含吩噻嗪金属配合物的合成及非线性光学性质研究

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本文报道了一种新的配体: 10-乙基-3-甲酰吩噻嗪缩肼基二硫代甲酸甲酯 (HL)及其金属配合物的合成。采用了元素分析、质谱、核磁共振、红外光谱对配体及其金属配合物进行了表征。此外,并应用紫外、荧光和 Z-扫描技术,测定了配体及其金属配合物的荧光最佳发射波长(λmaxtm)、荧光量子产率(Φ_i)、寿命(τ)和非线性光学性质。结果表明它们在 DMF 溶液中都能发射出较强的橄榄色荧光,配体及其金属配合物都有双光子吸收,并且金属配合物的非线性光学效应比配体明显增强。用半经验量子化学方法(RHF/PM3)计算结果与实验值较为吻合。

关键词: 过渡金属配合物 吩噻嗪 双光子吸收 非线性光学性质 量子化学计算 分类号: 0614

Synthesis and NLO Studies on Metal Complexes Containing Phenothiazine Ligand

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A new ligand, S-methyl- β -N-[10-ethylphenothiazine-3-methylene] dithiocarbazate (abbreviated as HL) and its complexes ML₂(M = Ni, Cu, Zn, Cd and Pd) have been synthesized and characterized by elemental analyses, EI-MS, ¹H NMR, IR, UV-vis spectra, photoluminescence measurements. All of the compounds emit an olivine color in DMF solution. The emission maxima (λ_{max}^{em}), fluorescence quantums (Φ_f), and lifetimes (τ) of each compound are measured. The nonlinear absorptions of HL and ML₂ solutions (in DMF) are measured by open-aperture Z-scan technique at a 532nm wavelength. Theoretical calculations were consistent with the experimental results.

Keywords:transition metal complexphenothiazinetwo-photon absorptionnonlinear optical propertyquantum chemistry calculation

0 Introduction

 π -Conjugated organic compounds have emerged

as a promising class of advanced materials because of their optical nonlinearities^[1-4] and/or of their fluorescence efficiency and semiconducting properties, which

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have been exploited most notably in the development of efficient light emitting diodes (LEDs)^[5]. In all cases, the strong coupling between geometry and electronic structure is the source of the fascinating physics of these π -conjugated molecules and macromolecules^[6].

Recently, Schiff base derivative compounds have been extensively studied for the applications of electroluminescent (EL) device^[7] due to their luminescent properties. However, the devices are mostly organic compounds or polymers. Low melting points or low decomposition temperatures of the organic compounds inhibit their applications. In an attempt to seek for new fluorescent materials among the π -electron delocalized systems containing mixed sulfur and nitrogen donors, by introducing the optical and electronic active chromophore into metal complexes, we report herein the coordination complexes with olivine emissions, very strong two-photon absorption, non-linear optical properties.

Strategies of Syntheses of HL, ML₂.

1 Experimental

1.1 General Procedures

All chemicals and solvents were dried and purified by usual methods. Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectra were recorded with a Nicolet FT-IR 170SX instrument (KBr discs) in the 4000 ~ 400cm⁻¹ region. UV-vis spectra were recorded with an UV-265 spectrophotometer. The photoluminescence measurements were carried out in

DMF solutions and the spectra were collected with a Edingburg FLS920 spectrofluorimeter. No aggregation or self-absorption effects were observed upto 0.1 μ mol • L⁻¹ solutions in the solvents studied. Therefore, we prepared 0. 1μ mol \cdot L⁻¹ sample solutions for absorption, emission, excited-state lifetime (τ) , and quantum yield (Φ_f) studies. The reference standard used for quantum yield determination was Rh6G $(0.1 \mu \text{mol} \cdot \text{L}^{-1})$ in ethanol $(\Phi_f = 0.95)$. MS spectrum was obtained on a ZAB-HS mass spectrometer (FAB source) . ¹H NMR spectra were performed on a Brucker AM-500 spectrometer using TMS as internal standard and CDCl₃ as solvent. The PM3 series methods have been used to study HL and ML₂. The geometry optimization is calculated by PM3. The electronic spectra are calculated by PM3/SCI method.

1.2 Syntheses of HL and ML₂

Syntheses of S-methyl- β -N-[10-ethylphenothiazine -3-methylene] dithiocarbazate (HL). A total of 5. 1g (0.02mol) of 3-formyl-10-ethylphenothiazine^[8], 2. 4g (0.02mol) of S-methyldithiocarbazate, 100mL ethanol were introduced into a round-bottom flask fitted with a condenser. The mixture was then stirred for 3h at 80°C. The mixture was cooled to room temperature. The crude product recovered by filtration was washed with ethanol and recrystallized from ethanol/acetone (*V*: *V*, 1:1). Yellow powder was obtained and dried *in vacuo* over P₂O₅, yield 6. 5g (90%). Anal. Calcd. for C₁₇H₁₇N₃S₃: C, 56. 82; H, 4. 76; N, 11. 69. Found: C, 56. 58; H, 4. 53; N, 11. 67%. ¹H NMR



Scheme 1

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 $(CDCl_3), \delta[ppm]: 1.46 (3H, t), 2.70 (3H, s),$ 3.96 (2H, q), 6.84 ~ 7.73 (8H, m), 10.27 (1H, s). Syntheses of ML₂. M(OAc) $_2 \cdot nH_2O(M = Ni(II))$, Cu (II), Zn (II) and Cd (II)) or PdCl₂(CH₃CN)₂) 1 mmol, 2mmol HL was dissorved in ethanol (20mL). After refluxing for 3h, the mixture was cooled to room temperature. The precipitate was thoroughly washed with ethanol/acetone (V: V, 5:1) three times and dried in vacuo over P2O5, (90%). Anal. Calcd. for C34H32N6S6Ni: C, 52. 65; H, 4. 15; N, 10. 84. Found: C, 53.02; H, 4.42; N, 10.65%. Anal. Calcd. for C34H32N6S6Cu: C, 52. 32; H, 4. 13; N, 10. 77. Found: C, 51.75; H, 4.52; N, 10.29%. Anal. Calcd. for C34H32N6S6Zn: C, 52. 20; H, 4. 12; N, 10. 75. Found: C, 52.46; H, 4.41; N, 10.57%. Anal. Calcd. for C₃₄H₃₂N₆S₆Cd: C, 49. 24; H, 3. 88; N, 10. 14. Found: C, 49.66; H, 4.25; N, 10.26%. Anal. Calcd. for C34H32N6S6Pd: C, 49. 60; H, 3. 91; N, 10. 21. Found: C, 49.84; H, 4.35; N, 10.15%.

2 **Results and Discussion**

2.1 Mass Spectroscopy of HL

The EI MS data of HL were list in Table 1.

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Table 1 EI MS Data of HL
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| HL(m/z) | 357 | 283 | 253 | 223 | 153 |
|---------|-----|-----|-----|-----|-----|
| % | 30 | 15 | 19 | 100 | 10 |

According to the data in Table 1, the fragmentation pathways of HL were given in Scheme 2.

2.2 IR spectroscopy of HL and ML₂

The IR spectra data of HL and ML_2 were list in Table 2.

 Table 2
 FT-IR Data of HL and ML₂

| | $\nu_{\text{N-H}}$ | Vc - s | VC = N | V N-N | $ u_{Ph}$ |
|------------------|--------------------|----------|--------|--------------|-----------|
| HL | 3106 | 1099 | 1593 | 950 | 1465 |
| NiL ₂ | | <u> </u> | 1561 | 964 | 1464 |
| CuL ₂ | | | 1563 | 962 | 1461 |
| ZnL2 | | <u> </u> | 1570 | 957 | 1459 |
| CdL ₂ | | | 1563 | 958 | 1459 |
| PdL ₂ | | | 1563 | 960 | 1464 |

For HL neutral molecule, the IR absorption peaks, attributable to the characteristic $\nu_{\text{N-H}}$ and $\nu_{\text{C}=\text{S}}$, appear at 3106 and 1099cm⁻¹ respectively. In its complexes, the peaks are absent, indicating that after losing proton, the C-N and C = S bonds were changed into C = N and C-S bonds. At the same time, comparing the $\nu_{C=N}$, ν_{N-N} and ν_{Ph} , HL appear at 1593, 950 and 1465 cm⁻¹ respectively, but $\nu_{C=N}$ of its complexes (ML_2) has a red shift, e.g. $1561 \text{cm}^{-1}(\text{Ni}L_2)$, and $\nu_{\rm N-N}$ has blue shift, e. g. 964cm⁻¹(NiL₂). All these indicate, after HL losing proton and coordinating to M, that N(2), N(3), C(4) and S(5) form a five-ring and a wider π -conjugated system. While N(2) and S(5) coordinating to M, the strength of C(1) = N(2) bond will be weakened and N(2)-N(3) bond will be strengthened. So their vibrations appear red or blue shift respectively.

According to elemental analyses, MS, 'H NMR and IR spectral analysis, the Schiff base ligand HL was deprotonated on coordinating to the divalent metal ions Ni (II), Cu (II), Zn (II), Cd (II) and Pd (II) to form stable neutral complexes ML₂ (as shown in Scheme 1)^[9,10].

2.3 Linear Optical Properties

UV-vis spectroscopy of HL and ML₂: The elec-

 $\mathbf{H}^{+}(T) = \mathbf{F}$



Scheme 2 The fragmentation pathways of HL

tronic absorption spectra of HL, and ML_2 were measured in DMF solution. The data were listed in Table 3.

All the compounds (HL and ML₂), as shown in Fig. 1 and Table 3, exhibit essentially the same absorption profile: an intense and low-lying (near UV region) absorptions band. The large molar absorption coefficients ($\lg \varepsilon = 4 \sim 5$) are indicative of highly π conjugated systems. There are very week absorptions at 532nm. Each of their absorption spectra exhibits three peaks. The three peaks could be assigned to K, B or R band of each compound. The K band is the absorption of $\pi \to \pi^*$ of larger π -conjugated system. The B band is the absorption of $\pi \to \pi^*$ of benzene. The R band is the absorption of $n \to \pi^*$ of p- π conjugation of *n*-electron groups N (or S) with benzene.



Fig. 1 Room-temperature absorption, emission spectra of HL and ML₂ in DMF solution
For clarity, the intensity (1) was magnified 20 times for CuL₂, and 100 times for PdL₂

Comparing the K bands of HL with that of ML₂, K bands show a red shift of λ for ML₂ about 2 ~ 12nm to those for HL. The R bands were red shifted about 8 ~ 66nm. Such a red shift is consistent with the fact: while N(2) and S(5) of HL coordinated to M, the new rings enhance the π -electron delocalization along the unsaturated system and reinforce the electronic density on larger π -conjugated system and p- π conjugation. At the same time, the B bands of HL comparing with those of ML_2 were shown a smaller blue shift. They indicate that the forming of complexes, the electronic density on benzene is decreased.

All above indicates that HL was coordinated to M with N(2) and S(5) forming $S \rightarrow M$ and $N \rightarrow M$ bands (shown in Scheme 1).

Photoluminescence: Absorption, emission Spectra for HL and ML_2 and the selected fluorescence decay profiles monitored at 395nm for HL and NiL₂ in DMF solution are shown in Fig. 1, Fig. 2 respectively. All the absorption and emission optical data for HL and ML_2 in DMF are summarized in Table 4.



Fig. 2 Fluorescence decay profile of HL and NiL₂ in DMF solution monitored at 395nm

Compounds HL and ML₂ emit an olivine color when irradiated (one-photon processes) by UV in DMF solution. All the complexes show the same features: exciting λ_{max} (~395nm), emission band ($\lambda_{max} = 535$ ~

| HL | NiL ₂ | CuL2 | ZnL ₂ | CdL ₂ | PdL2 | assignment |
|------------|------------------|-----------|------------------|------------------|-----------|--------------------|
| 272(4.16) | 274(4,72) | 282(4.56) | 278(4.53) | 276(4.58) | 284(4.49) | K(π - π) |
| 330(4, 34) | 324(4.63) | 314(4.60) | 324(4,55) | 324(4.54) | 310(4.48) | B(π-π*) |
| 396(4.26) | 416(4.49) | 430(4.55) | 416(4.53) | 404(4.59) | 462(4.45) | $R(n-\pi^*)$ |

Table 3 UV-vis Data of HL, ML₂, λ (nm) (lg ε)

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| compound | λ _{max} ≪∕nm | λ _{max} em/nm | stokes shifts∕nm | Φſ | I | τ/ns | k _t /(μs) ⁻¹ | $k_{nf}/(\mu s)^{-1}$ |
|------------------|-----------------------|------------------------|------------------|-------------------------|-----|--------------------|------------------------------------|-----------------------|
| HL | 395 | 537 | 142 | 0.20 | 175 | 6, 82 | 29 | 117 |
| NiL ₂ | 395 | 537 | 142 | 0. 17 | 234 | 5.96 | 28 | 139 |
| CuL₂ | 390 | 543 | 153 | 5. 1 × 10 ⁻³ | 6 | 5.24 | 1 | 190 |
| ZnL ₂ | 395 | 539 | 145 | 0.34 | 496 | 4, 85 | 70 | 136 |
| CdL₂ | 396 | 535 | 140 | 0. 20 | 359 | 5.54 | 36 | 144 |
| PdL ₂ | 393 | 550 | 157 | 1, 1 × 10 ⁻³ | 0.7 | | | |

Table 4 Optical Data of the Complexes in DMF ($C = 1.0 \times 10^{-7} \text{mol} \cdot L^{-1}$)

550nm) resembling that of HL, and a large stokes shift (~150nm). In series HL and ML₂, they show the order in quantum yield (Φ_f) as $ZnL_2 > HL = CdL_2 >$ NiL₂ > CuL₂ > PdL₂. The emission spectra exhibit the same features, revealing that $\pi\pi$ * state of moiety (Scheme 3) in the ligand HL and its complexes ML₂ is believable to be responsible for the olivine luminescence.



Scheme 3

2.4 Theoretical Calculations

The presence of low-energy emission and absorption bands in the electronic spectra, and the shift of the IR absorption peaks support the structures of HL and its complexes. To gain insight into the nature of the bonds and the relative trends in the longest absorption $\lambda(nm)$ of UV-vis, and emission spectra as the metals are varied, semi-empirical molecular orbital calculations were carried out using the PM3. The selected results are listed in Table 5.

The bond length (C1-N2) of HL is shorter than those of its complexes, and the bond order of HL is larger than those of its complexes. The bond N2-N3 shows a contrary results. These are consistent with the shifts of the IR spectra. Considering the big stokes shift, the calculated longest absorption wavelengths λ (nm) are much consistent with experimental data of UV-vis and emission spectrum. The changes of dihedral angles from HL to ML₂ show that the phenothiazine moiety of the complexes has well planar configuration than that of the ligand.

2.5 Non-Linear Optical (NLO) Properties

Non-linear absorption coefficient: The nonlinear absorption of HL and ML₂ solutions (in DMF, ~ 10^3 mol \cdot L⁻¹) is measured by open-aperture Z-scan technique^[11] at a 532nm wavelength, and the results for HL and NiL₂ were shown in Fig. 3. The experimental arrangement was setup according to the reference 11. The normalized transmittance T(z) in Fig. 3 was analyzed theoretically with the following equations:

$$T_{(z,s=1)} = \sum_{m=0}^{\infty} \frac{[-q_{0(z)}]^{m}}{(m+1)^{\frac{3}{2}}} \quad \text{for } |q_{0}| < 1$$

Where $q_0(z) = \beta I_0(t) L_{eff} / (1 + z^2 / z_0^2)$, β is the TPA coefficient, $I_0(t)$ is the intensity of laser beam at focus (z=0), $L_{eff} = [1 - \exp(-\alpha_0 L)] / \alpha_0$ is the effective thickness with α_0 the linear absorption coefficient and L the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. The nonlinear absorption of HL and ML₂ in an open-aperture Z-scan can be explained mainly by the two-photon absorption (TPA) mechanism, and the total absorption coefficient can be written as: $\alpha(I) = \alpha_0 + \beta I$, where

Table 5 Selected Bond Lengths (Å), Bond Orders, Dihedral Angles (°) and UV for HL, ML_2

| UV longest λ∕nm |
|--------------------|
| λ/nm |
| |
| 450 |
| 454 |
| 518 |
| 443 |
| 427 |
| 465 |
| |

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are theoretical fitting results.

 α_0 is the linear-absorption coefficient and β is the TPA coefficient. Choosing the most fitted values for parameter β performed the numerical calculations. From the solid curves in Fig. 3, the best-fitting values, TPA cross section $\sigma = h\nu\beta/(N_A d_0 10^{-3})$ for HL and ML₂, are listed in Table 6. Comparing the β and σ of the ligand with those of the complexes, we find that the complexes show stronger nonlinear optical properties than the ligand.

| A = A = A = A = A = A = A = A = A = A = | Table 6 | б ТРА | Coefficient | β, | Cross | Section | σ | of | HL, | M |
|---|---------|-------|-------------|----|-------|---------|---|----|-----|---|
|---|---------|-------|-------------|----|-------|---------|---|----|-----|---|

| | HL | NiL ₂ | CuL ₂ | ZnL2 | CdL ₂ | PdL ₂ |
|--|------|------------------|------------------|------|------------------|------------------|
| $\beta/(cm/GW)$ | 0.15 | 0. 59 | 0.6 | 0.7 | 0.6 | 0. 55 |
| σ × 10 ⁴⁶ _/(cm ⁴ · s/photon) | 0.15 | 0. 92 | 1.16 | 1.21 | 0. 69 | 1.07 |

3 Conclusions

In conclusion, we have synthesized a new class of novel blue luminescent complexes based on Schiff base. All compounds emit a olivine color in DMF solution, and show the same features: exciting λ_{max} (~395nm), emission band ($\lambda_{max} = 535 \sim 550$ nm) resembling that of HL, and a large stokes shift (~150 nm). They show the order in quantum yield (Φ_I) as $ZnL_2 > HL = CdL_2 > NiL_2 > CuL_2 > PdL_2$. Theoretical calculations were consistent with the experimental results. All of the compounds exhibit good one-photon fluorescent properties, strong third-order NLO properties. Especially, the complexes show stronger nonlinear optical properties than the ligand.

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