

## 단 신

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

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

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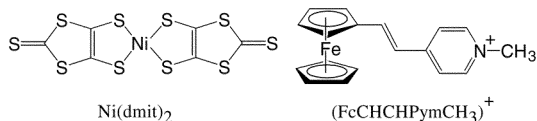
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주제 어: 마이크로 라만 분광학, FT-IR, Ni(dmit)<sub>2</sub>, 비선형 발색단

**Keywords:** Micro-Raman Spectroscopy, FT-IR, Ni(dmit)<sub>2</sub>, NLO Chromophore

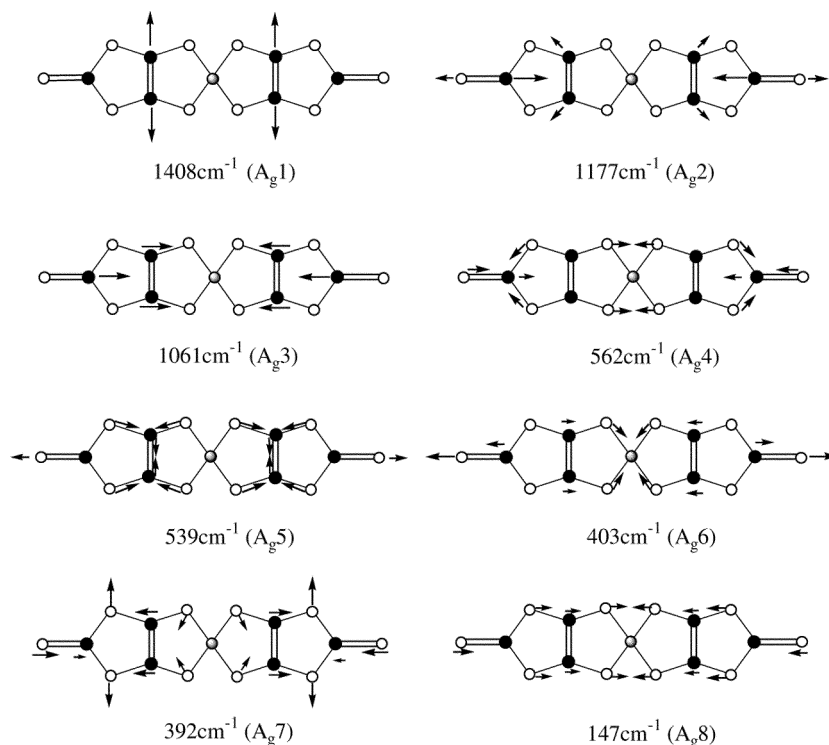
Ni(dmit)<sub>2</sub> (dmit: 1,3-dithiol-2-thione-4,5-dithiolate) complexes have so far been investigated mainly in the light of their metallic properties and superconductivity.<sup>1</sup> More recently, they have begun to be investigated as multifunctional materials which simultaneously exhibit more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



The (FcCHCHPyMCH<sub>3</sub>)[Ni(dmit)<sub>2</sub>] complex showed a strong absorption band at around 560 nm~610 nm depending upon the polarity of the solvent.<sup>2</sup> Furthermore, it showed an antiferromagnetic arrangement at temperature lower than 20K.<sup>4</sup> The partially oxidized (PO) complex, (FcCHCHPyMCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] (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 salts<sup>5</sup> are the case whose donor/acceptor ratio was first determined by utilizing the laser micro-Raman spectroscopy. Subsequently, the charge of [M(dmit)<sub>2</sub>]<sup>x-</sup> (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<sub>g</sub> modes of Ni(dmit)<sub>2</sub>.<sup>9</sup>

linearly correlated with the anion A<sub>g</sub> modes.<sup>6</sup> (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<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] complex which was electrochemically grown.

The (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] 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<sup>-1</sup> and 1347 cm<sup>-1</sup>, respectively, and the C=C vibration of the pyridinium moiety at 1594 cm<sup>-1</sup>.<sup>7</sup> The former two vibrations are very close to those observed in the [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] complex (1058 cm<sup>-1</sup> and 1349 cm<sup>-1</sup>, respectively, in Fig. 1b). For the (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] PO complex, the C=S vibrational peak at 1052 cm<sup>-1</sup> is the same as that of the corresponding 1:1 complex, whereas the C=C vibrational peak shifts to 1239 cm<sup>-1</sup> (Fig. 1d), which is very similar to that of the [Ni(dmit)<sub>2</sub>]<sup>0</sup> neutral complex (1241 cm<sup>-1</sup>).<sup>8</sup> This noticeable shift indicates that the charge of the

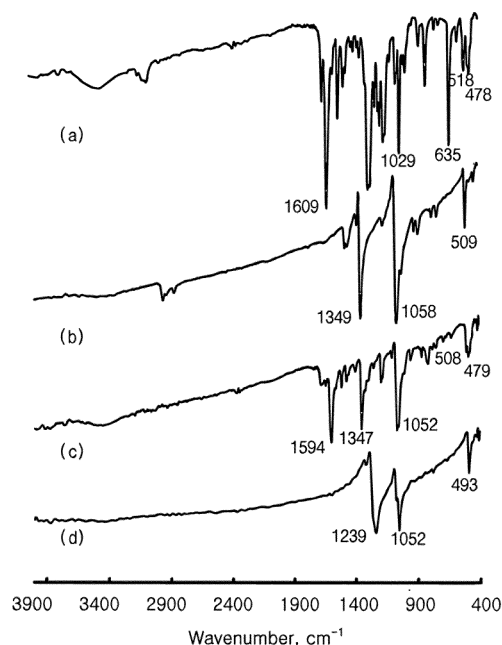


Fig. 1. IR spectra of the complexes: (FcCHCHPymCH<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>) (a), [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] (b), (FcCHCHPymCH<sub>3</sub>)[Ni(dmit)<sub>2</sub>] (c) and (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] (d).

Table 1. The A<sub>g</sub> mode frequencies of the Ni(dmit)<sub>2</sub> complexes (cm<sup>-1</sup>)

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

Ni(dmit)<sub>2</sub> 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<sup>-1</sup> (Fig. 1c) corresponds to the peak (1609 cm<sup>-1</sup>) of the (FcCHCHPymCH<sub>3</sub>) (CF<sub>3</sub>SO<sub>3</sub>) 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 FcCHCHPymCH<sub>3</sub> cation in the PO complex is very small.

The Raman spectrum of the (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] complex is shown in Fig. 2, and compared with those of the (FcCHCHPymCH<sub>3</sub>)<sub>2</sub>[Ni(dmit)<sub>2</sub>], [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] and (FcCHCHPymCH<sub>3</sub>) (CF<sub>3</sub>SO<sub>3</sub>) complexes. These spectra were measured in the 200~1700 cm<sup>-1</sup> region with a polarized laser-Raman spectroscopy in parallel polarization mode. The peaks corresponding to Ni(dmit)<sub>2</sub> were assigned based on the eight symmetric A<sub>g</sub> modes proposed by Ramakumar *et al.*<sup>9</sup> (Scheme 1), and are listed in Table 1. The peak at 1610 cm<sup>-1</sup> in Fig. 2a is assigned to the pyridine C=C bond stretching, which also appears in the spectrum of (FcCHCHPymCH<sub>3</sub>)<sub>2</sub>[Ni(dmit)<sub>2</sub>] (Fig. 2c) with a strong intensity, but is not observed in (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] (Fig. 2d), as is also the case in the IR spectra. The intense peak at 1398 cm<sup>-1</sup> in Fig. 2b is assigned to the C=C bond stretching (A<sub>g</sub> 1), and its intensity appears to decrease significantly in Fig. 2c and 2d. The A<sub>g</sub> 1 mode (C=C stretching) frequencies of [Ni(dmit)<sub>2</sub>]<sup>x-</sup> are known to be linearly correlated with its charge(x),<sup>6</sup> 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<sub>g</sub> 1 mode (Δ) is represented by Δ = (ν<sub>x</sub> - ν<sub>x=0</sub>) /

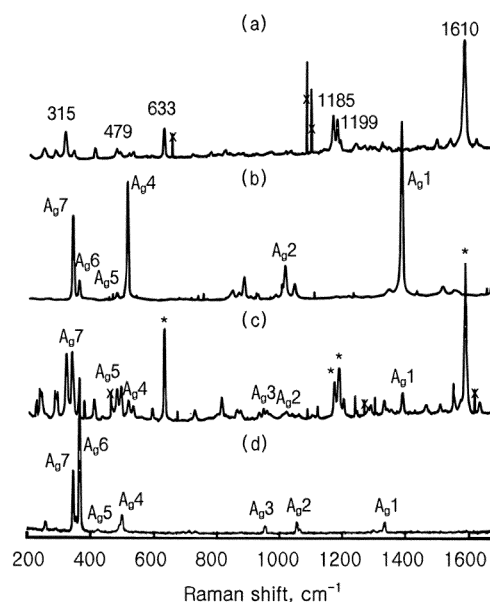


Fig. 2. Raman spectra of the complexes: (FcCHCHPymCH<sub>3</sub>) (CF<sub>3</sub>SO<sub>3</sub>) (a), [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] (b), (FcCHCHPymCH<sub>3</sub>)<sub>2</sub>[Ni(dmit)<sub>2</sub>] (c) and (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] (d). The peaks due to the (FcCHCHPymCH<sub>3</sub>)<sup>+</sup> cation are denoted by \* in (c), and the satellite peaks are marked 'x'.

ν<sub>x=0</sub>. The charges(x) of [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] and (FcCHCHPymCH<sub>3</sub>)<sub>2</sub>[Ni(dmit)<sub>2</sub>] are calculated as 1.028 and 0.989, respectively, when ν<sub>x=0</sub> is 1329 cm<sup>-1</sup>.<sup>6</sup> These values are in good agreement with the elemental analysis and/or X-ray structure analysis data for these complexes,<sup>2</sup> 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<sub>x</sub>=1335 cm<sup>-1</sup> and ν<sub>x=0</sub>=1329 cm<sup>-1</sup>), and the value of x obtained was 0.143. This small value is not entirely unexpected, because other M(dmit)<sub>2</sub> PO complexes with small x values have previously been reported, such as [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>0.17</sub>[Ni(dmio)<sub>2</sub>] (dmio: 1,3-dithiol-2-on-4,5-dithiolate),<sup>10a</sup> [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>0.29</sub>[Ni(dmit)<sub>2</sub>]<sup>10b</sup> and [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>0.22</sub>[Au(dmit)<sub>2</sub>].<sup>10c</sup>

In summary, the charge(x) of the Ni(dmit)<sub>2</sub> moiety was determined by means of the relationship between the charge(x) and the frequency of the A<sub>g</sub> 1 mode, as measured by polarized micro-Raman spectroscopy. This rapid and non-destructive characterization method offers the composition of the PO complex as (FcCHCHPymCH<sub>3</sub>)<sub>0.143</sub>[Ni(dmit)<sub>2</sub>].

## EXPERIMENTAL SECTION

(FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] complex was prepared by means of the electro-crystallization technique using a typical H-type cell.<sup>2</sup> (FcCHCHPymCH<sub>3</sub>)<sub>2</sub>[Ni(dmit)<sub>2</sub>]<sup>2</sup> and [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>]<sup>11</sup> 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 (λ<sub>0</sub>=6328Å) laser. The incident laser power applied was adjusted to as low as 0.06 mW, and was focused on a 1 μm<sup>2</sup> 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<sup>-1</sup> with a 200 sec time constant at a 1 cm<sup>-1</sup> resolution, and the Raman shifts thereby obtained were calibrated against a standard Si peak at 520 cm<sup>-1</sup>. Typically, more than six hours was required for collecting the Raman data of each sample.

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