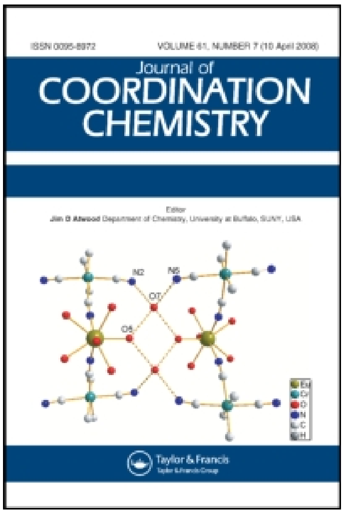

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SYNTHESES, SPECTROSCOPY AND CALCULATED SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF A NEW SERIES OF SQUARE-PYRAMIDAL SUBSTITUTED PHENYLTHIOUREA ZINC(II) COMPLEXES

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A new series of square-pyramidal coordination compounds $L \cdot Zn(acac)_2$ (acac = acetylacetonate; L is a variety of substituted phenylthioureas: *p-N,N′*-dimethylaminophenylthiourea **1**, *p*-methoxy-phenylthiourea **2**, *p*-nitrophenylthiourea **3**, *p*-acetylphenylthiourea **4**) have been synthesized and characterized by ^{1}H NMR and IR spectra and elemental analysis. Most of these compounds exhibit wide transparent ranges in the visible region. Their electronic spectra have been studied experimentally, and theoretically by ZINDO/S calculation. The MOPAC software package has been used to evaluate their first-order molecular hyperpolarizabilities (β). All β values of the four coordination compounds are greater than or equal to those of *p*-nitroaniline, and are larger than β values of their corresponding substituted phenthylthiourea ligands.

Keywords: Zn(II); Phenylthiourea; Syntheses; Electronic spectrum; Nonlinear optics; ZINDO/S calculation

INTRODUCTION

Since the first discovery of second harmonic generation phenomena in quartz crystals in 1961, interest in nonlinear optics has increased owing to its broad application in optoelectronics [1–4]. Second-order nonlinear optical (NLO) materials are widely used in frequency transformation and optical parameter oscillators (OPO) [5–7], etc. It has long been recognized that molecular chromophores could exhibit second-order NLO responses several orders larger than that of inorganic compounds, such as KDP (potassium dihydrogen phosphate) and LN (lithium niobate) [8]. In recent years, the search for molecular chromophores has focused on coordination systems which offer a variety of molecular structures by changing metals, ligands or coordination numbers. Such complexes may enhance thermal stability, and provide diverse electronic behavior by virtue of the coordinated metal center [3, 9, 10]. On the basis of the broad investigation

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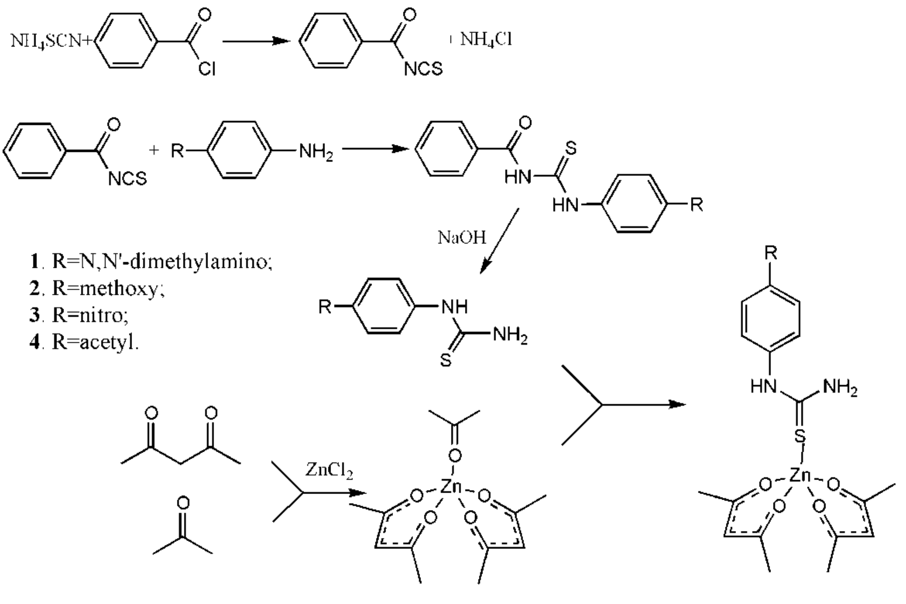
of organometallic and coordination compounds, we have summarized an empirical rule which indicates that the molecular configuration is an important factor to the linear and nonlinear optical properties of organometallic and coordination compounds [11]. Metal ions with d^{10} electronic structure (such as Zn^{2+}, Cd^{2+} and Hg^{2+}) cause excellent transparency in the visible region, as the metal ions do not form an electronic conjugation system with the ligands and thus are not involved in intramolecular charge transfer [11]. We synthesized a square-pyramidal complex, phenylthiourea zinc diacetylacetonate (PZDA) [12], which shows a second harmonic generation (SHG) ten times that of KDP. In this article, a series of colorless complexes with phenylthiourea as ligands give new square-pyramidal Zn(II) complexes whose optical spectra are investigated experimentally and theoretically. Their first-order molecular hyperpolarizabilities were calculated utilizing the ZINDO quantum chemistry method.

EXPERIMENTAL

The general synthetic route is given in Scheme 1. All chemicals used were of A.R. grade and used as received without further purification except acetone, which was dried by anhydrous $MgSO_4$ for two days and distilled before use. Acetone zinc acetylacetonate (acetone-ZDA) was synthesized according to the method given in the literature [13].

Physical Measurements

IR spectra were recorded on a Nicolet 170SX FT-IR spectrometer. ^1H NMR spectra were obtained on a Mercury-VX300 spectrophotometer. Elemental analysis were obtained on a Calo-Erba elemental analyzer (Model 106). The electronic spectra of the complexes in the UV-Vis region were recorded on a Shimadzu UV-160A spectrophotometer.



SCHEME 1

Preparation of Substituted Phenylthiourea

The general procedure includes two steps, formation of the intermediate and hydrolysis of the intermediate. In the first step, 0.86 g (0.011 mol) ammonium thiocyanate and 30 mL acetone were added to a 100-mL three-necked round-bottom flask equipped with a refluxing condenser and a dropping funnel. While stirring, 1.16 mL (0.01 mol) benzoyl chloride was added dropwise, and after refluxing for 5 min an acetone solution of 0.01 mol of the substituted aniline was added dropwise under slow reflux. The mixture was then poured into 150 mL of water with constant stirring to yield a significant amount of precipitate, which was filtered off and dried in air. In the hydrolysis process, the solid was added to 10% NaOH solution and refluxed for 30 min and filtered off. The following process was different for the four compounds. For *p*-*N*,*N′*-dimethylaminophenylthiourea and *p*-methoxyphenylthiourea, the precipitate was recrystallized from methanol and dried in vacuum for 4 h. For the other two compounds, the filtrate was acidified with concentrated HCl and neutralized to slightly basic pH with ammonium hydroxide to yield the precipitate which was subsequently filtered off and dried in vacuum for 4 h. The precipitate was then recrystallized from methanol and dried in vacuum for 4 h.

p-N,N′-Dimethylaminophenylthiourea Yield: 1.45 g (74%), m.p. 209°C. IR (KBr, cm^{-1}): 3429, 3164 (NH_2); 3326 (NH); 2992, 2985, 2923, 2855 (C–H); 1628 (C–N); 1596, 1532, 1478 (Ar); 1380 (C–H); 1317 (C–N); 1075 (C=S); 826 (Ar–H). ^1H NMR (DMSO-d_6, ppm): 2.8 (s, 6H); 3.3 (s, 2H); 6.6–6.7 (d, 2H); 7.0–7.1 (d, 2H); 9.3 (s, 1H). Anal. Calcd. for $C_9H_{13}N_3S$ (%): N, 21.54; C, 55.38; H, 6.67. Found: N, 21.43; C, 55.29; H, 6.22.

p-Methoxyphenylthiourea Yield: 1.5 g (82%), m.p. 228°C. IR (KBr, cm^{-1}): 3402, 3155 (NH_2); 3278 (NH); 2985, 2833 (C–H); 1625 (C–N); 1607, 1589, 1509 (Ar); 1380, 1444 (CH_3); 1243 (C–O–C); 1021 (C=S); 812 (Ar–H). ^1H NMR (DMSO-d_6, ppm): 3.7 (s, 3H); 6.8–6.9 (d, 2H); 7.2 (d, 2H); 9.4 (s, 1H); 3.3 (s, 2H) Anal. Calcd. for $C_8H_{10}N_2OS$ (%): N, 15.38; C, 52.75; H, 5.49. Found: N, 15.57; C, 52.28; H, 5.35.

p-Nitrophenylthiourea Yield: 1.3 g (65%), m.p. 208°C (dec.). IR (KBr, cm^{-1}): 3376, 3185 (NH_2); 3291 (NH); 1640, 1608 (C–N); 1595, 1507 (Ar); 1540, 1340 (NO_2); 1058 (C=S). ^1H NMR (DMSO-d_6, ppm): 7.8 (m, 2H); 8.2 (m, 2H); 10.2 (s, 1H); 3.2 (s, 2H). Anal. Calcd. for $C_7H_7N_3O_2S$ (%): N, 21.32; C, 42.64; H, 3.55. Found: N, 21.93; C, 42.98; H, 3.25.

p-Acetylphenylthiourea Yield: 0.8 g (40%), m.p. 216°C (dec.). IR (KBr, cm^{-1}): 3346, 3164 (NH_2); 3283 (NH); 2986 (CH_3); 1675 (C=O); 1635 (C–N); 1602, 1580 (Ar); 1066 (C=S). ^1H NMR (DMSO-d_6, ppm): 2.5 (s, 3H); 7.6–7.7 (d, 2H); 7.8–7.9 (d, 2H); 9.9 (s, 1H); 3.2 (s, 2H). Anal. Calcd. for $C_9H_{10}N_2OS$ (%): N, 14.43; C, 55.67; H, 5.15. Found: N, 13.90; C, 55.79; H, 5.41.

Syntheses of the Complexes

The general synthetic route involves the addition of the corresponding ligand to the acetone solution of acetone-ZDA and stirring at 40°C for 1–2 h to yield a precipitate which is purified by recrystallization from an acetone/acetyl acetone mixture (2 : 1 v/v).

p-N,N′-Dimethylaminophenylthiourea-ZDA m.p. 156°C. IR (KBr, cm^{-1}): 3391, 3165 (NH_2); 3297 (NH); 2993, 2913, 2884 (CH_3, CH_2); 1639 (C–N); 1606, 1576, 1521 (Ar);

1265, 1187 (C–O); 1018 (C=S); 815 (Ar–H). ^{1}H NMR (DMSO-d$_6$, ppm): 1.8 (s, 12H); 2.8 (s, 6H); 3.3 (s, 2H); 5.2 (s, 2H); 6.6–6.7 (d, 2H); 7.0–7.1 (d, 2H); 9.3 (s, 1H). Anal. Calcd. for $C_{19}H_{27}N_3O_4SZn$ (%): N, 9.17; C, 49.38; H, 5.90. Found: N, 9.39; C, 49.43; H, 5.58.

p-Methoxyphenylthiourea-ZDA m.p. 280°C (dec.). IR (KBr, cm^{-1}): 3402, 3167 (NH$_2$); 3275(NH); 2975 (CH$_3$, CH$_2$); 1624 (C–N); 1602, 1580, 1522 (Ar); 1262, 1243 (C–O–C); 1010 (C=S); 811 (Ar–H). ^{1}H NMR (DMSO-d$_6$ ppm): 1.8 (s, 12H); 3.3 (s, 2H); 3.7 (s, 3H); 5.2 (s, 2H); 6.8–6.9 (d, 2H); 7.2 (d, 2H); 9.4 (s, 1H). Anal. Calcd. for $C_{18}H_{24}N_2O_5SZn$ (%): N, 6.29; C, 48.49; H, 5.39. Found: 6.11; C, 48.01; H, 5.10.

p-Nitrophenylthiourea-ZDA m.p. 300°C (dec.). IR (KBr, cm^{-1}): 3392, 3152 (NH$_2$); 3250 (NH); 3283, 3217 (NH); 2920, 2819, 2870 (CH$_3$, CH$_2$); 1639, 1617 (C–N); 1588, 1576 (Ar); 1513, 1341 (NO$_2$). ^{1}H NMR (DMSO-d$_6$, ppm): 1.8 (s, 12H); 5.2 (s, 2H); 7.8 (d, 2H); 8.2 (d, 2H); 10.2 (s, 1H); 3.3 (s, 2H). Anal. Calcd. for $C_{17}H_{21}N_3O_6SZn$ (%): N, 9.13; C, 44.35; H, 4.57. Found: N, 8.59; C, 44.93; H, 4.83.

p-Acetylphenylthiourea-ZDA m.p. 220°C (dec.). IR (KBr, cm^{-1}): 3349, 3165 (NH$_2$); 3250 (NH); 2989, 2920 (CH$_3$, CH$_2$); 1677 (C=O); 1635 (C–N); 1599, 1580, 1524.67 (Ar); 1262 (C–O); 1023 (C=S); 809 (Ar–H). ^{1}H NMR (DMSO-d$_6$, ppm): 1.8 (s, 12H); 2.5 (s, 3H); 3.3 (s, 2H); 5.2 (s, 2h); 7.6–7.7 (d, 2H); 7.8–7.9 (d, 2H); 10.0 (s, 1H). Anal. Calcd. for $C_{19}H_{24}N_2O_5SZn$ (%): N, 6.13; C, 49.89; H, 5.25. Found: N, 6.43; C, 49.39; H, 4.82.

Electronic Spectra and Second-Order NLO Calculations

All calculations were performed on a PC Pentium III 750 MHz. The all-valence ZINDO/S (intermediate neglect of differential overlap) method in the Hyperchem 5.11 software package (Hypercube, Florida) [14] was employed to calculate the electronic spectra. Details of the ZINDO method for calculating electronic spectra and second-order molecular nonlinear optical properties can be found elsewhere [15]. The molecular hyperpolarizabilities were calculated using PM3 parameterization in the MOPAC software package (7.0) [16]. The closed-shell restricted Hartree–Fock (RHF) formalism was employed. The monoexcited configuration interaction (MECI) approximation was used to describe the excited states. The ten highest occupied molecular orbitals and the ten lowest unoccupied molecular orbitals were involved in CI mixing. The molecular structure was optimized utilizing AMl parameterization [17].

RESULTS AND DISCUSSION

Syntheses of the Ligands and the Complexes

According to the literature [18], during the synthesis of electron-acceptor substituted phenylthiourea, the intermediate formed by reaction of ammonium thiocyanate, benzoyl chloride and substituted aniline in acetone is changed to the terminal product through hydrolysis. In this process the intermediate is dissolved in 10% NaOH solution to form the sodium salt of substituted phenylthiourea and then acidified with concentrated HCl and finally neutralized to pH ~ 8 to yield the final product, in this case *p*-nitrophenylthiourea and *p*-acetylphenylthiourea. As for the syntheses of electron-donor substituted phenylthiourea, *p-N,N′*-dimethylaminophenylthiourea and *p*-methoxyphenylthiourea, the terminal products were formed directly in NaOH solution. Furthermore, we found that in the case of the weaker electron-donor substituted *p*-methoxyphenylthiourea there was still some product formed through the literature process. With increasing strength of the electron donor, direct formation of the product is optimized. This can be attributed to the assumption that the electron-donor effect makes it difficult to form the sodium salt, as the anion is not stable in such an environment. Formation of the complexes can be confirmed by IR spectra, in which the C=S signals have red shifts of 10–50 cm^{-1}, and by the appearance of resonance peaks at 1.8 ppm (s, 12H) and 5.2 (s, 2H) in the ^{1}H NMR spectra, which indicate the presence of acetyl acetone groups in the final products.

Spectroscopy and Solvatochromism

The optical absorption spectra of the four complexes, recorded in chloroform, are shown in Fig. 1. All of the complexes are transparent in the visible region. The spectrum of Complex **1** exhibits an intense band at 270 nm ($\varepsilon = 83168\,\mathrm{M^{-1}\,cm^{-1}}$), while the spectrum of Complex **2** shows an intense band at 265 nm ($\varepsilon = 89025\,\mathrm{M^{-1}\,cm^{-1}}$), which has a blue shift of about 5 nm compared to Complex **1**. The spectrum of Complex **3** exhibits two absorption bands at 275 nm ($\varepsilon = 22409\,\mathrm{M^{-1}\,cm^{-1}}$) and 332 nm ($\varepsilon = 11205\,\mathrm{M^{-1}\,cm^{-1}}$), respectively. As for Complex **4**, there is one absorption band at 282 nm ($\varepsilon = 17778\,\mathrm{M^{-1}\,cm^{-1}}$). The absorption maximum shows a red shift tendency as the substituted group changes from electron-donor to electron-acceptor. The reason for this may be that the ligand structure is changed from D-π-D to A-π-D, which makes it easier to undertake the charge transfer process.

The UV-vis absorption wavelengths of Complexes **1** and **3** in solvents of different polarities are listed in Table I. Both of the compounds exhibit solvatochromism, that is, maximal absorption peaks show hypsochromic or bathochromic shifts with increasing solvent polarity. This means negative or positive dipole moment change between the ground and the excited state, respectively, and hence indicates charge transfer (CT) character for the associated optical transition. It is well known that solvatochromism is based on a two-level model in which only the HOMO and

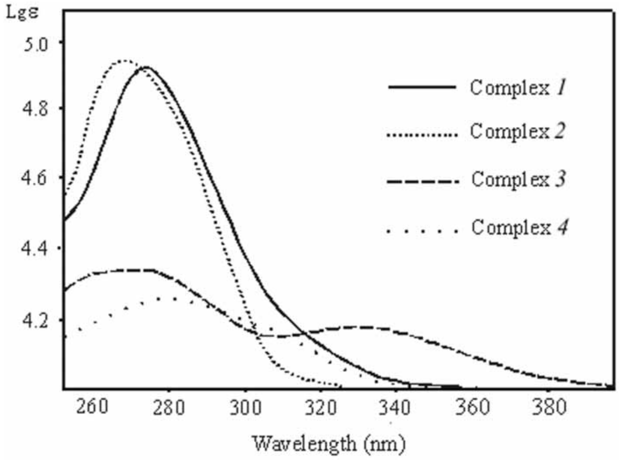


FIGURE 1 Optical spectra of the complexes recorded in chloroform.

TABLE I Absorption maxima of the high intensity optical transition of Complexes **1** and **3** in solvents of different polarities

Solvent	E_T^N	λ_{max} (nm)		
		Complex **1**	*Complex* **3**	
Toluene	0.096	287	339	285
1,4-Dioxane	0.164	275	318	222
THF	0.207	295	350	294
Chloroform	0.259	270	336	275
Acetone	0.355	272	345	270
DMF	0.404	284	351	287
Acetonitrile	0.472	272	337	274
Ethyl acetate	0.577	271	340	269
Methanol	0.765	285	339	286

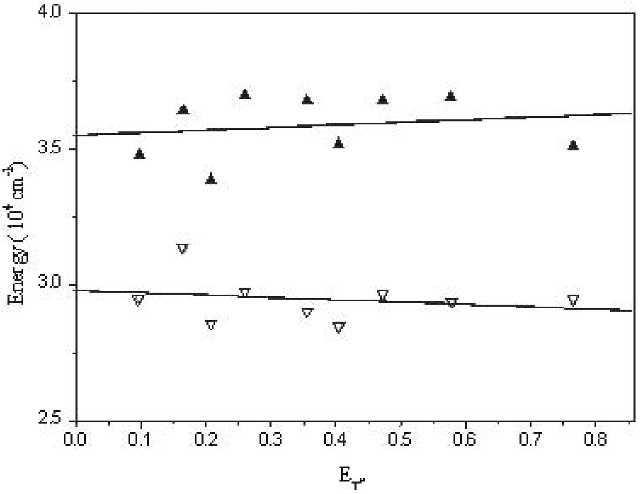


FIGURE 2 Solvatochromism for **1** and **3** *versus* the Reichardt parameter (black triangles represent **1**; hollow triangles represent **3**).

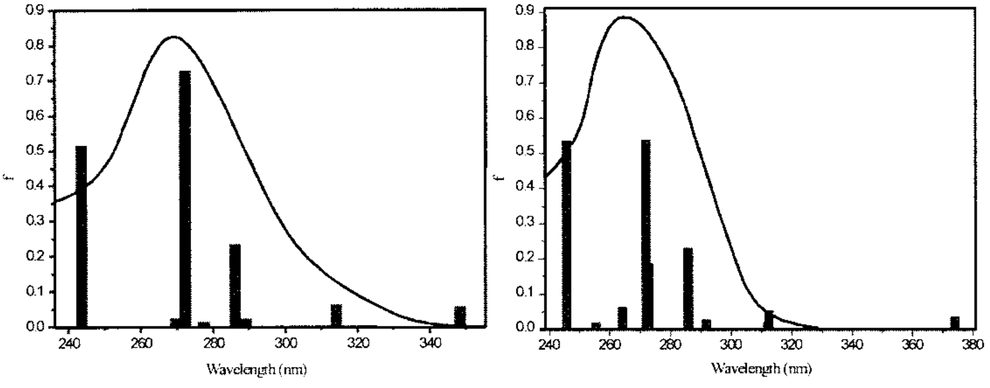
LUMO, i.e., ground and first excited state, are involved in charge transfer character, valid in a large number of organic NLO chromophores [19]. However, it is quite complicated to predict the extent of the NLO properties of organometallic and coordination NLO materials, in which more than one optical transition may be involved in the NLO response, as for Complex **3**. Nonetheless, the second-order NLO effects of organometallic and coordination compounds can be evaluated qualitatively [19]. So we chose the Reichardt parameter ($E_{\mathrm{T}}^{\mathrm{N}}$) [20] of the solvents, which has been confirmed to be a suitable solvent polarity parameter to evaluate NLO responses [19], as the x-axis, and the energies of absorption maxima as the y-axis to draw a graph, as shown in Fig 2. Complex **1** shows negative solvatochromism, and the linear fit indicates a slope of 945.9, while Complex **3** shows positive solvatochromism with a corresponding gradient of -831.6. These results are in agreement with the calculation that $\Delta\mu$ is negative in Complex **1**, and is positive for the band at 322 nm in Complex **3** (Table II).

ZINDO/S-derived electronic spectral data are listed in Table II. The experimental optical spectra in relatively nonpolar chloroform solution and ZINDO/S-derived electronic spectra of the complexes are compared in Fig. 3. Although the y-axis of

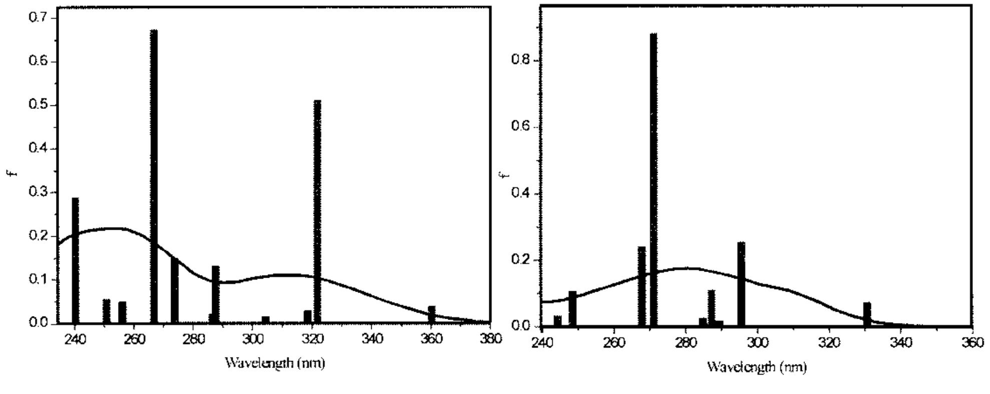
TABLE II ZINDO/S-derived main maximal absorption (λ_{max} in nm), oscillator strengths (*f*), dipole moment changes between ground state and excited state ($\Delta\mu$ in D), and composition of the first excited states

Complex	λ_{max}	*f*	$\Delta\mu$	*Composition of CI*[e] *expansion*
1[a]	286	0.24	−0.28	$0.396\ x_{75\rightarrow78}+0.4\ x_{74\rightarrow78}$
	272	0.73	−0.05	$0.513\ x_{75\rightarrow80}+0.346\ x_{74\rightarrow78}$
	244	0.52	−4.74	$0.553\ x_{68\rightarrow78}$
2[b]	286	0.23	−0.18	$0.318\ x_{71\rightarrow75}$
	272	0.54	−2.99	$-0.325\ x_{72\rightarrow73}-0.395\ x_{72\rightarrow77}$
	246	0.53	−3.91	$0.507\ x_{66\rightarrow73}$
3[c]	322	0.51	7.45	$-0.604\ x_{71\rightarrow75}$
	267	0.67	−1.67	$0.337\ x_{74\rightarrow80}+0.388\ x_{71\rightarrow76}$
	240	0.29	−1.73	$0.585\ x_{69\rightarrow76}$
4[d]	296	0.25	−0.7	$0.326\ x_{74\rightarrow75}-0.439\ x_{70\rightarrow75}$
	271	0.88	−1.00	$0.465\ x_{74\rightarrow79}-0.474\ x_{73\rightarrow78}$
	268	0.24	−1.22	$0.469\ x_{70\rightarrow75}$

[a]HOMO, 75; LUMO, 76. [b]HOMO, 72; LUMO, 73; [c]HOMO, 74; LUMO, 75. [d]HOMO, 74; LUMO, 75. [e]Configuration interaction.



Complex 1 Complex 2



Complex 3 Complex 4

FIGURE 3 The experimental absorption spectra and ZINDO/S-derived electronic transitions of the complexes. The columns represent the oscillator strengths of the various transitions, while the curves represent the experimental optical spectrum. The *y*-axis of the experimental optical spectrum is ε ($\times 10^{-5}$).

the experimental spectrum and the calculated spectrum (ε ($\times 10^{-5}$) for the former and the oscillator strength (f) for the latter) are different, it is still obvious that the absorption band sites of the experimental spectra are very close to the calculated results. In Complex **1**, for example, in which the strongest absorption band of the calculated spectrum is located at 272.3 nm ($f = 0.73$), this is equivalent to the wavelength of the maximal absorption peak of the experimental optical spectrum (270 nm, $\varepsilon = 83168\,\mathrm{M^{-1}\,cm^{-1}}$). As for Complex **3**, calculation shows that the oscillator strength of the absorption band at 267 nm ($f = 0.67$) is larger than that of the band at 322 nm ($f = 0.51$), which is in agreement with the experimental data that ε of the band at 275 nm ($\varepsilon = 22409\,\mathrm{M^{-1}cm^{-1}}$) is larger than that of the band at 32 nm ($\varepsilon = 11205\,\mathrm{M^{-1}\,cm^{-1}}$). The band at 270 nm in the experimental spectrum of Complex **1** can be related to three electronic transitions at 286, 272 and 244 nm, among which the transition at 244 nm has obvious charge transfer character ($\Delta\mu = -4.74$ D). An experimentally observed band at 265 nm of Complex **2** is related to nine calculated transitions, some of which have obvious charge transfer character (bands at 272 and 246 nm, $\Delta\mu$ of which are -2.99 and -3.91 D, respectively). As for Complex **3**, there are about five calculated bands involved in the experimental transitions at 275 and 332 nm and some nine calculated electronic transitions are related to the 282 nm absorption in Complex **4**.

Hyperpolarizabilities Calculation

The calculated first-order molecular hyperpolarizabilities of the complexes are listed in Table III. The trend for β enhancement at higher frequencies is observed, as the double frequencies become closer to the electronic transitions of the complexes. As anticipated from the spectroscopic study discussed previously, all of these complexes exhibit moderate β values, with Complexes **1**, **3** and **4** showing larger β values than *p*-nitroaniline (6.8×10^{-30} esu, calculated value). Comparing these with the corresponding substituted phenylthioureas, the β values of all of the complexes also increase. Table IV shows the absorption maxima of the complexes and the ligands

TABLE III Molecular hyperpolarizabilities of the four complexes at various wavelengths and β_0 of the ligands in 10^{-30} esu

Wavelength (nm)	β_{total}			
	1 (*ligand*)	**2** (*ligand*)	**3** (*ligand*)	**4** (*ligand*)
∞	10.9 (9.9)	4.3 (3.4)	10.2 (4.2)	8.7(4.4)
4959.37	11.3	4.4	10.6	9.0
2479.68	12.5	4.7	11.6	9.8

TABLE IV The absorption maxima recorded in chloroform and the colors of the complexes and the ligands

	1 (*ligand*)	**2** (*ligand*)	**3** (*ligand*)	**4** (*ligand*)
$\lambda_{\max}$ (nm)	270 (274)	265 (262)	336 (332)	282 (245)
Color	g[a] (w[b])	w (w)	ly[c] (ly)	w (w)

[a]gray; [b]white; [c]light yellow.

recorded in chloroform. It is clear that this series of complexes show larger first-order molecular hyperpolarizabilities than the corresponding free ligands, while the colors are unchanged.

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