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Spectral Dispersion of Third-Harmonic Generation in Thin Films Containing Transition Metal Complexes

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The optical third-harmonic generation technique has been used in a study of several transition metal complexes having different near-infrared (NIR) absorption features. The complexes were dispersed in polymer matrices, and the molecular second hyperpolarizabilities $\gamma(3\omega;\omega,\omega,\omega)$ were derived from thin film Maker fringe measurements at 1064 and 1907 nm. Dispersion measurements of the complexes TBA[Ni(dmit)₂] and TBA[Pd(dmit)₂], both having strong NIR transitions, were performed in the region from 1065 to 1480 nm, revealing resonances in the NIR. For the TBA[Ni(dmit)₂] complex a maximum γ -value of 20×10^{-33} esu was observed at approximately 1325 nm, red-shifted by 172 nm (0.14 eV) compared with the position of the NIR absorption peak at 1153 nm. For the TBA[Pd(dmit)₂] complex the exact location of the resonance could not be determined definitively but was shifted to or even beyond 1480 nm. The maximum γ -value of the Pd-complex was more than 2.5 times that of the Ni-complex. The γ -values were strongly influenced by a number of resonances (one-, two-, and three-photon resonances); however, no clear correlation with the near-infrared transition was observed.

1. Introduction

In the last decade there has been an increasing focus on organometallic compounds in the search for materials exhibiting nonlinear optical properties suitable for photonic applications.^{1,2} Studies of square-planar transition metal bis(dithiolene) complexes and their derivatives have revealed large third-order optical nonlinearities ($\gamma \approx 10^{-31}$ – 10^{-29} esu) when measured by the degenerate four-wave mixing technique (DFWM) of the complexes in solutions^{3–10} and with the Z-scan technique applied to the complexes in the form of guest–host polymer films.^{7,8} This class of complexes possesses an intense near-infrared (NIR) absorption band that has been assigned¹¹ to a mainly ligand-based π – π^* transition¹² with some degree of metal–ligand mixing.¹³ The position of the NIR band has been tuned over the range from 630 to 1500 nm by either varying the substituents on the ligand, changing the central metal atom, or changing the charge on the metal complex.^{6,10} This wavelength tuneability of the absorption band has been proposed to be an effective way of obtaining near resonance enhancement and at the same time giving rise to only moderate absorption

losses in nonlinear optical devices.⁸ However, the extensive DFWM studies showed no simple dependence of the nonlinearities on either the position of the NIR-transition or the linear absorption at the excitation wavelength.

Only a few third-harmonic generation (THG) studies have been performed on dithiolene metal complexes.^{14–17} THG measurements on solutions revealed γ -values below 10^{-32} esu at the fundamental wavelengths of 1064 and 1907 nm¹⁴ while THG measurements conducted on guest–host PMMA (poly(methyl methacrylate)) polymer films of bis(dithiolene) and related complexes resulted in γ -values below 10^{-33} esu.^{15,17} No apparent correlation between the nonlinearity and the NIR transition were observed in these studies. Recent THG dispersion studies¹⁶ of a dithiolene analogue revealed a resonance peak red-shifted by approximately 200 nm compared with the NIR transition and a maximum value of γ of above 10^{-33} esu. All γ -values obtained by THG are 2–3 orders of magnitude smaller than those obtained by DFWM. CNDO calculations of Ni bis(dithiolene) complexes result in a γ -value of 2×10^{-34} esu (at zero-frequency)^{18,19} and are thus of the same order of magnitude as the ones obtained experimentally by THG.

It has recently been shown that the large γ -values obtained by DFWM in the retro-reflection configuration may have

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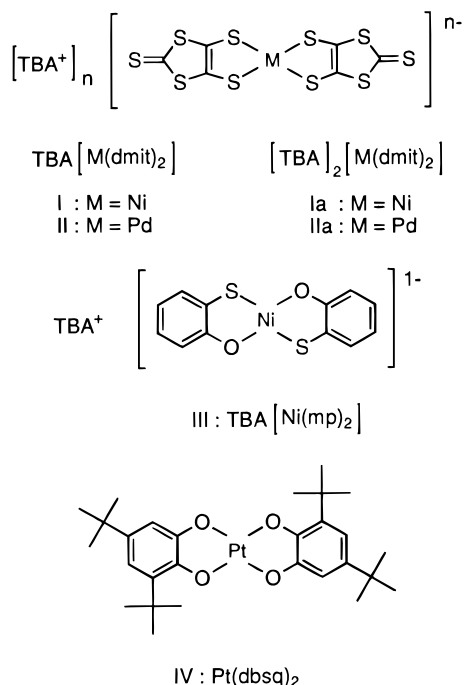


Figure 1. Compounds studied in the present work.

substantial contributions from nonparametric effects^{20,21,17} and that Z-scan measurements are likely to be dominated by thermal effects.¹⁷ Contrary to DFWM and Z-scan techniques only the electronic nonlinearities are probed by THG. Therefore it is expected and observed that resonance contributions will result in large differences between the γ -values obtained by DFWM and THG.

The THG technique has been applied to a series of transition metal complexes (Figure 1) in order to investigate the influence of the NIR transition on the magnitude of the nonlinearity. The series include complexes of 1,3-dithio-2-thione-4,5-dithiol (dmit) in which both the coordinating atoms are sulfur, as in the dithiolene complexes. However, the π -conjugation is extended to other sulfur atoms in the ligand. The metal atoms in the complexes are either Ni or Pd with d^8 and d^{10} electronic configuration, respectively. Both monoanionic (**I**, **II**) and dianionic (**Ia**, **IIa**) complexes were studied. The influence of the coordinating atoms is also of interest and the complex (**III**) of 3,5-di-*tert*-butyl-1,2-benzoquinone (dbsq) with all the coordinating atoms being oxygen was studied, as was a complex (**IV**) of *o*-mercaptophenol (mp) in which both oxygen and sulfur coordinating atoms are present. These complexes, with the exception of the dianionic, have previously been studied²² by DFWM and have been shown to have γ -values in the range from 10^{-29} – 10^{-30} esu. In the present work the complexes dispersed in PMMA matrices were studied in the form of thin films.

2. Experimental Section

Samples. All the compounds were prepared by published methods and gave satisfactory elemental analysis.^{22,23} The UV-vis electronic spectra of the complexes were obtained from solutions in dichloromethane and are shown in Figures 2 and 3 for the complexes **I**, **II** and **III**, **IV**, respectively. Thin solid films of the metal complexes were prepared by mixing a chlorobenzene solution of PMMA with approximately 10 mass % of the complex, resulting in a concentration of about 10^{20} molecules cm^{-3} . The solution was cast onto one side of a fused silica substrate, and the solvent was allowed to evaporate. The thicknesses of the films were determined from the optical density

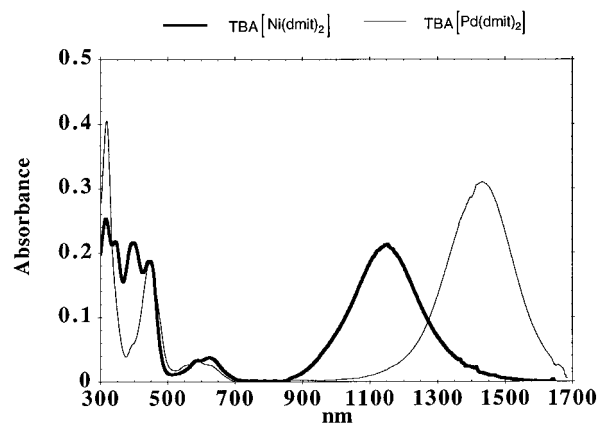


Figure 2. UV-vis-NIR absorption spectra of **I** and **II** in dichloromethane (10^{-5} M).

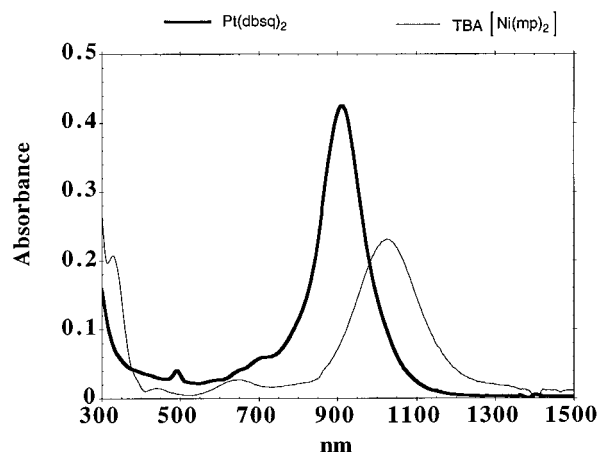


Figure 3. UV-vis-NIR absorption spectra of **III** and **IV** in dichloromethane (10^{-5} M).

of the solid films.²⁴ The optical density was deduced from the absorption spectra obtained on a Perkin-Elmer 9 spectrophotometer. Films with thicknesses from 50 to 500 nm were used in the present work, except for the two complexes **III** and **IV** where thicknesses of the order of 1 μm were used.

Third-Harmonic Generation. THG measurements were performed with two different experimental setups. One system has previously been described in detail and operates at the fundamental wavelength of 1064 nm,^{25,15} modified to also include the Raman-shifted beam at 1907 nm.²⁶ This system was used for thin film THG Maker fringe measurements and allowed the magnitude and the phase of the nonlinear susceptibility, $\chi_i^{(3)}$, of the thin film to be determined relative to that of the substrate.²⁷ Briefly, a Q-switched Nd:YAG laser delivered 10 ns pulses at 10 Hz at 1064 nm which could be Raman shifted to 1907 nm in a 1 m high-pressure (27 bar) hydrogen cell. The fundamental beam was directed through filters, polarizing optics, and focused on the sample. The sample was mounted on a rotation stage so that the angle of incidence of the laser beam could be varied in order to generate the Maker fringes. The sample and the rotation stage were contained in a vacuum chamber in order to eliminate undesired THG contributions from air. The harmonic beam was filtered from other wavelengths by a combination of IR filters and a monochromator and detected in a transmission geometry using a photomultiplier connected to a photon counter. A personal computer was used to control the rotation stage and collect the data. Maker fringes were recorded in the range from -30° to 30° (-50° to 50°) at 1064 nm (1907 nm) with respect to normal incidence of the laser beam that was polarized parallel with the rotation axis.

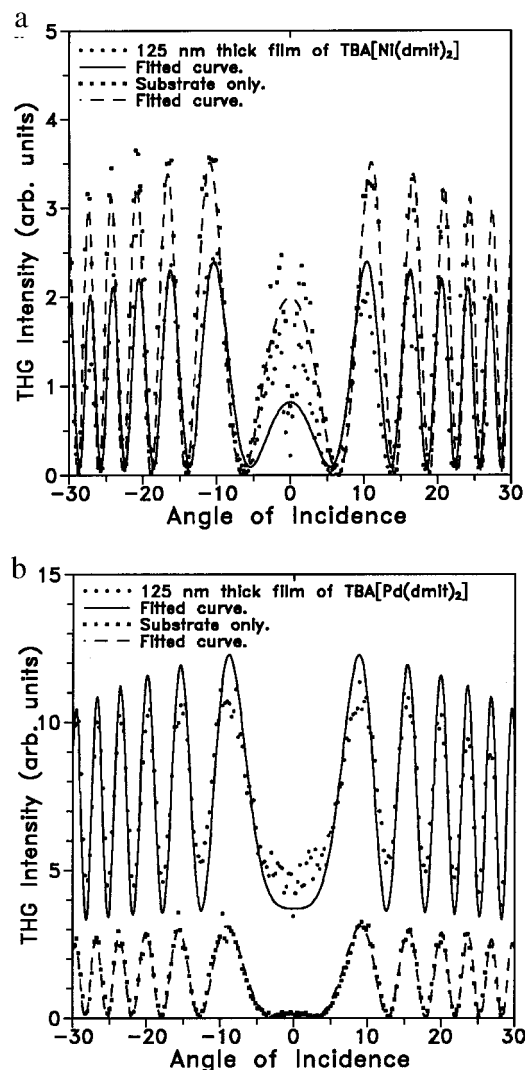


Figure 4. THG Maker fringe patterns from fused silica substrates (film removed in situ with chloroform) together with the Maker fringe patterns from thin films of (a) **I** and (b) **II**.

First a fringe pattern of a sample consisting of a thin film on a fused silica substrate was recorded. Both the film and the substrate contribute to the third-harmonic signal. The contribution from the substrate was determined by recording Maker fringes of the bare substrate under the same experimental conditions which is obtained by removal of the thin film, in situ. Typical examples of such pairs of Maker fringe patterns are shown in Figure 4a,b. For a film with thickness, l_f , much smaller than the THG coherence length, $l_c = \lambda/6|n_{\omega,f} - n_{3\omega,f}|$, the third-harmonic field generated in the film is a monotonic function of the angle of incidence and proportional to the film thickness,^{27,28} peaking at normal incidence. Without exact knowledge of the refractive indices, $n_{\omega,f}$ and $n_{3\omega,f}$, it is in such cases possible to determine the magnitude of the modulus of $\chi_f^{(3)}$ relative to that of the substrate, $\chi_s^{(3)}$, from the following relation^{29,30}

$$|\chi_f^{(3)}| = \frac{2}{\pi} \frac{l_{c,s}}{l_f} \left(\frac{I_{3\omega,f}}{I_{3\omega,s}} \right)^{1/2} \chi_s^{(3)} f(\alpha_1, \alpha_3, l_f) \quad (1)$$

where $l_{c,s}$ and $\chi_s^{(3)}$ of the fused silica substrate are assumed to be $6.823 \mu\text{m}$ ($18.38 \mu\text{m}$) and 3.11×10^{-14} esu (2.80×10^{-14} esu), respectively, at $\lambda = 1064 \text{ nm}$ ($\lambda = 1907 \text{ nm}$).³¹ $I_{3\omega,s}$ is the third-harmonic intensity from the substrate obtained from the envelope function at normal incidence, when no film is

present. $I_{3\omega,f}$ is the third-harmonic intensity from the thin film sample, corrected for the presence of the substrate.^{32,25} The factor, $f(\alpha_1, \alpha_3, l_f)$, is included to correct for the attenuation of the fundamental and third-harmonic in the films.³³ For thin films we have

$$f(\alpha_1, \alpha_3, l_f) = \left| \frac{(3\alpha_1 - \alpha_3)l_f/2}{\exp(-3\alpha_1 l_f/2) - \exp(-\alpha_3 l_f/2)} \right| \quad (2)$$

where α_1 and α_3 are the absorption coefficients at the fundamental and third-harmonic wavelength, respectively. In order to obtain information about the phase of $\chi_f^{(3)}$ the experimental data were also analyzed by fitting the data to the theoretical expression²⁷ for the Maker fringe patterns, taking into account the absorption at both the fundamental and the third-harmonic wavelengths. The refractive indices of the films were not known accurately; thus, the imaginary parts were determined from the absorption spectra of the films while the real parts were assumed to be close to that of pure PMMA due to the moderate loading. The values used at the different wavelengths were $n_{355} = 1.512$, $n_{636} = 1.486$, $n_{1064} = 1.478$ and $n_{1907} = 1.475$. These were calculated from literature values²⁴ using a Cauchy equation to describe the dispersion. Another system was used to obtain THG dispersion measurements in the range from 1065 to 1480 nm. A tuneable source consisting of a three-pass travelling wave optical parametric generator pumped at 527 nm by 1.5 ps pulses from a negative feedback oscillator/regenerative amplifier Nd: Glass laser system. Due to a large bandwidth ($> 50 \text{ cm}^{-1}$) of the laser pulses, no distinct Maker fringes could be resolved from millimeter thick substrates. However, also in this case an approximate modulus of $\chi_f^{(3)}$ can be determined from a modified version of eq 1

$$|\chi_f^{(3)}| = \frac{2}{\pi} \frac{l_{c,\text{ref}}}{l_f} \left(\frac{I_{3\omega,\text{sam}}}{2I_{3\omega,\text{ref}}} - \frac{1}{2} \right)^{1/2} \chi_{\text{ref}}^{(3)} f(\alpha_1, \alpha_3, l_f) \quad (3)$$

where $I_{3\omega,\text{sam}}$ and $I_{3\omega,\text{ref}}$ are the third-harmonic intensities from the sample and the reference, respectively, measured at normal incidence in vacuum. The reference was a 2 mm thick BK7-glass plate, for which the coherence length, $l_{c,\text{ref}}$, was calculated using the dispersion of the refractive index of BK7-glass, and $\chi_{\text{ref}}^{(3)}$ was assumed to be 4.8×10^{-14} esu over the spectral range considered. In the derivation of eq 3 it has been assumed that $\chi_f^{(3)}$ is real (i.e., the relative phase between the film and the substrate is close to zero (or π)). Due to resonances, $\chi_f^{(3)}$ is most likely complex. However, if $I_{3\omega,\text{sam}}$ is much larger than $I_{3\omega,\text{ref}}$, the error due to an imaginary component of $\chi_f^{(3)}$ will be small. In both of the above-described experimental situations the isotropic orientational average of the molecular hyperpolarizability

$$\langle \gamma \rangle_{\text{THG}} = \frac{1}{5} \left(\sum_i \gamma_{iiii} + \sum_{i \neq j} \gamma_{iijj} \right) \quad (4)$$

is obtained from the nonlinear susceptibility $\chi_f^{(3)}$ by use of the expression

$$\langle \gamma \rangle_{\text{THG}} = \frac{\chi_f^{(3)}}{LN} \quad (5)$$

where N is the number density of molecules in PMMA polymer host and L is a correction factor due to the local-field effects. We use a value of $L = 4$ obtained from the Lorentz approximation

$$L = \left(\frac{n_{\omega}^2 + 2}{3} \right)^3 \frac{n_{3\omega}^2 + 2}{3} \quad (6)$$

with refractive indices close to 1.5.

3. Experimental Results

In Figure 2 is shown the UV–visible absorption spectra of the monoanionic complexes **I** and **II** obtained from solutions in dichloromethane. These complexes possess a strong electronic transition in the near-infrared region. The position and strength of the intense near-infrared absorption band is strongly dependent upon the central metal atom. The TBA[Ni(dmit)₂] has a $\lambda_{\max} = 1153$ nm while $\lambda_{\max} = 1431$ nm for the TBA[Pd(dmit)₂]. From the integrated absorption³⁴ the transition moments of the NIR transitions are calculated to be enhanced from 6.5 to 13.5 D by substituting the Ni by Pd. Both of the complexes **I** and **II** possess a much weaker transition in the visible region around 600 nm and strong UV-transitions. The NIR band is absent in the dianionic form (**Ia**, **IIa**). The monoanionic complex **III** and the neutral complex **IV** also possess strong NIR bands (see Figure 3) which have been assigned to a ligand-based π – π^* transition between states that both exhibit a certain degree of metal–ligand mixing, and thus the transition is not entirely ligand centered.^{13,11} Table 1 shows the position and the extinction coefficient of the most intense NIR transition for the complexes **I**–**IV**. For the dianionic complexes **Ia** and **IIa** the values listed are those for the lowest lying electronic transition. The spectra of the thin films are in good agreement with the solution spectra, although some broadening of the near-infrared peak were observed in the films.

Examples of Maker fringe patterns measured by THG from thin films on fused silica substrates together with those obtained from the bare silica substrates after in situ removal of the thin films are shown in Figure 4a,b. Also shown are the least-squares fits of the Maker fringe expression^{27,25} to the experimental data. It should be noted that for the TBA[Ni(dmit)₂] complex, **I**, the fringes obtained from the thin film sample are actually lower than the fringes obtained from the bare substrate as shown in Figure 4a. The reasons for this are, first, the combination of magnitude and phase of the film nonlinearity is such that the third harmonic generated in the thin film interferes destructively with that of the substrate; second, the TBA[Ni(dmit)₂] complex absorbs at both the fundamental and harmonic wavelengths. For the TBA[Pd(dmit)₂] complex the thin film sample gives rise to a signal larger than that of the substrate. This is due to both a large contribution from the film and a constructive interference with the substrate.

The magnitude of the γ -values obtained from the Maker fringe measurements at 1064 nm are listed in Table 1. The listed values are representative for measurements of several films of each compound with different film thicknesses, all prepared from solutions with close to 10% by weight of the metal complex. Figure 5 shows the results obtained from TBA[Pd(dmit)₂] films with different thicknesses in the range from 50 to 160 nm. The values obtained are all within 20%, and the phases obtained by the fit are consistent with a dominating positive imaginary part. For the complexes **Ia**–**IIa** only an upper limit of the γ -values is given. This is due to the fact that the contributions from the thin films to the third harmonic do not alter the fringes obtained from the substrate alone. Thicker films (more than 300 nm) of high enough quality could not be made. The results for the complexes **III** and **IV** are obtained from films with thicknesses of the order 1 μ m. These are not considered to be thin films since a thickness of that

order is too close to the $l_{c,f}$, which in pure PMMA is approximately 5 μ m at 1064 nm. Therefore only the magnitude is shown. In the derivation of the molecular hyperpolarizabilities, we have not corrected for the nonlinearity of the polymer host PMMA. For compounds **I** and **II** the contribution of the nonlinearity of PMMA to γ is below 10% and therefore within the uncertainty quoted. For compounds **III** and **IV** there may be a significant influence on the γ -values obtained.

The complexes TBA[Ni(dmit)₂] and TBA[Pd(dmit)₂] were also studied at the fundamental wavelength of 1907 nm. However, only upper limits of 10^{-33} esu for γ can be obtained due to an insignificant contribution from the thin films. Films of these complexes with thicknesses above 500 nm and of high enough quality could not be made.

THG dispersion measurements of the TBA[Ni(dmit)₂] and TBA[Pd(dmit)₂] complexes were performed in the wavelength range from 1065 to 1480 nm. Figure 6 shows the spectra of the derived γ -values for TBA[Ni(dmit)₂] for two films with different thicknesses (230 and 425 nm). The spectra show a resonance peak, with a maximum γ -value of approximately 20×10^{-33} esu, located around 1325 nm. This is red-shifted by 0.14 eV (almost 200 nm) compared with the position of the near-infrared absorption peak. Also shown is the γ -value obtained from the Maker fringe measurement at 1064 nm. This value is somewhat lower than the value obtained from the dispersion measurement at a similar wavelength. The uncertainty associated with the dispersion measurements is large in this wavelength range because of the small signal from the film. At the peak around 1325 nm the TH signal from the thin and thick films was approximately 65 and 265 times, respectively, that from the BK7 reference, and the error due to the unknown phase is estimated to be less than 15%.

For the TBA[Pd(dmit)₂] complex an increase in the nonlinearity was observed when the wavelength was increased from 1200 toward 1480 nm. However, the position of the resonance could not be definitively determined since it is shifted toward or even beyond 1480 nm. The upper limit of 10^{-33} esu obtained by the Maker fringes at 1907 nm, however, confirms that there is a peak. The maximum γ -value of the TBA[Pd(dmit)₂] complex is more than 2.5 times that of the TBA[Ni(dmit)₂] complex.

4. Discussion

Figure 6 shows the dispersion of $\gamma(3\omega; \omega, \omega, \omega)$ for TBA[Ni(dmit)₂] and the linear near-infrared absorption band (indicated by the dashed line). It is observed that there is a nontrivial relation of γ on the absorption band. The observed red-shift suggests that the dispersion of γ is influenced by electronic levels other than the one giving rise to the near-infrared absorption. The intense absorption band in the UV below 475 nm may cause the dispersion to be influenced by three-photon resonances. It can also be affected by the weak absorption band in the visible, which we have assumed to be due to a partly allowed two-photon transition. Therefore a four-level model is considered, where the ground state is denoted $|0\rangle$, the two one-photon allowed states associated with the infrared and UV absorption bands are denoted $|1\rangle$ and $|3\rangle$, respectively, and the two-photon state is denoted $|2\rangle$. The sum-over-states (SOS) expression for $\langle\gamma\rangle$ is then given by^{35,36}

$$\begin{aligned} \langle\gamma\rangle \propto & -\mu_{01}^4 D_{11} - \mu_{03}^4 D_{33} - \mu_{01}^2 \mu_{03}^2 (D_{13} + D_{31}) + \\ & \mu_{01}^2 \mu_{12}^2 D_{121} + \mu_{03}^2 \mu_{32}^2 D_{323} + \mu_{01} \mu_{12} \mu_{23} \mu_{30} D_{123} + \\ & \mu_{03} \mu_{32} \mu_{21} \mu_{10} D_{321} \quad (7) \end{aligned}$$

TABLE 1: Materials Studied, Absorption Maxima, Extinction Coefficient (ϵ), Magnitude ($\langle\gamma\rangle$), and Phase (ψ) of the Orientational Average of the Second Hyperpolarizability Obtained by THG at the Fundamental Wavelength of 1064 nm

compound	λ_{max} (nm)	ϵ_{max} (l mol ⁻¹ cm ⁻¹)	$\langle\gamma\rangle$ (10 ⁻³³ esu)	ψ	γ_{DFWM}^a (10 ⁻³³ esu)
I , TBA[Ni(dmit) ₂]	1153	19 900	0.75 ± 0.25	-30° ± 20°	4.89 × 10 ³
II , TBA[Pd(dmit) ₂]	1431	26 000	3.1 ± 0.6	90° ± 20°	1.36 × 10 ³
Ia , [TBA] ₂ [Ni(dmit) ₂]	566	45 600	<0.5		
Ila , [TBA] ₂ [Pd(dmit) ₂]	414	23 500	<0.5		
III , TBA[Ni(mp) ₂]	1025	12 800	0.15		6.67 × 10 ³
IV , Pt(dbsq) ₂	911	25 000	0.10		4.54 × 10 ³
V , Ni(dipdt) ₂	854	30 800	0.15 ^c		1.50 × 10 ³ ^b

^a The DFWM values are taken from ref 22. ^b Value reported in ref 7 converted to esu.³⁷ ^c THG results from ref 15.

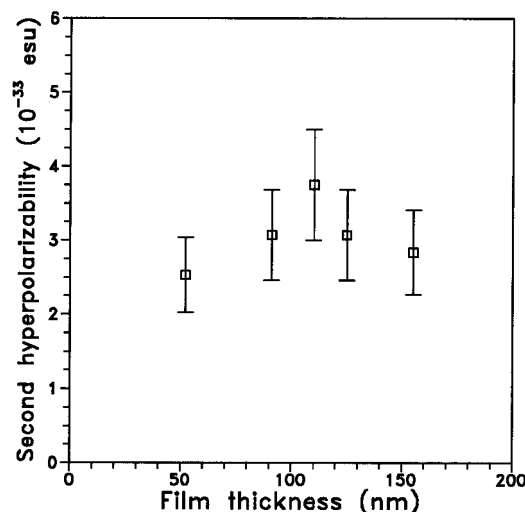


Figure 5. The deduced γ -values for thin films of **II** as a function of film thickness.

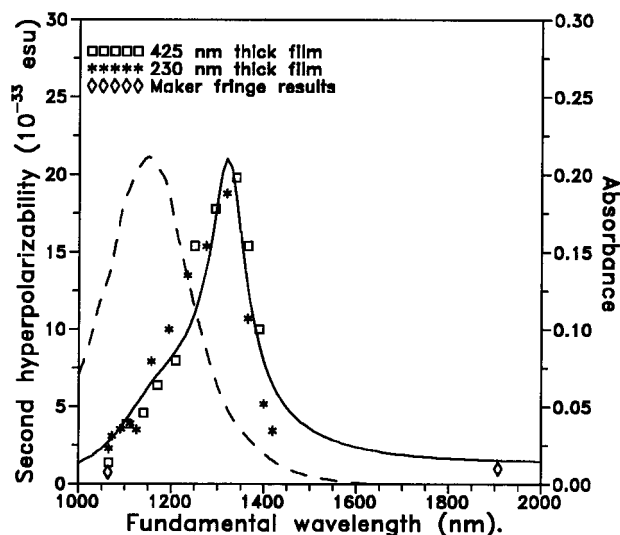


Figure 6. Spectral dispersion of γ for the TBA[Ni(dmit)₂] complex (**I**). The solid line is due to the four-level model and is normalized to the maximum value of the experimental data. The dashed line indicates the NIR absorption spectrum.

where D_{mn} and D_{lmn} are dispersion factors,^{35,36} and μ_{mn} is the dipole moment for the transition from state $|m\rangle$ to state $|n\rangle$. The solid line in Figure 6 represents the dispersion governed by eq 7 with one-photon states $|1\rangle$ and $|3\rangle$ located at 1153 and 400 nm, respectively. The line widths of the states are taken to be 0.24 eV (measured) and 0.40 eV (estimated). The two-photon state is located at 663 nm, close to the small visible absorption, with a line width of 0.1 eV (assumed). All the dipole moments are taken to be equal. Figure 6 shows a good agreement in trend between the dispersion obtained experimentally and the dispersion from the proposed model. It should be emphasized

that in the figure the values obtained from the model have been scaled to the experimental results. However, the transition moment of 6.5 D calculated from the integrated absorption results in a peak value of the right order of magnitude. Furthermore, the model gives a phase of $\approx -45^\circ$ at 1064 nm in good agreement with the phase obtained by the Maker fringe experiment. Ignoring the one-photon state in the UV only results in a minor change in the dispersive behavior in the considered wavelength range. With $\mu_{03} = 0$ in eq 7 the experimental data can be modeled equally well if μ_{01} and μ_{12} are increased by 10%. The significance of the near-infrared transition in the monoanionic complexes **I** and **II** is clear from comparison with the results from the dianionic complexes **Ia** and **Ila** which do not possess a NIR transition, resulting in lower γ -values, in qualitative agreement with eq 7. The larger value obtained for the TBA[Pd(dmit)₂] complex may in part be due to the transition moment μ_{01} , which is more than a factor of 2 larger than for the Ni complex.

A similar red-shift of the resonance peak of γ of 0.18 eV (from 950 to 1100 nm) has previously been observed for the TBA[Ni(2-amidothiophenolato)₂] complex.¹⁶ This complex, however, showed a resonant γ -value of only 1.3×10^{-33} esu which is more than 1 order of magnitude less than that for the TBA[M(dmit)₂] complexes studied in this work. This suggests that the extension of the conjugation to other sulfur atoms in the ligand gives rise to larger electronic nonlinearities.

The complexes **III–V** have a NIR transition located 40–210 nm below the fundamental laser wavelength of 1064 nm. However, these complexes do not show a similar resonance enhancement since all γ -values are of the order 10^{-34} esu. This indicates a complicated competition between the various terms in the SOS expression.

5. Conclusion

The THG γ -values obtained in this study show that the correlation between the position and the extinction coefficient of the NIR transition in the metal dithiolene complexes and the electronic third-order nonlinear response cannot be described by a simple one-photon resonance. It is concluded that all the γ -values measured by THG in the wavelength range used are strongly influenced by a number of resonances (one-, two-, and three-photon). All measured THG responses are lower by several orders of magnitude relative to earlier DFWM results²² in agreement with other recent THG reports.^{14–17}

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