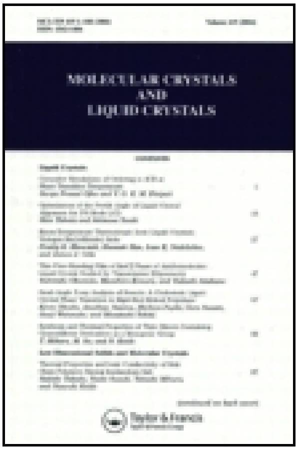

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CONDUCTING POLYNUCLEAR CuI COMPLEXES WITH THIOPHENE-FUSED DCNQI LIGANDS

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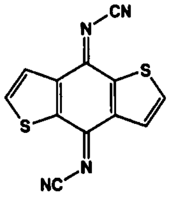
Abstract New derivatives of thiophene-fused DCNQI and their CuI complexes have been prepared. Among those, β,β'-dimethyl derivative (**2**) afforded a single crystal of complex ($\mathbf{2}$)$(CuI)_2$ suited for an X-ray analysis and its crystal structure has been determined. The structure is built up of the zigzag ladder of CuI polymer. Bidentate ligand molecules of **2** bridge the CuI ladders by coordinating the CN group to Cu of the ladder. The acceptor π–plane is arranged face-to-face with interplanar distance of 3.56Å. The room temperature conductivity of ($\mathbf{2}$)$(CuI)_2$ was 7.6×10^{-3} Scm^{-1} with semiconductive behavior in the temperature dependent conductivity.

INTRODUCTION

The radical anion salts of copper with N,N'-dicyanoquinodiimines (DCNQIs), particularly in the form of their 2,5-disubstituted benzoquinone derivatives, have aroused wide interest because of the discovery of molecular conductors with extremely high electrical conductivity in those.[1] In the $(DCNQI)_2Cu$ type of salts the π-acceptor molecules DCNQI are stacked along the tetragonal c axis, forming the one-dimensional pπ conduction bands. The copper atoms are tetrahedrally coordinated by the terminal nitrogen atoms of the N-cyano group in DCNQI molecules, so that one-dimensional DCNQI columns are connected three-dimensionally through Cu atoms.

As a structural modification of DCNQI acceptors we have recently prepared thiophene-fused DCNQI, which we designate as DTQI (**1**), and found that these acceptors form a new family of highly conducting complexes with copper (I) iodide represented as formula ($\mathbf{1}$)$(CuI)_2$.[2] Unfortunately, our attempts to grow a single crystal suitable for X-ray analysis were unsuccessful. In our further efforts in this direction we have prepared several new derivatives of DTQI and their CuI complexes. Among those, β,β'–dimethyl derivative (**2**) was found to form a single crystal for an X-ray analysis and its crystal structure could be determined. We describe herein the preparation and characterization of (**2**)$(CuI)_2$ along with those of a few other derivatives (**3**)$(CuI)_2$ and (**4**)$(CuI)_2$ derived also from thiophene-fused DCNQIs.



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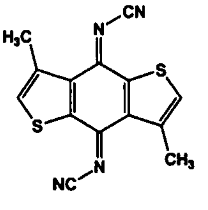

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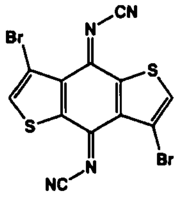

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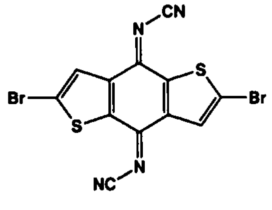

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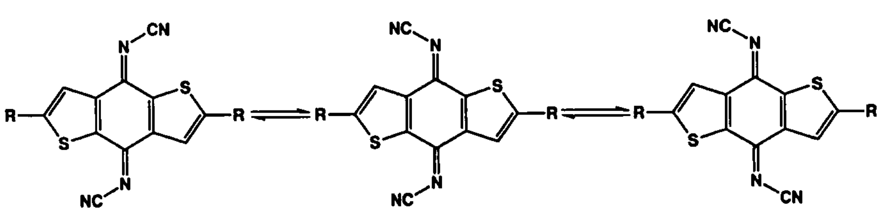
PREPARATION AND CHARACTERIZATION OF CuI COMPLEXES

It is thought that the failure to isolate a single crystal of (**1**)$(CuI)_2$ is attributed to the presence of configurational isomers with respect to the =N-CN orientation. In fact, the NMR spectra of the α–substituted DTQI derivative exhibited the presence of three isomeric species in a solution. These are ascribed to *syn-syn* and *anti-anti* and *anti-syn* configurational isomers, as depicted in Figure 1. These signals coalesced at about 90 °C, indicating fast inversion of the CN group in NMR time-scale. Thus the coexistence of the isomers in a solution is considered to prevent crystallization to form single crystals. Then we have designed DTQI derivatives that bear substituents at the β–positions of the condensed thiophene rings such as **2** and **3**. The β-substituents would exert buttressing effects to fix the CN group in opposite side of the substituent, yielding exclusively *syn-syn* comformers. For comparison, we have also prepared α–bromo derivative **4**.

The synthesis of the new DTQI derivatives has been carried out by the reaction of bis(trimethylsilyl)carbodiimide with the corresponding precursor quinones, by following the procedure described by Hünig.[3]



syn-syn *syn-anti* *anti-anti*

FIGURE 1 Three configurational isomers due to orientation of the CN groups in α–substituted thiophene-fused DCNQI.

The cyclic voltammograms of all the present DTQI acceptors exhibited two reversible redox waves. As shown in Table 1, the first-wave reduction potentials of bromo derivatives **3** and **4** relative to DTQI **1** are rather higher due to the electron withdrawing nature of bromine substituent.

TABLE I Data of Cycle Voltammograms[a] for DTQI derivatives.

compd.	**1**	**2**	**3**	**4**
$^1E_{1/2}$	+0.08	-0.04	+0.12	+0.22
$^2E_{1/2}$	-0.47	-0.58	-0.47	-0.36
ΔE	0.55	0.54	0.59	0.58

a in C_6H_5CN, V vs. Ag/AgCl

All the new acceptors afforded (DTQI)$(CuI)_2$ type of the complexes by the reaction with CuI in hot acetonitrile or acetonitrile/chlorobenzene. The compositions were confirmed by microanalysis. The complexes are quite stable; iodine is not lost upon heating up to 300 °C, which indicates that it is incorporated as a counter-anion of copper rather than as molecular iodine in an inclusion complex.

The electrical conductivities of these CuI complexes are listed in Table 2. The conductivities of (**2**)$(CuI)_2$ and (**4**)$(CuI)_2$ are lower than that of (**1**)$(CuI)_2$. In other words, DTQI itself afforded the CuI complex with an extremely high conductivity among this DTQI family. For (**2**)$(CuI)_2$, electrical conductivity measurements could be carried out on a single crystal by a two-probe method and the temperature dependent conductivities revealed that this complex is a semiconductor with an activation energy of 0.18 eV.

TABLE II Electrical Conductivities of CuI complexes (Scm^{-1}).

(**1**)$(CuI)_2$	(**2**)$(CuI)_2$	(**4**)$(CuI)_2$
45	7.6×10^{-3}	1.7×10^{-1}

CRYSTAL STRUCTURE OF (2)$(CuI)_2$

The crystal structure of (**2**)$(CuI)_2$ is shown in Figures 1 and 2. Crystal data are listed in Table III. The crystal is built up of the zigzag ladders of the CuI polymer parallel to the b axis, to which bidentate ligand molecules of **2** bridge by coordinating the N atom of the CN group to the copper atom. The π-acceptor molecules of **2** are stacked in face-to-face arrangement. The interplanar distance of 3.56 Å is longer than that of (dimethyl-DCNQI)$_2$Cu (3.217 Å).

The Cu---Cu distance in the ladder is 2.89 Å, being similar to that of (**1**)(CuI)$_2$ estimated by an EXAFS analysis for (**1**)(CuI)$_2$ and also to that of (MeNC)(CuI) determined by an X-ray analysis.[4] On the other hand, this distance is shorter than 3.88 Å in (DCNQI)$_2$Cu and rather close to that of copper metal (2.56 Å).[3] There are no short contacts smaller than the sum of the van der Waals radii between the ladder; The inter I---I distance is 4.18 Å and the S---I contacts are 3.95 Å and 4.01 Å.

TABLE III Crystal Data of (**2**)(CuI)$_2$

monoclinic	$P2_1/a$
a /Å	16.647(2)
b	4.1826(2)
c	12.8187 (15)
β /°	105.786(11)
V /Å^3	858.9(2)
Z	2
R	7.13
Rw	8.30

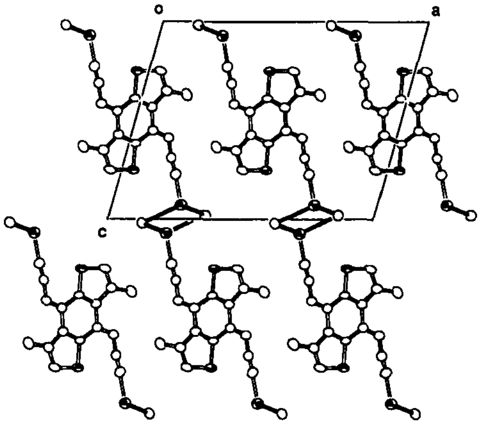


FIGURE 1 Crystal structure of (**2**)(CuI)$_2$ viewed along the b axis.

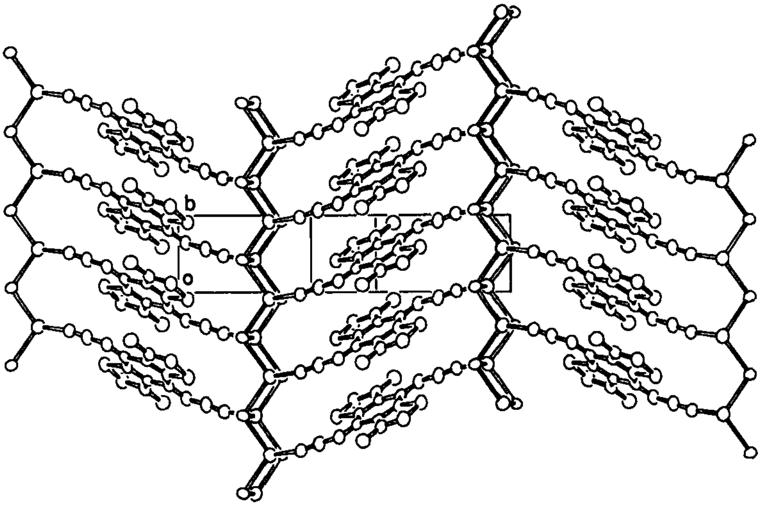
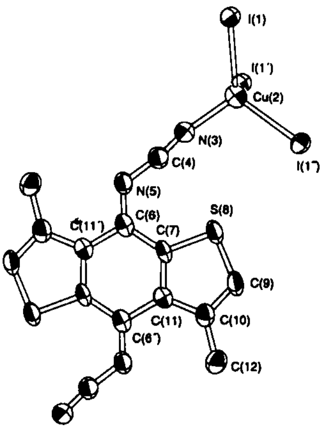


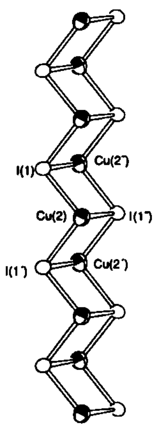
FIGURE 2 Crystal structure of (**2**)(CuI)$_2$, showing bridging of **2** molecules to the ladder of CuI.

The powder X-ray diffraction patterns of (**2**)$(\mathrm{CuI})_2$ is consistent with the structure determined from a single crystal (Figure 3). The characteristic feature is appearance of relatively sharp reflection at 2θ = 7.15° and its higher-order reflections. A set of these reflections affords a value of 12.35 Å for the basal spacing, corresponding to the inter-ladder distance. Thus the sharp reflections are attributed to the layers constructed of the side-by-side alignments of the CuI ladders. These observations characterize an interesting supuramolecular structure of (**2**)$(\mathrm{CuI})_2$: an organic-inorganic hybrid solid, in which the organic π-molecular layers and the inorganic CuI waving-layers of CuI are alternately piled up.

TABLE IV Selected interatomic distances (Å) and bond angles (°).

I(1)---Cu(2)	2.654(2)
I(1')---Cu(2)	2.673(2)
I(1")---Cu(2)	2.681(2)
Cu(2)---N(3)	1.960(13)
N(3)---C(4)	1.13(2)
N(5)---C(4)	1.33(2)
Cu(2)--Cu(2')	2.896(3)
Cu(2)--Cu(2")	2.899(3)
I(1)-Cu(2)-N(3)	115.0(4)
I(1)-Cu(2)-I(1')	103.47(8)
I(1)-Cu(2)-I(1')	114.61(9)
I(1')-Cu(2)-I(1'')	114.07(9)
Cu(2)-I(1")-Cu(2')	65.82(7)
Cu(2')-I(1")-Cu(2")	103.47(8)
I(1')-Cu(2)-N(3)	103.8(4)





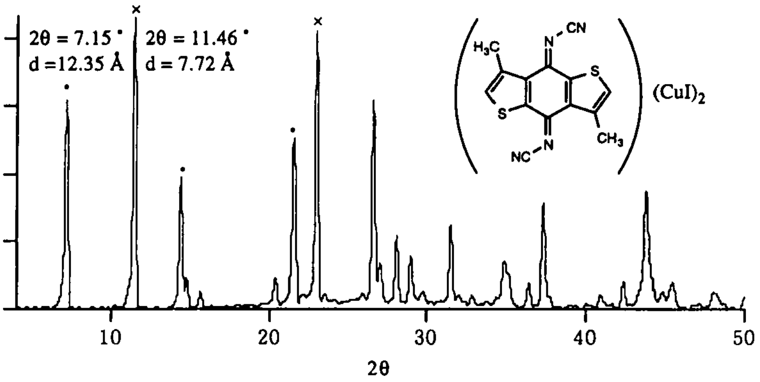


FIGURE 3 X-ray powder diffractions of (**2**)$(\mathrm{CuI})_2$

In summary we have found an entirely new type of conducting CuI complexes from structurally modified DCNQI compounds, i. e. thiophene-fused DCNQI (DTQI). At this stage the electrical-transport properties in (DTQI)$(CuI)_2$ type of the complexes cannot be deduced. Although there may be several possibilities, it seems most likely that charge transfer is slightly caused from the CuI ladder to the acceptor ligand (**2**) to produce the net positive charge in the CuI chain and hence it assists hole conduction along the CuI backbone. It is interesting to note that both the π-stacked organic columns and the inorganic CuI chains could transport electricity in these newly introduced complex of DCNQI family.

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