A New Blue Photoluminescent Salen-like Zinc Complex with Excellent Emission Quantum Yield

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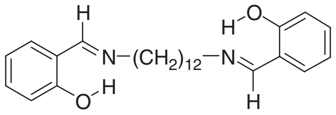
A new salen-like compound, **H_2L**, bearing a 12-carbon atom length aliphatic chain bridging iminic nitrogen atoms, was successfully synthesized and characterized. Interestingly, its zinc complex, **ZnL**, showed an extraordinary high fluorescent quantum yield value of 75%, originating from a metal-perturbed ligand-centered state.

The chelating ligands H_2(salen) (H_2(salen) = *N*,*N*′-bis(salicylidene)-1,2-ethylenediamine) or H_2(salen)-like are very popular in complexation reactions with most M(II) metal ions. Moreover, the straightforward synthesis makes available a wide selection of ligands which differ from each other with regards the nature of the diamine or of the substituents placed on the salicylidene core. These characteristics have led to the extensive interests in these compounds in applications as catalysis to materials for opto-electronic devices.[1]

Some of these zinc complexes, in particular those exhibiting high fluorescence intensity, have been proposed as blue emitters in electroluminescent devices.[2] Results support the good performances of these materials, motivating further studies regarding the luminescence properties of Zn(salen)-related species.[3]

We are currently concerned with the synthesis of emitting zinc coordination compounds,[4] in this context we have now prepared and characterized the **H_2L** ligand and its Zn(II) complex, **ZnL**.



H_2L

Condensation of 2,4-dihydroxybenzaldehyde with 1,12-dodecylenediamine (2:1 molar ratio) produces the ligand **H_2L** at a yield of 80%.[5] Elemental analysis, IR and ^{1}H NMR spectra confirmed the reported molecular formula. The corresponding tetracoordinated **ZnL** complex was prepared by reacting **H_2L** with an equivalent of zinc(II) acetate dihydrate in hot ethanol. A bright yellow solid was obtained at a yield of 60%, and the stoichiometry of this complex was confirmed by elemental analysis, IR spectroscopy and MALDI/TOFMS.[6]

Photophysical characterization was performed at room temperature; all the compounds were stable during the measurements.[7] Emission quantum yields were determined using the optically dilute method[8] on aerated solutions with 9,10-diphenylanthracene in cyclohexane ($\Phi = 0.95$)[9] serving as the standard.

The absorption spectrum of **H_2L** in dichloromethane (Figure 1) shows two peaks at 255 nm ($\varepsilon = 12730\,\mathrm{M^{-1}\,cm^{-1}}$) and 314 nm ($\varepsilon = 4630\,\mathrm{M^{-1}\,cm^{-1}}$), and a very low intensity band at 410 nm ($\varepsilon = 120\,\mathrm{M^{-1}\,cm^{-1}}$). The 255 and 314 nm bands are ascribed to a π–π^* transitions localized on the aromatic ring, while the 410 nm band is due to an *n*–π^* excitation between the lone pair on the iminic nitrogen and a π^* orbital on the C=N fragment.[10] When the ligand was irradiated on the *n*–π^* band maximum, an emission at the limit of instrument resolution was detected at 500 nm; the excitation spectrum recorded at this wavelength closely matched the absorption spectrum.

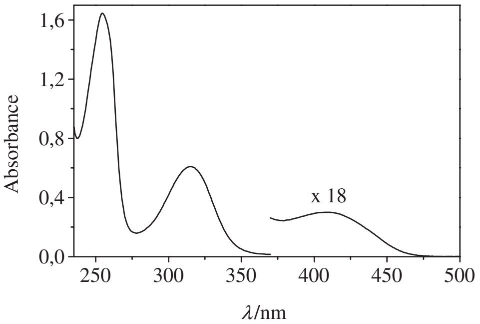


Figure 1. Absorption spectrum of **H_2L** ligand in dichloromethane solution.

Complexation of the zinc ion lowers the energy states of the ligand, leading to a red-shift of the absorption bands of the complex with respect to those of the ligand. Actually, the electronic excitation pattern (Figure 2) of **ZnL** shows two intense bands at 272 nm ($\varepsilon = 9000\,\mathrm{M^{-1}\,cm^{-1}}$) and 370 nm ($\varepsilon = 5930\,\mathrm{M^{-1}\,cm^{-1}}$), due to metal-perturbed ligand-centered transitions, which have the same origin as the two principal bands of the ligand spectrum. As expected, the *n*–π^* transition, which gives rise to the low-intensity band in the ligand spectrum, is undetected in the complex spectrum, because of the involvement of the lone pair on the nitrogen atom in the coordination with zinc ion. The resultant energy increase of the *n*–π^* transition (Figure 3) causes a blue-shift of the corresponding band, which is probably hidden by the 370 nm broaded band.[11] The complex shows a very intense photoluminescent band with a maximum at 450 nm (Figure 2). The shape of this band and the comparison with similar compounds[1b,12] indicate that the luminescence originates

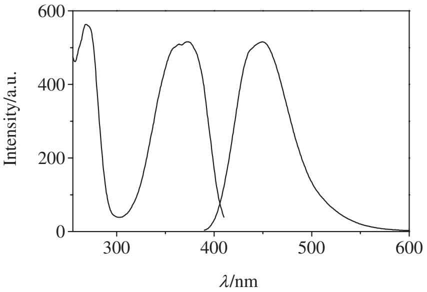


Figure 2. Excitation ($\lambda_{\mathrm{em}} = 450$ nm) and emission ($\lambda_{\mathrm{ex}} = 370$ nm) spectra of the **ZnL** complex in dichloromethane solution.

from singlet ligand-centered excited state.[1c] The emission quantum yield (Φ) of the complex attained the extraordinary value of 75%.

The remarkable fluorescent quantum yield exhibited by **ZnL** is, to the best of our knowledge, the highest reported to date for blue-emitting H_2(salen)-like complexes. Actually, despite the high level of interest in this class of compounds, and reports of similar luminescent complexes, no systematic study of the photophysical properties have been reported with only a few authors reporting Φ values.[1c,3] Interestingly, in **H_2L**, the substitution of two H^+ for Zn(II) dramatically improves the emission quantum yield; this is attributed to the increase in energy of the $n\pi^*$-related state and to the decrease of the $\pi\pi^*$-related state which becomes the lowest energy excited state (Figure 3), allowing a radiative decay.[13]

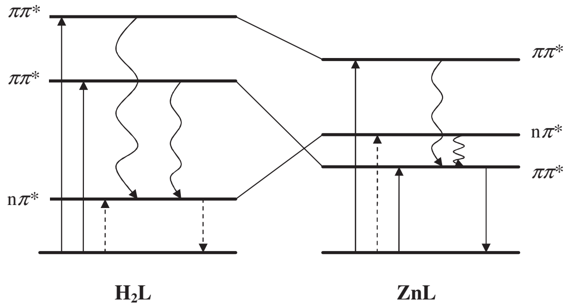


Figure 3. Qualitative states diagram of the **H_2L** and **ZnL** compounds: solid line indicates allowed radiative transitions; dotted line, forbidden (or weak) transitions; curves represent the nonradiative decays.

Concluding, with reference to the molecular structure, it is worthy of note that for complexes similar to **ZnL** very little data are available from the literature.[14] The first X-ray structural analysis of a tetracoordinated **ZnL′** complex (**H_2L′** = *N,N′*-bis(3-*tert*-butylsalicylidene)-1,2-ethylenediamine) was, in fact, only recently carried out. Unexpectedly, **ZnL′** was found to display a dimeric structure, with the two metal centres in a tetrahedral coordination geometry, resulting in an overall helical structure.[12] As far as the photophysical properties of this dimeric **ZnL′** complex are concerned, the emission quantum yield was not reported, however, for the sake of comparison with **ZnL**, we measured Φ (at room temperature, in dichloromethane solution) for the reference **Zn(salen)** complex. The value of Φ measured for **Zn(salen)** is 0.1%. Thus, comparing the results obtained for **ZnL** and for **Zn(salen)**, it is apparent that the emission performances of this series of zinc complexes strongly depend on the nature of the bridging diimine and ultimately, on the molecular structure of the resulting coordination compounds. Work is currently underway to determine the molecular structure for **ZnL** and the structure–luminescent relationship of this class of molecules which, with such intense emission, is extremely promising as a valuable blue emitter for various applications in opto-electronic technologies.

References and Notes

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5 2-Dihydroxybenzaldehyde (4,09 mmol, 500 mg) and 1,12-dodecylenediamine (2,05 mmol, 410 mg) were dissolved in 10 mL of methanol. The resulting solution was stirred at reflux for 3 h. As the solution cooled, a yellow solid was obtained which was separated by filtration. The crude product was purified by recrystallization from ethanol. Yield 80%, mp 82 °C. Anal. Calcd. for $C_{26}H_{36}N_2O_2$: C, 76.48; H, 8.88; N, 6.86%. Found: C, 75.98; H, 8.26; N 6.81%. IR (KBr): ν 2918, 2848, 1635 (C=N), 1608, 1581, 1499, 1469, 1238, 997, 978, 949, 752, 740, 693, 459 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13,76 (s, 2H, OH), 8.33 (s, 2H, CH=N), 7.30–7.23 (m, 4H, ArH), 6.99–6.64 (m, 1H, ArH), 6.89–6.84 (m, 1H, ArH), 3.58 (t, 4H, CH_2–N).

6 **H_2L** (0.37 mmol, 150 mg) was dissolved in 15 mL of hot ethanol and zinc(II) acetate dihydrate (0.37 mmol, 81 mg) was added. After 5 h of refluxing, the solvent was concentrated and petroleum ether was added; the resulting solution was kept at −4 °C for 24 h. The bright yellow precipitated complex was filtered off and washed with ethanol. Yield 60%, mp 125 °C. Anal. Calcd. for $C_{26}H_{34}N_2O_2Zn$: C, 66.17; H, 7.26; N, 5.94%. Found: C, 66.01; H, 7.21; N 5.94%. IR (KBr): ν 2922, 2852, 1623 (C=N), 1600, 1537, 1467, 1249, 978, 908, 794, 739, 654, 465 cm^{-1}. MALDI/TOFMS: $m/z = 471$ ([**ZnL** + H]$^+$). ^{1}H NMR data not available because of the low solubility.

7 Absorption spectra (Perkin Elmer Lambda 900 spectrophotometer) and emission spectra (Perkin Elmer LS 50B spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube) were recorded using spectrofluorimetric grade solvents; uncorrected emission spectra were confirmed by excitation spectra. The experimental uncertainty of the band maximum for absorption and luminescence spectra was 2 nm while that for the extinction coefficient was 10%, and that of luminescent intensity was 15%.

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10 The weak band at 410 nm is assigned to an excitation on the single molecule because of the detected linear correlation between absorption intensity and concentration.

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