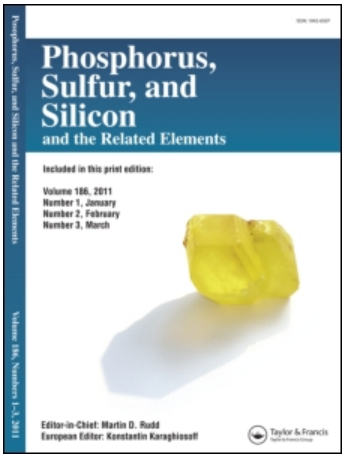

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Thiophene-fused DCNQI Derivatives: Their Copper Iodide Complexes as a New Family of Molecular Conductors

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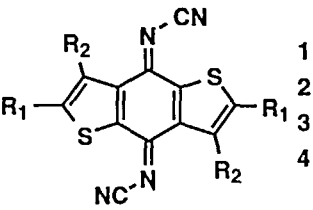
Organic sulfur compounds have played important roles in developing new organic materials. Recently we have reported that thiophene-fused DCNQI (DTQI)**1** forms a new family of highly conducting CuI complex.[1] However, all our attempts to grow a single crystal suitable for an X-ray analysis have been unsuccessful. The presence of the configurational isomers with respect to the =N-CN orientation was suspected to prevent the growth of a single crystal of **1**. Thus we have designed **2** and **3** that bear the substituents at β-position of the condensed thiophene rings; the β-substituents could fix the cyano-group on the opposite side of the substituent. We have also characterized compound **4** for comparison.



1: $R_1 = H, R_2 = H$
2: $R_1 = H, R_2 = Me$
3: $R_1 = H, R_2 = Br$
4: $R_1 = Br, R_2 = H$

Thiophene-fused DCNQI derivatives were prepared by the reaction of the precursor quinones with bis(trimethylsilyl)carbodiimide, following the procedure described by Hünig.[2] As anticipated, the NMR spectra of **2** were ascribed to only one isomer.

Cyclic voltamograms of all the new DTQI derivatives showed two reversible redox waves [**1**: $^1E_{1/2}$, $^2E_{1/2}$ = +0.08, -0.47; **2**: -0.04, -0.58; **3**: +0.12, -0.47; **4**: +0.22, -0.36 V vs. Ag/AgCl in benzonitrile].

The CuI complexes were prepared by diffusion method. DTQI derivatives and CuI were allowed to diffuse in an H-type glass cell and within a few weeks $(DTQI)(CuI)_2$ type of the complexes were formed as black fine crystalline powder. Only for $(\mathbf{2})(CuI)_2$

a single crystal suitable for X-ray analysis could be obtained.

The electrical conductivity of a single crystal of (**2**)$(CuI)_2$ was measured by four probe method to be 7.8×10^{-3} Scm^{-1} at room temperature and the temperature dependence revealed that this complex is a semiconductor with an activation energy of 0.18 eV. The other complexes were found to be semiconductors at room temperature [(**3**)$(CuI)_2$: 1.7×10^{-1} Scm^{-1}, (**4**)$(CuI)_2$: 8.2×10^{-2} Scm^{-1}].

The crystal structure was determined for (**2**)$(CuI)_2$. The structure is constituted of the zig-zag ladder chains of copper iodide polymers along the b-axis and the DTQI molecule bridges these polymers as a bidentate ligand by coordinating the terminal nitrogen atom to the copper atom. The acceptors are stacked in a face-to-face arrangement and an interplanar distance is 3.56 Å. The van der Waals contact is found between the iodine and the sulfur atoms (3.95, 4.01 Å). The most characteristic feature of this complex is a layered suprastructure in which the copper iodide layers and the organic layers are completely separated.

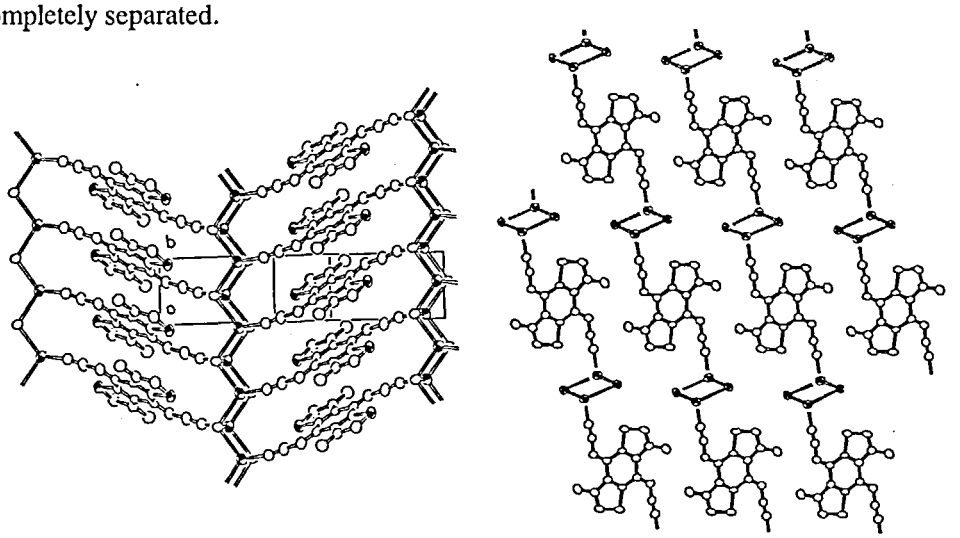


FIGURE 1 Crystal structure of (**2**)$(CuI)_2$

In conclusion, we have characterized the structure and electrical properties of the CuI complexes of new DTQI derivatives. These conducting complexes have layered suprastructure , being a completely different type of the DCNQI-based conductors.

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2. A. Aumüller and S. Hünig, *Angew. Chem. Int. Ed. Engl.*, **23**, 447 (1984).