and one tetranuclear compound, namely,  $[Cd_4(L)_6I_2]$ ·2MeOH (3), was obtained. As shown in Fig. 6a, there are two crystallographically independent Cd(II) in the tetranuclear centrosymmetric complex 3. The two terminal Cd1 atoms are five-coordinated by one iodine atom, one nitrogen atom and three hydroxyl



Fig. 5 The 2D supramolecular structure of 2.



**Fig. 6** a) A view of the coordination geometries of the Cd(II) atoms in **3**; b) the C-H··· $\pi$  interactions in **3** along the c-axis; c) the 2D network of **3** mediated by C-H···Cl interactions; d) the 3D network of **3**.

oxygen atoms from the three L ligands with an average Cd–O bond distance of 2.276(5) Å, a Cd–I bond distance of 2.716(8) Å and a Cd–N bond distance of 2.369(6) Å. The bond angles around Cd1 are in the range of 70.15(17)–140.66(17)°. While the two Cd2 centers adopt a distorted octahedral geometry with the equatorial plane occupied by the NO3 donors of three L ligands and the apical position occupied by one nitrogen and one oxygen atom of two ligands. The average Cd–O and Cd–N distances around Cd2 are 2.247(5) and 2.367(5) Å, respectively. The bond angles around Cd2 range from 70.85(17) to  $146.8(2)^\circ$ .

The intramolecular (or intermolecular) interactions play a significant role in the packing of the crystals. Three pairs of ligands with offset face-to-face  $\pi$ - $\pi$  stacking (Fig. S11, ESI†) are arranged around four Cd(II) atoms to form a tetranuclear cluster. As shown in Fig. 6c, through C(8)–H(8A)···Cl(4) (3.742(8) Å) intermolecular interactions, the neutral molecular units in 3 are linked into 2D layers in the *ab* plane, which are further assembled into a 3D supramolecular network (Fig. 6d) *via* an interlayer hydrogen bond C(14)–H(14A)··· $\pi$  (between the –CH<sub>3</sub> group of dichlorophenyl and the adjacent dichlorophenyl ring, 3.640(15) Å) interaction (Fig. 6b), contributing to the additional stability of the structure.

### Anion effects on molecular structure

On the basis of the above results, the roles of the anions in determining the structures of the three cadmium complexes are unambiguously exhibited. The nature (coordinating ability, size, and geometry) of the anions is the primary reason. Compared with OAc<sup>-</sup> and I<sup>-</sup>, the coordinating ability of NO<sub>3</sub><sup>-</sup> is worst in the construction of the cadmium complex. The NO<sub>3</sub><sup>-</sup> ion cannot coordinate to the cadmium center in the self-assembly of the mononuclear complex **1**. The OAc<sup>-</sup> ion has a larger size and two coordinated oxygen atoms in comparison with the I<sup>-</sup> ion. This induces the six-coordinated Cd(II) center in **2** to adopt a distorted octahedron geometry. The two terminal Cd atoms in **3** are five-coordinated by one iodine atom and four NO3 atoms from three ligands, and adopt a distorted trigonal bipyramid geometry. Additionally, the



Fig. 7 The PXRD patterns of complexes 1-3.

noncovalent forces such as hydrogen bonding,  $\pi$ ··· $\pi$  stacking, C–H··· $\pi$ , and halogen-related interactions also determine the self-assembly of the three supramolecular structures.

#### Fluorescent properties in the solid state

To prove that the crystal structures of trimeric **1–3** are truly representative of their bulk materials, powder X-ray diffraction (PXRD) experiments were carried out on the as-synthesized samples. As we can see from Fig. 7, the PXRD experimental patterns of **1–3** are in good agreement with the simulated patterns.



Fig. 8 a) The emission spectra of complexes 1–3 in the solid state; b) the emission decay trace of 1–3 in the solid state.

The fluorescent properties of compounds **1**, **2** and **3** were investigated in the solid state at room temperature (Fig. 8a). **1**–**3** exhibit intense photoluminescences with emission maxima at 580, 573, and 566 nm, respectively, upon excitation at 365 nm. Compared with the free ligand HL (Em: 465 nm), the bright and extensive yellow emissions of complexes **1**–**3** predominantly originate from the metal-to-ligand charge transfer (MLCT) transition and exhibit a remarkable red shift.<sup>17*a*</sup> However, differences in the optical properties of **1**–**3** in the solid state are observed. The mononuclear complexes **1** is red shifted in comparison with the two tetranuclear complexes **2** and **3**.

To further understand the fluorescent properties of 1–3, their lifetimes were investigated in the solid state. The  $\tau$  values of 1–3 are 5, 4 and 3 ns, respectively. The lifetimes of 1–3 are different and shorter than that of the zinc complex  $Zn_2L_4$  fabricated from HL.<sup>19*a*</sup> The above different fluorescent properties of complexes 1–3 can be explained by various molecular packing characteristics, which are consistent with the recently reported correlations between the molecular density of the packing and the length of the interligand contacts of the neighboring clusters in the crystal structures and the photophysical properties of the *mer*-Alq3 polymorphs (as a result of different dispersive and dipolar interactions, as well as different  $\pi$ – $\pi$  orbital overlaps).<sup>5*a*</sup>

## Conclusions

In the present work, we have demonstrated the self-assembly of three cadmium complexes built from a 2-substituted 8-hydroxyquinoline ligand and Cd(II) ions. In the solid state, the building units of **1**–3 exhibit a remarkable dependence on the counter anions. One mononuclear and two different tetranuclear Cd(II) core structures were fabricated in response to the counteranions  $NO_3^-$ ,  $OAc^-$  and  $I^-$ , respectively. Additionally, the three Cd(II) complexes exhibit disparate photophysical properties due to their different core and supramolecular structures. This unique capability may provide a useful strategy to tune the optical properties of multinuclear materials, which could be exploited as important components for optoelectronic devices.

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