IV-G Development of Molecular Materials Containing Photo-Reactive Species

The molecular materials are considered to be good candidates for advanced functional materials such as (nano-)devices. Their outstanding advantages include the wide variety of substances, possibility of molecular-level fine design, softness of lattices and unique and varied crystal structures. On the other hand, the physical properties of the molecular materials significantly depend on their crystal structures. The crystal structures are, however, not predictable or controllable thus far. Sometimes a pair of molecular materials with very similar crystal structures to each other exhibit qualitatively different physical properties for various or unknown reasons. Additionally many of the molecular charge-transfer salts are very difficult to change their Fermi level by standard methods of doping. Consequently one can hardly choose an appropriate molecular crystal which has favorable physical properties (band-filling) and a crystal structure with an enough good quality and sufficient size for study or other practical purposes. If one can obtain molecular radical salts with a photo-redox-reactive species, one could dope it by irradiation of light (permanent photo carrier injection) without unexpected structural change using solid state in situ reaction. In order to pursue a new possibility of molecular materials, we have started to develop molecular radical salts with photo-reactive species.

IV-G-1 Metastable State of MV[Ni(dmit)$_2$]$_2$ (MV = Methyl Viologene, dmit = 1,3-dithiol-2-thione-4,5-dithiolate)

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MV[Ni(dmit)$_2$]$_2$ has long attracted a special attention of several different research groups in terms of the strong photo-induced redox ability peculiar to MV. Yet most of the electrical, structural or optical data are based on the powder sample, and few details are known on its physical properties. We have recently obtained the single crystals of this material, and found that there exists a new phase as a metastable state. The fresh single crystals of the title compound exhibited clear metallic conductivity down to 1 K with anomaly below 100 K. The magnetic susceptibility was well described by Pauli paramagnetism with a small anomaly below 100 K corresponding to the electrical behavior. The thermoelectric power was constantly ~ 0 μVK^{-1} from RT–4 K, which is consistent with the fact that this material has a half-filled (“compensated”) electronic band strucuture. The crystal consists of mixed stacking of [Ni(dmit)$_2$]$^-$ (A) and MV^{2+} (D) by repeating unit of D–A–A. The intermolecular interactions between A’s are very weak but isotropic. This phase could be one of the rare examples of molecular version of naturally occurring (main group) metallic elements in that weak and isotropic inter-site interactions favor the metallic nature against correlation effect. The light irradiation effects on its electrical and magnetic properties are under study.

IV-G-2 Electrical Behavior of UV-VIS Irradiated Ag(DMe-DCNQI)$_2$

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The UV-VIS (200–1100 nm) irradiation effect on the electrical behavior of the title compound was examined with its single crystals and clear difference has been found depending on the duration of irradiation. The longer the irradiation time was, the higher RT resistivity it exhibited. The whole temperature-dependence also changed. With irradiation a sudden but small resistivity increase appeared well higher temperature than its original metal-insulator transition (100 K), and this temperature rapidly moved toward room temperature. These irradiation effects has been confirmed to be intrinsic by comparing the results of parallel measurements of non-irradiated samples. The overall behavior can be featured by sum of original bulk behavior (major part) and new metallic behavior with a possible transition at higher temperature (minor part). Further details are now under study.