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PHOTOCHEMICAL TRANSFORMATION OF MOLECULAR CRYSTALS INTO DEVICES

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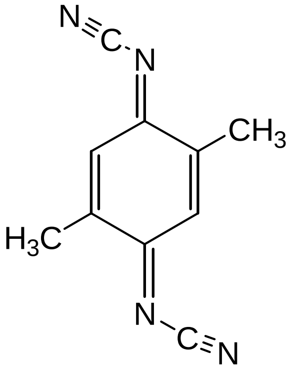
1 INTRODUCTION

All electronic devices such as transistors and diodes are based on junction structures, where a conducting solid consists of several parts with different electrical properties. Thus it is important to control the conducting properties of an arbitrary selected part of molecular materials for their applications as electronic devices. We have recently reported a novel photochemical way of fabrication of molecular devices.[1] Using a single crystal of a silver salt of an organic π–acceptor molecule 2,5-dimethyl-*N*,*N'*-dicyanoquinonediimine[2] (DM; Figure 1), $Ag(DM)_2$, we simply illuminated a part of the crystal to change the electrical conductivity. During illumination the photo-excited silver ions become strong enough oxidizers to remove electrons from neighbouring DM radical anions. Because the conduction properties are governed by unpaired π–electrons on the DM radical anions in this material, such photo-induced redox reactions result in due decrease in conductivity. Selecting the appropriate illumination conditions, one could turn the material, which has originally metallic conduction property, into a semiconducting solid with retaining its original crystal structure. It should be noted here that the conductivity changed at only the illuminated part, and the rest remained unchanged. Thus such illumination treatments should correspond to doping with spatial resolution. The doped state survived at least for several months after the cessation of illumination. This apparent irreversibility enables us to make a junction structure starting from a single crystal. Now we are studying the detailed mechanism of this phenomenon in order to utilize it as a simple and versatile doping method for device fabrications. In this brief paper, we report the ultraviolet-visible (UV-Vis) illumination effects on the electronic and magnetic properties of $Ag(DM)_2$.

2 METHOD AND RESULTS

The single crystals of $Ag(DM)_2$ were prepared by following reported procedures and identified by spectroscopic and X-ray structural analyses.[3,4] The single crystals are fine long needles, and have the highest conduction along the needle axes. These axes coincide with the crystallographic *c*-axis, which are parallel with the stacking axes of the planar

DM radical anions. The single crystals were wholly illuminated with suspended and stirred in water using a Hg/Xe lamp (200-1100 nm, 200 W) equipped with a multimode optical fibre and a cold mirror. This method enabled us an easy control of temperature and homogeneous illumination on the samples. In some experiments, where only a small amount of samples were required, the single crystals were well ground to fine powder and exposed to UV-Vis light from the same light source with continued agitation. Through water or air, illumination gave the samples an approximately similar strength of light (1.5-2.5 mWcm^{-1} at 200-350 nm, 40-70 mWcm^{-1} at 350-550 nm, 3-15 mWcm^{-1} at 550-1100 nm), but at some particular wavelengths light was characteristically strong or weak due to the light source property.



2,5-Dimethyl-*N*,*N'*-dycyanoquinonediimine (DM)

Figure 1 *Structure of DM*

1.1 DM Molecules in illuminated Ag(DM)$_2$

As long as the sample temperature was kept around RT during illumination, the IR spectra (Figure 2) showed that the DM molecules in Ag(DM)$_2$ remained almost unchanged. In addition, such samples gave identical results of elemental analyses and X-ray absorption fine structure (XAFS) on Ag *L*-edge with those of the pristine samples.[5] However, Raman and X-ray photoelectron spectroscopy (RS and XPS) clearly indicated that a part of the DM molecules, which were originally radical anion species before illumination, were oxidized toward neutral molecular species by photo-excited silver ions.[1] These experimental facts indicates that UV-Vis illumination should induce an irreversible redox reaction between the DM molecules and silver ions, but that the resultant formally neutral DM molecules should remain where it used to be in the crystal and still take part in the delocalization of the remaining unpaired π–electrons in Ag(DM)$_2$. Therefore one can observe only an averaged and thus intermediate oxidation state of DM species in Raman spectra.[1] In fact, powder X-ray diffraction pattern[5] indicate that the crystal structure should be largely retained as long as the redox reaction does not proceed so extensively, *i.e.* within “light-doping” stage, suggesting a certain meta-stable state after the photo-induced redox reaction. For more detailed information on the chemical state of the DM molecule, the measurements of solid state ^{13}C-NMR spectra are now under way.

1.2 Electronic Structure of Ag(DM)$_2$ after illumination

While the molecular and the crystal structures are largely retained at the light-doping stage, the band electronic structure after illumination could sensitively alter in accordance with the duration of illumination. We once directly observed this process by a series of electrical resistivity measurements using a partially illuminated single crystal of $Ag(DM)_2$.[1] Since electrical resistivity is generally much sensitive to extrinsic factors such

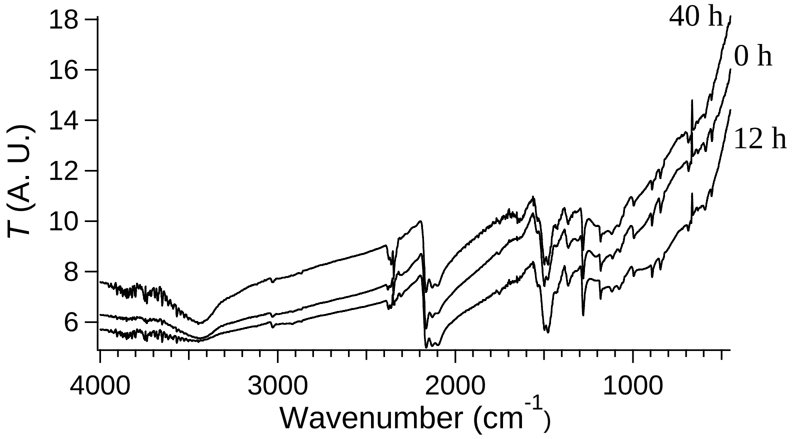


Figure 2 *IR spectra of pristine and illuminated $Ag(DM)_2$ (KBr disks)*

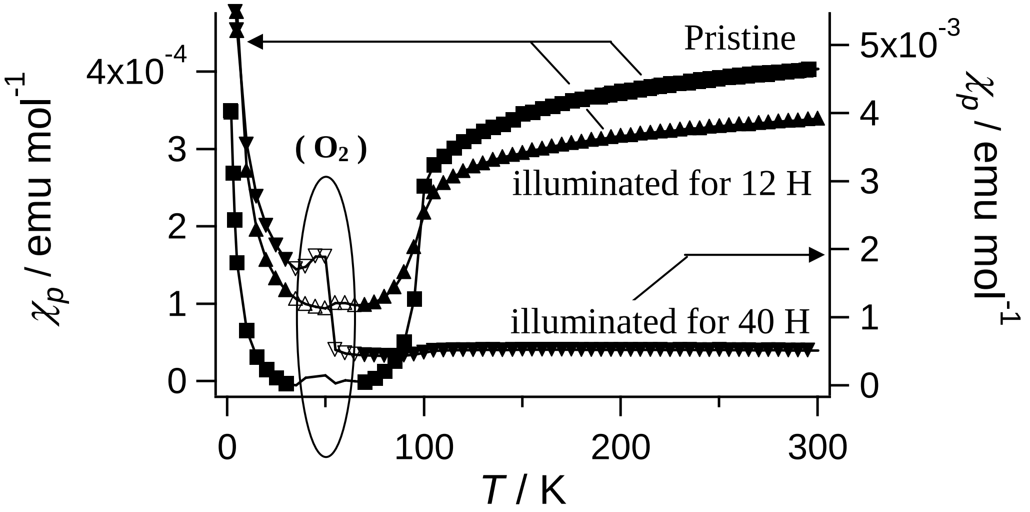


Figure 3 *Magnetic susceptibility of pristine and illuminated $Ag(DM)_2$*

as surface conditions in conjunction with electrical contacts, other measurements that require no electrical contacts are desirable to support our previous observation. Accordingly we measured magnetic susceptibility (Figure 3) and diffuse reflectance spectra (Figure 4) of the same samples used in the measurements of the IR spectra shown in Figure 2. Both of magnetic susceptibility and diffuse reflectance spectra well reflect bulk properties and electrical structures. The temperature-dependence of magnetic susceptibility of the pristine $Ag(DM)_2$ was of Pauli paramagnetic with the value of 4-5×10^{-3} (emu mol^{-1}) above 100 K, and became diamagnetic below 100 K except for a Curie-tail below ~ 30 K. Illumination clearly decreased the value of Pauli paramagnetism (3-4×10^{-3} (12 h) and 5×10^{-4} [emu mol^{-1}] (40 h)), suggesting the decrease in the number of metallic conduction electrons. On the other hand, illumination made the Curie-like behaviour at low temperatures more and more marked, while the magnetic transition at 100 K less and less evident. The Curie-tail, which originated from the lattice defects introduced by this doping, increased as follows; 6.9×10^{-4} (pristine), 3.0×10^{-3} (12 h), and 3.2×10^{-2} [emu K mol^{-1}] (40 h). Such magnetic behaviour could be reproduced as a sum of Curie contribution and Pauli paramagnetism. It should be noted that the transition temperature (100 K) remained constant despite the fact that the whole behaviour qualitatively changed. The results shown in Figure 3 imply that the illumination gradually and heterogeneously turns the metallic material into a semiconductor (probably from the surface), partly leaving the original metallic property of the inner sample intact. The Kubelka-Munk transformation of diffuse reflectance spectra (Figure 4) indicated that the electronic structure qualitatively changed due to the illumination.

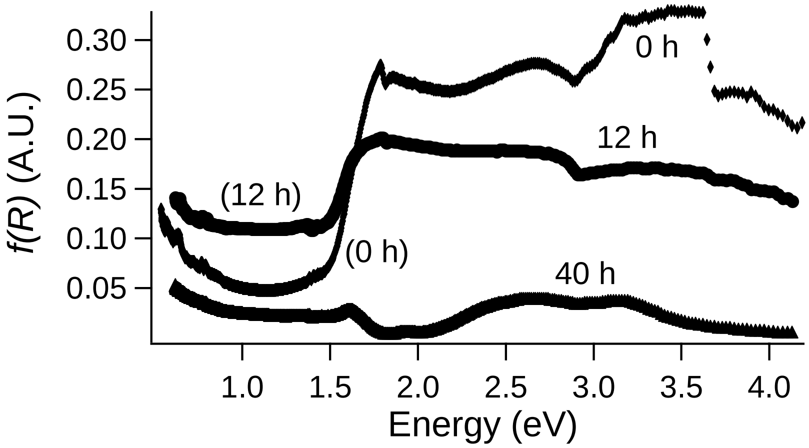


Figure 4 *Diffuse reflectance spectra of pristine and illuminated Ag(DM)$_2$*

3 CONCLUSION

UV-Vis illumination has qualitatively changed the electronic structure and magnetic properties of Ag(DM)$_2$ with retaining its crystal and molecular structure.

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