

## 단 신

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

한윤경 · 노동윤\*  
서울여자대학교 화학과  
(2003. 11. 14 접수)

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

Yoon-Kyoung Han and Dong-Youn Noh\*

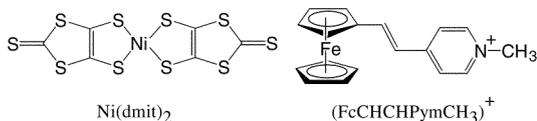
Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea

(Received November 14, 2003)

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

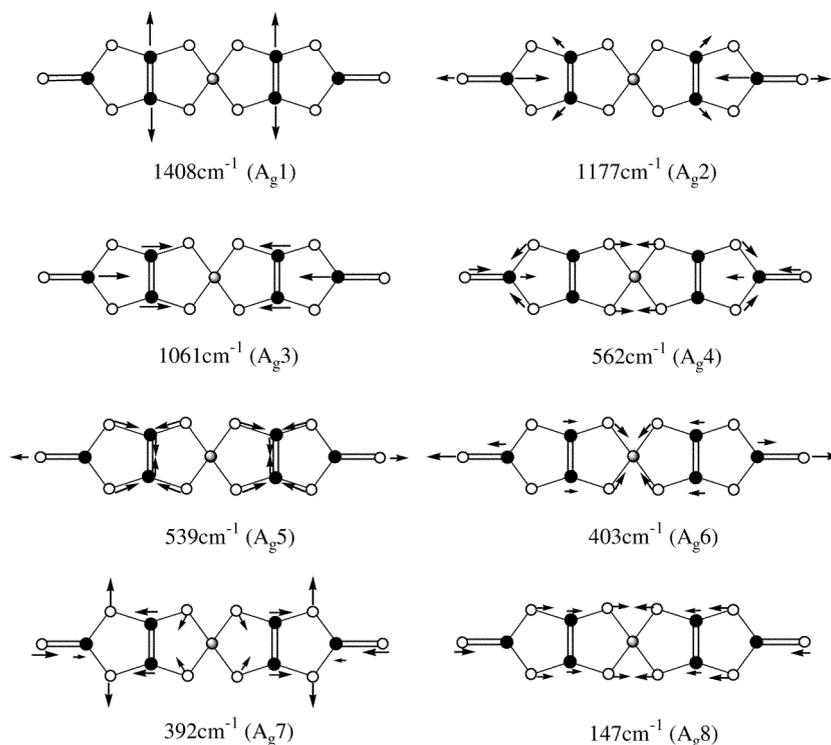
Ni(dmit)<sub>2</sub> (dmit: 1,3-dithiol-2-thione-4,5-dithiolate) complexes have so far been investigated mainly in the light of their metallic properties and superconductivity.<sup>1</sup> More recently, they have begun to be investigated as multifunctional materials which simultaneously exhibit more 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  $A_g$  modes of  $Ni(dmit)_2$ .<sup>9</sup>

linearly correlated with the anion  $A_g$  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  $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$  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  $1052\text{ cm}^{-1}$  and  $1347\text{ cm}^{-1}$ , respectively, and the C=C vibration of the pyridinium moiety at  $1594\text{ cm}^{-1}$ .<sup>7</sup> The former two vibrations are very close to those observed in the  $[(n-C_4H_9)_4N][Ni(dmit)_2]$  complex ( $1058\text{ cm}^{-1}$  and  $1349\text{ cm}^{-1}$ , respectively, in Fig. 1b). For the  $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$  PO complex, the C=S vibrational peak at  $1052\text{ cm}^{-1}$  is the same as that of the corresponding 1:1 complex, whereas the C=C vibrational peak shifts to  $1239\text{ cm}^{-1}$  (Fig. 1d), which is very similar to that of the  $[Ni(dmit)_2]^0$  neutral complex ( $1241\text{ cm}^{-1}$ ).<sup>8</sup> This noticeable shift indicates that the charge of the

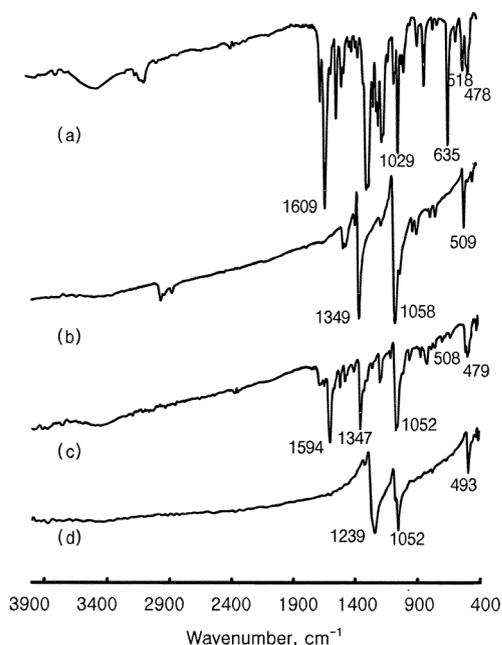


Fig. 1. IR spectra of the complexes:  $(FcCHCHPymCH_3)(CF_3SO_3)$  (a),  $[(n-C_4H_9)_4N][Ni(dmit)_2]$  (b),  $(FcCHCHPymCH_3)[Ni(dmit)_2]$  (c) and  $(FcCHCHPymCH_3)_x[Ni(dmit)_2]$  (d).

Table 1. The A<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> )[Ni(dmit) <sub>2</sub> ]	337	358	480	516	936	1024	1396
(FcCHCHPymCH <sub>3</sub> ) <sub>x</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>)[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>)[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>)/

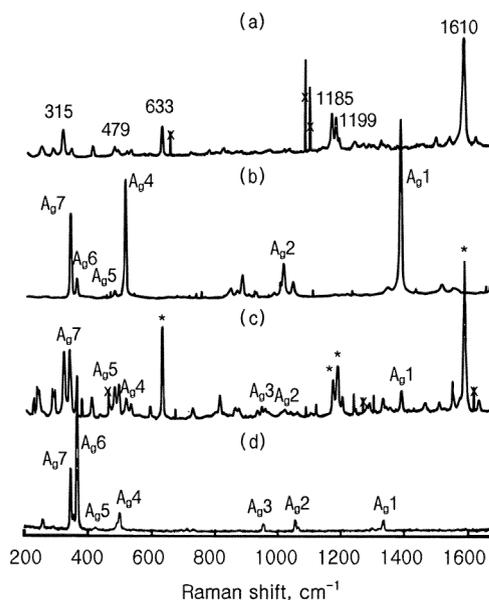


Fig. 2. Raman spectra of the complexes: (FcCHCHPymCH<sub>3</sub>)(CF<sub>3</sub>SO<sub>3</sub>) (a), [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(dmit)<sub>2</sub>] (b), (FcCHCHPymCH<sub>3</sub>)[Ni(dmit)<sub>2</sub>] (c) and (FcCHCHPymCH<sub>3</sub>)<sub>x</sub>[Ni(dmit)<sub>2</sub>] (d). The peaks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

**Acknowledgement.** This work was supported by The Institute of Natural Sciences, Seoul Women's University (2002). We wish to express our thanks to Dr. H. H. Wang (Argonne National Laboratory, USA) for the micro-Raman spectroscopy measurements.

## REFERENCES

- (a) Robertson, N.; Cronin, L. *Coord. Chem. Rev.* **2002**, 227, 93. (b) Akutagawa, T.; Nakamura, T. *Coord. Chem. Rev.* **2002**, 226, 3. (c) Akutagawa, T.; Nakamura, T. *Coord. Chem. Rev.* **2000**, 198, 297. (d) Pullen, A. E.; Olk, R. M. *Coord. Chem. Rev.* **1999**, 188, 211. (e) Canadell, E. *Coord. Chem. Rev.* **1999**, 185-186, 629. (f) Cassoux, P. *Coord. Chem. Rev.* **1999**, 185-186, 213. (g) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, 110, 115.
- Noh, D. Y.; Lee, H. J.; Kang, H.; Kang, W.; Lee, W. *Mol. Cryst. Liq. Cryst.* **2002**, 376, 269.
- Long, N. L. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 21.
- Han, Y. K.; Noh, D. Y. unpublished data.
- (a) Wang, H. H.; Ferraro, J. R.; Williams, J. M.; Geiser, U.; Schlueter, J. A. *Chem. Commun.* **1994**, 1893. (b) Wang, H. H.; Kini, A. M.; Williams, J. M. *Mol. Cryst. Liq. Cryst.* **1996**, 284, 211. (c) Ward, B. H.; Schlueter, J. A.; Geiser, U.; Wang, H. H.; Morales, E.; Parakka, J. P.; Thomas, S. Y.; Williams, J. M. *Chem. Mater.* **2000**, 12, 343. (d) Kini, A. M.; Parakka, J. P.; Geiser, U.; Wang, H. H.; Rivas, F.; DiNino, E.; Thomas, S.; Dudek, J. D.; Williams, J. M. *J. Mater. Chem.* **1999**, 9, 883.
- Pokhodnya, K. I.; Faulmann, C.; Malfant, I.; Andreu-Solano, R.; Cassoux, P.; Mlayah, A.; Smirnov, D.; Leotin, J. *Syn. Met.* **1999**, 103, 2016.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; John Wiley, Inc.; NY, 1997.
- Noh, D. Y.; Underhill, A. E.; Hursthouse, M. B. *Syn. Met.* **2001**, 120, 1053.
- Ramakumar, R.; Tanaka, Y.; Yamaji, K. *Phys. Rev. B* **1997**, 56, 795.
- (a) Sun, S. Q.; Zhang, B.; Wu, P. J.; Zhu, D. B. *J.C.S. Dalton Trans.* **1997**, 277. (b) Valade, L.; Legros, J. P.; Bousseau, M.; Cassoux, P.; Garbaskas, M.; Interrante, L. V. *J.C.S. Dalton Trans.* **1985**, 783. (c) Matsubayashi, G.; Yokozawa, A. *J.C.S. Dalton Trans.* **1990**, 3535.
- Steimecke, G.; Sieler, H.; Kimmse, R.; Hoyer, E. *Phospho. Sulfur* **1979**, 7, 49.