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Synthesis, structural characterizations and spectroscopic properties of binuclear Co^{III} complex and its Schiff ligand as a chemosensor for fuorescent recognition of Zn^{II}

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Keywords: Coumarin Schiff-base Cobalt complex Crystal structure Zn ^{II} recognition Test paper	Binuclear Co ^{III} complex [Co ₂ (L) ₃ (DMF) ₃] containing a Schiff ligand H ₂ L was synthesized and analyzed by elemental analysis, single crystal X-ray crystallography, FT-IR, UV–Vis absorption spectroscopy, Hirshfeld surface analysis and DFT calculation. The Co ^{III} complex was a 3:2 ((L) ²⁻ : Co ^{III}) binuclear structure. The spatial configuration of central Co ^{III} ions was six-coordinated slightly twisted octahedron. The 3D supramolecular network structure was linked by intermolecular hydrogen bonds, C–H··· π and π ··· π stacking interactions. The Schiff ligand H ₂ L exhibits weak luminescence, but this weak fluorescence is turned on after coordination with the Zn ^{II} ion. Furthermore, H ₂ L could as an "OFF-ON" chemosensor for fluorescent recognition of Zn ^{II} .

1. Introduction

Schiff base compounds and their derivatives are usually used for chelating ligands because they can provide a good coordination environment for metal ions [1,2]. In the last few years, they have been widely used in organic synthesis intermediates, industrial catalysis, electrochemistry, luminescence and magnetic materials [3-5]. Meanwhile, Cobalt complexes have excellent biological activity and catalytic properties. Previous reports have shown that Schiff base cobalt complexes have been used in the study of DNA interaction and antitumor activity [6,7]. On the one hand, Schiff base ligands and their complexes have excellent optical properties. For example, the structure of C=C, C=O and lactone ring in coumarin compounds can effectively increase the conjugation degree of molecules and make them have strong fluorescence [8,9]. In the process of designing fluorescent probe compounds, it is an ideal candidate for fluorescent groups [10–13]. On the other hand, Zinc ion has been considered as an important biological element since ancient times, it is a kind of human metal ion with strong biocompatibility. Zinc ions deficiency can cause diseases such as slow growth, decline of immune function and loss of appetite [14-16]. Therefore, it will be of great use to develop efficient and sensitive zinc ion fluorescence detection probes. In this paper, a dinuclear Co^{III} complex [Co₂(L)₃(DMF)₃] based on coumarin ligand 4-hydroxy-3-[(2-hydroxy-methylenebenzene)-iminomethyl]-benzopyran-2-one (H₂L) was

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synthesized and characterized by elemental analyses, single crystal X-ray crystallography, FT-IR, UV–Vis absorption spectroscopy, Hirshfeld surfaces analyses and DFT calculation. It is noteworthy that the ligand $\rm H_2L$ could as an "OFF-ON" chemosensor for fluorescent recognition of Zn^{II}.

2. Experimental

2.1. Materials and methods

The 4-hydroxycoumarin (99%) and salicylic aldehyde (98%) used in the experiment were purchased from Alfa Aesar (New York, USA). The remaining reagents and solvents are of analytical grade, provided by Tianjin Chemical Reagent Factory, and can be used without further purification. Melting points were measured by an X-4 microscopic melting point apparatus made by Beijing Taike Instrument Limited Company and it was not calibrated before use [17]. German Vario EL V3.00 automatic element analyzer was used for the analysis of C, H, and N elements. The single crystal X-ray structure data is measured by Bruker Smart 1000 CCD area detector. Prepare the sample into KBr (400 ~ 4000 cm⁻¹) microspheres, and perform FT-IR spectroscopy on the VERTEX70 FT-IR spectrophotometer. Ultraviolet–visible absorption spectrum is measured by Hitachi UV-3900 spectrometer [18]. With tetramethylsilane ($\delta = 0.00$) as the internal standard, ¹H NMR spectra



Scheme 1. Synthetic routes of H₂L.

Table 1

Crystal date and structure parameters description of Co^{III} complex.

Compound	$[Co_2(L)_3] \cdot (DMF)_3$
Empirical formula	C ₆₀ H ₅₀ Co ₂ N ₉ O ₁₅
Formula weight	1254.95
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	13.6074(19)
b (Å)	13.9185(17)
c (Å)	15.837(2)
α (°)	81.196(4)
β (°)	86.607(4)
γ (°)	81.665(4)
V (Å ³)	2930.7(7)
Ζ	2
$D_{\rm c} ~({\rm g}~{\rm cm}^{-3})$	1.422
$\mu \text{ (mm}^{-1}\text{)}$	0.642
F (000)	1294.0
Crystal size (mm)	$0.22\times0.26\times0.28$
θ range (°)	2.21 to 26.06
Index ranges	$-17 \le h \le 17; -18 \le k \le 18; -15 \le l \le 20$
Reflections collected	26810, 13,597
Independent reflections	13,597
R _{int}	0.035
Completeness %	98.3%
Date / restraints / parameters	13,597 / 0 / 780
GOF	0.888
R_1 , w R_2 [$I > 2\sigma(I)$]	0.0564 / 0.2010
R_1 , w R_2 indices (all data)	0.1037 / 0.1612
Largest differences Peak and hole (e	-0.340 / 0.490
Ā ⁻³)	

were recorded in DMSO- d_6 solution using Bruker AV instrument at room temperature. Hirshfeld surfaces analyses and two-dimensional ingerprint plots were calculated using using *CrystalExplorer* 3.1. The B3LYP function is used as the basis of geometric optimization, and the Gaussian 09 software program is used for DFT calculation [19]. The luminescence spectra of the solution were measured and recorded on Hitachi F-7000 spectrometer. When ligand H₂L was used to recognize thirteen metal cations (Ca^{II}, Cr^{III}, Ba^{II}, Mn^{II}, Ni^{II}, Co^{II}, Cu^{II}, Cd^{II}, Mg^{II}, Al^{III}, Fe^{III}, Zn^{II}, Hg^{II}), nitrate was used as raw material to prepare cation solution. The excitation wavelength of the fluorescence spectrum is 350 nm, the incident slit is 5 nm, and the exit slit is 5 nm.

2.2. Preparation of H_2L

H₂L was synthesized according to the following synthetic routes shown in Scheme 1. 3-Aldehyde-4-hydroxyl-coumarin was synthesized in the light of the formerly reported method [20,21]. Yield: 63.8%. m.p. 114 ~ 115 °C. Anal. Calcd. for C₁₀H₆O₄ (%): C, 63.16; H, 3.18. Found (%): C, 62.56; H, 3.57. The ligand H₂L was synthesized in a similar way [22].

3-Aldehyde-4-hydroxyl-coumarin (1.71 g, 9 mmol) and O-hydroxybenzaldehyde (1.0 mL, 9 mmol) were dissolved in anhydrous ethylalcohol, added drop-wise added hydrazine hydrate (0.6 mL, 9 mmol) at 70 °C, and then continued heating and refluxing for 5–6 h. The mixed solution was cooled overnight, and a light-yellow solid was precipitated, and then washed with absolute ethanol to obtain 1.44 g of H₂L (Figs. S1 and S2). Yield: 71.2 %. m.p. 269 ~ 270 °C, Anal. Calcd. for C₁₇H₁₂N₂O₄ (%): C, 66.23; H, 3.92; N, 9.09. Found (%): C, 66.57; H, 3.22; N, 9.25 (Table S4). ¹H NMR (500 MHz, DMSO-*d*₆) δ 13.89 (s, 1H), 10.32 (s, 1H), 9.06 (s, 1H), 8.73 (s, 1H), 7.97 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.75–7.67 (*m*, 2H), 7.40–7.32 (*m*, 3H), 6.94 (dd, *J* = 17.8, 7.9 Hz, 2H).

2.3. Syntheses of Co^{III} complex

A solution of Co(OAc)₂·4H₂O (1.0 mg, 0.004 mmol) in methanol (2.0 mL) was added dropwise to a solution of H₂L (1.8 mg, 0.006 mmol) in DMF (2.5 mL). The mixture solution immediately turns green. Then it was stirred at room temperature for 30 min. Subsequently, filtered and placed at room temperature for about two weeks. The solvent evaporated partially, and pale black single crystals of Co^{III} complex suitable for X-ray crystallographic analysis were obtained [23]. Anal. Calcd. for C₆₀H₅₀Co₂N₉O₁₅ (%): C, 57.42; H, 4.02; N, 10.05. Found (%): C, 57.87; H, 4.12; N, 10.02.

2.4. Crystal structure determinations of Co^{III} complex

A single crystal with a size of approximately 0.22 mm \times 0.26 mm \times 0.28 mm was placed on the Bruker Smart 1000 CC. The reflections were



Fig. 1. (a) Molecular structure of Co^{III} complex; (b) coordination configuration of Co^{III} ions.



Fig. 2. Intermolecular hydrogen bonding and C—H… π interactions of Co^{III} complex.



Fig. 3. The supramolecular structure of Co^{III} complex.

collected using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 296 K [24,25]. Furthermore, in this experiment, LP correction is suitable for SAINT program, SADABS scheme adopts semi empirical correction and the direct method was used to solve the crystal structure (shelss-2014) [26]. The crystal data and experimental parameters of the Co^{III} complex are listed in Table 1.

3. Results and discussion

3.1. Crystal structures and related properties of Co^{III} complex

3.1.1. Crystal structures of Co^{III} complex

The molecular structure of Co^{III} complex is shown in Fig. 1, and selected bond lengths and angles are listed in (Table S1). The Co^{III} complex was crystallized in a triclinic crystal system, *P*-1 space group. The Co^{III} complex was a 3:2 ($(L)^{2-}$: Co^{III}) binuclear structure, and composed of two Co^{III} ions, three deprotonated ($L)^{2-}$ units, and three crystallizing DMF solvent molecules (Fig. 1a). The spatial configuration of two central Co^{III} ions were all six-coordinated slightly twisted octahedron, and both of the Co^{III} ion were coordinated by three imine N atoms and three phenolic oxygen atoms (Fig. 1b).

The $\mathrm{Co}^{\mathrm{III}}$ complex existed five weak intermolecular non-classical hydrogen bond, C11-H11...O15, C13-H13...O2, C28-H28...O14, C41-H41...O13 and C58-H58A...O2 (Fig. 2 and Table S2). Two crystallizing DMF solvent molecules was bound to the Co^{III} complex main units through C28-H28-O14 and C11-H11-O15 hydrogen bonding interaction. The remaining DMF molecule connected two adjacent Co^{III} complex molecules to form a dimer unit by C41-H41...O13 and C58-H58A...O2 hydrogen bonds. This dimer units were further linked by C13-H13...O2 hydrogen bonding interaction to obtain an infinite 1D banded supramolecular structure along the a-axis direction. Simultaneously, this linkage was further stabilized by the C–H \cdots π (C52-H52A…Cg1) interaction. In addition, this 1D banded supramolecular structures were further linked by the $\pi \cdots \pi$ (Cg2...Cg3 and Cg3...Cg3) stacking interactions between the coumarin rings into an infinite 2D layer supramolecular structure parallel to the ac plane (Fig. 3 and Table S3).

3.1.2. Hirshfeld surface analyses

The solid crystal structure of any complexes is steadied by a large number of supramolecular interactions, so these interactions need to be



Fig. 4. The Hirshfeld surface of the Co^{III} complex mapped with d_{norm} , shape index and curvedness.



Fig. 5. Fingerprint plots (d_e vs d_i) of the Co^{III} complex showing atoms interactions.

considered [27]. Hirsfield surface analysis is an effective tool for researching the interaction between molecular crystals. The combination of *de* and *di* in the form of two-dimensional fingerprint shows the contact area between molecules in the crystal [28]. The surfaces analyses of the Co^{III} complex are given in Fig. 4 mapping with d_{norm} , shape index and curvedness. The d_{norm} mapping on the surface of Hirshfeld molecules proves that they are in contact with each other, the visible bright red areas indicate the presence of C-H--O hydrogen bond contacts on the surface [27-30]. Some white dots on the surface are caused by the H…H interaction and the blue areas on the surface indicate that there is no interaction. Shape exponents and curvature can be used to identify stack interactions. For the Co^{III} complex, red or blue triangle (bow tie pattern) and flat surface patches are observed in the shape index diagram, which indicates the existence of $\pi \cdots \pi$ stacking interaction. The 2D fingerprint shows the proportion of all in termolecular interactions (Fig. 5) [31]. The proportion of O···H/H···O, C···H/H···C and H…H interactions comprising 21.7%, 26.8% and 44.0% of the total Hirshfed surfaces for each molecule of the Co^{III} complex, respectively.

3.1.3. DFT computation

The electronic structure of the Co^{III} complex was further studied by DFT calculation [32]. The singlet molecular geometry was optimized at the level of B3LYP through Gaussian 09, and metal atoms were processed through the B3LYP/LanL2DZ basis set [33]. Fig. S3 shows the orbital energies of the molecular orbitals of the Co^{III} complex, mainly from LUMO + 1 to HOMO-1. As everyone knows, HOMO means the ability to give electrons, and LUMO means the ability to accept electrons. The diagram of the HOMO of Co^{III} complex shows that these HOMOs are delocalized and mainly distributed on the Co1 ion orbitals. Compared with HOMO, LUMO is mainly distributed in the fragments of Schiff base ligands and Co^{III} ions [34-36]. The molecular orbital energies of $E_{\rm HOMO},~E_{\rm LUMO},~E_{\rm HOMO-1}$ and $E_{\rm LUMO+1}$ of $Co^{\rm III}$ complex are respectively -5.686 eV, -2.813 eV, -5.708 eV, -2.773 eV. The energy gaps between them are ΔE (E_{LUMO} - E_{HOMO}) = 2.873 eV, ΔE (E_{LUMO+1} - E_{HOMO-1}) = 2.936 eV, respectively. The molecular orbitals energies of Co^{III} complex are all negative, indicating the good stability of Co^{III} complex molecular. The complex has a lower energy gap between HOMO and LOMO ($\Delta E = E_{LUMO} - E_{HOMO}$), and the smaller the E value, the higher the activity of the molecule [37].

3.1.4. IR spectra analyses

The IR spectra of H₂L and its Co^{III} complex show different characteristic stretching vibration bands in the scope of $400 \sim 4000 \text{ cm}^{-1}$ [38]. As shown in Fig. S4, the O—H stretching band is observed at 3471 cm⁻¹ in H_2L, which belongs to phenolic hydroxyl group. However, in the Co^{III} complex, a new stretching vibration band (wider peak) was watched at 3436 cm⁻¹, corresponding to crystalline water [39]. The absorption band of free ligand H₂L at 1645 cm⁻¹ is attributed to the stretching vibration of the C=O double bond of the coumarin ring, while the C=O stretching vibration of Co^{III} complex occurs at about 1621 cm⁻¹. In addition, the ligand H₂L showed characteristic tensile bands of C=N groups at 1685 cm⁻¹, and its corresponding Co^{III} complex was watched at 1694 cm^{-1} . Compared with the ligand H₂L, the C=N stretching frequency of Co^{III} complex shifted about 9 cm⁻¹ to higher frequency, which indicates that the coordination between the metal atom and the amino nitrogen lone pair increases the frequency of the C=N bond. Compared with the contraction band of the H_2L at 1213 cm⁻¹, the Ar-O contraction band of the complex at 1200 cm^{-1} moved about 13 cm^{-1} to the low frequency, which indicates that M–O bond is formed between the metal ions and the oxygen atoms of the phenolic groups [40].

3.1.5. UV-Vis absorption spectra and fluorescence spectrum analysis

The electronic absorption spectra of ligand H₂L and its Co^{III} complex were detected in DMSO solution. As shown in Fig. 6a, it can be clearly observed that free H₂L has two absorption peaks at 296 nm and 356 nm, they are the π ··· π^* transition of aromatic ring and the internal ligand transition of n··· π^* (C=N), respectively [39–41]. While that of the Co^{III} complex has a strong absorption peak at 258 nm and a weak absorption peak at 405 nm. Compared with the free H₂L, the absorption peak of Co^{III} complex blue shifted from 296 nm to 258 nm, which indicated the coordination between H₂L and Co^{III} ions. And the latter at 356 nm disappeared in the complex, but a new weak absorption peak at 405 nm was observed, which was attributed to the d-d transition of Co^{III} ions [42].



Fig. 6. (a) The ultraviolet spectrum of ligand H_2L and Co^{III} complex; (b) Fluorescence spectra of ligand H_2L and Co^{III} complex (c = 4.0 × 10⁻⁵ mol/L).



Fig. 7. (a) Fluorescence response of H₂L to various metal cations in DMSO solution; (b) The images of color changes upon different cationic added to the H₂L in DMSO solution under 365 nm UV lamp; (c) Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of the H₂L in the presence of Zn^{II} and various cationic in DMSO solutions.

The fluorescence spectra of ligand H₂L and its Co^{III} complex were detected in DMSO solution. As can be seen from the Fig. 6b, under 350 nm excitation, the free ligand H₂L has a strong emission peak at 456 nm, which is caused by the π ··· π transition. The fluorescence intensity of H₂L is almost quenched upon coordination with Co^{III} ions, indicating the Co^{III} ions coordinated with the N and O atoms of H₂L and a photo-induced electron transfer process occurs [43].

3.2. Fluorescence recognition of metals cations by ligand H_{2L}

3.2.1. Fluorescence response of Zn^{II}

The selectivity of H₂L to thirteen different metal cations (Ca^{II}, Cr^{III}, Ba^{II}, Mn^{II}, Ni^{II}, Co^{II}, Cu^{II}, Cd^{II}, Mg^{II}, Al^{III}, Fe^{III}, Zn^{II}, Hg^{II}) were studied by fluorescence spectra at room temperature [44]. Firstly, the solvation effect of ligand H₂L was studied (Fig. S5). The fluorescence intensity of H₂L was measured in different solvent systems, it was observed that two weak emission peaks appeared in other organic solvent systems at 432 nm and other different wavelengths. In DMSO solution system, the fluorescence intensity of H₂L at 519 nm was significantly enhanced. In addition, the fluorescence intensity decreased significantly in the mixture of DMSO and H₂O. As shown in Fig. 7a, the H₂L and cations stock solutions were prepared in DMSO solution at a concentration of 5.0×10^{-5} mol/L and 1.0×10^{-2} mol/L. The H₂L showed a weak fluorescence emission peak at 456 nm, after the addition of other metal



Fig. 8. Fluorescence spectra of the H_2L in DMSO solution with increasing concentration of Zn^{II} (0–1.0 equiv).

ions, the emission peak strength has no obvious enhancement except Zn^{II} ions. Furthermore, the emission peak was red-shifted from 456 nm to 519 nm and the intensity increased by 8 times upon addition of Zn^{II} ions [45]. Under the UV lamp, the solution of other metal ions was added to DMSO solution of H₂L in turn, a strong bright yellow fluorescence is produced only added Zn^{II} ions, and other metal cations has basically no obvious effect, the fluorescence remains unchanged or quenched (Fig. 7b). It can be proved that H₂L could selectively identify Zn^{II} among other measured metal ions in DMSO solution. It is helpful to study the high sensitivity of H₂L to Zn^{II} ions by anti-interference experiment. In Fig. 7c, after adding Zn^{II} to H₂L solutions containing different metal ions, other metal cations had no markedly effect on the fluorescence recognition to Zn^{II} ions except for the slight quenching of Cu^{II} ion. Therefore, even if there are other disturbing ions, probe H₂L has a high selectivity for Zn^{II} in DMSO system [46].

3.2.2. Titration experiment of H_2L to Zn^{II}

As shown in Fig. 8, the fluorescence titration experiment was carried out by the gradual addition of Zn^{II} ions to the H₂L solution [47]. The H₂L exhibited a weak emission peak at 456 nm. When the concentration of Zn^{II} ions gradually increased, the weak emission peak of H₂L at 456 nm gradually weakened and change, and a new peak emission present to 519 nm and its intensity gradually increased when the concentration of Zn^{II} ion increases continuously. And when the content of Zn^{II} reached at 1.0 equivalent, the fluorescence emission intensity reaches the maximum at 519 nm, indicating that the optimal binding ratio of Zn^{II} to probe H₂L is 1:1. The titration results were brought into Benesi-Hildebrand equation [48], as Eq (1), and the binding constant is calculated $K_a = 0.45 \times 10^4 \text{ M}^{-1}$ (Fig. S6a), Where, F₀ is the fluorescence intensity without Zn^{II} , F is the fluorescence intensity at any given Zn^{II} concentration, and F_{max} is the fluorescence intensity after titration saturation. The detection limit calculated using $LOD = 3\sigma/slope$ is 3.26 $\times 10^{-7}$ mol/L (Fig. S6b), and the calculation result is lower than the limit of WHO drinking water (7.0 \times 10⁻⁶ mol/L) [49,50]. Among, σ is the standard deviation of five successive measurements of the fluorescence strength by ligand H₂L, and the slope is obtained by the relationship between the emission intensity and concentration. At the same time, the time response experiment is to verify the rapid detection performance of probe H₂L for Zn^{II}. As shown in (Fig. S5), when Zn^{II} was added to the ligand H₂L solution, the response time was 30 s.

$$\frac{1}{(F-F_0)} = \frac{1}{(F_{\max}-F_0)} + \frac{1}{K_d[C]} \times \frac{1}{(F_{\max}-F_0)}$$
(1)



Fig. 9. ¹H NMR titration of H₂L with different concentrations of Zn^{II} in d₆-DMSO.



Fig. 10. Plausible mechanism for Zn^{II} recognition by H_2L .

3.2.3. The detection mechanism of Zn^{II} ion by H_2L

¹H NMR titration experiments in DMSO-d₆ were performed to investigate the recognition mechanism of the H₂L to Zn^{II}. In Fig. 9, when Zn^{II} was added in the same amount from 0 to 1.0 equivalent, the protons of phenol hydroxyl group H1 ($\delta = 10.32$ ppm) and H2 ($\delta = 13.89$ ppm), which indicated that Zn^{II} induced deprotonation of hydroxyl group [51]. and hydroxyl O atoms participated in the coordination. For complex L-Zn^{II}, the proton signal becomes more extensive with the addition of metal ions, and the ¹H NMR titration data supports the metal coordination ratio of 1:1. In addition, the ¹H NMR of zinc ion complex powder was characterized and compared with the ¹H NMR data of adding 1.0 equivalent zinc ion, which further showed that the binding mechanism was consistent with the above experimental results (Fig. S8). The analysis of Job plot further confirmed the stoichiometric ratio between them (Fig. S9). The mole fraction of Zn^{II} ions added reached the maximum value at 0.5, indicating that the binding ratio of Zn^{II} ions to SW was 1:1 [52]. After binding with Zn^{II}, the pristine peak of the complex was found at 391.28 (calcd for $[H_2L/Zn^{II} + H_2O)$ (Fig. S10), which further confirmed the binding mode of probe H₂L with Zn^{II}. As shown in Fig. 10, after 365 nm excitation, H₂L shows weak fluorescence emission in the range of 417 \sim 528 nm, and reaches the maximum at 456 nm. The fluorescence enhancement recognition mechanism of Zn^{II} by H₂L may be mainly due to fact that the presence of Zn^{II} hinders the light-induced electron transfer (PET) effect of H₂L, leading to fluorescence quenching. Due to the existence of imino group (–CH = N) in H₂L and continuous rotation, there is a weak fluorescence at 456 nm in H₂L solution. The addition of Zn^{II} ions can coordinate with the ligand H₂L, inhibit the free rotation of the imino of the molecules and produce chelation enhanced fluorescence (CHEF) effect. At the same time, strong fluorescence emission occurs at 425 ~ 675 nm, which leads to the enhancement of bright yellow fluorescence [53,54].

3.2.4. DFT calculation

In order to understand the interaction and coordination properties of H_2L with Zn^{II} , the geometric optimization of H_2L and L-Zn^{II} complexes was carried out by using B3LYP / 6-31G and LanL2DZ basis sets [55], respectively. As shown in Fig. 11, the L-Zn^{II} complex is coordinated by a Zn^{II} ion, one H_2L molecule and one water molecule. Among them, the coordination atoms are phenolate oxygen and imine nitrogen on the salicylaldehyde group in the ligand H_2L , hydroxyl oxygen on the coumarin group and the oxygen of the water molecule. In the HOMO and LUMO orbitals of ligand H_2L , the electron density is mainly delocalized



Fig. 11. Molecular structure and orbital diagram of the optimized ligand H_2L and complex L-Zn^{IL} $\,$



Fig. 12. Tests paper experiment of probe H_2L . (a) The color changes after dropping different concentrations of Zn^{II} ions; (b) The experiment of paper test after adding different metal ions (1.0 \times 10⁻² mol/L).

on the conjugated skeleton of the whole ligand molecule, and the LUMO and HOMO energies of H₂L were -2.298 eV and -5.898 eV, respectively. The energy gap difference ΔE (E_{LUMO} - E_{HOMO}) between them is 3.60 eV, which is consistent with the weak fluorescence of H₂L. When Zn^{II} is coordinated with H₂L, LUMO and HOMO energies were -2.772 eV and -6.042 eV, respectively. Correspondingly, the energy gap was 3.270 eV, and the electron cloud density of HOMO of L-Zn^{II} is mainly concentrated on the salicylaldehyde group, whereas the electron cloud density of HOMO is mainly delocalized on the whole Schiff group. The HOMO-LUMO transition shows the fluorophore-metal charge transfer, indicating that with the PET effect, the excited electrons are readily

averted to metal ions [56]. The decrease of ΔE indicates that Zn^{II} and H_2L have good bonding ability and form a stable coordination environment.

3.2.5. Test papers of H_2L for Zn^{II}

In practical application, it is of great practical value to develop a simple, convenient and cheap paper sensor by changing the wavelength of the fluorescent probe [57]. The probe H_2L was designed as a paper sensor for Zn^{II} ion recognition. Firstly, the filter paper was soaked in DMSO solution of probe H_2L for 3 h, then it was taken out and dried. Then it was placed under a 365 nm UV lamp [58], and different

concentrations of Zn^{II} ions or other different metal ions were added, and the response signals were observed. As shown in Fig. 12a, the sensitivity and color change of H₂L to Zn^{II} were observed by naked eye. In addition, the selectivity of H₂L to different metal ions was also studied (Fig. 12b). When Zn^{II} was added to the H₂L strip, the color of the strip changed from blue to yellow. When other metal ions were added, the strip had almost no obvious color change. The results show that the probe H₂L has high selectivity for the recognition of Zn^{II} as a paper sensor.

4. Conclusions

In this paper, we designed and synthesized the ligand 4-hydroxy-3-[(2-hydroxy-methylenebenzene)-iminomethyl]-benzopyran-2-one (H₂L) with absolute ethanol as the medium, and combined it with Co (CH₃COO)₂·4H₂O was cultured in DMF/CH₃OH solvent system by natural volatilization to obtain the complex $[Co_2(L)_3(DMF)_3]$. The spatial configuration of Co^{III} complex was determined by X-ray diffraction method and a series of structural characterization were carried out. The Co^{III} complex was a 3:2 ((L)²⁻ : Co^{III}) binuclear structure and the spatial configuration of central Co^{III} ions were six-coordinated slightly twisted octahedron. At the same time, H₂L had a specific fluorescence response to Zn^{II} in the DMSO system and it can be used as a fluorescent chemosensor for recognition of Zn^{II}. And the detection limits on colorimetric and fluorescence response of the H_2L to Zn^{II} is down to 3.26×10^{-7} mol/ L. The binding ratio of probe H₂L to Zn^{II} was 1:1 by ¹H NMR, MS analysis and theoretical calculation. In addition, the probe SW can be used for the detection of ${\rm Zn}^{\rm II}$ in DMSO solution under 365 nm ultraviolet light, and the tast paper detection of Zn^{II} in DMSO, which has a potential application prospect.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120581.

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