

## An EXAFS observation of Ag local structure of Ag(DMe-DCNQI)<sub>2</sub> photoproduct

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### Introduction

A charge transfer complex Ag(DMe-DCNQI)<sub>2</sub> (DMe-DCNQI = 2,5-dimethyl-*N,N'*-dicyanoquinonediimine) shows one dimensional metallic conductivity at room temperature. (Figure 1) Its conductivity changes into semiconducting or insulating character by the irradiation of UV-Vis light.<sup>2</sup> This feature can apply to the fabrication of single-material devices made only from Ag(DMe-DCNQI)<sub>2</sub> by photolithography. We have investigated the structures of Ag(DMe-DCNQI)<sub>2</sub> and its photo-products by the analysis of Ag K-edge EXAFS to clarify the conductivity change mechanism. Here we will report the structure of the photoproduct with semiconducting conductivity.

### Experimental

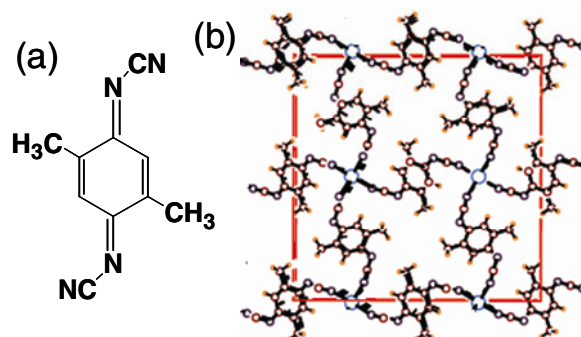
Ag(DMe-DCNQI)<sub>2</sub> was synthesized using a previously reported method.<sup>2</sup> A 200 W Hg/Xe lamp was used as a UV-vis light (200–1100 nm) source. Ag K-edge EXAFS measurements were carried out at NW10A in a transmission mode. The powder sample was cooled at 15K. We named the pristine state as  $\alpha$  and the photo-product with semiconducting conductivity as  $\beta$ .

### Result and discussion

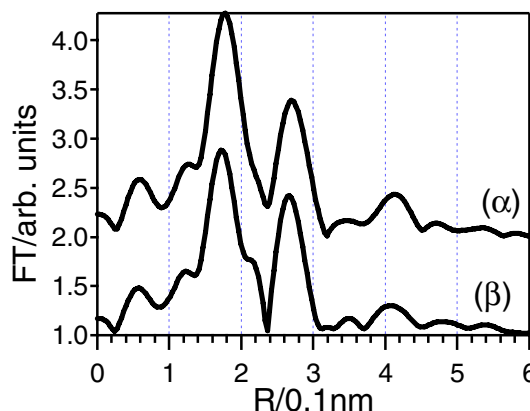
Figure 2 shows Ag K-edge EXAFS Fourier transforms of  $\alpha$  and  $\beta$ . The first peak corresponds to the Ag-N bonds in cyano groups of Ag(DMe-DCNQI)<sub>2</sub> crystal. The second peak corresponds to the second nearest C atoms in the cyano groups. The second peak is enhanced due to the shadowing effect. The shape of the first peak of  $\beta$  spectrum is asymmetric compared to that of  $\alpha$  spectrum. Moreover, the intensity of the first peak of  $\beta$  spectrum is lower than that of  $\alpha$  spectrum. These features imply that the Ag-N bond in  $\beta$  state includes some distortions compared to the original Ag-N bond of  $\alpha$ . Powder XRD measurements showed that diffraction peaks of  $\beta$  appeared almost at the same positions as those of  $\alpha$ . This result suggests that the crystal structure of  $\beta$  is not remarkably different from  $\alpha$ .

The asymmetry of the first peak of  $\beta$  is a key to determine the conductivity change mechanism. The distortions of DMe-DCNQI ligands around the Ag cations, induced by the irradiation of UV-Vis light. In another words, the irradiation causes the partial disorder in the DMe-DCNQI columns, which are the conduction

pathways in this material. The disorder in the columns may locally interrupt the conduction pathway; hence, it creates an activation energy for conduction, or a new band gap. We concluded that the local disorder is an important role in the conduction change into semiconducting properties.



**Figure 1.** (a) Molecular structure of DMe-DCNQI. (b) Crystal structure of Ag(DMe-DCNQI)<sub>2</sub> viewing down the stacking axis, i.e., c-axis.



**Figure 2.** Ag K-edge EXAFS Fourier transform spectra of Ag(DMe-DCNQI)<sub>2</sub> and its photo-product. ( $\alpha$ ) Ag(DMe-DCNQI)<sub>2</sub>,  $\alpha$ , and ( $\beta$ ) photo-product,  $\beta$ , showing semiconducting conductivity.

### References

1. A. Aumüller et al. *Angew. Chem. Int. Ed. Engl.* 25, 740 (1986)
2. T. Naito et al. *Adv. Mater.* 16, 1786 (2004)

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