Controlling Charge Separate Phase Transition Temperatures in the [Pd(dmit)₂]₂ and [Pt(dmit)₂]₂ Salts

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Most [Pd(dmit)₂]₂ salts (see Fig.1 (a)) are Mott insulators at ambient pressure, except for only a few examples being metal. The ABCOH salt [1] (ABCO = 1-Azabicyclo[2.2.2]octane, Fig. 1 (b)) and PyH salt (PyH = Pyridinium, Fig. 1 (c)) are the examples of showing metallic conductivity. In both salts, NH···S hydrogen bonds are formed between the cation and [Pd(dmit)₂]²⁻. The cation orientation is disordered in the metallic phases. The PyH salt undergoes a valence transition, 2[Pd(dmit)₂]²⁻ → [Pd(dmit)₂]₀²⁰ + [Pd(dmit)₂]²⁻, accompanied by the PyH cation orientation ordering at 220 K. In the ordered phase, NH···S hydrogen bonds are formed only between [Pd(dmit)₂]²⁻ and PyH, namely these hydrogen bonds stabilize the separated charge. The cation ordering should play a key role in this structural change. This suggests that, this phase transition can be suppressed by preventing the PyH cation orientation. We synthesized PyH derivative salts (Fig.1 (d-f)), in which the cation rotation should be considerably suppressed by introducing the functional groups. The 2EtPyH salt showed metallic conductivity and no charge separate transition. In this talk, we will discuss the thermal behavior and the electronic states of the PyH derivatives salts from the results of reflectivity (600–15000 cm⁻¹) down to 10 K. We will also discuss a controlling the transition temperatures in the [Pt(dmit)₂]₂ salts.

Fig. 1. Chemical structures of (a) M(dmit)₂ (M = Pd, Pt), (b) ABCOH, (c) PyH, (d) 2MePyH, (e) 2EtPyH, (f) 4EtPyH.

Fig. 2. Reflectivity spectra of the 2EtPyH salt at 295 K and 10 K.

References