

**Structures and electrical conductivities of cation radical salts based on asymmetrical [Au(III)(C-N)(S-S)] type dithiolate complexes.**

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[Au(III)(C-N)(S-S)] type [C-N = C-deprotonated-2-phenylpyridine (ppy<sup>-</sup>); S-S = sulfur-rich dithiolate(2-) including an organic donor moiety] complexes are of much interest as new electrical conductors forming an inorganic/organic molecular composite. They are expected to become advanced and functional materials. In this work, metal complexes [Au(ppy)(S-S)] [S-S = C<sub>8</sub>H<sub>4</sub>S<sub>8</sub><sup>2-</sup> (**1**) and C<sub>8</sub>H<sub>4</sub>S<sub>6</sub>O<sub>2</sub><sup>2-</sup> (**2**), including an ET or BO moiety] and their cation radical salts have been prepared, and electrical conductivities of the cation radical salts are discussed based on their crystal structures.

Various [Au(ppy)(S-S)]<sub>2</sub>[Q][solvent]<sub>n</sub> [Q = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> and TaF<sub>6</sub><sup>-</sup>; solvent = PhCl and PhCN; n = 0-0.5] type cation radical salts have been prepared by current-controlled electrolysis of **1** and **2**, and their crystal structures were revealed by X-ray crystal structure analysis.

These salts exhibit two types of unique columnar structures. The one (S-S = **1**, Q = PF<sub>6</sub><sup>-</sup> / S-S = **2**, Q = BF<sub>4</sub><sup>-</sup>) contains the two-fold head-to-head stacking of cation radicals while the other (S-S = **1**, Q = AsF<sub>6</sub><sup>-</sup>, TaF<sub>6</sub><sup>-</sup>) is based on the stacking of tetramers cation radicals containing four units in the unit length. In the former structures, some intercolumn S--S contacts shorter than the van der Waals distance are observed, resulting in a two-dimensional sheet of the molecular interaction, while, in the latter structures, there is no short intercolumn S--S contact.

These cation radical salts show metallic or semiconducting behavior. To our knowledge, this is the first example of the metallic cation radical salt based on the asymmetrical metal complex.