

Synthesis, characterization and properties of Schiff base zinc complexes

In order to solve the problem of aggregation and quenching of fluorescent materials, four kinds of zinc complexes of Schiff base were designed and synthesized, and the IR spectra and nuclear magnetic resonance spectroscopy were analyzed. The photo-physical properties of ligands and complexes were analyzed. The results show that the four complexes have good aggregation-induced luminescence enhancement properties. The oxidation potentials of the four complexes are, respectively, the energy gap obtained by UV absorption, and the four complexes level is located in between the energy level, so the four complexes can be used for hole transport materials, can also be used for electronic transmission materials.

Keywords: aggregation quenching; infrared spectroscopy; photo-physicality; electrochemical performance; energy level

1. Introduction

In recent years, organic luminescent materials have attracted more and more attention, and quickly extended to various fields, however, most of the organic luminescent materials in the dilute solution shows a strong fluorescence emission, and in solid or high concentration of solution, which inhibits the application of organic luminescent materials in optics due to the fluorescence quenching [1] due to the interaction between adjacent molecules. In order to solve the problem of fluorescence quenching in luminescent materials, four kinds of zinc complexes of Schiff base were designed and synthesized, and their properties are studied. TPD is the most widely used in the light-emitting device hole transport material, the hole mobility, glass transition temperature, easy vacuum deposition film [2].

A lot of scholars have made great contributions to the study of Schiff base zinc complexes. Yang Hongjun (2008) has studied the synthesis, characterization and properties of Schiff base metal complexes. It is concluded that

salicylaldehyde amino acid can be used as The ch-elate ligand and the tin atom coordinate to form a five-coordinated monomer structure, but also as a tetradentate ligand through the ligand of carbonyl oxygen and the adjacent molecules of tin atoms with the formation of six coordination of the twelve ring Structure, which depends on the steric hindrance, which mainly includes the base of the hydrocarbon on the tin and the base of the N-substituted amino acid [3]; Wang Xingang (2009) synthesized and characterized eight conjugated Schiff ligands. The results show that the ligand and metal ions Formed a 1: 1 type (metal/ligand) or 2:1 type (metal/ligand) complex [4].

Based on the previous research, four kinds of Schiff base zinc complexes were designed and synthesized for the aggregation quenching problem of the fluorescent materials, and the IR spectra and nuclear magnetic resonance spectroscopy were analyzed.

2. Experimental process

2.1 TARGET COMPOUND STRUCTURE AND EXPERIMENTAL REAGENTS, EQUIPMENT

Schiff base zinc complexes in the field of electro-luminescent materials and biochemistry and other fields is widely used, mainly due to Schiff base compounds easy synthesis, easy to modify the characteristics, as shown in Fig.1. However, the current Schiff base complex luminescent materials also suffer from a number of defects, such as aggregation quenching problems caused by the film in the state of low luminous efficiency.

The experimental reagents used in the experiment are shown in Table 1.

Experimental apparatus: Perkin-Elmer 240C Elemental Analyzer, Bruker Avance 500 Nuclear Magnetic Resonance Spectrometer, Irprestige-21 Infrared Spectrometer, Shimadzu UV-2550 Ultraviolet Spectrophotometer, Shimadzu RF-5301PC Fluorescence Spectrophotometer.

2.2 SYNTHETIC ROUTES AND METHODS

To synthesize Schiff base zinc complexes in 4, the synthesis of five ligands is carried out first, and the synthesis route is shown in Fig.2.

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TABLE 1 EXPERIMENTAL REAGENTS AND PURITY

Reagents	Purity	Reagents	Purity
Carbazole	Analysis of pure	DMF	Analysis of pure
4-nitrofluorobenzene	Analysis of pure	Tetrahydrofuran	Analysis of pure
Triphenylamine	Analysis of pure	2-hydroxy-1-naphthaldehyde	Analysis of pure
Salicylaldehyde	Analysis of pure	Zinc acetate	Analysis of pure
Anhydrous ethanol	Analysis of pure	Column chromatography silica gel	Industrial pure
Anhydrous magnesium sulfate	Analysis of pure	Dichloromethane	Analysis of pure

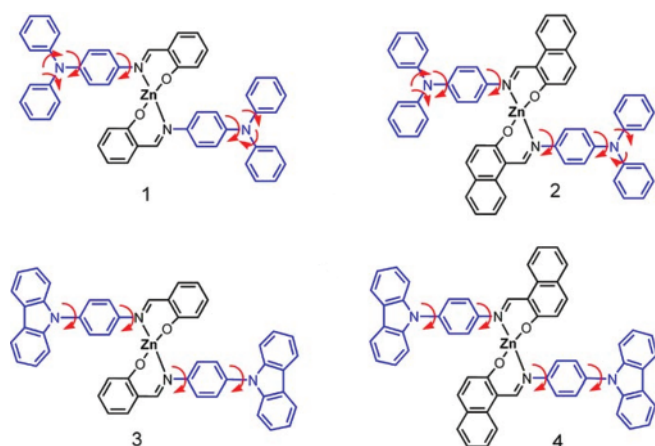


Fig.1 Target compound structure

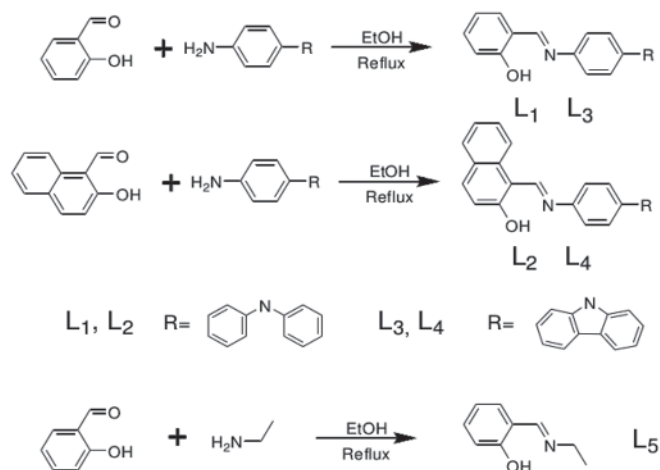


Fig.2 Synthesis of five ligands

Weigh 4,4-diphenyl-p-phenylenediamine in anhydrous ethanol, add () salicylaldehyde and heat reflux to cool to precipitate a large amount of solid. The residue was separated by suction filtration and washed with absolute ethanol to give a pale yellow solid, which was a ligand. Productive rate is 82%. The synthesis of 2-hydroxy-1-naphthaldehyde with 4,4-diphenyl-p-phenylenediamine as a starting material can be used to obtain a yellow solid as a ligand. Productive rate is 85%. The reference ligand synthesis method, 4-(9-carbazolyl) p-phenylenediamine and salicylaldehyde as raw materials, to obtain a pale yellow solid is ligand, yield. Productive rate 92%. Using the ligand synthesis method, 4-(9-carbazolyl) p-

phenylenediamine and 2-hydroxy-1-naphthaldehyde were used as starting materials to obtain an orange solid. Productive rate is 90%.

2.2.1 Synthesis of four complexes

(1) Synthesis of complex 1

Weigh the ligand into a two-necked flask and add anhydrous ethanol and heat until the ligand is completely dissolved. And then take acetic acid dissolved in anhydrous ethanol, the solution was added to the two bottles and heated to reflux, cooled to. The solid was separated by suction filtration and washed with a small amount of absolute ethanol to obtain a yellow flocculent solid which was compound 1. (M, and lt; RTI ID = 0.0 and (KBr), ν/cm^{-1} : 1607, 1587, 1531, 1498, 1460, 6.95 (dd, $J = 17.4, 8.7$ Hz, 6H), 6.65 (t, $J = 7.3$ Hz, 2H) 1438, 1384, 1325, 1276, 1180, 1147, 756, 696, 501. Anal. Calcd. For $\text{C}_{50}\text{H}_{38}\text{N}_4\text{O}_2\text{Zn}$: C, 75.80; H, 4.83; N, 7.07. Found: C, 75.92; H, 4.71; N, 7.11. MS (MALDI-TOF): m/z 791.2 [M +].

(2) Synthesis of complex 2

Synthesis with the complex 1, select the zinc acetate and ligand as raw materials, the orange solid is complex 2, yield. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.32 (s, 2H), 8.01 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 9.2$ Hz, 2H), 7.68 (d, $J = 7.6$ Hz (T, $J = 7.9$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.9$ Hz, 8H), 7.09 (d, $J = 9.2$ Hz, 2H), 7.02-7.00 (m, 12H), 7.00-6.94 (m, 8H). IR (KBr), ν/cm^{-1} : 1614, 1593, 1535, 1490, 1456, 1427, 1394, 1363, 1328, 1278 C, 78.10; H, 4.70; N, 6.31. MS (MALDI-TOF) and lt;/RTI and gt; and lt; RTI ID = 0.0 and gt; : M/z 891.2 [M +].

(3) Synthesis of complex 3

Synthesis with the complex 1, select the zinc acetate and ligand as raw materials, the yellow solid is complex 3, the yield. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.50 (s, 2H), 8.15-8.07 (m, 4H), 7.89 (d, $J = 9.3$ Hz, 2H), 7.75 (d, $J = 7.8$ Hz, 2H) (D, $J = 9.2$ Hz, 2H), IR (KBr), 7.42 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 4H), 7.38-7.26 (m, 14H) Lt;/RTI and gt; , 4.35; N, 7.11. Found: C, 76.02; H, 4.45; N, 7.23. MS (MALDI-TOF): m/z 787.2 [M +].

(4) Synthesis of complex 4

Synthesis process with the complex 1, select the zinc acetate and ligand as raw materials, the orange solid is complex 4, the yield. (D, $J = 7.7$ Hz, 4H), 7.56 (d, $J = 8.6$ Hz, 4H), 7.46 (t, $J = 7.0$ Hz, (D, $J = 8.6$ Hz, 2H), 6.74 (d, $J = 8.6$ Hz, 4H), 7.36 (d, $J = 3.3$ Hz, 8H), 7.33-7.23 (m, 8H) T, $J = 7.3$ Hz, 2H). IR (KBr), ν/cm^{-1} : 1612, 1575, 1535, 1510, 1452, 1427, 1392,

1363, 1336, 1228, 1182, 1165, 833, 748, 503 (MALDI-TOF): m/z 887.2 [M+]. Calculated for C₅₈H₃₈N₄O₂Zn: C, 78.42; H, 4.31; N, 6.31 Found: C, 78.51; H, 4.20; N, 6.40 MS.

3. Analysis of experimental results

3.1 ANALYSIS OF INFRARED SPECTROSCOPY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

In the infrared spectrum, the double bond stretching vibration peaks in the ligands are in, and at the same time. In the four complexes, the double bond stretching vibration peaks are at and. This change indicates that the Schiff base is coordinated with the nitrogen atom through the zinc ion.

3.2 PHOTOPHYSICAL PROPERTIES OF LIGANDS AND COMPLEXES

The absorption spectra and emission spectra of the ligands are shown in Fig.3. It can be seen that the ligands have absorption peaks around them and can be attributed to the transition of aromatic rings. In the case of, the absorption

peak can be attributed to the transition formed by the imino nitrogen atom and the aromatic ring.

Four kinds of Schiff base zinc complexes were dissolved in the solution, and their fluorescence excitation spectra were studied, as shown in Fig.4.

It can be seen from Fig.4 that the solution of the complex exhibits weak fluorescence emission at room temperature, and the maximum emission peak of the complex 2 and the ligand is at the same position as the maximum emission peak, while the complexes 1, 3 correspond to the corresponding complex,

TABLE 3 ENERGY LEVELS OF THE FOUR COMPLEXES

	$E_{onset}^{ox}(V)$	$HOMO(eV)$	$E_g eV$	$LUMO(eV)$
1	0.33	-5.13	2.67	-2.46
2	0.31	-5.11	2.53	-2.58
3	0.63	-5.43	3.00	-2.43
4	0.34	-5.14	2.73	-2.41

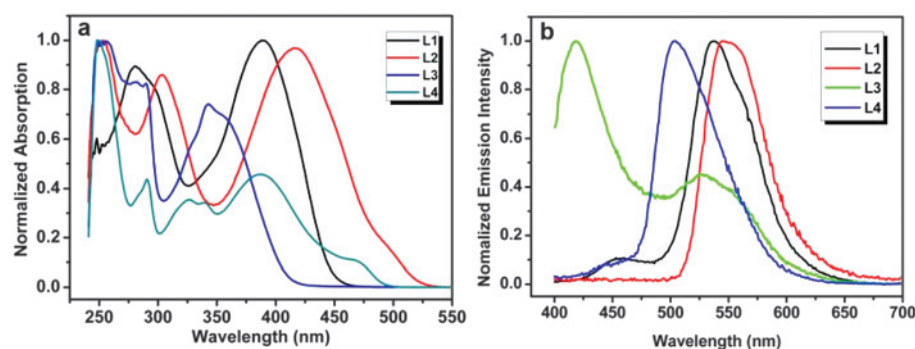


Fig.3 Absorption spectra and emission spectra of ligands

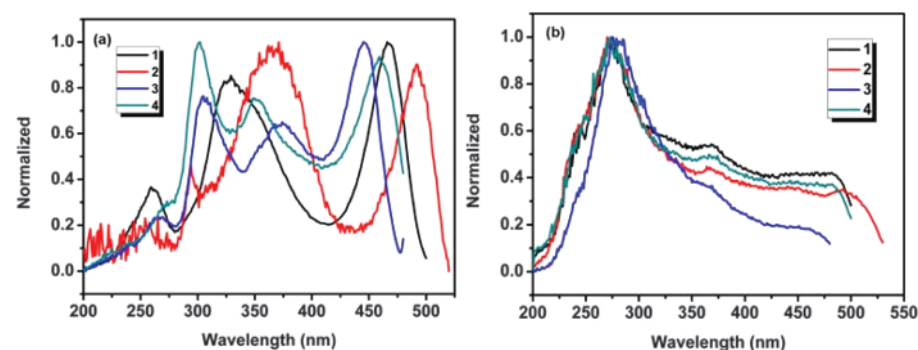


Fig.4. Fluorescence excitation spectra of complexes (a) Solution, (b) Solid (powder)

The maximum emission peak is blue-shifted, and the maximum emission peak of the complex in the solid state is red-shifted relative to its solution as shown in Table 2.

Table 3 shows that the complex 1 has the same salicylaldehyde group as the complex 3, whereas the emission peak of the complex 1 is obviously redshift compared to the complex 3 because the carbazole group in the complex 3 is more complex than the complex 1 Diphenylamine groups give electrons weak, leading to increased levels. It is also known that the complex 2 and the complex 4 have similar results.

3.3 STUDY ON THE ELECTROCHEMICAL PROPERTIES OF COMPLEXES

Combined with the anodic cyclic voltammetry, the electro-chemical properties of the complexes were studied. First, the voltammetric curves of the four complexes were obtained as shown in Fig.5.

TABLE 2 COMPARISON OF ABSORPTION SPECTRA AND FLUORESCENCE SPECTRA OF LIGANDS AND COMPLEXES

	^a Ligands		Complexes		
	$\lambda_{abs/em}(nm)$	$\lambda_{abs}(nm)$	$\lambda_{em}(nm)$	$^c\Phi_{solution}$	Φ_{power}
1	389/537	422	^a 518/ ^b 527	3.0%	16.7%
2	416/544	441	^a 544/ ^b 554	16.0%	20.9%
3	342/418(526)	409	^a 496/ ^b 504	3.0%	21.4%
4	387/503	430	^a 503/ ^b 521	2.0%	4.5%

^aTHF solution (10⁻⁵ M); ^bpowder; ^cCH₂Cl₂ solution.

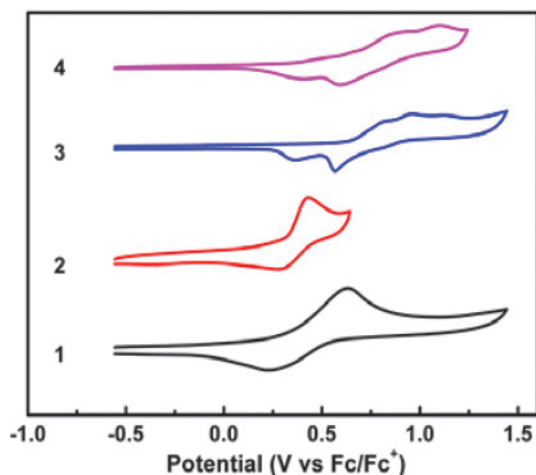


Fig.5. Four complexes Anode scan voltammetry curve

It can be seen from Fig.5 that the four complexes have good reversibility during voltammetry, and their redox is derived from carbazole units and triphenylamine in the molecule. The corresponding data is shown in Table 3.

It can be seen from Table 3 that the oxidation potentials of the four complexes are 0.33, 0.31, 0.63 and 0.34, respectively, and the energy gap obtained by UV absorption is 2.67, 2.53, 3.00 and 0.34. The four *HOMO* complexes are calculated from the formula $E_{HOMO} = -(E_{ox} + 4.8)eV$. It is found that the four *HOMO* complexes are located between $-5.11 \sim -5.43 eV$, so they have good hole transport function, and their *LUMO* energy levels are located between $-2.41 \sim -2.58 eV$.

4. Conclusion

In this paper, four kinds of Schiff base zinc complexes were synthesized and analyzed by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The photo-physical properties of ligands and complexes and the electro-chemical properties of the complexes were studied. The following conclusions were drawn:

- (1) In the ligand, respectively. At the same time, the Schiff base group was coordinated with the nitrogen atom through the zinc ion and the nitrogen atom in the four complexes, respectively.
- (2) The four complexes have good aggregation-induced luminescence enhancement properties.
- (3) Through the study of the electro-chemical properties of the four complexes, we can see that the oxidation potentials of the four complexes are 0.33, 0.31, 0.63 and 0.34, respectively, and the energy gap obtained by UV absorption is 2.67, 2.53, 3.00 and 0.34. The energy levels of the four *HOMO* kinds of cooperation are located between $-5.11 \sim -5.43 eV$, with good hole transport function; four *LUMO* complexes are located between $-2.41 \sim -2.58 eV$.

Acknowledgments

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