

단 신

trans-4-[2-(1-Ferrocenyl)vinyl]-1-Methylpyridinium 발색단을 포함하는 Ni(dmit)₂-화합물의 Raman/IR 분광학 특성화

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Raman/IR Spectroscopic Characterization of the Ni(dmit)₂-Complexes with *trans*-4-[2-(1-Ferrocenyl)vinyl]-1-Methylpyridinium Chromophore

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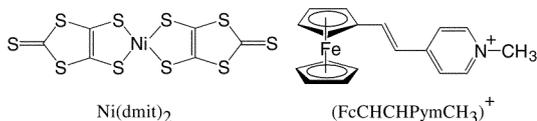
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Keywords: Micro-Raman Spectroscopy, FT-IR, Ni(dmit)₂, NLO Chromophore

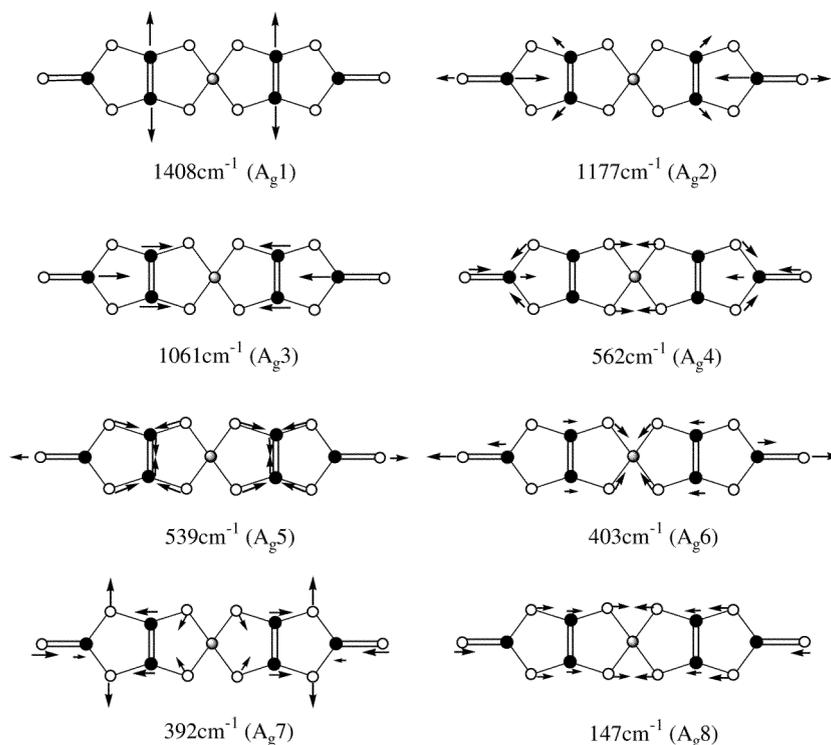
Ni(dmit)₂ (dmit: 1,3-dithiol-2-thione-4,5-dithiolate) complexes have so far been investigated mainly in the light of their metallic properties and superconductivity.¹ More recently, they have begun to be investigated as multifunctional materials which simultaneously exhibit more than two physical properties such as magnetic, electrical and optical properties.^{1f} We also recently reported a multifunctional Ni(dmit)₂ complex with the *trans*-4-[2-(1-ferrocenyl)vinyl]-1-methylpyridinium cation chromophore (FcCHCHPymCH₃).² This cation is one of the well-known second order non-linear optical(NLO) chromophores.³



The (FcCHCHPymCH₃)[Ni(dmit)₂] complex showed a strong absorption band at around 560 nm~610 nm depending upon the polarity of the solvent.² Furthermore, it showed an antiferromagnetic arrangement at temperature lower than 20K.⁴ The partially oxidized (PO) complex, (FcCHCHPymCH₃)_x[Ni(dmit)₂] (0<x<1), grown in a typical electrochemical cell,

showed semiconductor behavior ($E_a=106$ meV) over the measured temperature range (30~300 K) with $\sigma_{RT}=1$ S/cm. The composition of this complex was not verified because the amount of crystals obtained was insufficient for performing a micro-analysis of the chemical composition and a single crystal of a high quality suitable for X-ray structural analysis was not obtained. These are the common difficulties which are usually faced in the characterization of a PO complex. These problems can be largely overcome by using laser Raman spectroscopy in conjunction with an optical microscope attachment, a low power laser source (0.06~6 mW) and a highly sensitive CCD area detector. This equipment constitutes a very powerful tool for carrying out a rapid and non-destructive characterization of a PO complex.

ET(ethylenedithiotetrathiafulvalene) based radical cation salts⁵ are the case whose donor/acceptor ratio was first determined by utilizing the laser micro-Raman spectroscopy. Subsequently, the charge of [M(dmit)₂]^{x-} (M=Ni, Pd) complexes was determined by a combination of Raman and IR spectroscopies, based on the finding that the anion's charge(x) is



Scheme 1. The eight symmetric A_g modes of $Ni(dmit)_2$.⁹

linearly correlated with the anion A_g modes.⁶ (Scheme 1) In this report, we also utilized laser micro-Raman spectroscopy, in conjunction with FT-IR spectroscopy, to verify the anion charge of $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$ complex which was electrochemically grown.

The $(FcCHCHPymCH_3)[Ni(dmit)_2]$ complex shows three major vibrational peaks in the FT-IR spectrum (Fig. 1c): the C=S and C=C vibrations of the dmit ligand at 1052 cm^{-1} and 1347 cm^{-1} , respectively, and the C=C vibration of the pyridinium moiety at 1594 cm^{-1} .⁷ The former two vibrations are very close to those observed in the $[(n-C_4H_9)_4N][Ni(dmit)_2]$ complex (1058 cm^{-1} and 1349 cm^{-1} , respectively, in Fig. 1b). For the $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$ PO complex, the C=S vibrational peak at 1052 cm^{-1} is the same as that of the corresponding 1:1 complex, whereas the C=C vibrational peak shifts to 1239 cm^{-1} (Fig. 1d), which is very similar to that of the $[Ni(dmit)_2]^0$ neutral complex (1241 cm^{-1}).⁸ This noticeable shift indicates that the charge of the

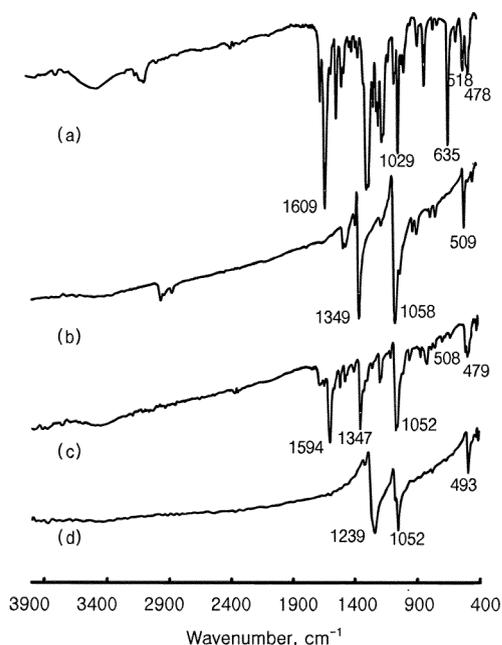


Fig. 1. IR spectra of the complexes: $(FcCHCHPymCH_3)(CF_3SO_3)$ (a), $[(n-C_4H_9)_4N][Ni(dmit)_2]$ (b), $(FcCHCHPymCH_3)[Ni(dmit)_2]$ (c) and $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$ (d).

Table 1. The A_g mode frequencies of the Ni(dmit)₂ complexes (cm⁻¹)

A _g mode	A _g 7	A _g 6	A _g 5	A _g 4	A _g 3	A _g 2	A _g 1
vibrational mode	Ni-S	Ni-S	C-S	C-S	C-S	C=S	C=C
[(n-C ₄ H ₉) ₄ N][Ni(dmit) ₂]	339	359	479	513	932	1051	1398
(FcCHCHPymCH ₃)[Ni(dmit) ₂]	337	358	480	516	936	1024	1396
(FcCHCHPymCH ₃) _x [Ni(dmit) ₂]	346	366	492	499	954	1055	1335

Ni(dmit)₂ anion in the PO complex is different from that of the corresponding 1:1 complex, due to the effects of oxidation on the dmit ligand being particularly pronounced. The C=C vibration of the pyridinium moiety at 1594 cm⁻¹ (Fig. 1c) corresponds to the peak (1609 cm⁻¹) of the (FcCHCHPymCH₃)(CF₃SO₃) complex (Fig. 1a), but it is not observed in the case of the PO complex (Fig. 1d). This strongly suggests that the content of the FcCHCHPymCH₃ cation in the PO complex is very small.

The Raman spectrum of the (FcCHCHPymCH₃)_x[Ni(dmit)₂] complex is shown in Fig. 2, and compared with those of the (FcCHCHPymCH₃)[Ni(dmit)₂], [(n-C₄H₉)₄N][Ni(dmit)₂] and (FcCHCHPymCH₃)(CF₃SO₃) complexes. These spectra were measured in the 200~1700 cm⁻¹ region with a polarized laser-Raman spectroscopy in parallel polarization mode. The peaks corresponding to Ni(dmit)₂ were assigned based on the eight symmetric A_g modes proposed by Ramakumar *et al.*⁹ (Scheme 1), and are listed in Table 1. The peak at 1610 cm⁻¹ in Fig. 2a is assigned to the pyridine C=C bond stretching, which also appears in the spectrum of (FcCHCHPymCH₃)[Ni(dmit)₂] (Fig. 2c) with a strong intensity, but is not observed in (FcCHCHPymCH₃)_x[Ni(dmit)₂] (Fig. 2d), as is also the case in the IR spectra. The intense peak at 1398 cm⁻¹ in Fig. 2b is assigned to the C=C bond stretching (A_g 1), and its intensity appears to decrease significantly in Fig. 2c and 2d. The A_g 1 mode (C=C stretching) frequencies of [Ni(dmit)₂]^{x-} are known to be linearly correlated with its charge(x),⁶ because the frequency of this stretching vibration is proportional to the variation in the electron density of this bond. This correlation has been described as below:

$$x = (\Delta\nu_x + 4) / 74.6$$

where x is the formal charge, and the relative ionization shift of the A_g 1 mode (Δ) is represented by Δ=(ν_x-ν_{x=0})/

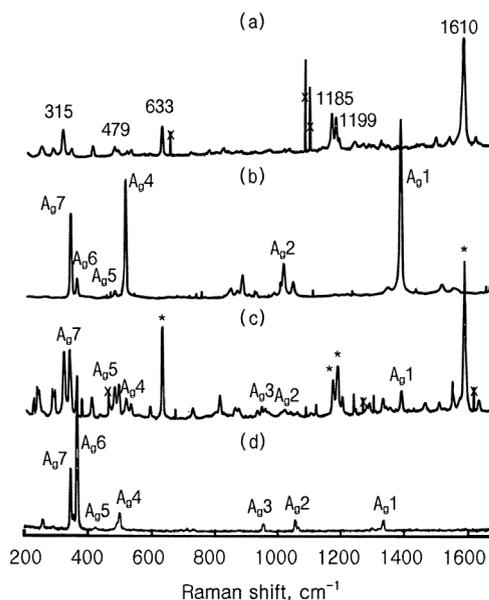


Fig. 2. Raman spectra of the complexes: (FcCHCHPymCH₃)(CF₃SO₃) (a), [(n-C₄H₉)₄N][Ni(dmit)₂] (b), (FcCHCHPymCH₃)[Ni(dmit)₂] (c) and (FcCHCHPymCH₃)_x[Ni(dmit)₂] (d). The peaks due to the (FcCHCHPymCH₃)⁺ cation are denoted by * in (c), and the satellite peaks are marked 'x'.

ν_{x=0}. The charges(x) of [(n-C₄H₉)₄N][Ni(dmit)₂] and (FcCHCHPymCH₃)[Ni(dmit)₂] are calculated as 1.028 and 0.989, respectively, when ν_{x=0} is 1329 cm⁻¹.⁶ These values are in good agreement with the elemental analysis and/or X-ray structure analysis data for these complexes,² indicating the reliability of this equation when applied to these complexes. Based on this reliable equation, the x value for the PO complex was calculated with the parameters (ν_x=1335 cm⁻¹ and ν_{x=0}=1329 cm⁻¹), and the value of x obtained was 0.143. This small value is not entirely unexpected, because other M(dmit)₂ PO complexes with small x values have previously been reported, such as [(C₂H₅)₄N]_{0.17}[Ni(dmio)₂] (dmio: 1,3-dithiol-2-on-4,5-dithiolate),^{10a} [(n-C₄H₉)₄N]_{0.29}[Ni(dmit)₂]^{10b} and [(n-C₄H₉)₄N]_{0.22}[Au(dmit)₂].^{10c}

In summary, the charge(x) of the Ni(dmit)₂ moiety was determined by means of the relationship between the charge(x) and the frequency of the A_g 1 mode, as measured by polarized micro-Raman spectroscopy. This rapid and non-destructive characterization method offers the composition of the PO complex as (FcCHCHPymCH₃)_{0.143}[Ni(dmit)₂].

EXPERIMENTAL SECTION

(FcCHCHPymCH₃)_x[Ni(dmit)₂] complex was prepared by means of the electro-crystallization technique using a typical H-type cell.² (FcCHCHPymCH₃)₂[Ni(dmit)₂]² and [(n-C₄H₉)₄N][Ni(dmit)₂]¹¹ were obtained according to the previously reported procedure. The IR spectra were obtained by the KBr pellet method on a MIDAC FT-IR spectrometer. The micro-Raman measurements were carried out at room temperature using a Raman microscope spectrometer (Renishaw Ltd.) equipped with an He:Ne (λ₀=6328Å) laser. The incident laser power applied was adjusted to as low as 0.06 mW, and was focused on a 1 μm² area, because using a higher laser intensity caused the samples to burn. The samples were mounted on a glass microscope slide. Each spectrum was scanned over 20 times between 200 and 2000 cm⁻¹ with a 200 sec time constant at a 1 cm⁻¹ resolution, and the Raman shifts thereby obtained were calibrated against a standard Si peak at 520 cm⁻¹. Typically, more than six hours was required for collecting the Raman data of each sample.

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