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Table of content entry

Three double cubane tetranuclear complexes with different spatial structures were tuned by anion and have different photophysical properties.



Anion-tuned assembly of three double cubane tetranuclear

Cd(II)/Zn(II) complexes based on a 2-substituted 8-hydroxyquinoline

ligand: synthesis, crystal structures and fluorescent properties

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Abstract

2-substituted-8-hydroxyquinoline One unique ligand with 2,3-dimethoxyphenyl groups was synthesized and characterized by ESI-MS, NMR spectroscopy and elemental analysis (EA). Two double tetranuclear Cd(II) complexes $[Cd_4(L)_6(CH_3COO)_2]$ cubane (1). $[Cd_4(L)_6(I)_2]$ (2) and one double cubane tetranuclear Zn(II) complex $[Zn_4(L)_6(NO_3)_2]$ (3), were prepared by solvothermal reactions of Cd(CH₃COO)₂, CdI₂ and Zn(NO₃)₂. Complexes 1-3 were characterized with single crystal X-ray diffractions, powder X-ray diffractions (PXRD), thermogravimetry analyses (TGA) and EA. The building blocks exhibited unprecedented structural diversification and their self-assembly afforded tetranuclear Cd(II)/Zn(II) structures binding of different anions and

solvent systems. Complexes 1-3 featured three types of supramolecular network controlled by non-covalent interactions, such as C–H···O, C–H··· π , π ··· π stacking, hydrogen-bonding, and halogen-related interactions. Investigation of their photoluminescence properties exhibited disparate emission wavelengths and lifetimes in the solid state. 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.

Keyword: Anion-tuned; Double cubane tetranuclear; 8-hydroxyquinoline; Crystal structure; Photophysical property

Introduction

Over the past few decades, the design and preparation of metal-organic coordination complexes have caused widespread concerns, not only due to their fascinating structures, such as molecular cage, honeycomb, grid, ladder, rotaxane and catenane structures, but also their promising applications in gas adsorption, magnetism, ion-exchange, catalysis, lighting, display, sensing, and optical devices [1-8]. Motivated by the success of tris(8-hydroxyquinolinato)aluminum (Alq₃) in vacuum deposited LEDs, organic chelate metal complexes based on 8-hydroxyqunoline derivatives have, in particular, attracted a lot of attention [9].

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A large number of literatures show that the coordination of different metal ions and organic ligands involved in coordination of the ligand atoms of type, number, and the spatial location. Therefore in the process of design and construct target complexes, the choice of organic ligand and metal ions are very important. The d¹⁰ metal complexes, such as Zn(II) and Cd(II), not only have the stable electron configuration, and when the metal conjugation organic ligand to form complexes which cause metal to ligand or ligand to metal electron transition and transform the luminous performance of the ligand itself. This phenomenon has received extensive attention of the researchers [10]. In general, the photophysical properties of 8-quinolinolate-based complexes in the solid state are dependent on the character of the metal ion, the degree of aggregation, and the molecular and supramolecular structures, the intermolecular non-covalent interactions[11]. Hence, the development of new synthetic methods and strategies for the fabrication of well-defined heteroleptic molecular complexes or multinuclear clusters that are supported by organic 8-hydroxyquinoline derivatives, with unique self-assembled structures and properties, remains a big challenge for chemists [12].

Over the past two decades, it has been demonstrated that the self-assembly of complexes from polytopic organic linkers could be affected by many structure-directing factors [13-18], such as the metal,

the coordinating ability of the anion, the pH value, and the reaction temperature [19-23]. Of these factors, the anion plays a crucial role in influencing the formation of the coordination compound and leads to their structural and dimensional variation, supramolecular isomerism, and new topologies [19]. With a few notable exceptions, the systematic investigation of the effect of the anion on 8-hydroxyquinolinate-based complexes remains unexplored [24].

In recent years, we have reported the synthesis and characterization of a series of transition-metal complexes that involve 2-substituted 8-quinolinolate ligands with a NO donor set [25]. In this context, one 8-quinolinolate-based ligand (**HL**), which contained a 2. 3dimethoxyphenyl group, was chosen for fabricating Cd(II)/Zn(II) complexes in different solvent systems. We studied the effects of solvent for ligand to luminescence properties as well as the effects of anion to the structure of complexes. By using a solvothermal method, three double cubane tetranuclear Cd(II)/Zn(II) were constructed by the self-assembly of Cd(CH₃COO)₂, CdI₂ and Zn(NO₃)₂ with the **HL** ligand. In addition, their fluorescent properties showed disparate emission wavelengths, lifetimes, and quantum yields in the solid state. This unique capability may provide a useful strategy for tuning the optical properties of 8-hydroxyquinoline materials, which could be exploited as important components of optoelectronic devices.



Experimental

As outlined in Scheme 1, bidentate ligand **HL** was prepared by a similar procedure from the cheap commercial available 8-hydroxyquinaldine and characterized by ESI-MS, NMR spectroscopy and elemental analysis. Single crystals of complexes were readily obtained in good yields by heating Cd(CH₃COO)₂, CdI₂ and Zn(NO₃)₂ and **HL** in a mixture of DMF and MeOH.

Materials and methods

All solvents and reagents were purchased from commercial sources and used as received. Elemental analyses were performed with an Perkin-Elmer 2400 elemental analyzer. ¹HNMR experiments were performed on a MERCURYplus 400 spectrometer. All UV-Vis absorption spectrum were carried out on a Lambda 20 UV-Vis Spectrometer (Perkin Elmer, Inc., USA). The IR (KBr pellet) spectrum was recorded (400-4000 cm⁻¹ region) on a NICOLET380 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu K α radiation. Thermogravimetric analyses (TGA) were performed using a NETZSCH STA409P thermal analyzer under N₂ atmosphere at a heating rate of 15 °C·min⁻¹ in the temperature region of 25~1000 °C.

Preparation of 2-[2-(2, 3-dimethoxyphenyl)vinyl]-8-acetoxyquinoline

To a solution of 2, 3-dimethoxybenzaldehyde(1.33 g, 8 mmol) in acetic anhydride (15 ml) was added 1.1 equiv of 8-hydroxyquinaldine (1.4 g). The mixture was refluxed at 145 °C under N₂ for 30 h. The reaction mixture was extracted with dichloromethane. After removal of solvent under reduced pressure, the residue was purified on silica gel by column using acetone/hexane as the eluent to afford the target compound (1.15 g, 41 %). mp 90 °C, ¹H NMR (400 MHz, CDCl₃) δ : 8.17 – 8.04 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 12.3 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 7.0 Hz, 6H), 2.58 (s, 3H); ESI-MS m/z: 350.1 ([M+H⁺]); Anal. Calcd (%) for C₂₁H₁₉NO₄ : C 72.19, H 5.48, N 4.01; Found: C 72.21, H 5.42, N 4.04.

Preparation of Ligand HL: 2-[2-(2, 3-dimethoxyphenyl)vinyl]-

8-quinolinol

A solution of 2-[2-(2, 3-dimethoxyphenyl)vinyl]-8-acetoxyquinoline

(1.0 g, 2.9 mmol) in pyridine(15 mL) was refluxed for 30 min, then water (10 mL) was added. The reaction mixture was refluxed at 130 °C for 5 h. After cooled, the solution was extracted with dichloromethane. After removal of solvent under reduced pressure, the crude product was purified with column chromatography over silica gel using acetone/petro -leum ether as the eluent to give **HL** (0.81 g, 91 %). mp 104 °C ; ¹H NMR (400 MHz, DMSO) δ : 9.60 (s, 1H), 8.26 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 16.5 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 16.5 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 3H), 7.19 – 6.97 (m, 3H), 3.80 (d, *J* = 7.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ : 154.19, 153.22, 152.04, 137.95, 136.28, 130.52, 129.59, 128.63, 127.26, 124.25, 120.10, 118.35, 117.66, 112.40, 110.09, 61.33, 55.84; ESI-MS m/z: 308.1 ([M+H⁺]); Anal. Calcd (%) for C₁₉H₁₇NO₃ : C 74.25, H 5.58, N 4.56; Found: C 73.97; H 5.61; N 4.38.

Preparation of complex 1

A mixture of Cd(OAc)₂·2H₂O (5.4 mg, 20 µmol), **HL** (2.4 mg, 7.8 µmol), DMF (0.5 mL), and EtOH (1.5 mL) in a capped vial was heated at 80 °C for three days. Yellow block-like crystals of **1** were collected, washed with EtOH, and dried at 60 °C. Yield: 2.5mg (81 %, based on **HL**); IR (KBr, cm⁻¹): 3431.11(m), 1625.9(m), 1578.36(m), 1553.04(m), 1504.15(m), 1477.86(m), 1445.04(s), 1424.34(s), 1372.34(m), 1339.00(m), 1304.56(m), 1276.92(s), 1222.47(m), 1100.59(m),

1072.31(m), 1006.81(m); Anal. Calcd (%) for C₁₁₈H₁₀₂Cd₄N₆O₂₂ : C 58.91, H 4.27, N 3.49; Found: C 58.94, H 4.26, N 3.51.

Preparation of complex 2

A mixture of CdI_2 (7.3 mg, 27 µmol), **HL** (2.4 mg, 7.8 µmol), DMF (0.5 mL), and MeOH (30 drops) in a capped vial was heated at 80 °C for two days. Orange-yellow block-like crystals of 2 were collected, washed with MeOH, and dried at 60 °C. Yield: 1.4 mg (86 %, based on HL); IR cm^{-1}): 3440.39(m), 1578.32(m), (KBr. 1596.40(m), 1550.39(m), 1503.95(m). 1443.84(s), 1424,83(s), 1371.62(m), 1337.49(m), 1303.06(m), 1276.05(s), 1099.09(m), 1071.26(m); Anal. Calcd (%) for C₅₇H₄₈Cd₂ I N₃ O₉ : C 53.88, H 3.81, N 3.31; Found: C 53.84, H 3.79, N 3.35.

Preparation of complex 3

A mixture of Zn(NO₃)₂·6H₂O (9 mg, 30 µmol), **HL** (4.8 mg, 15.6 µmol), DMF (0.5 mL), and EtOH (40 drops) in a capped vial was heated at 65 °C for three days. Yellow-green block-like crystals of **3** were collected, washed with EtOH, and dried at 60 °C. Yield: 4.6 mg (78 %, based on **HL**); IR (KBr, cm⁻¹): 3437.02(m), 1627.18(m), 1598.13(m), 1579.07(m), 1557.89(m), 1503.85(m), 1478.87(s), 1448.14(s), 1380.42(s), 1335.24(s), 1274,97(s), 1223.83(m), 1102.72(s), 1071.61(s), 1006.00(m); Anal. Calcd (%) for C₁₁₄ H₉₉ N₈ O₂₆ Zn₄ : C 60.62, H 4.42, N 4.96; Found: C 60.71, H 4.37, N 5.03.

Crystal data collection and refinement

The single crystal X-ray data of the three polymers were collected on a Bruker APEX area-detector X-ray diffractometer with MoK_□ radiation $(\lambda = 0.71073 \text{ Å})$. The raw data frames were integrated with SAINT⁺, which were also corrected for Lorentz and polarization effects. Absorption corrections were applied by using the multi-scan program SADABS [18]. The respective structures were solved by direct methods, and refined with a full-matrix least-squares technique based on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). The non-hydrogen atoms were refined anisotropically and the H-atoms were geometrically included in the final refinement. Crystallographic crystal datas and structural parameters for 1-3 are given in table 1, whereas the selected bond distances and angles of 1-3 are presented in table S1-S3. The CCDC numbers of 1-3 are 1402718, 1402719 and 1402720, respectively.

	1	2	3
Empirical formula	$C_{118}H_{102}Cd_4N_6O_{22}$	$C_{114}H_{96}Cd_4I_2N_6O_{18}$	$C_{114}H_{99}N_8O_{26}Zn_4$
$M_{\rm r}$ /g mol ⁻¹	2405.66	2541.37	2258.49
T/K	293(2)	298(2)	296(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P1	C2/c
a/Å	13.5052(16)	12.4248(13)	27.7095(15)
<i>b</i> /Å	22.217(2)	14.9354(16)	11.8305(5)
$c/\text{\AA}$	20.391(2)	29.935(3)	31.9391(17)
$\alpha/^{\rm o}$	90	89.802(2)	90
$oldsymbol{eta}$ /°	99.090(2)	82.238(2)	91.548(3)
$\gamma/^{\mathrm{o}}$	90	74.6920(10)	90

 Table 1
 Crystallographic data and structure refinement details for 1-3

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	$V/\text{\AA}^3$	6041.4(11)	5305.8(9)	10466.4(9)	
	Ζ	2	2	4	
	$ ho_{ m c}/{ m g~cm}^{-3}$	1.322	1.591	1.433	
	μ /mm ⁻¹	6.105	1.442	0.987	
	Reflections collected	21099	27131	33688	
	Unique reflections	10465	18365	9427	
	$R_{\rm int}$	0.1322	0.1226	0.0575	
	S	1.011	1.033	1.004	
	$R_1^{a} (\mathbf{I} > 2\sigma(I))$	0.1337	0.0966	0.0434	
	wR_2^{b} (all data)	0.2758	0.1829	0.1208	

Results and discussion

Spectroscopic properties

In order to investigate the interaction mode of the **HL** ligand with the Cd^{2+} ion, the coordination reaction of **HL** with the $Cd(OAc)_2$ was monitored through a UV-vis spectroscopic titration. The absorption bands of **HL** in MeOH dramatically changed upon the addition of the Cd^{2+} ions. As depicted in Fig.1a, the band of 1 showed a significant bathochromism shift from 297 to 311 nm. The peak at 338 nm was found to become weak and disappeared in the presence of increasing amounts of the Cd^{2+} ion. The new band at 424 nm was attributed to the charge transfer from the metal to ligand band. No differences were observed in the absorption spectra after the 2 : 3 ratio of Cd^{2+}/HL , so this experiment clearly indicates the formation of $(Cd_2L_3)_n$. By following the same procedure, the formation of $(Cd_2L_3)_n$ and $(Zn_2L_3)_n$ for **2** and **3** was also determined by UV-vis spectroscopic titrations (Fig. 1b and 1c).



Fig. 1 UV-vis titrations of HL (0.1 mM) in methanol with $Cd(OAc)_2$ (a), CdI_2 (b) and $Zn(NO_3)_2$ (c), respectively. Each spectrum was acquired 5 min after the $Cd^{2+}addition$.





Fig. 2 Fluorescence emission changes of **HL** in methanol solutions upon addition of Cd(OAc)₂(a), CdI₂(b) and Zn(NO₃)₂(c), respectively.



Fig. 3 Fluorescence emission spectra of HL in different solvents

Photophysical properties

Results from the UV-vis spectrophotometric titrations were corroborated by the fluorescence spectroscopic titration. Fluorescence photographs were obtained under irradiation 340 nm. As for ligand **HL**, addition of Cd^{2+} produced a clear growing orange band at 598 nm and emission band at 469 nm decreased simultaneously (Fig. 2a). By following the same procedure, the formation of $(Cd_2L_3)_n$ and $(Zn_2L_3)_n$ for **2** and **3** was also determined by fluorescence spectroscopic titration (Fig. 2b and 2c).

We also investigated the steady-state spectroscopic properties of ligand. This strengthened our understanding and arguments regarding the relaxation behavior of the system in the same kind of media, in which the dynamical properties have been investigated. Figure 3 showed the fluorescence emission spectra of ligand in the 400-550 nm region in seven nonaqueous solvents, namely n-hexane, methylene chloride, tetrahydrofuran, ethanol, methanol, N,N-dimethyl formamide and acetonitrile. From the figure 3, with increase of polarity of the solvent, fluorescence emission of the ligand showed significant red-shift. In nonpolar aprotic n-hexane, the fluorescence emission intensity was weakest and the wavelength was shortest. The reason for this phenomenon may be that the ${}^{1}n-\pi^{*}$ state and $\pi-\pi^{*}$ state of ligand were very similar and the lowest excited singlet belongs to ${}^{1}n-\pi^{*}$ in the hydrocarbon solvent. But in polar solvent (protic or aprotic), the fluorescence emission of ligand was enhanced, probably because of ¹n- π^* state and π - π^* state reversed, π - π^* state became the lowest excited singlet [26,27]. In addition, the emission peak of ligand in both ethanol and methanol solvent was found to move, which may be attributed to the hydrogen bond interaction between ligand molecule and solvent molecules.

To confirm that the crystal structures of complexes 1-3 were truly representative of their bulky materials as employed in the photochemical studies, powder X-ray diffraction (PXRD) experiments were carried out on the resultant samples. The simulation curves were to simulate the cif into XRD by mercury software. As shown in figure 4, the peak positions of the experimental pattern was in good agreement with its simulated PXRD pattern, respectively. The differences in intensity may be due to the preferred orientation of the crystal samples. The luminescence behavior of 1-3 and the corresponding free HL ligand were investigated in the solid state at room temperature (Figure 5). The free HL ligand shows a weak emission band at λ_{max} = 452 nm upon being excited at 346 nm, whereas complexes 1-3 exhibit photoluminescences with maximum emission peaks at 575, 590 and 545 nm, respectively. Relative to that of the free ligand, the bright and extensive yellow emissions of complexes 1-3 predominantly originate from a ligand-to-metal charge-transfer (LMCT) transition and exhibit a remarkable red-shift emission, which may be ascribed as the incorporation of Zn (II) and Cd(II) effectively increasing the conformational rigidity of the ligand and decreasing HOMO-LUMO energy gaps of those compounds [28]. Meanwhile, the enhancement of emission intensity for the Zn(II) complex was probably due to inhibition of PET (photoinduced electron transfer) process, as the

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lone pairs involved in PET process get localized due to relatively strong interaction with the Zn(II). With Cd(II), where the metal ligand bonds were much longer compared to those of the Zn(II) complex, the lone pairs are less effectively localized [29]. Furthermore, differences in the optical properties of **1-3** are probably attributed to the different central metal ions or anion effects. The enhanced fluorescence also showed corresponding asignificant changes in emission lifetime, as illustrated in Fig. 6 (1.91, 1.83, 5.15 ns for **1, 2, 3,** respectively). In addition, we study the fluorescence properties of complexes **1-3** in ethyl acetate. As shown in Fig. 7, the fluorescence emission intensities of these complexes were also relatively stronger than the **HL** ligand and there were almost no apparent emission peaks of the **HL** ligand, which indicates that the three compounds possess stable structures.



Fig. 4 PXRD patterns of complexes 1-3





Fig. 6 Time-resolved fluorescence decay of 1-3 Fig. 7 The one-photon fluorescence of 1-3



Thermal stability

The thermal stability of complexes 1-3 was carried out by thermogravimetric analysis (TGA) from 27 to 1000 °C under a nitrogen atmosphere with a heating rate of 10 $^{\circ}C \cdot min^{-1}$, as shown in Fig. 8. For complex 1, there was no obvious change until 311 °C. With further heating, the first weight loss of 22.48 % from 311 to 386 °C. This may be due to the loss of one Cd (II) atom, one L ligand and two acetate anions (calcd: 22.30 %). The second mass loss occuring from 386 to 651 °C was 17.26 % and was assigned to the decomposition of one organic ligand L and one Cd (II) atom (calcd. 17.39 %). Then the backbone of complex 1 started to decompose gradually with the increasing temperature. TGA profile of complexes 1 and 2 was nearly comparable. However, for 2, a small weight loss about 2.22 % was observed below 185 °C, which can be attributed to the loss of the remaining DMF. The next weight loss of 21.40 % occurred from 257 to 405 °C could be attributed to the removal of one Cd (II) atom, one L ligand and one iodine atom (calc. 21.45 %). The further weight loss about 5.08 % until 534 °C was observed, attributable to the loss of the other coordinated iodine atom. Then the framework of compound 2 began to collapse gradually with the increasing temperature. For complex 3, the first weight loss of 19.13 % (calc. 19.05 %) occurred at around 289 °C might be attributed to the removal of one L ligand and two nitrate anions. Next, the backbone of compound 3 started to collapse with the residue of about 16.66 % (calc. 16.44 %), corresponding to one L ligand and one Zn (II) atom.



Fig. 8 TGA scans for 1-3

Structural description

Structure of [Cd₄(L)₆(OAc)₂](1).

Single crystals of coordination polymer 1 were readily obtained in

good yield by heating $Cd(OAc)_2$ and **HL** in the mixture of DMF/EtOH. X-ray diffraction analysis reveals that complex 1 crystallizes in the monoclinic space group $P2_1/c$ with Z = 2. The asymmetric unit contains two Cd(II) atoms, three L ligands and one coordinated acetate anion and it can be seen that there are two crystallographically independent Cd(II) atom (Fig. 9a). Cd1 is six-coordinated to four phenolato oxygen atoms (one O1, one O7, and two O4) and two nitrogen atoms (N1 and N3) from four L ligands displaying a distorted octahedron geometry. Cd2 is also six-coordinated with a distorted octahedron geometry containing O1, O4, O7 and N2 from three L ligands, and the other two coordination atoms for Cd2 are O10 and O11 from one acetate anion. The bond lengths and Å angles around Cd(II) are 2.35(2) - 2.38(2)for Cd–N, 2.173(15)-2.430(15)Å for Cd-O, 55.8(6)-169.9(6)° for O-Cd-O, 74.0(7)–146.3(7)° for O–Cd–N and 102.4(7)° 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. 9a).

There are intramolecular nonclassical C–H···O (between the oxygen atoms of acetate anion and the ethenyl group, C–H···O = 2.374–3.477Å, 12.494–67.142°) hydrogen bondings or C–H··· π (between the –CH₃ group of acetate anion and the adjacent dimethoxyphenyl ring, C–H··· π = 3.688Å) interactions, which play a vital role in the construction of the

tetranuclear Cd(II) units (Fig. 10a). As shown in Fig. 10c, through $C-H\cdots O = 2.750-3.094$ Å, the neutral molecular units in 1 are linked into a 2-D network structure in ab plane, giving a 3-D supramolecular structure (Fig. 10d) via an interlayer hydrogen bond C-H···O (between the C-H group of the dimethoxyphenyl ring and O atoms of $-OCH_3$ groups in another adjacent HL ligand, 2.750–2.817Å) interaction (Fig. 10b), which also generate a topological structure of **1** in bc plane(Fig. 10f), which can be simplified into a ball-stick space array, that is, each purple ball represent for a tetranuclear "diamond unit" of **1**, which is considered as a node, and each brown stick represent for C-H···O intermolecular interactions(Fig. 10e).



Fig. 9 Perspective drawing of 1(a), 2(b), 3(c) showing the local coordination environment around Cd(II) and Zn(II) (H atoms omitted for clarity).



Fig. 10 (a) The intramolecular C–H···O and C–H··· π interactions of complex 1; (b) the 2D network of 1 mediated by the nonclassical C–H···O hydrogen bonds in bc plane; (c) The 2D net structure through the nonclassical C–H···O hydrogen bonds in ab plane; (d) the 3D network of 3; (e) Space array of a "diamond unit" of 1 in bc plane ; (f) Topological structure of 1 in bc plane. Hydrogen atoms have been omitted for clarity. Color codes: green, Cd; red, O; blue, N; gray, C.

Structure of $[Cd_4(L)_6I_2](2)$

The crystal structure analysis indicates that 2 crystallizes in the triclinic P1 space group. The crystal structure of 2 is similar to complex 1, but the asymmetric unit contains two Cd(II) atoms, three L ligands and one iodine atom insteading of one coordinated acetate anion in 1. As shown in Fig. 9b, there are also two crystallographically independent Cd(II) in the tetranuclear centrosymmetric complex 2. The two Cd1 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 phenol oxygen atom and one pyridyl nitrogen atom of two ligands, respectively. While the two terminal Cd2 atoms are five-coordinated by one iodine atom, one nitrogen atom and three hydroxyl oxygen atoms from the three L ligands. The bond lengths and 2.281(15)-2.370(13)Å for angels around Cd(II) are Cd–N. 2.186(12)-2.560(9)Å for Cd-O, 73.2(4)-167.3(4)° for O-Cd-O, 70.1(4)–152.9(4)° for O–Cd–N and 98.0(4)° for N–Cd–N, respectively. Similar to complex 1, six oxygen atoms of six ligands HL link 2Cd1 and 2Cd2 into a double-open cubane-like unit(Cd_4O_6) (Fig. 9b).

There are intramolecular C-H···I (between the cooperated iodine

atom and the C–H group of ethenyl, 3.264Å) and $\pi \cdots \pi$ interactions (face-to-face distance of 2,3-dimethoxyphenyl ring: 3.824Å) in 2(Fig.11 a), which contribute to the construction of the tetranuclear Cd(II) units. As shown in Fig.11b, via C–H···O(2.642–3.056Å) and C–H···I (3.125Å) intermolecular interactions, the neutral molecular units in **2** are linked into 2D layers in the ab plane (Fig. 12). The two planes formed by the cooperated iodine atoms are parallel to the ab plane.



Fig. 11 (a) Two types of intramolecular interaction $\pi \cdots \pi$ (dashed red lines) and C-H \cdots I(dashed yellow lines) in compound **2**. (b) the 2D supramolecular structure of **2** mediated by C-H \cdots O and C-H \cdots I interactions



Fig. 12 2D layers in the ab plane of 2

Structure of $[Zn_4(L)_6(NO_3)_2](3)$

X-ray single crystal diffraction analysis shows that **3** crystallizes in the monoclinic crystal system of C2/c space group, with one half of a formula unit in the asymmetric unit, that is, two Zn(II) atoms, three L ligands and one coordinated nitrate anion. As shown in Fig. 9c, there exists to be two crystallographically independent Zn(II) in the tetranuclear centrosymmetric complex 3. Zn1 is six-coordinated to four phenolato oxygen atoms (two O1, one O7, and one O4) and two nitrogen atoms (N2 and N3) from four L ligands displaying a distorted octahedron geometry. Zn2 is also six-coordinated with a distorted octahedron geometry. In addition to O1, O4, O7 and N1 from three L ligands, the other two coordination atoms for Zn2 are O10 and O12 from one nitrate anion. The bond distances and angels around Zn(II) are 2.10(2)–2.20(2)Å for Zn–N, 1.992(19)–2.215(19)Å for Zn–O, 73.2(4)–167.3(4)° for O-Zn-O, 70.1(4)-152.9(4)° for O-Zn-N and 98.0(4)° for N-Zn-N, respectively.

There exists weak non-classical C–H···O intramolecular hydrogen bonds in the complex **3**. As shown in Fig. 13a, the intramolecular interactions between the oxygen atoms(nitrate anion) and the ethenyl group(C–H···O = 2.586–3.254Å) play a critical role in the consolidation of the tetranuclear structure. Through C–H···O(2.751–3.342Å) intermolecular interactions, the neutral molecular units in **3** are linked into 2D layers in the ab plane (Fig. 13c), which are further assembled into a 3D supramolecular network (Fig. 13d) via an interlayer hydrogen bond C–H···O (between the oxygen atoms (nitrate anion) and the –CH₃ group (methoxyl) of the adjacent **HL**, 3.005–3.038Å) interaction (Fig. 13b) , contributing to the additional stability of the structure.



Fig. 13 (a) Perspective views of the intramolecular $C-H\cdots O$ hydrogen bondings in **3**; (b) View of the 1D supramolecular chain fabricated via $C-H\cdots O$ hydrogen bondings; (c) the 2D network of **3** mediated by $C-H\cdots O$ interactions; (d) the 3D network of **3**.

Conclusion

In conclusion, one unique ligand **HL** containing 2-substituted-8-hydroxyquinoline were synthesized, and three double cubane tetranuclear complexes **1-3** were prepared by solvothermal reactions. The aggregation behavior of zinc or cadmium salt and ligands in different solution was investigated by several techniques, including UV-vis and PL. We have shown that the anion of the metallic salt solution take part in coordination and lead to different crystal system and space group of complexes **1-3**. As a result, there are obviously different to the absorption wavelength, the emission wavelength, fluorescence lifetime, and thermostability of complexes. In addition, the polarity of the solvent effect fluorescence emission of the ligand. The photophysical properties of complexes **1-3** correlate with the values of the HOMO and LUMO of the respective substituents calculated. This strategy offers a powerful tool for the preparation of complexes with predictable photophysical properties. These complexes have potential applications in the OLED.

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Highlights

- 1. Three double cubane tetranuclear Cd(II)/Zn(II) complexes with different spatial structures were tuned by anion.
- 2. Analysis of the similarities and differences of the crystal structures of three complexes
- 3. Investigation different photophysical properties of ligand and complexes.

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