

Synthesis and Color-tunable Fluorescence Properties of Schiff Base Zinc (II) Complexes Used as Electroluminescent Materials

Yi YI, Xiao Qiang WEI, Ming Gui XIE, Zhi Yun LU*

Department of Chemistry, Sichuan University, Chengdu 610064

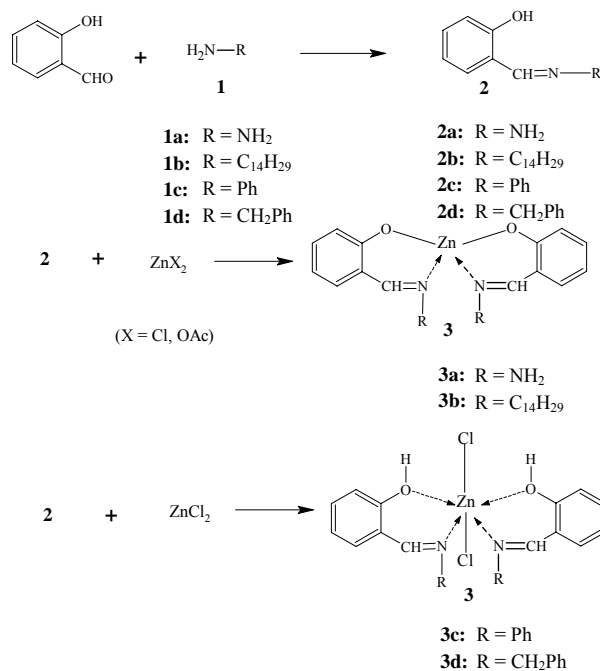
Abstract: Four kinds of bis(*N*-alkylsalicylaldiminato) zinc(II) complexes were synthesized, and their molecular structures were determined by FT-IR and elemental analysis. Their photoluminescence properties were determined, which indicated that they could emit strong fluorescence varying from blue to yellow to reddish orange depending on their different molecular structures. They had good thermostability, solubility and film forming capability, and can be used as organic electroluminescent materials. These new complexes may afford the feasibility to realize full-color display with materials based on similar molecular structures.

Keywords: Schiff base, fluorescence, color-tunability, organic electroluminescent material.

Since the first fabrication of thin-layer organic electroluminescent (OEL) device in 1987 by C. W. Tang *et al.*¹, OEL materials had been of ever increasing interest. Many efforts have been devoted to exploring new EL materials for display applications²⁻⁴, while up to now, full-color display has been realized with materials having different molecular structures. However, there are still some defects with both blue and red OEL materials, *i.e.* poor efficiency, poor durability and high driven voltage *etc.*, which bring difficulties to match with the green ones, and lead to the poor performance of OEL devices. The design and synthesis of OEL materials with similar molecular structures should be the key to the problem. In 2000, T. Tsutsui *et al.*⁵ reported a series of zinc chelates with arene substituted oxadiazole ligands, which showed good color-tunability from blue to orange by adjustment of different substituents. This result had opened a new pathway to get precise matching of RGB materials.

Bis(*N*-alkylsalicylaldiminato) zinc (II) complex has excellent fluorescent property with high photoluminescence quantum efficiency and good thermal stability, and could be used as fluorescence indicator and probe⁶. By employing this kind of chelates as EL material, Y. Yamada *et al.*⁷⁻⁹ reported the fabrication of OEL devices with maximum blue luminance of 1460 cd/m². We also reported the synthesis of blue luminescent Schiff base calixarene zinc (II) chelates with improved solubility¹⁰ before.

* E-mail: luzhiy@yahoo.com

Scheme 1 Synthetic route of the chelates

Because salicylaldehyde Schiff base zinc (II) chelate could be synthesized and chemically modified easily, thus may lead to cutdown cost. As it has excellent fluorescent properties, and was proved to be excellent OEL materials, we choose it as parent, and try to achieve color-tunability through variation of substituents in the ligands.

Herein, we reported the synthesis and photoluminescence properties of four kinds of salicylaldehyde Schiff base zinc complexes; the synthetic scheme was shown in **Scheme 1**. The results indicated that they could emit strong fluorescence with colors varied with different substituents.

Results and Discussion

Zinc atom may have coordination number of 4, 5, or 6 in the solid state¹¹. The FT-IR spectra indicated that there exists obvious difference between the ligands and chelates in the region of ~1600 cm⁻¹ which is assigned to $\nu_{C=N}$ stretching. This indicated the successful chelating. The results suggested that the former chelates with coordination number of 4 had weakened C=N bonds, while on the contrary, the latter ones had strengthened C=N bonds. This may lead to the different conjugation length of ligands.

Table 1 Difference of $\nu_{C=N}$ between ligands and chelates

Ligand / Chelate	2a	3a	2b	3b	2c	3c	2d	3d
$\nu_{C=N}$ (cm ⁻¹)	1620	1600	1634	1627	1615	1635	1635	1647
Difference (cm ⁻¹)		-20		-7		20		12

Because photoluminescence (PL) has almost the same mechanism to EL, we investigated their PL properties to predict their EL spectra. The results indicated that all of these chelates exhibited strong fluorescence both in solution and in solid states. Moreover, they had good solubility in common organic solvents, which afford them potential for using as dopants in polymer matrixes to fabricate OEL devices. The PL data were summarized in **Table 2**.

Complex **3a** and **3b** could emit blue fluorescence under UV irradiation in both solid states and solution, and could be used to fabricate blue OEL devices. However, Complex **3c** could emit bright reddish orange photoluminescence in solid state, while its PL spectra of chloroform solution lied in bluish green region. This indicated that it could be used to fabricate red OEL devices *via* vacuum evaporation. As for complex **3d**, it exhibited strong yellow fluorescence in its solid state and blue fluorescence in solution. Thus we have obtained a series of color-tunable chelates with their PL emission varied from blue to jacinth, this may offer the feasibility to fabricate full-color display with similar molecules.

The difference among the PL properties may be caused by the different conjugation system. From the FT-IR data, we can find that the C=N bond in **3a** and **3b** were weakened, while that of **3c** and **3d** were strengthened. This accounts for the red-shift of the PL emission. Moreover, as **3c** and **3d** have two additional Cl ions compared to **3a** and **3b**, they have stronger molecular interaction due to their salt-like structures and would easily compact together, which lead to the further red-shift of their PL spectra in solid states. While in solvent like chloroform, the molecular interaction can be reduced dramatically by the surrounding solvent molecules, thus lead to the blue-shift PL spectra of **3c** and **3d**.

Experimental

Instruments: PE-FT-IR 170SX; Finnigan Mat 4501 GC-MS; DuPont DSC-910 thermal analyzer; PE-2400 elemental analyzer; Janrell-Ash, ICAP9000+2000 ICP-AES; JASCO FP-6200 spectrofluorometer.

The intermediates **2a**, **2b**, **2c** and **2d** were synthesized according to literatures^{12~14}. The m.p. of these compounds were coincident with the corresponding literatures. Synthesis of **3a**: To a mixture of **2a** (10 mmol) and 20 mL methanol was added dropwise a solution of 5 mmol zinc acetate in 50 mL methanol. The mixture was refluxed for 2 hours under stirring, and the yellow precipitate was filtrated, washed with EtOH/H₂O alternately, and recrystallized from methanol to give white crystal with yield of 48%. M.p.>250°C; IR (KBr, cm⁻¹), 1605, 1145; Anal. Calcd. for Zn(C₇H₇N₂O)₂: (%) C 50.1, H 4.2, N 16.7, Zn 19.4; Found: C 49.8, H 4.3, N 16.7, Zn 19.5

Table 2 The photoluminescence properties of the complexes

	3a		3b		3c		3d	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
λ_{EXmax} (nm)	288	350	262	390	475	408	340	366
λ_{EMmax} (nm)	431	435	450	430	502	604	450	560
FWHM (nm)	65	70	70	55	80	100	60	110

λ_1 : 10⁻³ mol/L chloroform solution; λ_2 : Solid state; FWHM: full width at half maximum

Complexes **3b-3d** were synthesized with the same way as **3a**, except for using zinc chloride instead of zinc acetate solution.

3b: White needle crystals. Yield: 30%; m.p.82-84°C; IR (KBr, cm^{-1}), 1627, 1185; Anal. Calcd. for $\text{Zn}(\text{C}_{21}\text{H}_{34}\text{NO})_2$: (%) C 72.3, H 9.8, N 4.0, Zn 9.3; Found: C 72.5, H 9.8, N 4.3, Zn 9.0. MS m/z : 698 ($\text{M}+1^+$).

3c: Orange cubic crystals. Yield: 38%; m.p.228.3°C (DSC); IR (KBr, cm^{-1}), 1635, 1145; Anal. Calcd. for $\text{Zn}(\text{C}_{13}\text{H}_{11}\text{NO})_2\text{Cl}_2$: (%) C 58.9, H 4.2, N 5.3, Zn 12.2; Found: C 59.1, H 4.3, N 5.2, Zn 11.9.

3d: Saffron yellow cubic crystals. Yield: 62.7%; m.p.163-165°C; IR (KBr, cm^{-1}), 1647, 1156; Anal. Calcd. for $\text{Zn}(\text{C}_{14}\text{H}_{13}\text{NO})_2\text{Cl}_2$: (%) C 60.2, H 4.7, N 5.0, Zn 11.6; Found: C 59.8, H 4.7, N 4.9, Zn 11.0.

Acknowledgment

We want to express our thanks to the National Natural Science Foundation of China for financial support. (Grant No. 20102004)

References

1. C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.*, **1987**, *51*, 913.
2. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, *et al.*, *Nature*, **1990**, *347*, 539.
3. S. H. Jung, H. K. Kim, S. H. Kim, *et al.*, *Macromolecules*, **2000**, *33* (25), 9277.
4. S. C. Ng, H. F. Lu, H. S. O. Chan, *et al.*, *Adv. Mater.*, **2000**, *12* (15), 1122.
5. S. Tokito, K. Noda, H. Tanaka, *et al.*, *Synth. Met.*, **2000**, *111-112*, 393.
6. K. Morisige, *Analytica Chemica Acta*, **1974**, *22*, 295.
7. Y. Hamada, T. Sano, M. Fujita *et al.*, *Jap. J. Appl. Phys. Lett.*, **1993**, *32(4A)*, L511.
8. Y. Hamada, T. Sano, M. Fujita *et al.*, *Nippon Kagaku Kaishi*, **1993**, *7*, 883.
9. Y. Hamada, *IEEE Trans. Electron Devices*, **1997**, *44(8)*, 1208.
10. a. X. Q. Wei, Z. Y. Lu, P. Zou. M. G Xie, *Chin. Chem. Lett.*, **2003**, *14* (3), 263.
b. X. Q. Wei, Z. Y. Lu, P. Zou. M. G Xie, *Synth. Met.*, **2003**, *137(1-3)*, 1149.
11. G. E. Batley, D. P. Graddon, *Aust. J. Chem.*, **1967**, *20*, 877.
12. H. Carjar, *Ber.*, **1898**, *31*, 2803.
13. D. R. Lide, G. W. A. Milne, *Handbook of Data on common organic compounds*, Vol. II, 1753. (1995, by CRC Press Inc)
14. K. Tadeshige, N. Statoko, *J. Chem. Soc. Perkin Trans. I*, **2001**, *17*, 2071.

Received 13 May, 2003