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Photochemical modification of magnetic properties in organic low-dimensional conductors

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ABSTRACT

Magnetic properties of organic charge transfer salts Ag(DX)$_2$ (DX = 2,5-dihalogeno-N,N'-dicyanoquinonediimine; X = Cl, Br, I) were modified by UV irradiation from paramagnetism to diamagnetism in an irreversible way. The temperature dependence of susceptibility revealed that such change in magnetic behavior could be continuously controlled by the duration of irradiation. The observation with scanning electron microprobe revealed that the original appearance of samples, e.g. black well-defined needle-shaped shiny single crystals, remained after irradiation irrespective of the irradiation conditions and the duration. Thermochemical analysis and X-ray diffraction study demonstrated that the change in the physical properties were due to (partial) decomposition of Ag(DX)$_2$ to AgX, which was incorporated in the original Ag(DX)$_2$ lattices. Because the physical properties of low-dimensional organic conductors are very sensitive to lattice defects, even a small amount of AgX could effectively modify the electronic properties of Ag(DX)$_2$ without making the original crystalline appearance collapse.

1. Introduction

More than 30 years, the organic charge transfer salts have been at the center of scientific and technological interest in the field of synthetic (semi) conductors [1–3]. Their building blocks are generally planar molecular radical species with low symmetries and extended π-conjugations (Fig. 1), and their electronic band structures depend on π–π overlaps between neighboring molecules (Fig. 2). The anisotropy of the π-orbitals commonly leads to highly anisotropic (i.e. low-dimensional) crystal structures as well as small band widths (~1/2–1/10 of those of other kinds of conductors). For example, they consist of nanowires (one-dimensional, 1D), nanosheets (two-dimensional, 2D), and so on, all of which are made of molecular networks based on π–π interactions. Such characteristic molecular arrangements necessarily lead to high anisotropy in physical properties as well. Roughly speaking, the lower the dimensionality becomes, the less the number of the nearest neighbor sites become. Therefore the lower dimensionality involves a smaller number of intermolecular interactions, which are basically weak van der Waals interactions, dominating electrical and magnetic properties. Accordingly these structural situations peculiar to molecular charge transfer salts make the resultant electronic system far more sensitive to perturbations such as structural change [1–3], magnetic field [4–11], and lattice defects [12] than usual conductors having isotropic structures. This is one of the reasons the organic charge transfer salts are interesting in terms of sensors and devices.

Although the organic conductors, especially in their single crystalline forms, have many unique electrical and magnetic properties stated above, which might be applied to novel device actions, a serious drawback against practical application is the difficulty in controlling the physical properties of a given material with sufficiently high spatial resolution. As such a method, doping has played an indispensable role in fabrication of the current silicon-based semiconductor devices. However, standard ways of doping are not always practical in crystalline organic charge transfer salts. Thermal instability and mechanical fragility prevent us from the application of most of the advanced fabrication techniques established in inorganic semiconductors industry. In addition, most organic charge transfer salts are insoluble in any solvent and not volatile without decomposition, which limits our methods to treat them. The only practical and versatile way is chemical mixing in the course of syntheses. However, inclusion of foreign chemical species in the crystals of organic charge transfer salts often results in serious lowering of the crystal qualities and thus deteriorating of the conducting/magnetic properties. Coexistence of foreign chemical species (dopants) in synthesis sometimes led to unexpected change in crystal structures and thus in

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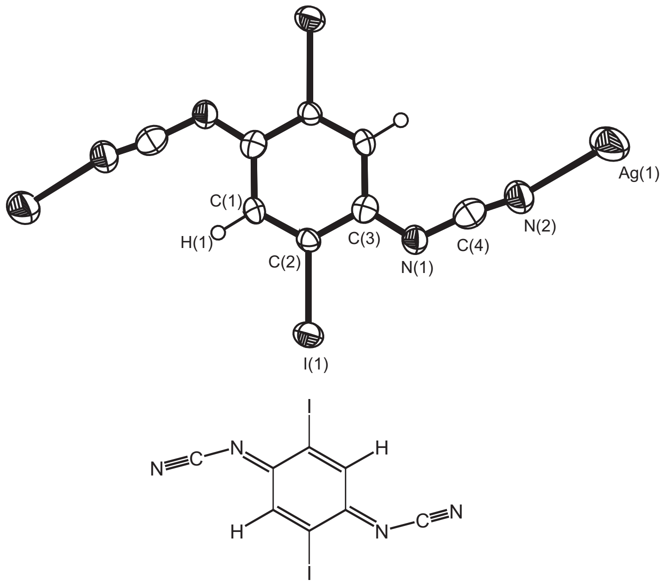

Fig. 1. Molecular structure of *DI* shown with silver ions coordinated by the imino-groups (=N–CN) of *DI*.

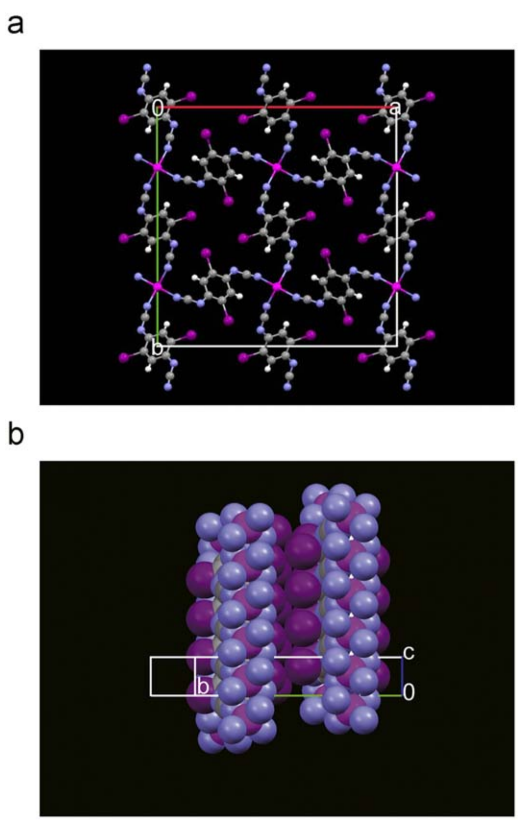

Fig. 2. Crystal structure of Ag(DI)$_2$; (a) view down along the *c* axis (stacking axis), and (b) perpendicular to the *c* axis. Purple, dark violet, grey, white, and pale blue spheres designate Ag, I, C, H, and N atoms, respectively.

physical properties [13,14]. It is very difficult to control exact amount of dopant and the precise part to be doped by chemical mixing methods.

A solution to these difficult problems was proposed in 2004; a photochemical method to control the number of carriers (unpaired electrons) with spatial resolution [15–21]. Utilizing this method a single crystal of Ag(DM)$_2$ (DM = 2,5-dimethyl-*N*,*N'*-dicyanoquinonediimine) can be irreversibly transformed to a diode, which have a junction interface between the irradiated and the non-irradiated parts in the crystal. Once the irradiation ceases, the resultant material are stable to retain the modified conductivity under normal atmosphere, or one can resume the irradiation to further modify the electrical property. The absolute values and temperature-dependence of resistivity gradually and continuously varied from metallic to semiconducting ones in accordance with temperature-controlled irradiation with UV and/or Visible (Vis) light. Meantime the magnetic properties varied from Pauli paramagnetic to Curie-like behavior, which was consistent with the change in electrical behavior mentioned above. Although such modification in magnetic property is of a qualitative level (from that of a metal to that of a semiconductor), both properties are paramagnetic, and thus a more marked change is desirable for future practical application in memory devices; for example, transformation between magnetic and non-magnetic properties. Here we report such materials, which alter their paramagnetism to diamagnetism simply by UV irradiation only in regard to the irradiated parts.

2. Experimental section

2.1. Synthesis

The chemicals were purchased from Sigma-Aldrich, Inc. or Wako Pure Chemical Industries, Ltd. in their purest grades and used as received. Silver wires (1 mm∅, 99.99%) were purchased from The Nilaco Corporation and used in the synthesis of the silver salts. 2,5-dihalogeno-*N*,*N'*-dicyanoquinonediimine (*DX*; Fig. 1) were prepared according to the literature [22,23]. Their silver salts Ag(DX)$_2$ in single crystals were prepared with a slight modification of a reported procedure [22,23]. In our typical procedure, *DX* (X = Cl: 100 mg, Br: 60 mg, I: 10 mg) and $AgNO_3$ (X = Cl, Br: 2 mg, I: 1 mg) were dissolved in CH_3CN (X = Cl, Br: 60 mL, I: 40 mL) and the solution was sealed, stood still for 30 min at −30 °C. Then a silver wire freshly cut in length of 5 mm was added in the solution, and the solution was again sealed, kept at −30 °C for 7–10 days to yield black thick needles of Ag(DX)$_2$. Thus obtained single crystals were analytically pure and many of them were suitable for structural analyses and physical property measurements.

2.2. UV-irradiation

For irradiation of the samples, one of the following UV light sources ((A), (B) and (C)) was used; (A) a Hg/Xe-lamp (200 W; Hamamatsu Photonics K. K.; Supercure-203S UV Lightsource; San-Ei Electric) with a multimode quartz fiber (1 m—length, $\phi = 5$ mm, numerical aperture (NA) = 0.22), (B) a Xe-lamp (100 W; Asahi Spectra K. K.; LAX-Cute) with a multimode quartz fiber (1 m—length, $\phi = 5$ mm, $NA = 0.2$), and (C) a UV laser (375 ± 5 nm, 20 mW, NEOARK TC20-3720-15) with a light guide (1 m—length) of adjustable focus, *NA*, and size of the beam spot. (A) was equipped with a filter and a mirror for filtering light with wavelengths of 220–275 nm. This helps to minimize thermal effects during the irradiation of the sample. (B) was equipped with a mirror module and a filter to irradiate the samples with the light of 240–360 nm wavelengths only. (B) was also equipped with a rod lens, which realizes a homogeneous irradiation with being in/out of focus to adjust the spot size to the sample area. The intensity of light at the sample was measured with a power meter (Ophir, NOVA attached with a Si photodiode head PD-300-UV).