

# Molecular Conductor Nanowires Sheathed by Supramolecular Networks

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Six co-crystals between one-dimensional(1D) stack of conducting TTF derivatives and insulating three-dimensional(3D) network sheathing the 1D stack were obtained by galvanostatic oxidation of the donor molecules (*i.e.* the TTF derivatives) in the presence of the corresponding halide anions and iodine-containing neutral molecules. In order to characterize their properties as wiring materials on nano-scale, their crystal structures were determined by X-ray single crystal diffraction and the temperature dependence of their anisotropic electrical resistivity was measured by four-probe or three-probe methods (TTF = tetrathiafulvalene).

While the 1D stack of the cation radicals of the donor molecules is formed by  $\pi$ - $\pi$  interaction, the 3D network of halide anions and the iodine-containing neutral molecules is formed by halogen bonding between the anion and the electron-deficient iodine. The co-crystallization of these two components to create the supramolecular sheathed nanowire structure is allowed by their several characters including complementary charges of the cationic and anionic moieties, high directionality and flexibility of the halogen bond, and compatibility of the lattices between the 1D stack and the 3D network. Among the present crystals, two distinct structures are found. One is a double-strand wire structure that is quite important issue to avoid disconnection of the wires by lattice defects, and the other one is 1 nm-thickness insulating sheath that is effective in prohibiting inter-wire hopping of the carriers.

The resistance anisotropy of the nanowires reaches as much as  $10^8$ . This result as well as the thermally activated behavior of the temperature dependence has been analyzed by tight-binding band calculation and resistance-array modeling, which gives fundamental understanding of this system. The structures and conduction properties of the six nanowires as well as the translational symmetry of crystal even make us propose their use in 3D cross-bar wiring by further developments.

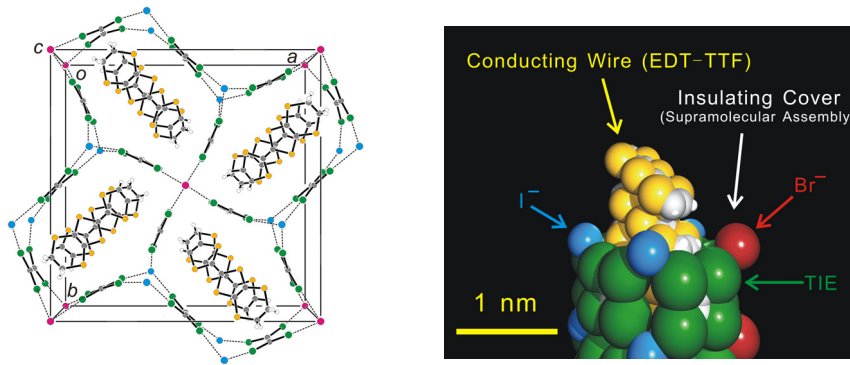


Figure 1 : Crystal structure of supramolecular nanowire  $(\text{EDT-TTF})_4\text{BrI}_2(\text{TIE})_5$ .

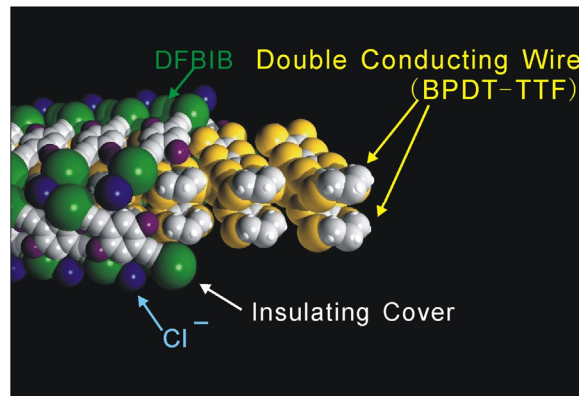


Figure 2 : Crystal structure of supramolecular nanowire  $(\text{BPDT-TTF})_2\text{Cl}(\text{DFBIB})_2$  which shows double strand structure of the nanowire.

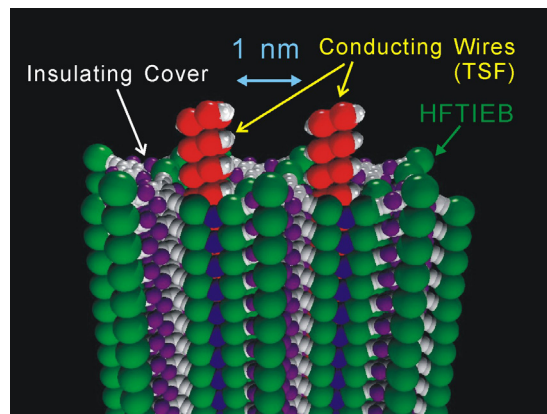


Figure 3 : Crystal structure of supramolecular nanowire  $(\text{TSF})\text{Cl}(\text{HFTIEB})$  in which the thickness of the insulating sheath is increased to 1 nm.

(EDT-TTF = ethylnedithiotetrathiafulvalene; TSF = tetraselenafulvalene; BPDT-TTF = bis(propylenedithio)tetrathiafulvalene; TIE = tetraiodoethylene; DFBIB = 2,5-difluoro-1,4-bis(iodoethynyl)benzene; HFTIEB = 2,2',4,4',6,6'-hexafluoro-3,3',5,5'-tetrakis(iodoethynyl)biphenyl)