A series of molecular conductors \((\text{Cation})^+\)[Pd(dmit)$_2$]$^-$ (see Fig. 1 (a)) have layered structures, in which conducting layers formed of strongly dimerized [Pd(dmit)$_2$]$^-$ units with spin-1/2 are sandwiched by cation layers. Most Pd(dmit)$_2$ salts are Mott insulators; at ambient temperature and pressure, only a few examples show metallic conduction e.g., the Cs salt and the ABCOH salt [1] (ABCO = 1-Azabicyclo[2.2.2]octane, Fig. 1 (b)). Relatively short intermolecular contacts between the cation and Pd(dmit)$_2$ molecules are found in these metallic salts. In ABCOH salt, N$^+$–H···S type hydrogen-bonds are formed between the ABCOH and Pd(dmit)$_2$ molecules. This fact, suggesting the role of cation-anion interactions in destabilizing the Mott insulating state, stimulates us to explore the Pd(dmit)$_2$ salts with the N$^+$–H···S hydrogen-bonding. For this purpose, we have prepared (DABCOH)[Pd(dmit)$_2$]$_2$ and (PyH)[Pd(dmit)$_2$]. (DABCO = 1,4-diazabicyclo[2.2.2]octane, Py = pyridine, Fig. 1 (c) and (d)) As expected, the both salts contain the N$^+$–H···S hydrogen-bonding. The DABCOH salt exhibits metallic temperature-dependence of conductivity above 260 K, while the ABCOH salt has been reported to show metallic behavior down to ca. 40 K [1], in spite of the structural similarity. We have found subtle difference in the infrared reflectivity spectra between these salts. The PyH salt retains metallic behavior down to 220 K. At this temperature, the PyH salt undergoes a valence-transition, 2[Pd(dmit)$_2$]$^-$ → [Pd(dmit)$_2$]$^0$ + [Pd(dmit)$_2$]$^{2-}$, to a non-magnetic insulating state of the anion layer, accompanied by ordering of the PyH$^+$ cation orientation. In this talk, we compare the structural, electrical, spectroscopic and ac dielectric properties of these salts to give insight into the physical role of the cation-anion interactions, particularly the N$^+$–H···S hydrogen-bonding.

Reference