A Rich Variety in Ground States of [Pd(dmit)$_2$]$_2$ Salts, and Methodology for Analyzing Intra-dimer Interactions, Inter-dimer Interactions and MO Levels

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2D molecular solids are roughly classified into two groups from the viewpoint of the crystal structure. In Group-A, 2D-layer consists of a “tight dimer”, a dimer with short inter-molecular contacts. The representative material is the $\kappa$–ET salts, where anti-ferromagnetic (AF) phase is neighbored with superconducting (SC) phase. In Group-B, on the other hand, any tight dimer is absent in 2D-layer. The representative material is the $\beta''$–ET salts, where charge frustration (CF) is occurred between the charge ordered (CO) phase and SC phase. Two groups have been independently studied.

2D-layer of [Pd(dmit)$_2$]$_2$ salts belongs to Group-A owing to the tight dimer. However, we have observed the perfect intra-dimer charge separation for triclinic-EtMe$_3$[Pd(dmit)$_2$]$_2$. The intra-dimer CO (IACO) is characteristic of Group-B. It is reasonable to assume that Group-A can be bridged with Group-B by using some proper parameters. Therefore, it is of considerable importance to analyze the detailed inter-molecular interactions for the ground states of [Pd(dmit)$_2$]$_2$ salts: AF, SF (spin frustration), VBS (valence bond solid), IACO and IECO (inter-dimer CO). In this symposium, we will present the methodology for analyzing intra-dimer interactions, inter-dimer interactions, and MO levels of [Pd(dmit)$_2$]$_2$ salts using vibrational and electronic spectroscopy, and discuss the parameters dictating the ground states above mentioned.

We have found that the fluctuated valence bond (VB), as well as the static VB, is observable. Interestingly, the coupling of charge and VB is reduced from IACO, VBS, SF to AF. We will also discuss some molecular solids, including $\beta''$– and $\kappa$–ET salts, from viewpoint of the coupling.