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Synthesis, fluorescence study and biological evaluation of three Zn(II) complexes with Paeonol Schiff base

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ABSTRACT

The synthesis of three Paeonol Schiff base ligand and their Zn(II) complexes are reported. The complexes were fully characterized by IR, ^{1}H NMR, elemental analysis and molar conductivity. The experiment results show the three Zn(II) complexes can emit bright fluorescence at room temperature in DMF solution and solid state. The fluorescence quantum yields (Φ) of three Schiff base ligands and their Zn(II) complexes were calculated using quinine sulfate as the reference with a known Φ_R of 0.546 in 1.0N sulfuric acid. Furthermore, in order to develop these Zn(II) complexes' biological value, the antioxidant activities against hydroxyl radicals (OH•) were evaluated. The results show the three complexes possess excellent ability to scavenge hydroxyl radicals.

1. Introduction

At present, luminescent complexes are attracting more and more interest from researchers due to their important applications in the field of light-emitting diode devices [1], fluorescent sensor [2] and biological probes [3,4]. Up to now, many metal complexes have been studied for these uses, such as lanthanide(III) complexes [5], Pt(II) and Ru(II) complexes [6]. It is known that some zinc(II) complexes with nitrogen-containing ligands can exhibit intense emission at room temperature and zinc also has a significant role in bioinorganic chemistry [7]. Compared to other luminescent complexes, zinc has its own advantages of cheap materials, no damage to human body, and easy forming of complexes [8]. These excellent properties inspire our interest to synthesize a new series luminescent zinc(II) complexes as a candidate for biological use or fluorescence material. At the same time, Schiff base, a kind of very important N, O donor ligand and effective antibacterial, antiviral and antifungal agent becomes our first choice [9].

The previous literatures [8,10] have reported some Schiff base zinc(II) complexes, its Photoluminescent properties have been studied; however, its biological activities against hydroxyl radical are rarely evaluated. In this paper, we synthesized three paeonol (2-hydroxy-4-methoxy-acetophenone, Fig. 2(a)) Schiff base ligands and its zinc(II) complexes. It is found that all the zinc(II) complexes can emit strong fluorescence in DMF solution and solid state at room temperature, moreover, their quantum yields (Φ) were calculated. In order to explore these zinc(II) complexes' biological value, their antioxidant activities against OH• were studied. The results show the complexes possess excellent activities.

2. Experimental section

2.1. Instrumentation

Elemental analyses were conducted on a Vario EL analyzer. Infrared spectra (4000–400 cm^{-1}) were determined with KBr disks on a Therrno Mattson FTIR spectrometer. The ultraviolet spectra were recorded on a Lambda 35 UV–vis spectrometer. ^{1}H NMR spectra were measured on a Bruker Avance Drx 200-MHz spectrometer. The fluorescence spectra were recorded on a RF–5301PC spectrofluorophotometer produced by SHIMADZU. The antioxidant activities were tested on a 721E spectrophotometer.

2.2. Materials and methods

2-hydroxy-4-methoxy-acetophenone, Diethylenetriamine, 1,3-Diaminopropane, $Zn(Ac)_2{\cdot}2H_2O$, quinine, Safranin, Mannitol, EDTA, $FeSO_4{\cdot}7H_2O$, H_2O_2, were produced in China. All materials and solvents employed in this study were of analytical grade. EDTA–Fe(II) and Na_2HPO_4–KH_2PO_4 buffers were prepared with twice distilled water.

2.3. Calculation of quantum yields

The fluorescence quantum yields of the ligands 1–3, and complexes 1–3 were determined using quinine sulfate as the reference

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with a known Φ_R of 0.546 in 1.0N sulfuric acid [11]. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated according to the following equation: [8]

$$\frac{\Phi_S}{\Phi_R} = \left[\frac{A_S}{A_R}\right] \times \left[\frac{(OD)_R}{(OD)_S}\right] \times \left[\frac{\eta_S^2}{\eta_R^2}\right]$$

here Φ_S and Φ_R are the fluorescence quantum yields of the sample and reference, respectively, A_S and A_R are the areas under the fluorescence spectra of the sample and the reference, respectively. $(OD)_S$ and $(OD)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvents used for the sample and reference.

2.4. Hydroxyl radical scavenging assay

The hydroxyl radicals ($OH^{\bullet}$) in aqueous media were generated through the Fenton system. The solution of the tested compound was prepared with DMF. The 5 ml assay mixture contained following reagents: safranin (10 μM), EDTA-Fe(II) (80 μM), H_2O_2 (0.6%), the tested compound (4–20 μM) and a phosphate buffer (pH 7.4). The assay mixtures were incubated at 40 °C for 50 min in a water-bath. After which, the absorbance was measured at 520 nm. All the tests were run in triplicate and expressed as the mean ± standard deviation (SD). The suppression ratio for $OH^{\bullet}$ was calculated from the following expression:

$$\text{Scavenging effect}(\%) = \frac{A_i - A_o}{A_c - A_o} \times 100$$

where A_i = the absorbance in the presence of the tested compound; A_0 = the absorbance in the absence of the tested compound; A_C = the absorbance in the absence of the tested compound, EDTA-Fe(II) and H_2O_2.

2.5. Synthesis of Bi(2′-hydroxy-4′-methoxy-α-methyl-benzylidene)-1,3-trimethylenediimine.(ligand 1)

Paeonol (1.66 g, 10 mmol) and 1,3-Diaminopropane {0.37 g, 5 mmol} in 30 ml ethanol was refluxed for 10 h, a yellow precipitate was collected and recrystallized from DMF to give the pure ligand 1. Yield, 50%. Mp: 175–177 °C. ^{1}H NMR (DMSO-d6, ppm): δ 7.50 (2H, d, J = 9.0 Hz, 6-H), 6.23 (2H, d, J = 9.0 Hz, 5-H), 6.19 (2H, s, 3-H), 3.71(6H, s, –OCH_3), 3.62–3.71 (4H, t, J = 7.1 Hz, C = N–CH_2), 2.35(6H, s, N = C–CH_3), 2.02(2H, m, J = 7.1 Hz, –CH_2–). IR νmax (cm^{-1}): ν(C=N):1605.

2.6. synthesis of Bi(2′-hydroxy-4′-methoxy-α-methyl-benzylidene)-N,N′-diethyleneamine-1,5-diimine (ligand 2)

Paeonol (1.66 g, 10 mmol) and Diethylenetriamine {0.515 g, 5 mmol} in 30 ml ethanol were refluxed for 10 h, solvent were removed and diethyl ether was added, yellow solid was collected and washed with diethyl ether several times. Yield, 85%. Mp: 121–123 °C. ^{1}H NMR (DMSO-d6, ppm): δ 7.45 (2H, d, J = 8.7 Hz, 6-H), 6.17 (2H, dd, J = 8.7 Hz, J = 2.8 Hz, 5-H), 6.14 (2H, d, J = 2.8 Hz, 3-H), 3.71 (6H, s, –OCH_3), 3.62 (4H, t, J = 6.6 Hz, C=N–CH_2), 2.87 (4H, t, J = 6.6 Hz, NH–CH_2), 2.34 (6H, s, N=C–CH_3), 1.96 (1H, s, –NH–). IR νmax (cm^{-1}): ν(C=N):1604.

2.7. Synthesis of 2-hydroxy-4-methoxy-α-methylbenzylidene (benzoyl) hydrazone (ligand 3)

Paeonol (1.66 g, 10 mmol) and benzoyl hydrazine (1.36 g, 10 mmol) in 20 ml ethanol were refluxed for 10 h, white precipitate was collected and then recrystallized from methanol to obtain pure ligand 3. Yield, 65%. Mp: 210–212 °C. ^{1}H NMR (DMSO-d6, ppm): δ 13.63 (1H, s, –NH), 11.20 (1H, s, –OH), 7.91 ((1H, d, J = 6.6 Hz, 6-H), 7.52–7.61 (5H, m, Ph–H), 6.5 (1H, d, J = 6.6 Hz, 5-H) 6.45 (1H, s, 3-H), 3.77 (3H, s, –OCH_3), 2.43 (3H, s, N =C–CH_3). IR νmax (cm^{-1}): ν(C=O): 1650, ν(C=N):1615.

2.8. Synthesis of (complex 1)

$Zn(Ac)_2{\cdot}2H_2O$ (0.110 g, 5 mmol) in 2 ml DMF was added to 20 ml DMF solution containing ligand 1 (0.185 g, 5 mmol). After stirring at room temperature for 2 h, the light yellow precipitate was collected and washed with DMF three times, then with ethanol three times. The complex was dried at vacuo 24 h. Yield, 80%, $C_{21}N_2O_4H_{24}Zn$ requires (%) C, 58.20; N, 6.47; H, 5.54. Found: C, 58.50; N, 6.24, H, 5.10. ^{1}H NMR (DMSO-d6, ppm): δ 7.47 (2H, s, 6-H), 6.17–6.22 (4H, 3,5-H), 3.71 (6H, s, –OCH_3), 3.62–3.71 (4H, C=N–CH_2), 2.35 (6H, s, N=C–CH_3), 2.05 (1H, m, –CH_2–). ΛM ($S\,cm^2\,mol^{-1}$) 10^{-3} M DMF solution 25 °C = 16.2. IR νmax (cm^{-1}): ν(C=N):1599.

2.9. Synthesis of (complex 2)

$Zn(Ac)_2{\cdot}2H_2O$ (0.110 g, 5 mmol) in 5 ml methanol was added to 30 ml methanol solution containing ligand 2 (0.2 g, 5 mmol). After stirring at room temperature for 2 h, the light yellow precipitate was collected and washed with methanol three times, and then dried at vacuo overnight. Yield, 85%. $C_{22}N_3O_4H_{29}Zn$ requires (%) C, 55.00; N, 8.75; H, 6.04. Found: C, 54.61; N, 8.26, H, 5.90. ^{1}H NMR (DMSO-d6, ppm): δ 7.41 (2H, d, J = 9.6, 6-H), 6.1–6.14 (4H, 3,5-H), 3.64 (6H, s, –OCH_3), 3.33 (4H, s, C=N–CH_2), 2.9 (4H, s, HN–CH_2), 2.32 (6H, s, N=C–CH_3). ΛM ($S\,cm^2\,mol^{-1}$) 10^{-3} M DMF solution 25 °C = 30.8. IR νmax (cm^{-1}): ν(C=N):1608.

2.10. Synthesis of (complex 3)

$Zn(Ac)_2{\cdot}2H_2O$ (0.055 g, 2.5 mmol) in 5 ml methanol was added to 40 ml methanol solution containing ligand 3 (0.142 g, 5 mmol). After stirring at room temperature for 2 h, the yellow precipitate was collected and washed with methanol three times, then dried at vacuo overnight. Yield, 70%. $C_{32}N_4O_6H_{30}Zn$ requires (%) C, 60.86; N, 8.87; H, 4.75. Found: C, 60.55; N, 8.53, H, 4.50. ^{1}H NMR (DMSO-d6, ppm): δ 8.09, 7.41, 6.2 (8H, PH–H), 3.7 (3H, s, –OCH_3) 2.66 (3H, s, N=C–CH_3). ΛM ($S\,cm^2\,mol^{-1}$) 10^{-3} M DMF solution 25 °C = 45.0. IR νmax (cm^{-1}): ν(HO–C=N): 1605, ν(H_3C–C=N): 1594.

3. Results and discussion

3.1. Structure of the complexes

Fig. 1(a)–(c) shows the structure of the complexes 1–3, respectively. These structures are in accord with the results of elemental analysis, molar conductivity, IR and ^{1}H NMR. It is notable that the ligand 3 can exist as two forms as shown in Fig. 2(b). When ligand 3 was prepared, it was white; but after being exposed to the light at room temperature for several months it partly became yellow, complex 3 is also yellow. In the ^{1}H NMR spectra, the–OH (δ 11.2) and –NH (δ 13.63) can be observed in ligand 3; however, these two peaks disappeared when the complex 3 was formed. In IR spectra, ν(C=O) of ligand 3 appears at 1650 cm^{-1}, this peak shifts to 1605 cm^{-1} for complex 3, so many shifts seem unusual. We think the carbonyl group takes part in coordination as enolic form, that is to say the O=C–NH group has changed to HO–C=N. Another evidence can be found in UV spectra in Fig. 3(c), the absorption band at 327 nm (ε = 22,790) for ligand 3 shifts to 383 nm (ε = 23649). The TG curve of complex 2 shows weight loss between 180.6 and 271.7 °C, corresponding to its DTA curve, there is one evident endothermic

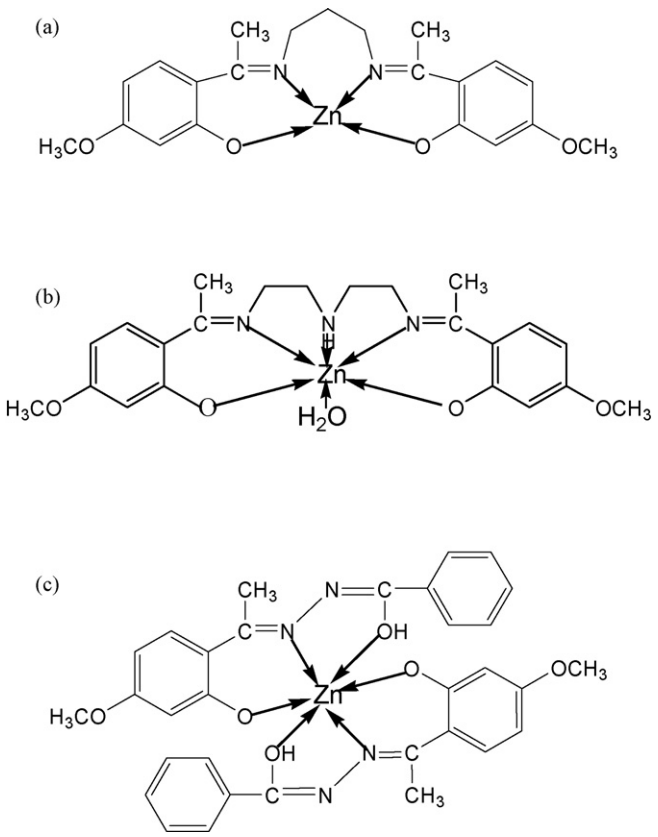

Fig. 1. Structures of complex 1(a), 2(b) and 3(c).

peak at 193.2 °C. This result confirms that water molecule takes part in coordination.

3.2. IR and ^{1}H NMR spectra

The ν(C=N) vibrations of ligands 1–3 are at 1605, 1604 and 1615 cm^{-1}, respectively, in the complexes, these vibrations shift to 1599, 1608, and 1594 cm^{-1}, respectively. The ν(C=N) vibration of ligand 2 shifts to high wavenumbers about 4 cm^{-1} when complex 2 forms. This change is also an evidence of coordination of C=N group [12]. In ^{1}H NMR spectra, except for the signals of ligands, there are not any other groups' signals, such as CH_3COO^-, solvent (methanol or DMF). These results indicate CH_3COO^- and solvent do not take part in formation of the complexes. In the complex 3, the O–H and N–H proton signals of the free ligands disappear in the ^{1}H NMR, which indicate the phenoxo oxygen coordinates to the Zn(II) ions and carbonyl has changed to enolic form. Moreover, in ^{1}H NMR spectra of complexes 1 and 2, the resonance for the 6-H, 5-H and 3-H (paeonol benzene ring) shifts by about 0.02–0.04 ppm, towards high field compared to the corresponding signals of the free ligands. However, the d and m peaks of benzene group in complex 3 change to three broad peaks compared to the ligand 3. In addition, it is interesting that the ^{1}H signals in the group of $-OCH_3$ and C=N–CH_2 also shift by about 0.07 and 0.29 ppm towards high field when complex 2 forms.

3.3. Fluorescence property

Table 1 summarizes the absorption and emission data for ligands (1–3) and complexes (1–3) in solution and the solid state. UV spectra of these six compounds are shown in Fig. 3. As shown in Table 1 and Fig. 3, the complexes 1–3 show three absorption bands, which are similar to the ligands 1–3. For ligand 1 and complex 1, the positions of their absorption bands are nearly no changes. But the absorption band at 376 nm for ligand 2 shifts to 350 nm for complex 2, blue-shifted 26 nm; and absorption band at 327 nm for ligand 3 shifts to 383 nm for complex 3, which are maximum absorption and red-shifted about 56 nm. The phenomenon of blue-shift and red-shift may be due to the different structures of ligands 2 and 3, and the perturbation of the intraligand π–π^* transition by the Zn(II) ions.

Fig. 4 shows the emission spectra of ligands 1–3 and complexes 1–3 in DMF solution. It can be seen that ligands 1–3 emit fluorescence at the same wavelength (414 nm). This suggests the fluorescence of the three ligands is all produced by π–π^* transition of Paeonol group, other different groups cannot effect their fluorescence. In comparison with the corresponding free ligands, the maximum emission of complexes 1 and 2 in solution are the same, only complex 3 exhibits slight red-shifts about 9 nm. On the other hand, the complexes 1–3 show higher fluorescence intensity than that of the free ligands, the changes of complexes 1 and 2 are higher than complex 3. These are supported by quantum yield values, as shown in Table 1. Enhancement of fluorescence after complexation may due to two reasons. First, when Zn(II) ions coordinate to the ligand, the ligand's photoinduced electron transfer (PET) process, which can often quench the fluorescence, is prevented. Second, the coordination of the ligands with the Zn atom increases the rigidity of the ligands, which can diminish the loss

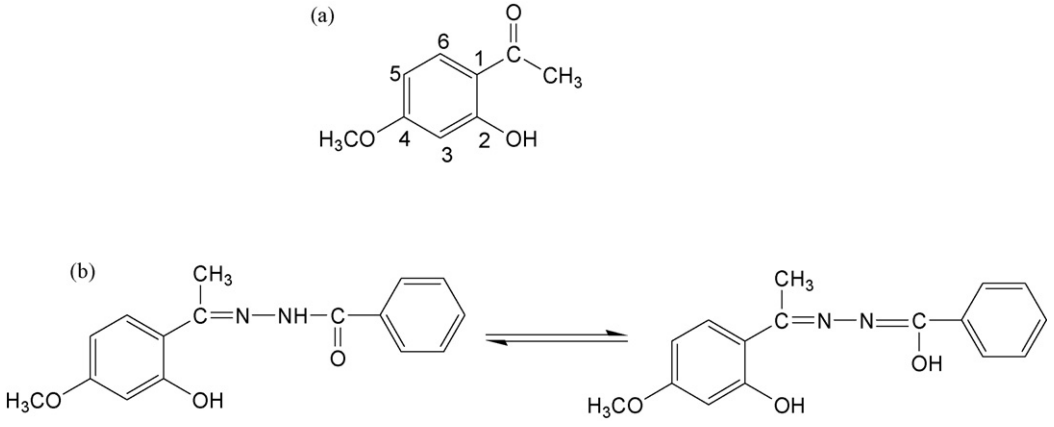

Fig. 2. The structures of paeonol (a) and the structure of ligand 3 (b).

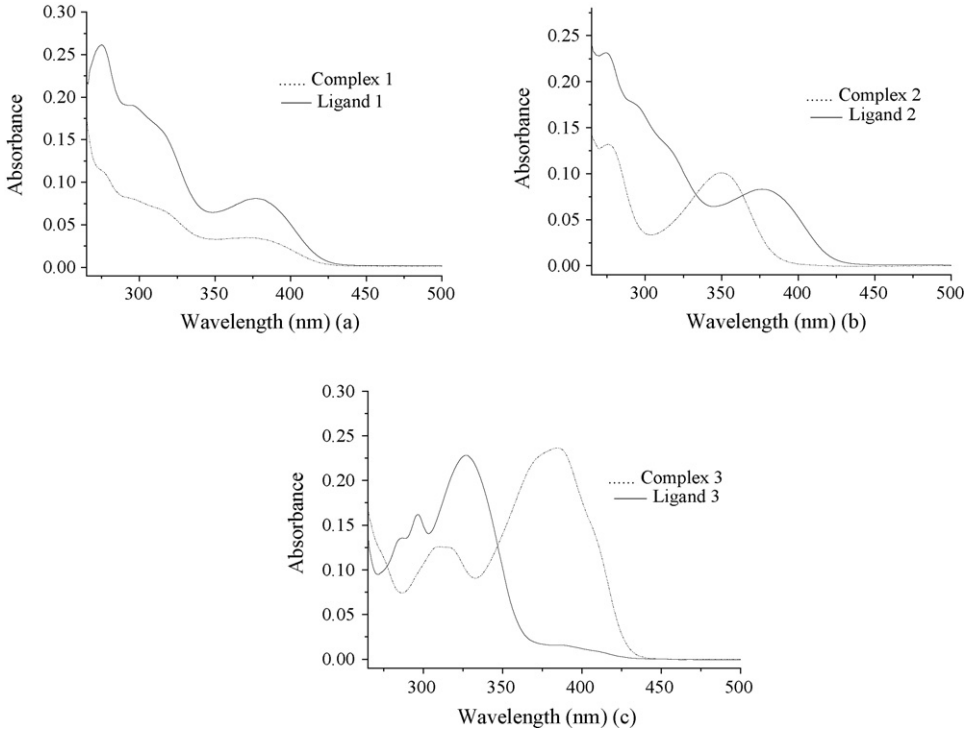

Fig. 3. The UV–vis spectra of ligands 1–3 and complexes 1–3 in DMF solution (1×10^{-5} M).

of energy via vibrational motions and increase the emission efficiency.

The emission spectra of ligands 1–3 and complexes 1–3 in the solid state are shown in Fig. 5. Ligands 1–3 and complexes 1–3 emit bright fluorescence in the solid state at room temperature. It can be seen from Fig. 5 that the emission maxima of three complexes are blue-shifted compared to those of the corresponding free ligand in the solid state, which is probably due to the disappearance of the intramolecular hydrogen bonding in ligands 1–3 after coordination with the zinc ions. In addition, it can be noted that the emission maxima of all the ligands and complexes in the solid state are red-shifted compared to their corresponding emission maxima in solution. This phenomenon can be normally observed for most fluorescent compounds in the solid state, probably due to π–π stacking of the aromatic rings in the molecules.

3.4. Evaluation of antioxidant activity

As an important non-enzymatic antioxidant, Zn complexes are attracting ample attention from researchers [13]. The scavenging

Table 1
Photoluminescent data of ligands 1–3 and complexes 1–3.

Compounds	Absorption (nm) ε ($dm^3\ mol^{-1}cm^{-1}$)	Excitation (λ_{max}, nm)	Emission (λ_{max}, nm)	Quantum yields (Φ)[a]	Conditions
Ligand 1	275 (25753) 295 (18742) 377 (7938)	312	414	0.0063	DMF, 298 K
		389	501		Solid, 298 K
Complex 1	276 (10567) 324 (5286) 378 (3229)	313	413	0.0180	DMF, 298 K
		385	474		Solid, 298 K
Ligand 2	275 (23135) 295 (17400) 376 (8312)	313	414	0.0086	DMF, 298 K
		343	498		Solid, 298 K
Complex 2	276 (13204) 350 (10097)	313	416	0.0402	DMF, 298 K
		389	446		Solid, 298 K
Ligand 3	287 (13567) 297 (16196) 327 (22790)	313	414	0.0062	DMF, 298 K
		371	487		Solid, 298 K
Complex 3	309 (12592) 383 (23649)	312	421	0.0094	DMF, 298 K
		391	474		Solid, 298 K

[a] Determined using quinine sulfate in 1 M sulfuric acid as a standard.

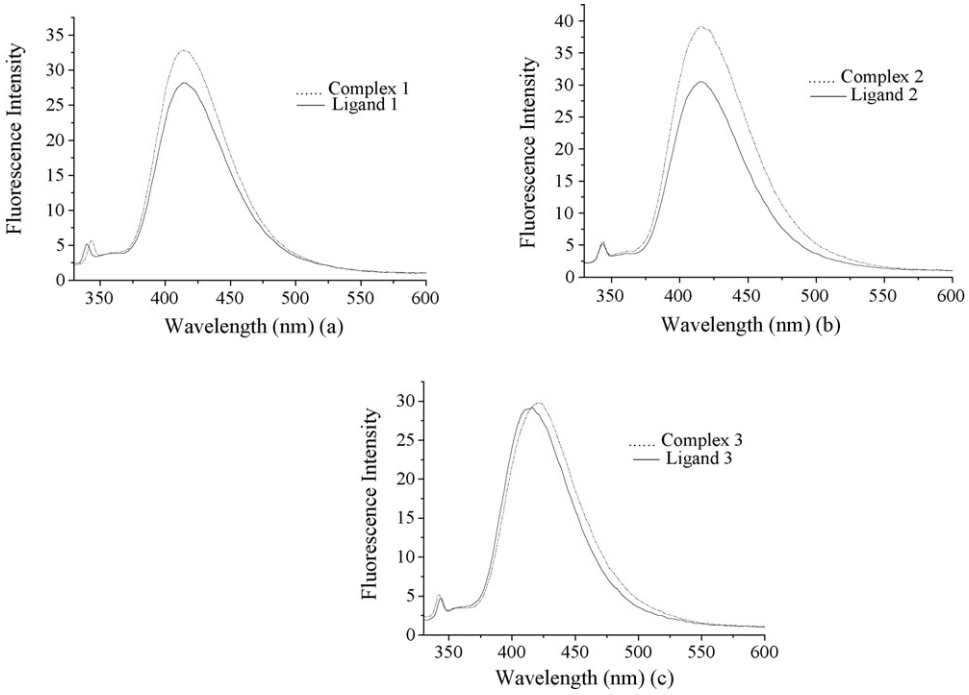

Fig. 4. Emission spectra of ligands 1–3 and complexes 1–3 in DMF (1×10^{-5} M, slit = 3 nm).

ability of the ligands1–3 and complexes 1–3 against hydroxyl radical is shown in Fig. 6. It can be seen that the inhibitory effects of all compounds on hydroxyl radical are related to concentration. At a concentration from 3 to 15 μM, the percentage scavenging effect values are about 0–50.9%, 1.5–25.4% and 3–20.1% for ligands 1–3, respectively; and values are about 5.3–57.9%, 8–72.45 and 6.9–72.4% for complexes 1–3, respectively. It is obvious that scavenging activities of the complexes are stronger than that of ligands. The results indicate Zn takes an important role in the scavenging ability of complexes [13].

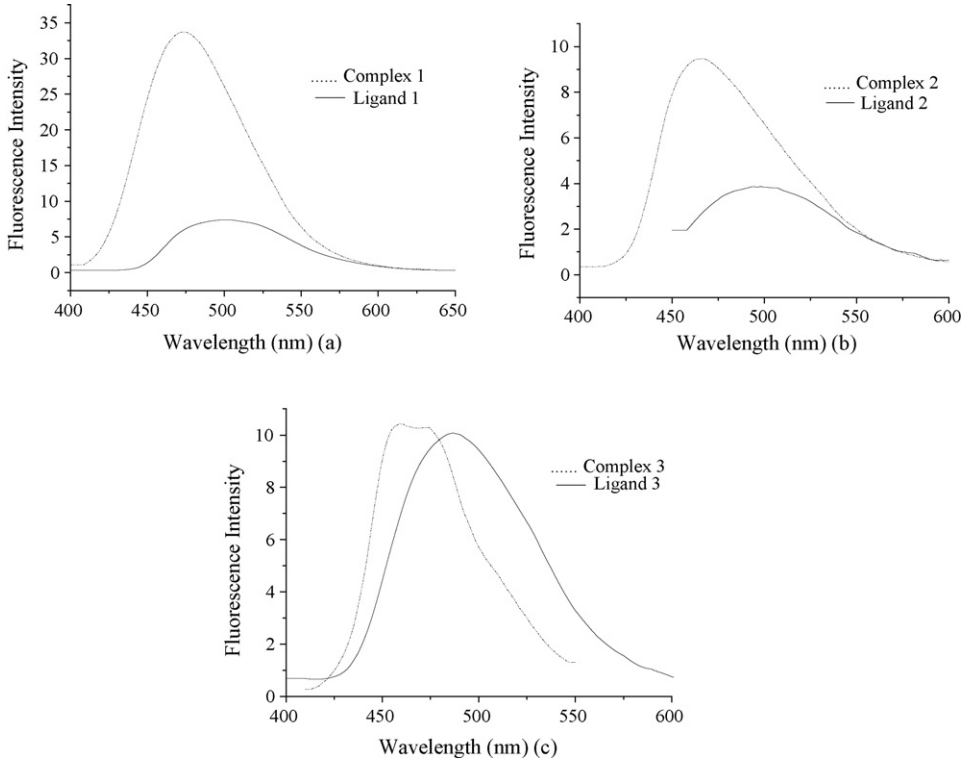

Fig. 5. Emission spectra of ligands 1–3 and complexes 1–3 in the solid state (slit = 1.5 nm, low sensitivity)

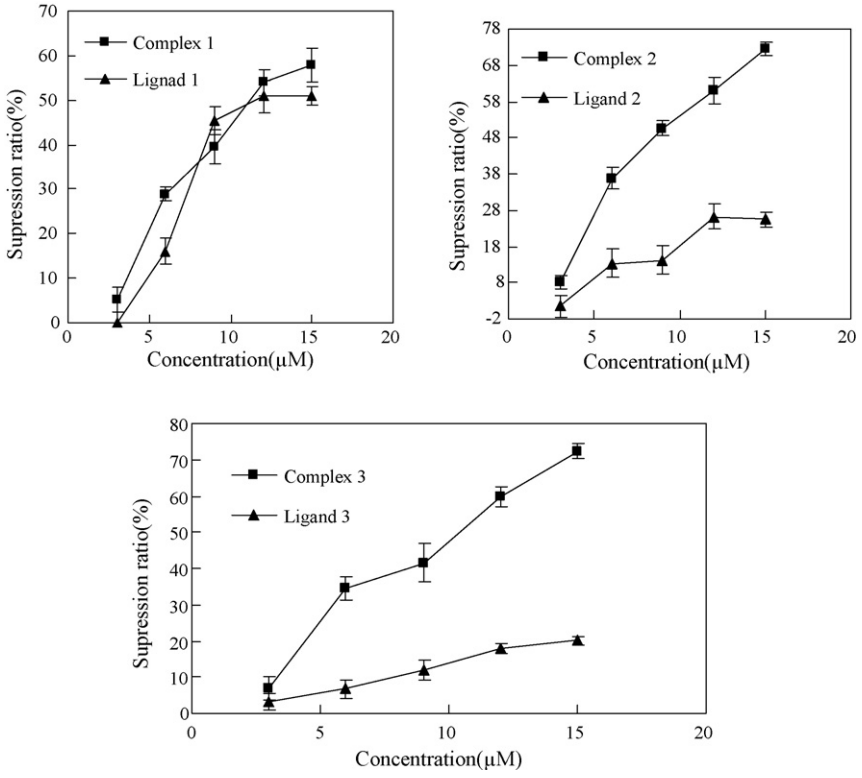

Fig. 6. Scavenging effect of tested compounds on hydroxyl radical. Values are means ± SD ($n = 3$).

4. Conclusion

A series of Schiff base ligands and their Zn complexes has been synthesized and fully characterized. The research results indicate the three Zn complexes can emit bright fluorescence in solution and solid state. It is suggested that the three complexes are a new class of fluorescence material. Furthermore, the high scavenging ability of three Zn complexes against hydroxyl radical makes them ideal candidates for biological use.

Acknowledgements

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