Two electrically different molecular conductors based on unsymmetrical Au(III)-dithiolene complexes with similar crystal structures

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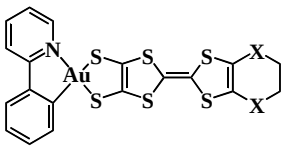
Donors based on unsymmetrical Au(III) dithiolene complexes, [Au(ppy)($C_8H_4S_8$)] and [Au(ppy)($C_8H_4S_6O_2$)] (Scheme 1), are capable of providing molecular conductors. We report here that cation radical salts, [Au(ppy)($C_8H_4S_8$)]$_2$[PF_6] (**1**) and [Au(ppy)($C_8H_4S_6O_2$)]$_2$[BF_4] (**2**) show different physical properties in spite of similar crystal structures. A columnar structure is commonly formed by two-fold head-to-head stacking of the cation radicals. Salt **1** is a semiconductor ($\rho_{r.t.}$ = 2.6 × 10^2 Ω cm) with small activation energy (E_a = 0.03 eV) under ambient pressure, and shows metallic behavior under high pressure (0.8-2.0 GPa). On the other hand, **2** is an insulator ($\rho_{r.t.}$ = 3.1 × 10^4 Ω cm, E_a = 0.08 eV) at ambient pressure. This notable contrast is caused by a subtle difference between the cation arrangements of **1** and **2**. Construction of effective conduction pathways through the S···S contacts was found in the crystal structure of **1**. However, the crystal of **2** contains no such conduction pathways through the S···S contacts. The energy band structures of **1** and **2** were calculated by the simple tight-binding method based on the crystal structural data (Fig. 1). These calculations suggest that even a subtle distinction of cation arrangements provides the remarkable distinction found between **1** and **2**. The electronic properties of **1** and **2** will be discussed in more detail based on the crystal structure, band calculation and magnetic susceptibility.



X = S: [Au(ppy)($C_8H_4S_8$)]
X =O: [Au(ppy)($C_8H_4S_6O_2$)]

Scheme 1

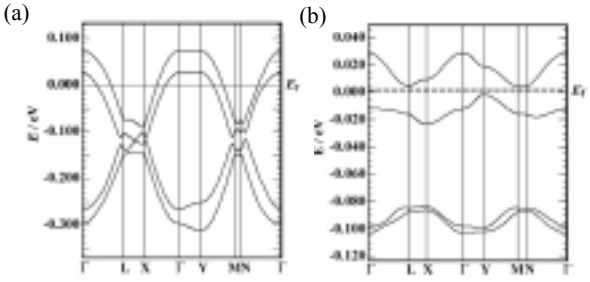


Fig. 1 Energy band structures of (a) **1** and (b) **2**