Nanowires based on supramolecular assemblies formed by halogen bonding


We have already reported several nanowires where organic supramolecular insulting networks are sheathing conducting organic radical cations of TTF (tetrathiafulvalene) derivatives. In most cases, the sheath is formed by halogen bonding between halide ions and neutral molecule containing iodine atoms.

Enlargement of neutral molecules leads to thicker, and thus more insulting sheath. The most interesting issue of using enlarged neutral molecules is to solve the problem of the lattice defects. Indeed, it offers the possibility to obtain larger channel and thus “multiwires” in which several columns of conducting organic cations stay in the same sheath.

To the end, we have synthesized molecule 1 as a new material for insulating sheath. Crystal structure of 1 solved by X-ray analysis shows formation of vacant channels containing solvent molecules (Figure 1). 1 can be co-crystallized with alkylammonium salts to form supramolecular assemblies. In the case of Et₄NBr, the X-ray analysis clearly shows halogen bonding between 1 and bromide ions. In addition, Et₄N ions are surrounded by the supramolecular assembly. Although the twist conformation of 1 is the same as in the pristine crystal, the co-crystallized structure and especially the channel are different in shape and size. This shows flexibility from the packing of the neutral molecule and gives serious hopes of compatibility with TTF derivatives, which leads to the formation of new nanowires. Optimization of conditions for electrochemical crystallization with several TTF derivatives is in progress.

The synthesis of other similar iodine-containing molecules is also in progress. These molecules should lead to channel with different shape and size. The wide range of channel structures expected from these molecules should show different compatibility with different TTF derivatives and lead to unique nanowires.

Figure 1. Crystal structure of 1