

## Towards Single-component Molecular Conductor [Ni(dmit)<sub>2</sub>] by Charge Disproportionation: 2[Ni(dmit)<sub>2</sub>]<sup>0.5</sup> → [Ni(dmit)<sub>2</sub>]<sup>+</sup> + [Ni(dmit)<sub>2</sub>]<sup>-</sup>

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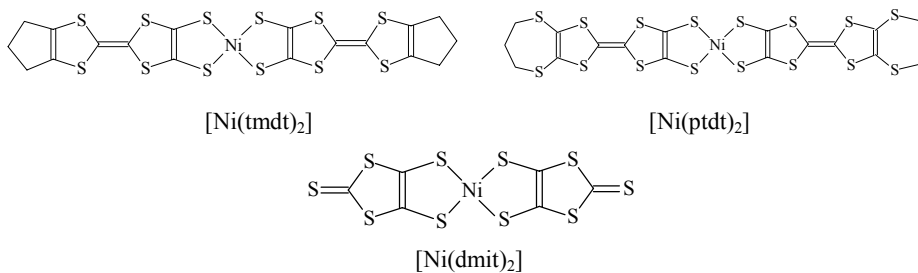
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**Abstract:** A new method of synthesizing single-component molecular conductor [Ni(dmit)<sub>2</sub>] by the reaction 2(Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>]<sub>2</sub> → [Ni(dmit)<sub>2</sub>] + (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] is reported. [Ni(dmit)<sub>2</sub>] exhibits a semiconductive behavior above 167 K, while from 167 K down to the measuring limit of 60 K, it exhibits metallic conductivity.

**Keywords:** Single-component molecular conductors, conductivity, charge disproportionation.

It was commonly thought that a molecular conductor or semiconductor should be composed of at least two components to make the conducting component in partially charged state. However, this idea became questionable by the recent report of the single-component molecular conductor [Ni(tmdt)<sub>2</sub>]<sup>1</sup> as well as several reports about single-component molecular semiconductors such as [Ni(ptdt)<sub>2</sub>]<sup>2</sup> and [Ni(C<sub>10</sub>H<sub>10</sub>S<sub>8</sub>)<sub>2</sub>]<sup>3</sup>. In fact, as early as 1985, [Ni(dmit)<sub>2</sub>] as a by-product in synthesizing TTF[Ni(dmit)<sub>2</sub>]<sub>2</sub> by slow interdiffusion of acetonitrile solutions of (TTF)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub> and (Bu<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] had been reported<sup>4</sup> (dmit = C<sub>3</sub>S<sub>5</sub><sup>2-</sup> = 4,5-dimercapto-1,3-dithiole-2-thionato). In 1992, Fang Qi *et al.* reported that [Ni(dmit)<sub>2</sub>] can be uniquely synthesized by removing an electron from [Ni(dmit)<sub>2</sub>]<sup>-</sup> by using [Fe(C<sub>3</sub>H<sub>5</sub>)]<sup>+5</sup>. In this paper, we mainly report an interesting route to synthesize single-component molecular conductor [Ni(dmit)<sub>2</sub>].

**Scheme 1** Molecular structures of [Ni(tmdt)<sub>2</sub>], [Ni(ptdt)<sub>2</sub>], and [Ni(dmit)<sub>2</sub>]



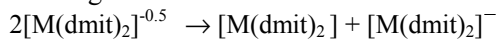
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As we know, most molecular conductors belong to the half-charged two-component motif. Because of the division of the counterion, such as the cation  $R_4N^+$  in  $R_4N[M(dmit)_2]_2$  and the anion  $X^-$  in  $(BEDT-TTF)_2X$ , these well-explored molecular conductors are limited in one- or two-dimensional structures. The significance of single-component molecular conductor is that it may open a new avenue to three-dimensional conducting structure and therefore throws light of discovering a new generation of molecular-based superconductors.

### Synthesis

Synthesis of  $(Me_4N)[Ni(dmit)_2]_2$ . Instead of common electro-chemical oxidation method, we developed a more convenient chemical method<sup>6</sup>.  $(Me_4N)[Ni(dmit)_2]$  can be oxidized to  $(Me_4N)[Ni(dmit)_2]_2$  either by  $I_2/NaI$  in acetone in air or by  $[Fe(C_5H_5)]BF_4$  in interdiffusion cell in acetonitrile without air. The product is shining platelet crystal that has been identified by X-ray diffraction data to be: monoclinic,  $a = 13.836(3)$ ,  $b = 6.536(2)$ ,  $c = 36.210(9)\text{\AA}$ ,  $\beta = 93.27(2)^\circ$ ,  $V = 3268.8(1)\text{\AA}^3$ , which is accordant with the literature data ( $a = 13.856(4)$ ,  $b = 6.498(2)$ ,  $c = 36.053(9)\text{\AA}$ ,  $\beta = 93.98(2)^\circ$ ,  $V = 3239(2)\text{\AA}^3$ ) from the crystal sample made by electro-chemical oxidation method<sup>7</sup>.

Synthesis  $[Ni(dmit)_2]$ . 55 mg of  $(Me_4N)[Ni(dmit)_2]_2$  and 5 mL freshly distilled acetonitrile were put in the left cavity of the  $\cap$ -shaped two-cavity glass tube which was then sealed in vacuum. Keep the sealed tube at  $70^\circ\text{C}$  for a few hours and slowly spill the green solution of  $(Me_4N)[Ni(dmit)_2]$  to the right cavity. Then keep the right cavity  $1^\circ\text{C}$  higher than the left cavity to evaporate the acetonitrile solvent to the left. After a few hours' reaction at  $70^\circ\text{C}$ , spill the green solution to the right again. This kind of circling process of solution from left to right and solvent from right to left was repeated about 100 times in a course of 40 days till the solution on the left-cavity became colorless. 24 mg of crystalline residue identified to be  $[Ni(dmit)_2]$  by elemental analysis and IR spectra was obtained with the yield of 95%. Anal. Calcd. for  $C_6S_{10}Ni$ : C 15.97, S 71.0; Found: C 16.15, S 69.45. This charge disproportionation or self-charge-transfer reaction can be formulated as:

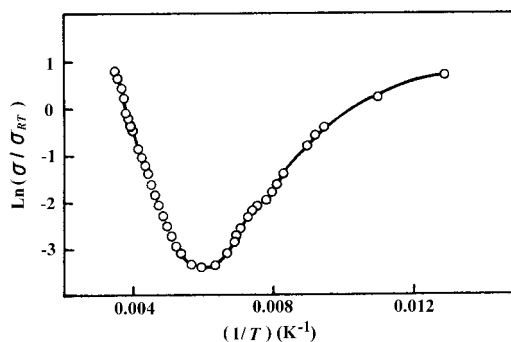


The success of above method is based on the fact that  $(Me_4N)[Ni(dmit)_2]$  is soluble,  $(Me_4N)[Ni(dmit)_2]_2$  is slightly soluble, and  $[Ni(dmit)_2]$  is insoluble in acetonitrile.

### Conductivity Measurement

The conductivity was measured by four-probe method and the sample was made by compacting  $[Ni(dmit)_2]$  microcrystals at 33 MPa. The measured conductivity at room temperature is  $2.0 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$ . The temperature dependence of conductivity in the range of  $300 \sim 60$  K (**Figure 1**) shows a minimum at 167 K, indicating that a semiconductor  $\rightarrow$  conductor transformation occurs during the temperature lowering.

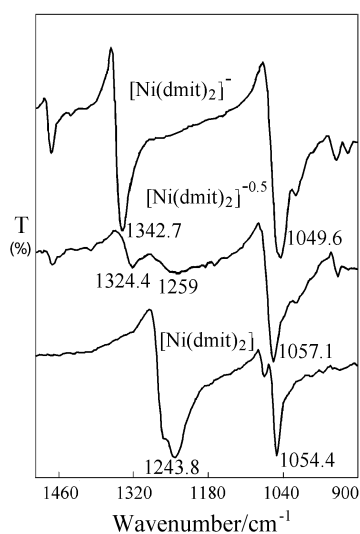
Figure 1 Temperature dependence of conductivity of [Ni(dmit)<sub>2</sub>]



### Result and Discussion

Figure 2 shows the infrared spectra of (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (up), (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>]<sub>2</sub> (middle), and [Ni(dmit)<sub>2</sub>] (bottom). With the electrical charge gradually being removed, the ν(C=C) are gradually red-shifted. It is also worth to note that the ν(C=C) of (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>]<sub>2</sub> consists of two peaks, 1324.4 cm<sup>-1</sup> and 1259.9 cm<sup>-1</sup>, implying that [Ni(dmit)<sub>2</sub>]<sup>-0.5</sup> can be regarded to consist of two resonance structures of [Ni(dmit)<sub>2</sub>]<sup>-</sup> and [Ni(dmit)<sub>2</sub>]. This may be the intrinsic reason why the self-charge-transfer reaction 2[Ni(dmit)<sub>2</sub>]<sup>-0.5</sup> → [Ni(dmit)<sub>2</sub>]<sup>-</sup> + [Ni(dmit)<sub>2</sub>] can be successfully carried out. Our further experiments have revealed that this kind of charge disproportionation can be developed to synthesize other [M(dmit)<sub>2</sub>] single-component molecular conductors such as [Pd(dmit)<sub>2</sub>].

Figure 2 IR spectra of (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (up), (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>]<sub>2</sub> (middle), and [Ni(dmit)<sub>2</sub>] (bottom)



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