Electronic structures of $M(tmdt)_2$ (M=Ni, Cu, Zn, Au)

S. Ishibashi,[1] and K. Terakura[2]
[1] RICS, AIST, 1-1-1, Umezono, Tsukuba-shi, Ibaraki 305-8568, Japan
[2]JAIST, 1-1, Asahidai, Nomi-shi, Ishikawa 923-1292, Japan
E-mail; kiyotera@jaist.ac.jp

Most of the metallic organic solids consist of at least two components. One of them serves as a donor and the other an acceptor. Partial electron transfer between them produces carriers, electrons and holes, contributing to metallic conduction. The first success of synthesizing single component metallic organic solids, $Ni(tmdt)_2$, was announced in 2001.[1] Among several related materials synthesized subsequently, only $Ni(tmdt)_2$ and $Au(tmdt)_2$ are metals.[2] The latter which shows antiferromagnetism below 100 K attracts strong attention.[3] We discuss in this talk the structural and electronic properties of $M(tmdt)_2$ with M=Ni, Cu, Zn and Au.

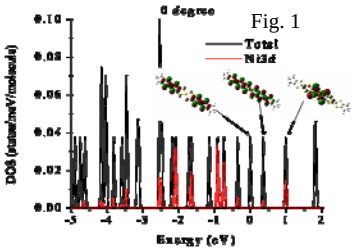

Fig. 1

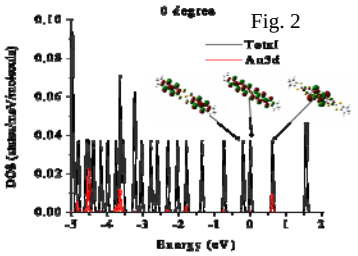

Fig. 2

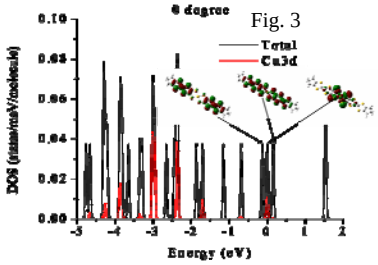

Fig. 3

Ni- and Au salts are planar in shape but those of Cu and Zn are distorted such that the dihedral angle of their two ligands is nearly 90 degree. However, in order to clarify the systematic trend, we first assume the planar shape of the molecule for all of them. Figs. 1, 2 and 3 show the molecular orbital levels of isolated molecules for M=Ni, Au and Cu without spin polarization. As the wavefunctions are for Ni, their detailed shape should not be taken seriously. We note the following features:

1) While d level of Au is deeper than that of Ni, its much more extended wavefunction pushes the anti-bonding level high enough to produce rather similar energy diagram to that of Ni. However, HOMO of Ni salt is fully occupied while in the case of Au one additional electron occupies the LUMO of Ni to make it SOMO.
2) LUMO and HOMO of Ni and SOMO and HOMO-1 of Au have very little contribution from d states. This leads to very weak coupling between the ligand π orbitals. This aspect is important in the metallicity of these systems and the antiferromagnetism of $Au(tmdt)_2$. There is little contribution from d states even in solids.
3) Compared with Au, Cu has much more localized d wavefunctions and the antibonding state with ligand π orbitals comes down to become SOMO.

As mentioned above, the dihedral angle of the two ligands is nearly 90 degree. Therefore, the crystal field of Cu and Zn is nearly that of tetrahedron. Anyway, d states make significant contributions to the properties of Cu salt.

1) H. Tanaka et al., Science **291** (2001) 285.
2) W. Suzuki et al., J. Am. Chem. Soc. **125** (2003) 1486.
3) S. Ishibashi et al., J. Phys. Soc. Jpn. **74** (2005) 843; *ibid* **74** (2005) 1879.