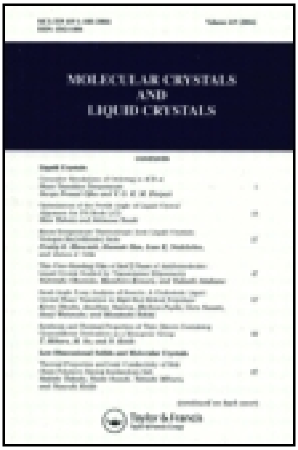

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EFFECTS OF THE SUBSTITUENTS ON THE NONLINEAR OPTICAL PROPERTIES OF BIS(1,2-DIARYL-1,2-ETHYLENEDITHIOLATO)METAL COMPLEXES

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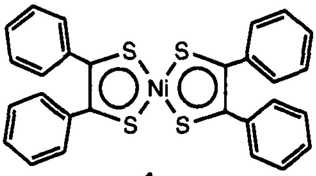
Abstract Electrochemical properties and third harmonic generation (THG) properties of bis(1,2-disubstituted-1,2-ethylenedithiolato)metal complexes were examined. This is the first time to report the THG properties of evaporated thin films of these complexes. Nonlinear optical (NLO) properties of these complexes in solutions were already reported by other research groups. It is notable that the title complexes show relatively large THG properties in both solid state and solution. It seems that the electronic state of these complexes by itself has some influences upon THG properties. The effects of the substituents in the dithiolato ligands were larger than those in the phenyl groups in the dithiolato ligands on both the reduction half-wave potentials and the THG properties. The reported molecular structure of bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel showed the planes of phenyl groups were not on the same plane as the metaladithiolene rings. These results suggest that the electronic state of the metaladithiolene ring have a large influence upon the THG property.

INTRODUCTION

Recently, we found that evaporated thin films of d^8 transition metal complexes with diondioxime ligands exhibit relatively high third-order nonlinear optical properties.[1,2] Those complexes formed one-dimensional structures in the film. These results suggest that the delocalised electrons in linear metal chains may be essential for exhibiting large nonlinear optical effects. It is well known that some dithiolatometal complexes exhibit the NLO properties estimated by THG in solutions and in the polymers.[3] This indicates that the electronic state of these complexes by itself has some influences upon THG properties. In contrast to the metal complexes with diondioxime ligands, dithiolato metal complexes show the THG properties both of solid state and solutions. In the cases of the bis(1,2-diaryl-1,2-ethylenedithiolato)metal complexes, it is easy to synthesise their various derivatives. Comparison of the results of electrochemical measurements between each derivative, indicate their electronic states in the solutions. In this paper, the relationships between electrochemical properties in the solutions and THG properties of thin films of these complexes were examined.

EXPERIMENTAL

The five complexes studied here were prepared according to methods described eleswhere.[4] Tetra-*n*-butylammonium perchlorate (TBAP) used as supporting electrolyte was of special polarographic grade purchased from Nakalai Tesque Inc. The purification of dichloromethane (CH_2Cl_2)was distilled with calcium hydride. Other chemicals were of reagent grade unless otherwise stated.



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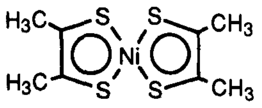

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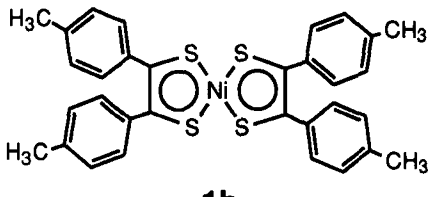

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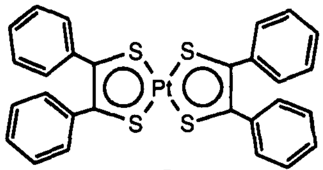

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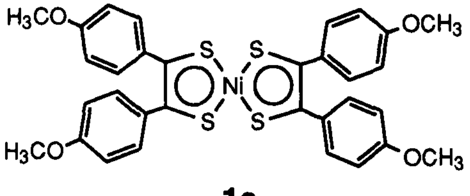

1c

All the voltammograms were recorded with a EG&G Princeton Applied Research model 273A in conjunction with a personal computer (DELL OptiPlex XM5100). All the electrochemical measurements were carried out in 0.3 mol dm^{-3} TBAP containing CH_2Cl_2 solutions at 25 ℃ under a nitrogen atmosphere. All the potentials were measured against an aqueous Ag/AgCl(3 mol dm^{-3} NaCl solution) reference electrode from Bioanalytical Systems (BAS). The potential of the reference electrode was determined against the half-wave potential of the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal standard in every voltammetric measurement. The average potential of the reference electrode at 25 °C was -0.47 ± 0.01 V against the half-wave potential of the Fc/Fc^+ couple. A platinum disc of diameter 1.8 mm from BAS was used as the test electrode for cyclic and normal pulse voltammetric experiments. A spiral platinum wire was used as the auxiliary electrode.

Thin films of the complexes were prepared by vacuum-evaporation onto a fused silica glass substrate at room temperature. The film thickness measured with a Tencor Alpha-step 3000 surface profilometer were from 0.1 to 0.5 μm. The absorption spectra of sample films were recorded on a Shimadzu UV-3100 spectrophotometer in the wavelength rage 200-2500 nm.

Third-order nonlinear optical properties were estimated by the THG Maker fringe method. THG measurements were carried out between 1.3 and 2.1 μm of the fundamental wavelength with wavemixing of a *Q*-switched Nd:YAG laser and a tuneable dye laser. Third-order nonlinear susceptibilities ($\chi^{(3)}$) were calculated by the method described elsewhere.[1,2]

RESULTS AND DISCUSSION

Typical cyclic and normal pulse voltammograms of complex **1c** in CH_2Cl_2 are shown in Figure 1 and 2. The cyclic voltammogram (CV) of **1c** showed a single cathodic peak with a corresponding oxidation peak. The Normal pulse voltammogram of **1c** showed a cathodic step, which corresponded to the peak in the CV. The conventional logarithmic plot analysis of this step revealed that it was Nernstian one-electron process. In the reduction step of these complexes, the electron is accepted by the dithiolene ligands as demonstrated by the results of electron spin resonance (ESR) experiments.[5] This result suggests that the half-wave potential of the dithiolatometal complex is reflected in the electron density on the dithiolato ligand. In the cases of the metal complexes with diondioxime ligands, the delocalised electrons in linear metal chains may be essential for exhibiting large nonlinear optical effects. It is noteworthy that the dithiolatometal complexes exhibit the large NLO properties in both solid state and solution. It seems that the electronic state of these complexes by itself has some influences upon NLO properties. Thus, in the cases of dithiolatometal complexes, the half-wave potential of the dithiolatometal complex is reflected in the nonlinear optical effects.

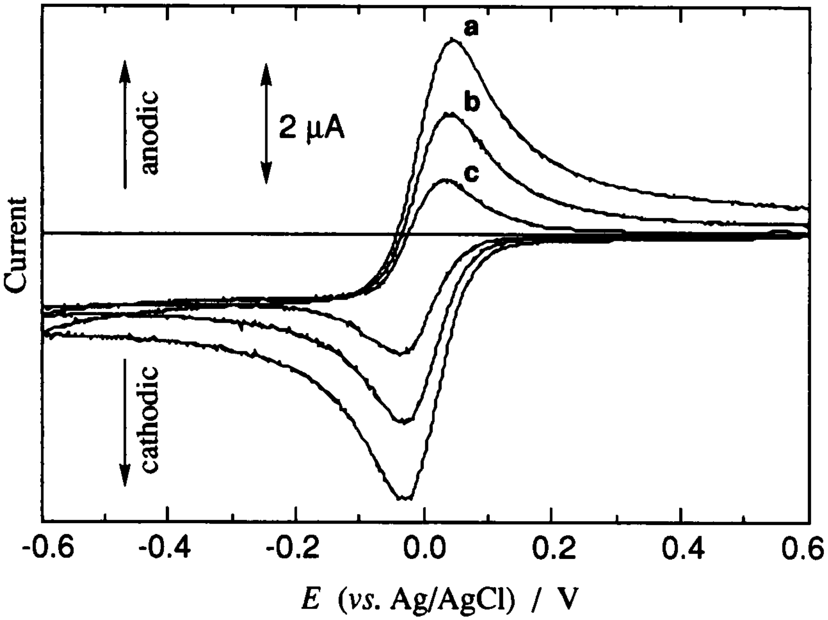

FIGURE 1 Cyclic voltammograms of **1c** in CH_2Cl_2 solution at 25 °C: (a) scan rate of 0.1 V s^{-1}; (b) scan rate of 0.05 V s^{-1}; (c) scan rate of 0.02 V s^{-1}.

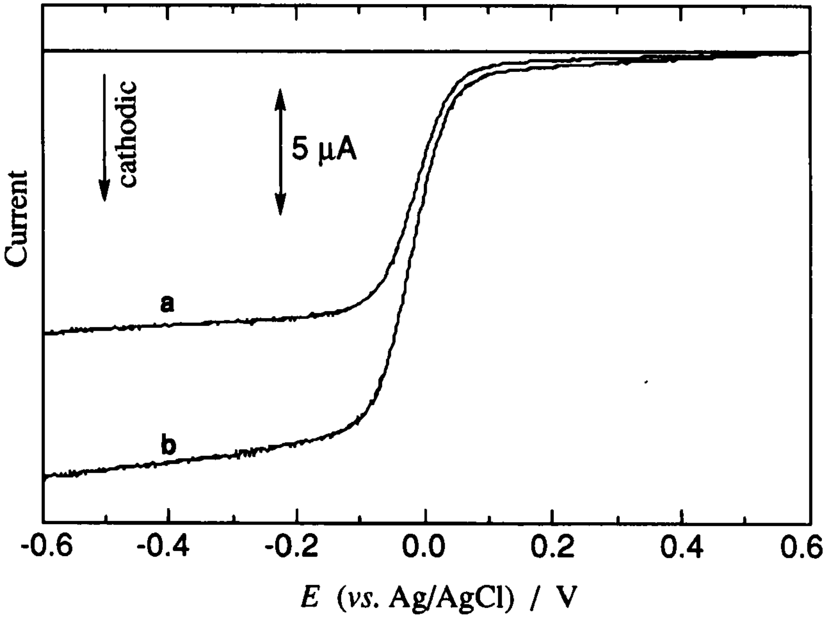

FIGURE 2 Normal pulse voltammograms of **1c** in CH_2Cl_2 solution at 25 °C: (a) pulse width of 100 ms; (b) pulse width of 50 ms.

The values of the reversible half-wave potential ($E_{1/2}$) of the complexes listed in Table 1 together with maximum absorption wavelength (λ_{max}) and the third-order nonlinear susceptibility ($\chi^{(3)}$) at 500 nm.

Table 1 The half-wave potentials ($E_{1/2}$), maximum absorption wavelengths (λ_{max}), and third-order nonlinear susceptibilities ($\chi^{(3)}$) at 500 nm of the dithiolene complexes

Complex	$E_{1/2}$ / V[a]	λ_{max} / nm	$\chi^{(3)}$ / esu[b]
1a	-0.389	762	3.63×10^{-12}
1b	-0.424	884	9.36×10^{-13}
1c	-0.458	848	3.46×10^{-12}
2	-0.580	1022	5.48×10^{-12}
3	-0.376	748	1.60×10^{-12}

[a] In 0.3 mol dm^{-3} TBAP/CH_2Cl_2 at 25 ℃ *vs.* $E_{1/2}$(Fc/Fc$^+$)
[b] At 500 nm

Comparing the $E_{1/2}$ values and $\chi^{(3)}$ values of the complex **1a** and **2**, the complexes, which show lower $E_{1/2}$ value, exhibit larger $\chi^{(3)}$ value. This means that the higher electron density of the dithiolene ligands results in larger $\chi^{(3)}$ value. In a similar manner, comparison of **1b** and **1c**, suggests that the electron donating substituent makes the complex stable against the reduction and the $\chi^{(3)}$ value larger, because the substituent controls the electron density of the dithiolene ligands. Comparing the $E_{1/2}$ values and $\chi^{(3)}$ values of the complex **1b** and **2**, indicates that a substituent affects the $E_{1/2}$ value and $\chi^{(3)}$ value to a larger extent when it is in the dithiolato ligand than when it is in the phenyl ring. It appears that the substituent in phenyl ring dose not affect the electron density of the dithiolato ligand in the same manner as the substituent in the dithiolato ligands. This is because of the planes of phenyl ring groups were not on the same plane of metaladithiolene rings as demonstrated by the results of X-ray crystal structure analysis.[6]

In contrast with the above results, **3** exhibits a larger maximum $\chi^{(3)}$ value at 680 nm than that of **1a**, in spite of **1a** showing a lower $E_{1/2}$ value than that of **3** (Figure 3).

It is necessary to compare the $E_{1/2}$ values and the maximum $\chi^{(3)}$ values at varying wavelengths for the differing central metals and substituent positions to complete this case. Unfortunately, the estimations for the maximum $\chi^{(3)}$ values of the all complexes are not complete yet. Further investigations are required to improve theses points.

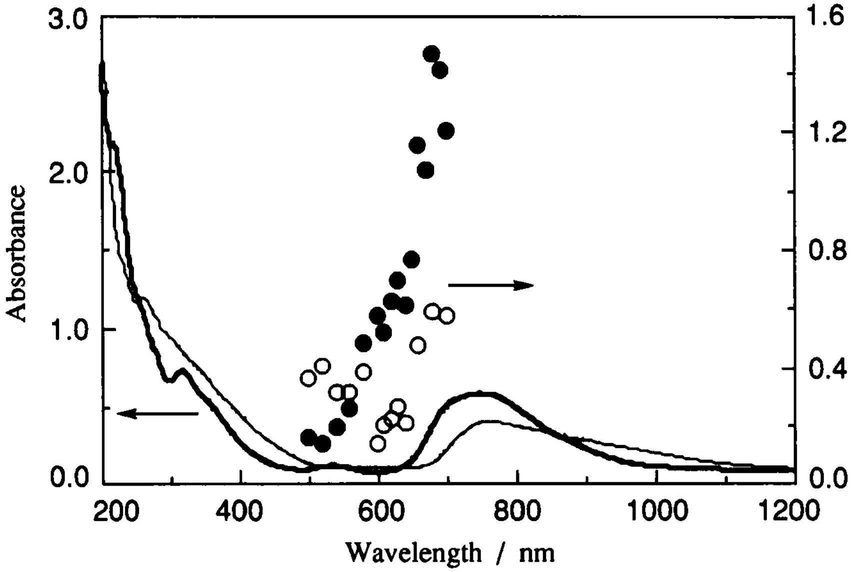

FIGURE 3 UV-vis spectrum and wavelength dependence of the $\chi^{(3)}$ value of the thin film of **1a** (thin line and O, film thickness: 113.1 nm, maximum $\chi^{(3)}$ value: 5.89×10^{-12} esu at 680 nm) and **3** (thick line and ●, film thickness: 105.2 nm, maximum $\chi^{(3)}$ value: 1.46×10^{-11} esu at 680 nm)

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