

# Photo-induced metal-insulator transition of a molecular crystal

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Molecular charge transfer salts form a unique group of material, whose properties might be advantageous in device fabrication. Examples include high purity and good quality of single crystals, wide choice of process under ambient conditions, self-aggregation ability, low-dimensionality of the crystal/electronic structure, well-established material design and rich variation. Recently conductivity of a molecular charge transfer salt ( $\text{Ag}(\text{DM})_2$ ;  $\text{DM} = \text{C}_{10}\text{H}_8\text{N}_4$ ) has been controlled using photochemical solid state reaction [1]. By analogy with carrier doping, this is tentatively called “optical doping”. During the investigation of the mechanism and related phenomena, a unique metal-to-insulator (MI) transition was found in the above material [2]. In this presentation, we analyze structural, electronic and physical properties of this transition, which may contribute to insulating and passivation techniques in the fabrication process of organic devices.

The MI transition occurs at 428.4 K (155.2 °C) and is characterized in the following feature; 1) it involves vitrification without melting, 2) the color of the solid changes from opaque black to transparent pale brown, and 3) the resultant insulating molecular glass is more stable than the original crystalline solid ( $\Delta H = -126.8 \text{ kJmol}^{-1}$ ) and thus the transition is irreversible.

$\text{Ag}(\text{DM})_2$  exhibits metallic conductivity above  $\sim 100$  K, at which temperature an MI transition takes place and the ground state of this material is an insulating crystalline solid [3]. Usually highly conducting molecular charge transfer salts will be easily decomposed at elevated temperatures, which is a serious drawback in any device fabrication processes. On the other hand, because any glassy solids, whether they are organic or inorganic, usually have higher energies than the corresponding crystalline

solids, vitrification occurs in an endothermic way ( $\Delta H > 0$ ). A series of thermodynamic measurements (DSC, TG-DTA and TG-MS) combined with XRD established that vitrification of  $\text{Ag}(\text{DM})_2$  should make sharp contrast with thermodynamic common trends in the abovementioned points 1)-3). The results of TG as well as spectroscopic (IR, UV-vis, <sup>13</sup>C-NMR, XPS, XAFS, MALDI-TOF MS) and chemical analyses elucidated that the molecular structure of the metal complex  $\text{Ag}(\text{DM})_2$  was retained in the glassy solid. SEM photographs clarified that the pristine crystalline  $\text{Ag}(\text{DM})_2$  easily turned into the glassy state under UV-vis illumination, retaining the original shape of the solid.  $\text{Ag}(\text{DM})_2$  is readily prepared as single crystalline or film forms by wet (solution) or dry (sublimation) processes. Using photolithography, this vitrification has a possibility to be utilized to directly *draw* an insulation in the  $\text{Ag}(\text{DM})_2$ -based device circuits without mechanical damages, or to be coated for passivation of air/humidity-unstable devices such as organic FET and EL.

- [1] T. Naito et al., Adv. Mater., 2004.
- [2] T. Naito et al., Adv. Func. Mater., in press.
- [3] A. Aümüller et al., Liebigs Ann. Chem., 1986.

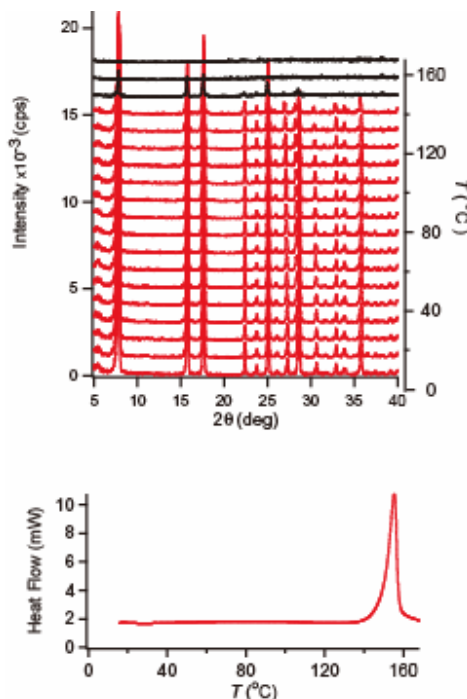


Fig. 1 XRD patterns (upper) and a DSC curve (lower) simultaneously measured in dry  $\text{N}_2$  from 18 to 168 °C starting from pristine  $\text{Ag}(\text{DM})_2$ . XRD:  $3 \leq 2\theta \leq 40$  deg, scan rate = 20 deg  $\text{min}^{-1}$ , sampling interval = 0.02 deg; DSC: heating rate = 3 °C  $\text{min}^{-1}$ , 6.49 mg of the polycrystalline sample in 100 ml of dry  $\text{N}_2$ .

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