

New Insight into the Nature of Cu(TCNQ): Solution Routes to Two Distinct Polymorphs and Their Relationship to Crystalline Films That Display Bistable Switching Behavior

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Syntheses and characterization of two polymorphs of Cu(TCNQ) have been carried out and the results correlated to films of the materials. Reactions of CuI with TCNQ or [Cu(CH₃CN)₄][BF₄] with TCNQ⁻ lead to blue-purple needles of Cu(TCNQ) phase I (**1**). A slurry of this kinetic product in CH₃CN yields a second crystalline phase of Cu(TCNQ), phase II (**2**), which exhibits a platelet morphology. Powder X-ray diffraction and scanning electron microscopy data revealed that both phases are present in films of Cu(TCNQ) formed by oxidation of Cu foil by TCNQ in CH₃CN. X-ray photoelectron spectra of the two phases are indistinguishable from each other and are indicative of the presence of Cu(I). Single-crystal X-ray studies were undertaken on very small crystals of the two samples, the results of which reveal that subtle geometrical changes for the nitrile arrangements around the four-coordinate Cu(I) centers lead to major changes in the architectural framework of the polymers. Phase I was indexed in the tetragonal crystal system, but due to disorder and twinning, the crystal diffracted to only ~40° in 2θ. The data were solved and refined in the monoclinic *Pn* space group. The polymeric motif consists of Cu atoms surrounded by four nitrile lone pairs of independent TCNQ⁻ molecules arranged in a distorted tetrahedral geometry. A quadruply twinned crystal of Cu(TCNQ) phase II was indexed in the monoclinic system and resolved by deconvolution methods. The Cu(I) ions in phase II occupy the tetrahedral positions of a Cooperite structure (PtS), and the TCNQ⁻ radicals occupy the square planar sites. In both phases there are two interpenetrating lattices present. In phase I the TCNQ⁻ units are involved in close π -stacking interactions at ~3.24 Å whereas in phase II the closest approach of the rings is ~6.8 Å. In qualitative agreement with these observations are the magnetic properties; **1** is essentially diamagnetic and **2** displays Curie–Weiss behavior down to very low temperatures. The charge-transport properties of the samples revealed that, while they are both semiconductors, **1** is a good semiconductor with a room-temperature conductivity of 0.25 S cm⁻¹ and a band gap of 0.137 eV whereas **2** is a very poor semiconductor with $\sigma(\text{rt}) = 1.3 \times 10^{-5}$ S cm⁻¹ and a band gap of 0.332 eV. Cu(TCNQ) film devices have been found to switch between two states that exhibit very similar conducting properties.

Introduction

The use of soluble transition metal coordination complexes as precursors to materials is a rapidly expanding area of inorganic chemistry, rich in structural diversity and potential applications.^{1–4} Topological arguments that take into consideration the geometrical preferences of the metal and ligand building blocks have allowed chemists to design new molecular

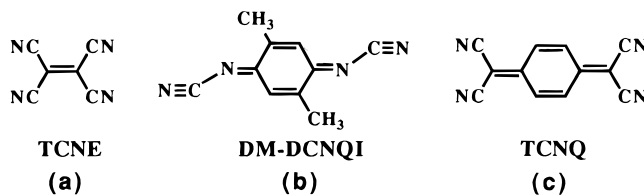


Figure 1. Organonitrile acceptor molecules used as ligands in metallopolymers.

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solids, including novel porous,² magnetic,³ and conducting⁵ materials. Among the compounds in the latter category are charge-transfer solids composed of metal complexes and the radical forms of the organonitrile acceptors depicted in Figure 1.^{4,5} The most well-investigated of these hybrid inorganic/organic materials are the binary, mixed-valence compounds

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Cu(2,5-R₂-DCNQI)₂ (DCNQI = dicyanoquinodimimine) (Figure 1b).⁵ These metallopolymers exhibit unusually high, anisotropic conductivities that are attributed not only to the columns of stacked DCNQI radicals formed by interpenetrating networks but also to the interaction of the d orbitals of the metal with the p orbitals of the diimine bridge.

In considering the remarkable properties exhibited by copper DCNQI polymers, we were reminded of a class of intriguing metal complexes of 7,7,8,8-tetracyanoquinodimethane (TCNQ) first reported in 1962. From the perspective of metal complexation, the main difference between DCNQI and TCNQ is that TCNQ is capable of behaving as a tetradentate as well as a bidentate bridging ligand, which allows it to form products with both 1:1 and 1:2 metal:TCNQ ratios.^{4a,c-h,j,m-p,6} The 1:1

materials of Ag and Cu are the subject of intense interest due to the fact that crystalline films of these compounds undergo electric-field-induced bistable switching under certain conditions.⁸⁻²² Despite extensive efforts to understand these materials, however, this phenomenon remains somewhat of an enigma, and it continues to be the source of debate in the literature. One of the crucial issues to be resolved is the source of conflicting data regarding the electrical behavior of Cu(TCNQ), a material that has received much scrutiny in the metal/acceptor thin film community. Independent findings of several groups suggest that the physical appearance of the crystalline films is highly dependent on film preparation conditions.^{15,19,20a,b,21,22} Surprisingly, despite these observations, no X-ray data have been published on these samples. Recently, two powder patterns of a film grown on a Cu substrate from 1-bromohexadecane/TCNQ solutions and on a film prepared by vapor deposition of TCNQ on a Cu surface at 240 °C were reported, but these samples do not physically resemble those that undergo switching.^{20a}

In this paper we report data that lend new insight into the nature of the elusive Cu(TCNQ) material. Specifically we have discovered that there are two distinct polymorphs of Cu(TCNQ). These two phases can be synthesized via solution reactions of Cu(I) precursors with TCNQ⁻ anions or by direct redox reactions of Cu(0) with neutral TCNQ. The characterization of these two phases by powder X-ray diffraction, single-crystal X-ray crystallography, infrared spectroscopy, conductivity, magnetism, and X-ray photoelectron spectroscopy is described. Finally, a comparison of the properties of the two phases to various films of Cu(TCNQ) described in the literature over the

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past 20 years is discussed in light of the new-found knowledge that all the films being compared to each other are not the same material.

Experimental Section

A. General Considerations. The reactions were carried out under an argon atmosphere unless otherwise indicated. Acetonitrile was dried over 3 Å molecular sieves and distilled under an atmosphere of N₂ prior to use. The TCNQ was purchased from TCI Chemical Company. The salts [Bu₄N][TCNQ]^{23a} and [Cu(MeCN)₄][BF₄]²⁴ were prepared according to the literature methods. Single-crystal X-ray data were obtained on a Siemens (Bruker) SMART 1K CCD area detector instrument with a Mo anode. Powder X-ray data were collected using a Rigaku RU200B X-ray powder diffractometer with Cu Kα radiation. The variable temperature magnetic susceptibility data were collected in the range 5–300 K using a Quantum Design model MPMS SQUID magnetometer housed in the Physics & Astronomy Department at Michigan State University. Infrared spectra were recorded in Nujol on KBr plates using a Nicolet IR/42 FT-IR spectrometer. X-ray photoelectron spectral data were obtained on a PHI 5400 instrument with a Mg source in the Composite Materials and Structures Center at Michigan State University. Scanning electron microscopy measurements were performed on a JEOL 6400V instrument with a LaB₆ gun housed in the Center for Electron Optics at Michigan State University.

B. Bulk Syntheses of Cu(TCNQ) (Phase I) (1). (a) Method A. CuI (0.95 g, 5 mmol) was added to 150 mL of a hot acetonitrile solution of TCNQ and stirred for 3 min.^{23a} The dark blue microcrystalline product that formed was separated from a brown solution by filtration, washed with copious amounts of acetonitrile, and dried in vacuo: yield 1.22 g, 91%. Anal. Calcd for C₁₂H₄N₄Cu: C, 53.83; H, 1.51; N, 20.93; Found: C, 53.46; H, 1.39; N, 20.57. Characteristic IR data (Nujol mull, KBr plates, cm⁻¹): ν(CN), 2199 s, br; 2172 sh; δ(C–H), 825 s.

(b) Method B. A quantity of [Bu₄N][TCNQ] (0.500 g, 1.12 mmol) was dissolved in 50 mL of acetonitrile to give a green solution, which was added to a solution of [Cu(MeCN)₄][BF₄] (0.352 g, 1.12 mmol) dissolved in 20 mL of acetonitrile. Upon mixing, a color change to dark blue occurred with the deposition of a dark blue microcrystalline solid. The solid was collected by filtration, washed with acetonitrile, and dried in vacuo to give 0.265 g (88% yield) of a dark blue solid whose X-ray pattern is identical to that of the product obtained in method A.

C. Bulk Synthesis of Cu(TCNQ) Phase II (2). A quantity of acetonitrile (20 mL) was added to 0.300 g of phase I. The resulting suspension and light green solution was stirred at room temperature for 4 days, after which time the solvent was removed in vacuo and the resulting dark blue solid dried in vacuo. The solution can also be heated to reflux for 3 h to hasten the conversion process. Both methods lead to virtually quantitative conversion of phase I to phase II as judged by X-ray powder diffraction and infrared spectroscopy. Anal. Calcd for C₁₂H₄N₄Cu: C, 53.83; H, 1.51; N, 20.93; Found: C, 53.68; H, 1.33; N, 20.85. Characteristic IR data (Nujol mull, KBr plates, cm⁻¹): ν(CN), 2211 s; 2172 s; δ(C–H), 825 s.

D. Thin Film Experiments. Cu(TCNQ) thin films were prepared by a method similar to ones described in the literature.⁸ Rectangular pieces of copper foil were cleaned mechanically and then chemically with a dilute H₂SO₄ solution and washed with water followed by acetone in an N₂ atmosphere. The dipping experiments were conducted in an N₂-purged glovebag in a two-compartment, fritted reaction vessel that contained a saturated CH₃CN solution of TCNQ. To avoid contaminating the Cu(TCNQ) films with solid TCNQ, the copper pieces were placed in a glass thimble with a coarse glass frit at one end and carefully

arranged such that copper surfaces did not touch. The thimble was lowered into the TCNQ saturated solution, and the reaction vessel was sealed with a ground glass stopper. Upon contact with the solution, black-purple films were observed to appear on the exposed copper surfaces. At periodic, timed intervals the reaction vessel was opened to retrieve one of the copper pieces, which was then washed with acetonitrile, dried, and placed in a vial under anaerobic conditions for later analysis.

E. X-ray Crystallography. (a) Cu(TCNQ) Phase I. A typical needle crystal of dimensions 0.25 × 0.02 × 0.02 mm was mounted on the end of a glass fiber with silicone grease. A hemisphere of data was collected at -100 ± 2 °C on a Siemens SMART 1K CCD area detector diffractometer by Dr. Victor Young at the University of Minnesota. The original data were integrated in the tetragonal cell setting $a = b = 11.266(2)$ Å, $c = 3.8878(8)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 493.47(17)$ Å³, but the structure was ultimately solved in the lower symmetry monoclinic space group Pn with $a = 3.8878(8)$ Å, $b = 11.266(2)$ Å, $c = 11.266(2)$ Å, and $\beta = 90.00(3)^\circ$ and refined as disordered and pseudomerohedrally twinned. The 3 × 3 twinning matrix [1 0 0, 0 0 1, 0 -1 0] was used to model the pseudo-4-fold rotation.

(b) Cu(TCNQ) Phase II. A typical crystal of dimensions 0.13 × 0.13 × 0.01 mm was mounted on the tip of a glass fiber with the use of silicone grease. A full sphere of data was collected at -100 ± 2 °C on a Siemens SMART 1K CCD area detector diffractometer. A total of 253 strong reflections were extracted with the SMART index routine, but this failed to give a reasonable cell. The solution was obtained by the use of programs in the TWINNING package written by R. Sparks.²⁵ The program TWINDX was used to index four monoclinic cells with $a = 5.3337(8)$ Å, $b = 5.3312(8)$ Å, $c = 18.875(3)$ Å, $\beta = 94.036(3)^\circ$, and $V = 535.38(14)$ Å³. By running the TWROT program, we obtained the twinning law matrix [0 -1 0, 1 0 0, 0.25 0.25 1]. Application of the matrix to one of the twinned cells transforms it into one of the other three cells. The reflection data were integrated, and four separate data sets were produced. The TWHKL program was modified by Dr. Robert Sparks to generate reflection data from the four data sets obtained from the twins, but the refinement was unstable. An alternative method was then used to generate the reflection data from one of the twinned sets of data according to the twinning law [0 -1 0, 1 0 0, 0.25 0.25 1]. Reflections from twinning component 1 are related to the three others according to the following conditions: When $h - k = 4n$, twin component 2 has the conditions $h' = k$, $k' = -h$, $l' = (h - k)/4 + 1$. When $h = 2n$, twin component 3 has the conditions $h'' = -h$, $k'' = -k$, $l'' = h/2 + 1$. Finally, when $h + k = 4n$, twin component 4 has the conditions $h''' = -k$, $k''' = h$, $l''' = (h + k)/4 + 1$. A FORTRAN routine was written to remove the partial overlap conditions and to generate the SHELX HKLF 5 format reflection data for refinement.

Results and Discussion

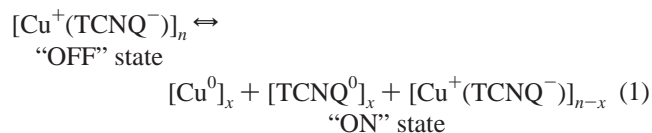
A. Phenomenon of Bistable Switching in Cu(TCNQ) Films. (a) Electrical and Optical Switching. To appreciate the interest in the structure of Cu(TCNQ), it is important to be aware of the literature regarding the behavior of this and related materials. Nearly 20 years ago, it was reported that the application of an electric field to a device consisting of a thin film of Cu(TCNQ) (5–20 μm) sandwiched between a Cu and an Al electrode induces a switching of the material from a high- to a low-resistance state at a critical threshold potential.⁸ The device displays a memory effect in that it remains in the low-resistance state (“ON” state) for a short period of time in the absence of an applied field. The time required for the device to return to the high-resistance state (“OFF” state) was reported to depend on the film thickness, the duration of the applied electric field, and the amount of power dissipated in the sample while in the low-resistance state.⁹ The original mechanism proposed by Potember et al., the discoverers of this phenomenon,

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(24) The method of Kubas (Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90) was used with the modification that 45–50% HBF₄ was used instead of 60–65% HPF₆.

(25) TWINDX, TWROT, and TWHKL are components of the TWINNING program written by Dr. Robert Sparks, private communication.

is given in eq 1.⁸ The reaction is written to denote that a nonstoichiometric Cu phase is produced along with neutral TCNQ and Cu⁰ to yield a mixed-valence film. In the “switched” state, it is argued that the repulsion of charge carriers is lowered by the availability of empty molecular orbitals on neutral TCNQ for conduction electrons, as opposed to the situation when an electron is moved from one TCNQ⁻ radical to another radical anion TCNQ⁻.^{9b}



Numerous techniques including Raman, infrared, Auger, and X-ray photoelectron spectroscopies have been used to probe the electronic state of the TCNQ molecule in the films. The data from these studies led to the general conclusion that neutral TCNQ is generated during the switching process.⁹ Similar electronic changes in the films can be optically induced at low irradiance levels to effect a color change from dark purple to yellow, signaling the conversion of the intensely colored TCNQ⁻ radical to TCNQ⁰.^{9a,c,11} The phototransformation produces a mixed-valence state that is spectroscopically similar to the state achieved during the electric-field-induced switching.¹² Higher irradiance levels produce local areas of macroscopic quantities of neutral TCNQ which can be used to generate high optical contrast patterns directly on the film.¹¹

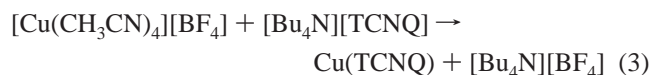
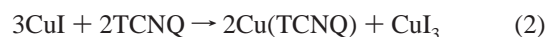
In addition to films with TCNQ, Cu and Ag devices with other acceptors such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄), 2,5-dimethoxy-7,7,8,8-tetracyanoquinodimethane (TCNQ(OMe)₂), 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP), and tetracyanoethylene (TCNE) have also been observed to switch.^{9a,15,16} The critical electric field strengths required to convert these devices from the high- to the low-resistance states are directly related to the relative reduction potentials of the various electron acceptors; devices with the more powerful acceptors such as TCNQF₄ require higher electric field strengths to switch compared to devices made with weaker electron acceptors such as TCNQ(OMe)₂. Thin films that incorporate TCNQF₄ exhibit a substantial memory effect, in that the material remains in the low-resistance state for a long time after the electric field has been removed. In sharp contrast, devices made with TCNQ(OMe)₂ return to the high-resistance state immediately after the electric field is removed.^{9a,15} These marked variations in physical properties with relatively subtle infrared spectral and optical changes in the materials illustrate the advantage of these metal/organic materials over conventional solid-state materials that cannot be easily tailored.

(b) The Controversy. Despite the extensive effort devoted to understanding the electrical switching of Cu(TCNQ) thin films, there remains skepticism regarding the validity of the mechanism as represented by eq 1. It has been suggested by some researchers that the electrical switching behavior is related not to changes in the bulk sample, but rather to the formation of channels created from the contact of the aluminum electrode with the irregular surface of the Cu(TCNQ) films.^{17–19} Others have argued that interfacial phenomena must be involved because the physical properties of the Cu(TCNQ) devices exhibit a high degree of variability from one study to another. For example, Potember et al. reported that their Cu(TCNQ) devices do not exhibit a dependence on the polarity of the applied potentials; in sharp contrast, a device prepared by Sato et al. showed polarized memory effects.¹⁸

After reviewing the body of literature on the subject, one is led to suspect that subtle changes in the Cu(TCNQ) film preparation could account for the differences in electrical properties of the devices. Indeed modifications of the synthetic conditions (e.g., solvent, reaction time, temperature) have been noted to result in morphology differences of the Cu(TCNQ) films produced on copper surfaces, but unfortunately only a few researchers have actually published SEM images of their films.^{15,19,20a,b,21,22} A recent SEM investigation by Hipps et al. revealed that a progression from a needle morphology to a mosaic platelike material was occurring with longer dipping times. An independent study by Zhu and co-workers demonstrated that major physical variations are evident in films prepared in different solvents.^{20a} On the basis of the SEM micrographs that have appeared in this² and earlier papers, it is obvious that a needlelike morphology dominates in films grown by dipping Cu substrates in CH₃CN solutions of TCNQ for short periods of time at elevated temperatures; longer reaction times lead to a degradation of these crystals and the formation of a phase or phases with a mosaic appearance. Minor differences are observed when the concentration of TCNQ in CH₃CN solutions was varied and the temperature was kept constant.

B. Synthetic Methods and Powder X-ray Characterization of Cu(TCNQ). After we reviewed the aforementioned data, it appeared obvious to us that there are two different forms of Cu(TCNQ). We therefore posed the question, “What are the structures of the two polymorphs of Cu(TCNQ), and how do they relate to the intrinsic properties of the materials?” To answer this question, it was necessary to prepare bulk samples of both materials and fully characterize them by conventional techniques.

(a) Bulk Synthesis of Phase I. Two methods were used to prepare bulk samples of Cu(TCNQ) (1), and the products were compared to the well-investigated phase first reported by Melby et al. in 1962 (eq 2).^{23a} In this method, TCNQ is reduced in situ by CuI, which leads to the immediate formation of Cu(TCNQ) as blue-black microcrystals and I₂ as a byproduct (eq 2). The I₂ is trapped by excess CuI to form I₃⁻, thus avoiding any side reactions with I₂. The second method, which is new, follows from our interest in the use of acetonitrile-solvated transition metal cations as useful starting materials in nonaqueous substitution reactions.²⁶ In the reaction depicted in eq 3, acetonitrile solutions of (Bu₄N)TCNQ and Cu(CH₃CN)₄(BF₄) are combined to give Cu(TCNQ) as a dark blue precipitate with [Bu₄N][BF₄] as the byproduct. A variety of characterization tools



including X-ray powder diffraction (vide infra) support the conclusion that the products of the reactions in eqs 2 and 3 (hereafter referred to as phase I) are the same material, except that the product of the CuI reaction is typically more crystalline as judged by the intensity of the powder patterns and by SEM. We were curious as to whether a different product could be obtained by the use of the Cu(II) starting material Cu^{II}(CH₃CN)₄(BF₄)₂. As depicted in eq 4, the products are Cu^I(TCNQ)

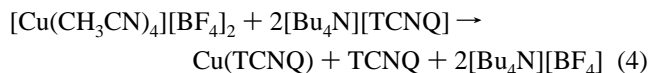
- (26) (a) Dunbar, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8247. (b) Dunbar, K. R.; Pence, L. E. *Inorg. Chem.* **1991**, *30*, 2018. (c) Bartley, S. L.; Bernstein, S. N.; Dunbar, K. R. *Inorg. Chim. Acta* **1993**, *213*, 213–231. (d) Dunbar, K. R. *Comments Inorg. Chem.* **1992**, *13*, 313–357. (e) Dunbar, K. R. *J. Cluster Sci.* **1994**, *5*, 125–144.

Table 1. IR and XPS Data for Cu(TCNQ) and Cu(DM-DCNQI)₂

	IR		XPS BE ^a (eV): Cu 2p _{3/2} , 2p _{1/2} ; N1s	XPS refs
	$\nu(\text{C}\equiv\text{N})$ (cm ⁻¹)	$\delta(\text{C}-\text{H})$ (cm ⁻¹)		
Cu(TCNQ)				
phase I needles ^b	2199 s, br; 2172 s	825 s	932.0, 951.9; 398.7	this work
phase II platelets ^c	2211 s, 2172 s	825 s	932.1, 952.0; 398.7	this work
Cu(TCNQ) ^b	2200 s, 2170 s ^d	826 s	931.2, 951.0; 398.1	28
Cu(DM-DCNQI) ₂	2139 w		931.6, 933.6 943, 962	30

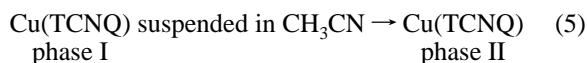
^a Binding energy. ^b CuI + TCNQ synthesis method of Melby et al., ref 23a. ^c Synthesis method in section B(b) of the Experimental Section B. ^d Data from ref 31a.

and neutral TCNQ and not Cu^{II}(TCNQ)₂ as one might have predicted. This is in accord with results reported for the reaction



of Cu^{II}SO₄ with LiTCNQ in H₂O, which gives an unstable green powder that is occasionally written as Cu(TCNQ)₂^{23a} but which is actually Cu^I(TCNQ⁻)(TCNQ⁰) with trapped TCNQ⁰ as established by Raman, XPS, and IR spectroscopies.^{23b-d} Our results from the reaction performed in CH₃CN indicate that Cu^{II}(TCNQ)₂ is not stable under nonaqueous conditions either. An important difference between the aqueous versus the nonaqueous reaction is that the Cu(TCNQ) material retains the neutral TCNQ molecule as part of the formula due to the insolubility of neutral TCNQ in H₂O. TCNQ is soluble in CH₃CN, however, and therefore remains in solution in our reaction. The characteristic yellow color of the acetonitrile filtrate and the $\nu(\text{C}\equiv\text{N})$ stretch at 2222 cm⁻¹ are convincing evidence that the byproduct is neutral TCNQ.²⁷

(b) Conversion of 1 to 2 in Acetonitrile. In the course of preparing Cu(TCNQ) by the reactions given in eqs 2 and 3, we made an unexpected observation. We discovered that if suspensions of phase I are stirred in CH₃CN at room temperature for several days or if the reaction solution is refluxed for several hours, a second phase, 2, is produced in essentially quantitative yields. This was quite surprising to us as we had observed that phase I can be heated in the solid state at 150 °C for 2 days in air or exposed to air and ambient light for weeks with no loss of integrity as evidenced by X-ray powder diffraction and IR spectroscopy. Clearly, acetonitrile is capable of dissolving phase I into its constituents, i.e., Cu(I) and TCNQ⁻ ions, which then recombine to give a different phase with concomitant physical changes that can be monitored.^{19,20a,22} This conversion produces a hitherto unknown (or unrecognized) bulk form of Cu(TCNQ) (eq 5) which is stable with respect to further changes under forcing thermal conditions in the solid state or in solution.



C. Spectroscopic Studies. Pertinent data for phase I and phase II of Cu(TCNQ) are summarized in Table 1. An interpretation of these data is provided in the following sections.

(a) X-ray Photoelectron Spectroscopy. The 1:1 ratio of Cu to TCNQ in the material does not necessarily connote that complete charge transfer between the metal and the acceptor has occurred; thus it is important to probe the oxidation state

(27) We note that it is not cost effective to use a Cu(II) starting material to prepare Cu(TCNQ) because it consumes Bu₄N(TCNQ) as a reducing agent and the product is not as pure as the compound obtained from either of the other two methods, as judged by X-ray powder diffraction techniques.

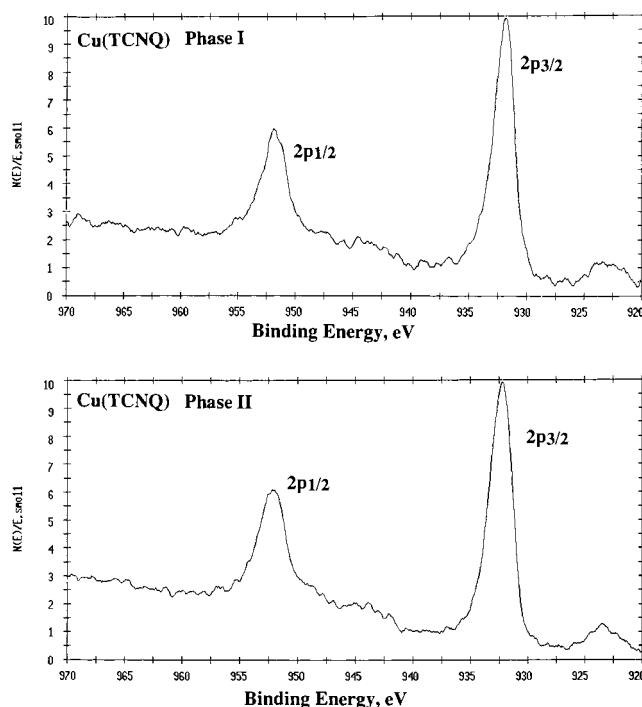


Figure 2. XPS data in the Cu 2p_{3/2} and 2p_{1/2} regions for phase I and phase II Cu(TCNQ).

of the metal in the Cu(TCNQ) phases. One method that is useful in this regard is X-ray photoelectron spectroscopy (XPS). In earlier reports, XPS data of Cu(TCNQ) prepared from CuI revealed characteristic binding energies for Cu(I) 2p_{1/2} and 2p_{3/2}^{9,b,d,28} with no evidence for shoulders or higher binding energy satellites that could be attributed to Cu(II).²⁹ Likewise, XPS data for compounds 1 and 2 prepared in our laboratories gave essentially identical results in accord with Cu(I). Data from the present work as well as earlier papers are presented in Table 1. The 2p_{3/2} and 2p_{1/2} signals are depicted in Figure 2. Both phases exhibit essentially identical binding energies for the Cu 2p orbitals, with no evidence for shoulders or satellites due to Cu(II). Likewise, the N1s orbitals appear as a single feature at 398.7 eV in both phases, which is indicative of one type of TCNQ. Mixtures of TCNQ⁻ and TCNQ can be readily discerned in this region.²⁸ The ease with which Cu(II) can be observed in bona fide mixed-valence Cu^I/Cu^{II} compounds and materials is illustrated by a comparison of the data for chemically prepared Cu(TCNQ) with electrochemically prepared Cu(DCNQI)₂ materials. For example, the mixed-valence metallic Cu(DM-DCNQI)₂ shows two sets of Cu 2p_{1/2} and 2p_{3/2} (931.6, 933.6 eV) signals and a more obvious second set of satellite features

(28) Ikemoto, I.; Thomas, J. M.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2237.

(29) Brant, P.; Fernando, Q. *J. Inorg. Nucl. Chem.* **1978**, *64*, 45.

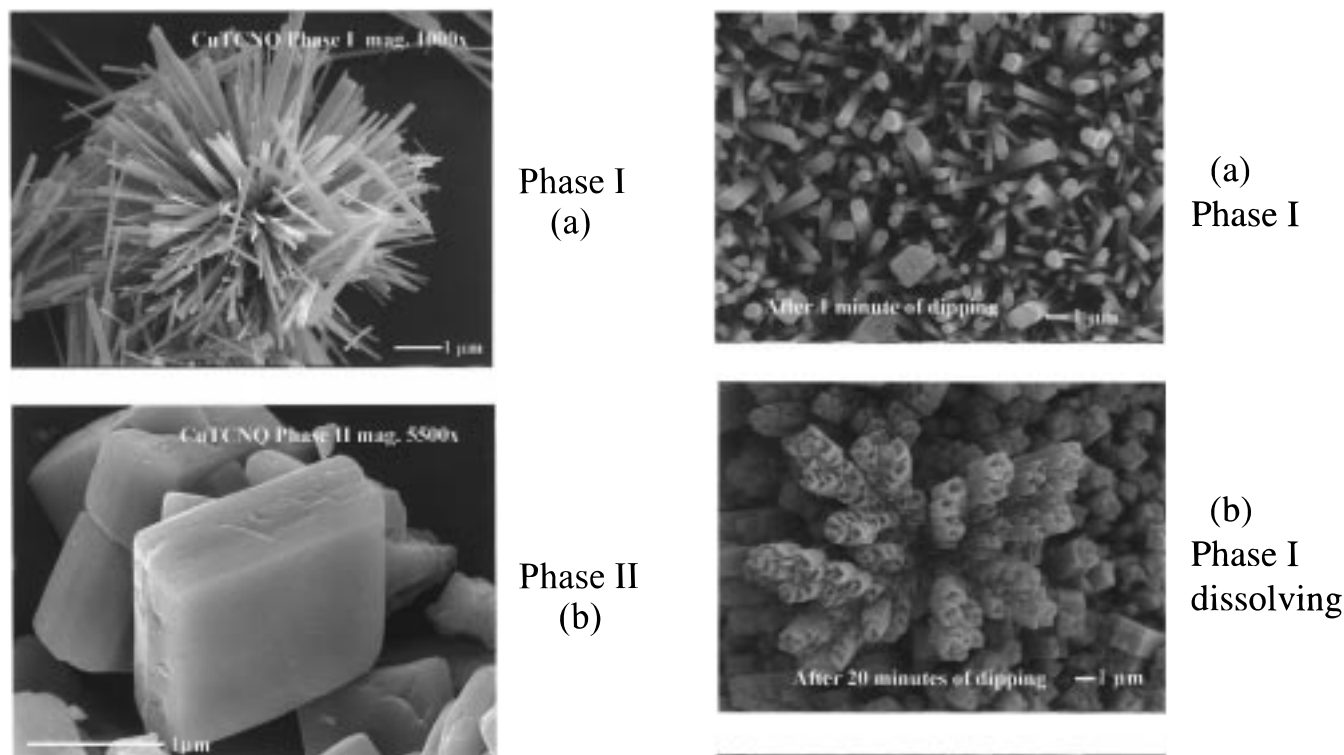


Figure 3. Scanning electron micrographs for solution-prepared samples of phase I and phase II Cu(TCNQ) ($1 \mu\text{m}$ resolution).

at 943 and 962 eV, characteristic of paramagnetic Cu(II).^{30a} As further support for the lack of Cu(II) in our TCNQ samples we undertook XPS measurements of the nitrile salts $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ and $[\text{Cu}^{\text{II}}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ as references. Although they were rather unstable under the vacuum conditions, the Cu(II) salt gave four different signals in the Cu 2p region whereas the Cu(I) analogue reveals only two features. We take these data as convincing evidence that Cu(II) is not present in our samples to any appreciable degree. This conclusion is in contrast to data obtained for electrochemically prepared samples reported by Willett and co-workers which point to the presence of both Cu(I) and Cu(II) species.^{30c}

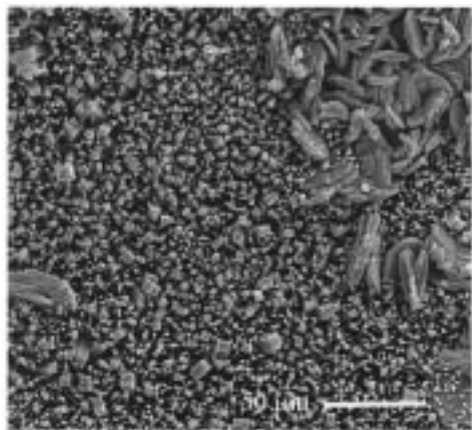
(b) Infrared Spectroscopy. Infrared spectroscopy is a useful tool for characterizing TCNQ materials, in particular for discerning the oxidation state of the molecule in its charge-transfer salts.³¹ Infrared spectra of the two phases of Cu(TCNQ) are quite similar as would be expected on the basis of their formulations as compounds of TCNQ^- .^{4f} No peaks associated with acetonitrile were observed in either phase. Compound **1** shows a strong, broad $\nu(\text{C}\equiv\text{N})$ absorption at 2199 cm^{-1} with a shoulder at 2172 cm^{-1} whereas **2** exhibits two strong, sharp stretches at 2211 and 2172 cm^{-1} . Perhaps even more indicative

Figure 4. Scanning electron micrographs of Cu(TCNQ) films grown on copper in CH_3CN at 60°C for (a) 1 min, (b) 20 min, and (c) 1 h emphasizing the conversion of phase I to phase II ($1 \mu\text{m}$ resolution).

of the similarity of the TCNQ unit in the two phases is the $\delta(\text{C}-\text{H})$ mode at 825 cm^{-1} , which is very sensitive to changes in oxidation state. These data are consistent with the presence of TCNQ^- and not TCNQ , TCNQ^{2-} , or mixed-valence stacks of TCNQ^- and TCNQ .³⁰ Furthermore, they are in accord with previously reported IR data for samples of **1** prepared by the original CuI method.^{10,30a} Since the existence of a second phase was unknown until the present work, there are no data with which to compare phase II, **2**.

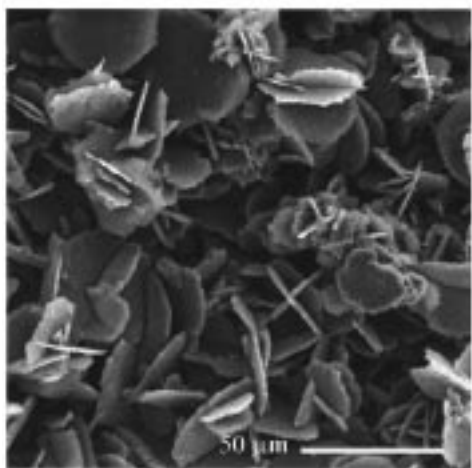
D. Structural Studies. (a) SEM Studies. Scanning electron microscopy was used to discern morphologies of the bulk Cu(TCNQ) samples in this study, and the results were compared to films of the material. It is evident from the micrographs depicted in Figure 3a,b that the two bulk phases are physically quite different. Phase I (**1**) is composed of regular needles whereas phase II (**2**) consists of crystallites with a platelet morphology. The same two crystallite types have been reported to appear during the growth of Cu(TCNQ) films from acetonitrile solutions.^{19,20a,22} If one compares these observations to Cu(TCNQ) grown as films on Cu substrates, it is obvious that the phase with densely packed needles oriented perpendicular to the Cu surface appears immediately and survives only during short dipping times at 60°C (Figure 4a).^{19,20a} Within 20 min, the needles become visibly pitted (Figure 4b), and after 1 h

- (30) (a) Kobayashi, A.; Kato, R.; Kobayashi, H.; Mori, T.; Inokuchi, H. *Solid State Commun.* **1987**, *64*, 45. (b) Yoshihiro, Y.; Furukawa, Y.; Kobayashi, A.; Tasumi, M.; Kato, R.; Kobayashi, H. *J. Chem. Phys.* **1994**, *100*, 2449. (c) Willett, R. D.; Long, G. Personal communication.
- (31) (a) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 539. (b) Inoue, M. B.; Inoue, M.; Fernando, Q.; Nebesny, K. W. *J. Phys. Chem.* **1987**, *91*, 527. (c) Inoue, M.; Inoue, M. B. *Inorg. Chem.* **1986**, *25*, 37. (d) Pukacki, W.; Pawlak, M.; Graja, A.; Lequan, M.; Lequan, R. M. *Inorg. Chem.* **1987**, *26*, 1328. (e) Farges, J. P.; Brau, A.; Dupuis, P. *Solid State Commun.* **1985**, *54* (6), 531. (f) Chappell, J. S.; Bloch, A. N.; Bryden, A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442. (g) Van Duyne, R. P.; Suchanski, M. R.; Lakovits, J. M.; Siedle, A. R.; Parks, K. D.; Cotton, T. M. *J. Am. Chem. Soc.* **1979**, *101*, 2832. (h) Lunelli, B.; Pecile, C. *J. Chem. Phys.* **1970**, *52*, 2375. (i) Bozio, R.; Girlando, A.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1237.



(a)

CuTCNQ film after one hour dipping at 60 °C



(b)

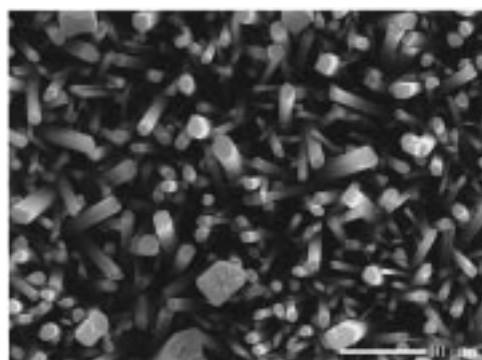
CuTCNQ film after one hour dipping at 80 °C

Figure 5. Scanning electron micrographs of Cu(TCNQ) films grown on copper in CH₃CN (a) at 60 °C for 1 h and (b) at 80 °C for 1 h that emphasize bulk differences in film morphology and size of crystallites (50 μm resolution).

(Figure 4c), the film consists of irregular-shaped blocks. A further illustration of the importance of reaction conditions in dictating the composition of the films is the comparison of SEM micrographs of films grown at 80 and 60 °C for 1 h (Figure 5). At 80 °C, the film consists of a single type of crystallite that is identical to bulk phase II as judged by powder XRD. In contrast, the 60 °C film shows regions of both polymorphs. At higher resolutions, one can observe from the micrographs in Figure 6a–d, that the needle morphology is dominant at 40 °C even after 1 h (Figure 6a,b) and that the platelets are present at 80 °C on Cu foil after 1 h as indicated in Figure 6c,d. These results are compelling evidence for the high degree of variability in films prepared under different conditions, a fact that helps to explain the lack of reproducibility in the electrical switching studies reported by various groups.

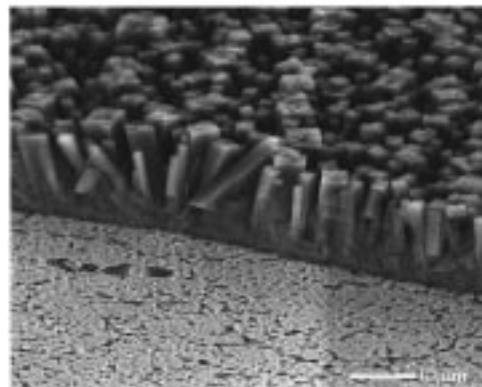
(b) Powder X-ray Studies of Chemically Prepared Phases.

The most convincing evidence that two distinctly different forms of Cu(TCNQ) exist can be found in the diffraction studies of microcrystalline samples prepared by the bulk solution routes. Several crystal structures containing copper and other ligands in addition to TCNQ have been reported,^{4,a,e,p,9} but there are no published structural data for a binary phase containing only copper and TCNQ. Powder patterns of **1** prepared at room temperature from CuI and TCNQ and a suspension of **1** that had been refluxed in MeCN for 3 h to convert it to **2** are depicted



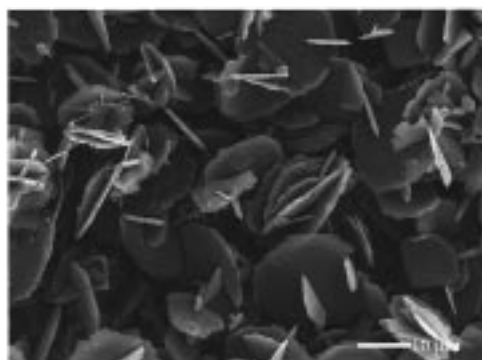
(a)

Top view



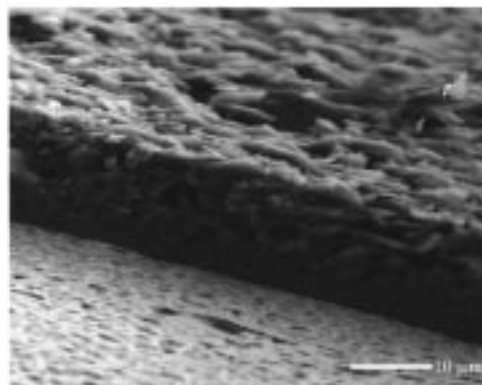
(b)

Side view



(c)

Top View



(d)

Side View

Figure 6. Scanning electron micrographs of Cu(TCNQ) films grown on copper in CH₃CN: (a) top and (b) side views of films grown for 1 h at 40 °C (phase I) and (c) top and (d) side views of films grown for 1 h at 80 °C (phase II) (10 μm resolution).

in Figure 7, panels a and b, respectively. Powder diffraction patterns from a Rigaku RU200B X-ray powder diffractometer were used for indexing by the programs Dicvol91 and Treor90.

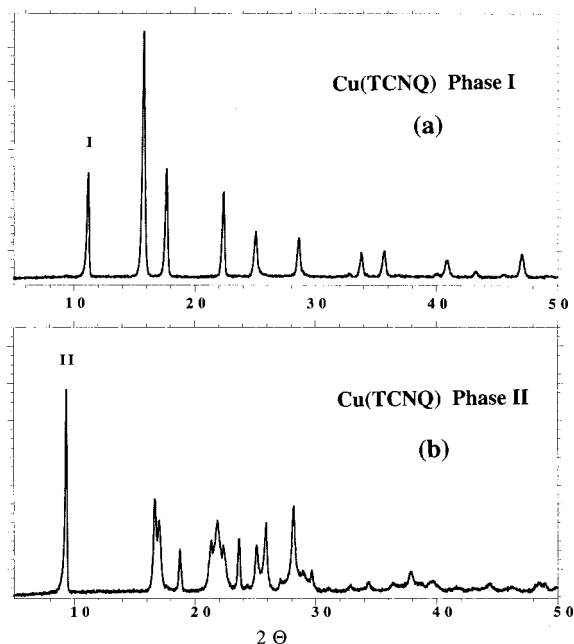


Figure 7. XRD patterns for Cu(TCNQ) (a) phase I needles and (b) phase II platelets.

This led to the tetragonal cell with $a = b = 11.2524 \text{ \AA}$, $c = 3.9501 \text{ \AA}$, and $V = 500.16 \text{ \AA}^3$ for phase I and the monoclinic cell with $a = 5.325 \text{ \AA}$, $b = 5.343 \text{ \AA}$, $c = 18.955 \text{ \AA}$, $\beta = 93.570$, and $V = 538.3$ for phase II.

(c) Powder X-ray Studies of Cu(TCNQ) Films Prepared on Cu Substrates: Relevance of Bulk Samples to Films of Cu(TCNQ). **(i) At Room Temperature.** It has been reported that Cu(TCNQ) films grown on Cu foil surfaces at short reaction times are spectroscopically identical to the bulk material prepared from CuI.¹⁰ Since our discovery that a second phase exists, however, it is important to investigate changes in film composition as a function of reaction time. Consequently, XRD patterns of the Cu(TCNQ) films were monitored periodically by removing one of the pieces of copper sheet from the TCNQ solution and collecting an X-ray powder pattern on the resulting material. Representative data are provided in Figure 8 with patterns a and e being provided as references for pure phase I and II, respectively. The powder pattern collected after 6 h is dominated by the features of 1, but within 46 h it is evident that 2 is being formed at the expense of 1 (Figure 8c); by 76 h 2 (Figure 8d) is the major species. We noted that the color of the films remained constant during the reaction and there were no other visible changes in the film with the exception of its thickness.

(ii) At Elevated Temperatures. Since the Cu(TCNQ) films in devices are required to be at least $5 \mu\text{m}$ thick, CH_3CN solutions of TCNQ are typically heated to $\sim 80^\circ\text{C}$ to accelerate the rate of growth on the Cu foil.^{15,19} Clearly it is important to know the composition of these films prepared at elevated temperatures. Accordingly, a piece of Cu foil was dipped as described in the Experimental Section at 80°C in CH_3CN , and the resulting film was analyzed by X-ray powder diffraction. Figure 9 shows the resulting XRD pattern obtained on the sample with the underlying Cu substrate. These data strongly support the conclusion that phase II is the main component of the device in the resting state before switching occurs. There is a very low concentration of phase I for films prepared under the conditions cited in the literature for the fabrication of devices.

(d) Single-Crystal Diffraction Studies. **(i) Crystal Growth.** Until the advent of area detector X-ray instruments, very small

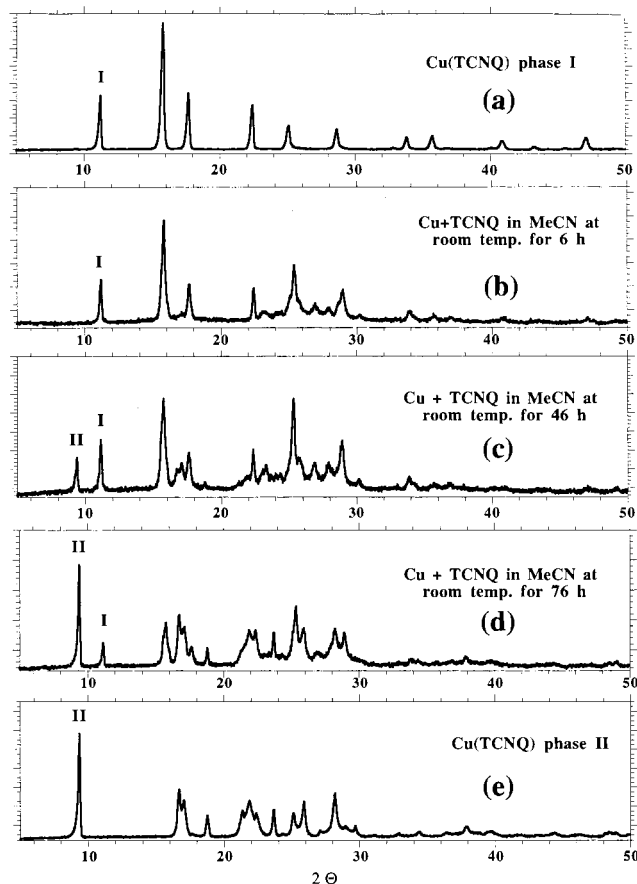


Figure 8. XRD patterns for crystalline Cu(TCNQ) films monitored periodically as they grow on Cu foil dipped in CH_3CN solutions of TCNQ at rt. Reaction times are (b) 6, (c) 46, and (d) 76 h. XRD patterns for pure phase I and phase II are provided as references in patterns a and e.

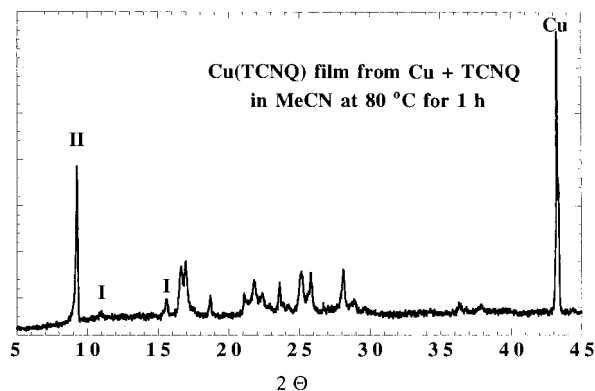


Figure 9. XRD pattern for a Cu(TCNQ) sample grown on a Cu substrate for 1 h at 80°C in a CH_3CN solution of TCNQ.

crystals and severe twinning problems precluded the structural determination of Cu(TCNQ).⁷ We and others have attempted to grow crystals by electrochemical methods, but this leads only to very fine dendrites. Eventually, tiny, but morphologically distinct, crystals of both phases were grown by a technique that involves the use of a three-compartment fritted cell. In the outer two compartments, small Soxhlet thimbles containing the starting materials CuI and TCNQ were suspended on a wire and immersed in the solution. The entire cell was placed in a water bath and gently heated to 60°C for 3–5 days to expedite mixing of the reactants in the center compartment. Within days, the solution gradually turned green, signifying the production of TCNQ^- , and tiny needles admixed with platelets began to

Table 2. Summary of Key Crystallographic Parameters for Cu(TCNQ) Phases I and II

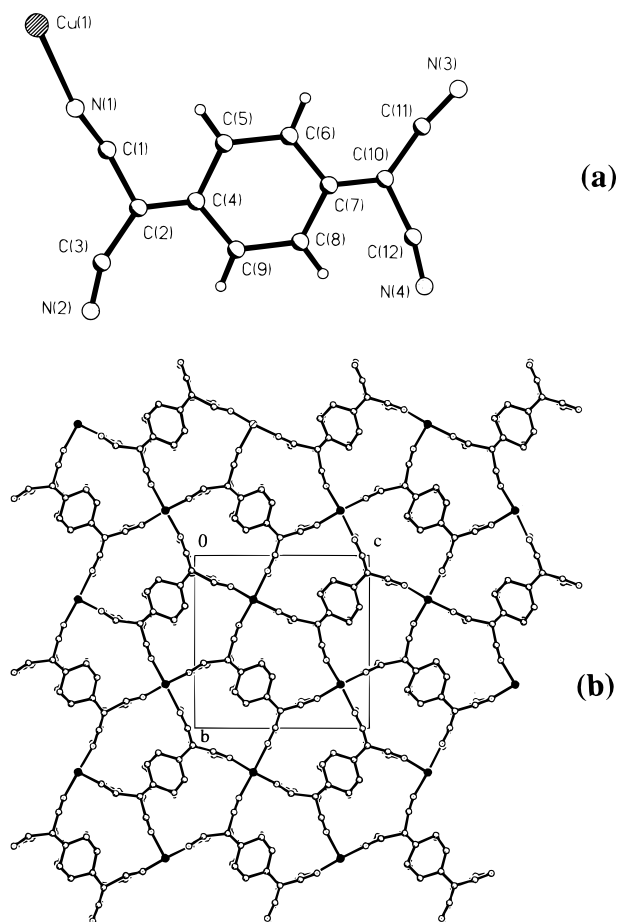
	phase I	phase II
formula	CuN ₄ C ₁₂ H ₄	CuN ₄ C ₁₂ H ₄
morphology	needle	square platelet
cryst size (mm ³)	0.25 × 0.02 × 0.02	0.13 × 0.13 × 0.01
cryst syst	monoclinic	monoclinic
space group	Pn	P2/n
a, Å	3.8878(8)	5.3337(8)
b, Å	11.266(2)	5.3312(8)
c, Å	11.266(2)	18.875(3)
α, deg	90	90
β, deg	90.00(3)	94.036(3)
γ, deg	90	90
V, Å ³	493.5(2)	535.38(14)
Z	2	2
T, K	173	173
radiation ^a	Mo Kα	Mo Kα
ρ _{calc} , g/cm ³	1.802	1.661
μ, mm ⁻¹	2.188	2.017
collected/unique data ^b	1995/1111	4456/955
indexing method	SMART	TWINDX
solution and refinement method	pseudomerohedral twinned and disordered, isotropically refined	quadruplet rotational twins, anisotropically refined
R1 (wR2) ^c	0.232 (0.481)	0.159 (0.345)
GOF ^d	2.576	1.060

^a Graphite monochromated. ^b $I > 2\sigma(I)$. ^c $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$. ^d Goodness of fit = $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$; n is the total number of reflections, and p is the total number of parameters refined.

form in the middle compartment. The needles (phase I) were harvested immediately, as they redissolve with time to produce crystals of phase II (the platelet habit).

(ii) Details of Collection and Refinement. A tiny needle of phase I and a very thin platelet of phase II were each mounted on the end of a glass fiber and X-ray data were collected on a Siemens (Bruker) SMART 1K CCD area detector. In both instances the crystals were exceedingly small, such that they tested the limits of the instrument. The weak data problems notwithstanding, the major features of the structures can readily be discerned. The results are in accord with the powder patterns; furthermore they help to explain the observed properties in a qualitative manner. The refinement of phase I is poor due to a low data-to-parameter ratio and to a merohedral twinning problem, but phase II actually refines reasonably well given the tiny size of the crystal and the fact that it is quadruply twinned. Numerous independent data sets of these materials have been collected on CCD diffractometers over the course of nearly two years, and the present results are the best that we have obtained. Since Cu(TCNQ) is the subject of much interest and its structural determination has eluded researchers for decades, these data sets, albeit marginal, are important to report. In keeping with the lower resolution of these structures, however, we have limited our discussion to the most important differences in phases I and II; no attempts to base conclusions on fine points of the structures are made.

(iii) Phase I. The structure was partially solved by direct methods and refined in SHELXTL V5.10. Key crystallographic parameters are summarized in Table 2. The presence of twinning renders the space group choice very difficult. Solutions were attempted in numerous tetragonal, orthorhombic, and monoclinic space groups, but the only reasonable solution was obtained in monoclinic *Pn*. The pseudomerohedral twin matrix [1 0 0, 0 0 1, 0 -1 0] was used in the refinement to represent the pseudo-

**Figure 10.** Phase I: (a) asymmetric unit with atom labels and (b) extended structure in the *bc* plane.

4-fold symmetry. The structure solution gave two independent Cu(TCNQ) orientations in a ratio of ~50% each. A total of 1111 unique data were refined isotropically on F^2 to $R1$ (wR2) = 0.232 (0.481), but, not surprisingly, the lack of data and other complications led to a slightly unstable refinement. Nevertheless, important features of the relationships within the structure can be gleaned from this very weak data set. The Cu atoms in the structure are coordinated to four nitrogen atoms in a highly distorted tetrahedral environment as evidenced by the N–Cu–N angles of 92° and 142° (Figure 10a,b). The quinoid rings of the TCNQ units are engaged in interplanar stacking at a distance of 3.24 Å, which is smaller than the van der Waals distance of 3.4 Å for carbon atoms. Adjacent TCNQ stacks are rotated by 90° with respect to each other, which is a standard feature in most binary metal/TCNQ salts.^{7,31} Powder simulations based on the raw *hkl* data and on the structure solution are very similar to the experimental powder pattern for the bulk phase I.

(iv) Phase II. The crystal was found to be a quadruplet twin; this was resolved by deconvolution methods, and the data were refined on F^2 in the space group *P2/n*. An ORTEP diagram of the asymmetric unit is provided in Figure 11a. The final residuals are $R1 = 0.159$ and $wR2 = 0.345$ for $I > 2\sigma(I)$. The N–Cu–N angles around the Cu atom are between 103° and 114.7°, and the average Cu–N bond length is 1.95 Å. The metal geometry is close to tetrahedral unlike the highly distorted Cu(TCNQ) phase I. Adjacent TCNQ ligands are parallel to each other with the shortest face-to-face contact between nearest neighbors in the same network being 6.8 Å (Figure 11b). This arrangement of TCNQ⁻ ions is unprecedented; typically they are situated

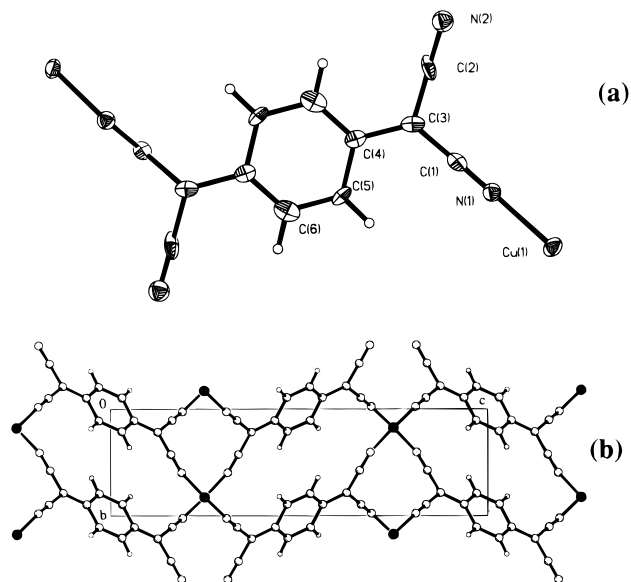
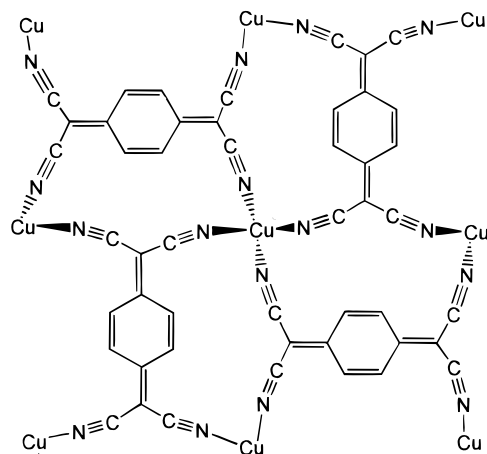


Figure 11. Phase II: (a) asymmetric unit with atom labels and (b) extended structure in the *bc* plane.

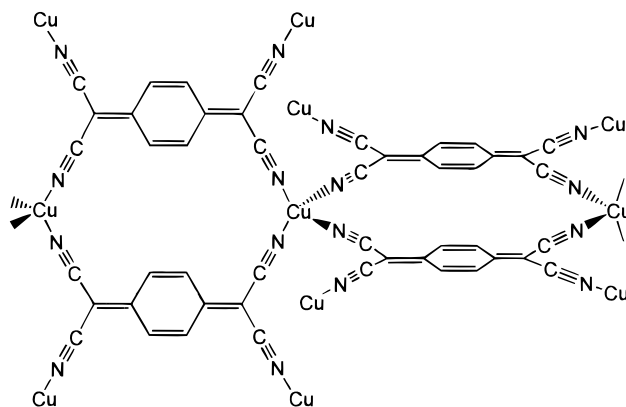
around a metal ion as four TCNQ units related by a pseudo-4-fold rotational axis such as that found in Ag(TCNQ) and alkali metal TCNQ salts.^{7,32}

(v) Comparison of the Cu(TCNQ) Polymorphs. Schematic views of the two structures are depicted in Figure 12. Both phases exhibit polymeric motifs based on the repeat pattern of a four-coordinate Cu ion ligated to nitriles of independent TCNQ molecules. There are two important differences in the structures, however, that lead to entirely different spatial arrangements for the TCNQ units in the two structures. The first difference is the relative orientation of TCNQ moieties around the Cu atoms. In phase I and in all other structures of 1:1 *M*(TCNQ) compounds including that of Ag and alkali metal salts,^{7,32} neighboring TCNQ molecules are rotated 90° with respect to one another as illustrated in Figure 10a. Phase II represents a new structural archetype for this type of solid in which infinite arrays of coplanar TCNQ molecules are oriented in the same direction, but in two perpendicular planes as depicted in Figure 11a. The second major difference in the two phases is the type of interpenetration that they exhibit. In phase I, the two independent networks bring the TCNQ molecules together to give a columnar stack with the closest distance being 3.24 Å (Figure 13a). In sharp contrast, the interpenetration in phase II does not bring the two independent networks together; rather the TCNQ rings are “slipped” and no π -stacking occurs (Figure 13b). The closest distance between parallel TCNQ units in the same network is 6.8 Å.

(e) Further Structural Analysis of Cu(TCNQ) and Comparison to Ag(TCNQ). At this point it is instructive to return to the powder patterns for the two Cu(TCNQ) phases and also for the Ag(TCNQ) material that was structurally characterized by Shields.⁷ An experimental powder pattern of Cu(TCNQ) phase I is given in Figure 14a from which it can be observed that there are very few intense features in the high-angle region. This is an indication that we are not observing much information



Cu(TCNQ) Phase I



Cu(TCNQ) Phase II

Figure 12. Schematic drawings of the TCNQ⁻ orientations in (a) phase I and (b) phase II.

about order in the third dimension. The fact that the sample is composed of very thin platelets leads to a preferred orientation which limits the amount of observed data. Since the Cu(TCNQ) phase I exhibits a connectivity reminiscent of Ag(TCNQ), it is important to comment on the fact that their powder patterns are very different. Ag(TCNQ) crystallizes in the orthorhombic space group *Pnmm*, with $a = 6.975(1)$ Å, $b = 16.689(1)$ Å, $c = 17.455(1)$ Å, and $V = 2031.5$ Å³.⁷ The powder pattern of Ag(TCNQ) simulated from the X-ray data of Shields shown in Figure 14b is clearly different from that of Cu(TCNQ) phase I. Bulk samples of Ag(TCNQ) (Figure 14c) prepared from the reaction between Ag[BF₄] and [Bu₄N][TCNQ] in CH₃CN were found to be identical to the sample used for the X-ray simulation. Interestingly, if the reaction is ceased after only 2 min instead of 3 h, the higher symmetry phase in Figure 14d is obtained. This new Ag(TCNQ) phase is similar to Cu(TCNQ) phase I in the low-angle region; this implies a pseudotetragonal cell and a similar connectivity. From its short lifetime, however, it is doubtful that this phase of Ag(TCNQ) will be possible to obtain as larger crystals for single-crystal analysis. Interestingly, if one simulates the Ag(TCNQ) powder pattern with the artificially imposed average cell edges $a = b = 17.06$ Å, the lines collapse to a pattern that resembles both the unstable Ag(TCNQ) and Cu(TCNQ) phase I structures (Figures 14a,e).

E. Magnetic and Charge-Transport Measurements on Phases I and II. Our discovery that Cu(TCNQ) exists as two different structural types is actually not surprising, given that

(32) (a) Hoekstra, A.; Spoelder, T.; Vos, A. *Acta Crystallogr.* **1972**, B28, 14. (b) Murakami, M.; Yoshimura, S. *Bull. Chem. Soc. Jpn.* **1975**, 48, 157. (c) Konno, M.; Saito, Y. *Acta Crystallogr.* **1974**, B30, 1294. (d) Konno, M.; Saito, Y. *Acta Crystallogr.* **1975**, B31, 2007. (e) Konno, M.; Ishii, T.; Saito, Y. *Acta Crystallogr.* **1977**, B33, 763. (f) Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983; Vol. 3, pp 263–317.

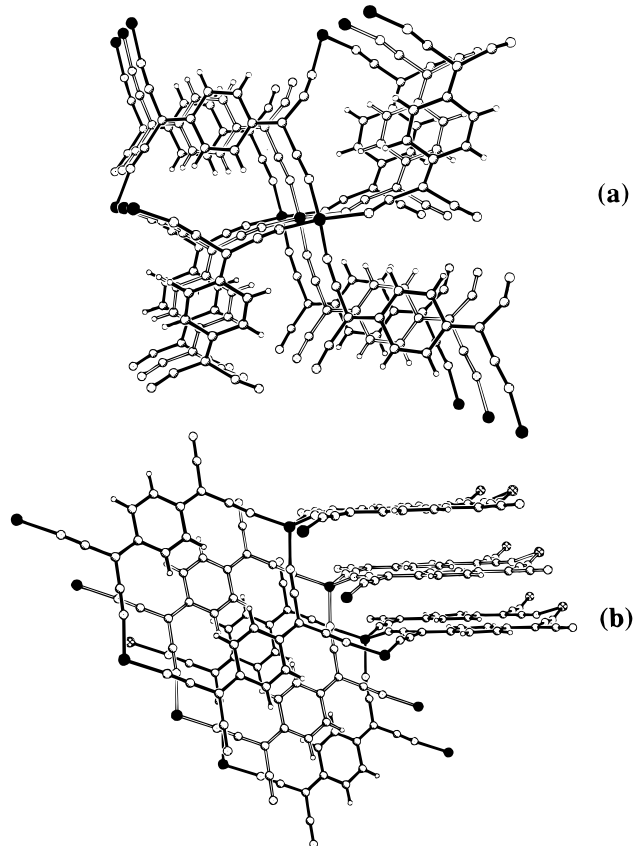


Figure 13. Views of the two interpenetrating networks in (a) phase I and (b) phase II. Solid bonds are used for one network and the open bonds for the second one.

numerous TCNQ materials are known to exhibit several different phases with the same chemical composition.^{6,32} Important aspects of this observation, however, are the ramifications that it has in terms of the observed properties of various samples of Cu(TCNQ), especially conductivity and magnetic coupling.

(a) Magnetic Behavior. The variable temperature magnetic susceptibilities of the samples were measured by the SQUID technique. Plots of χ versus T and μ_{eff} versus T are given in Figure 15. Phase I shows behavior typical of a TCNQ radical anion salt with TCNQ stacking, viz., strong coupling of the unpaired spins. Most simple TCNQ radical anion salts are paramagnetic, but the susceptibilities are only about 10% of that expected for a system with non-interacting spins.³³ The very low susceptibility of phase I (Figure 15a) indicates considerable magnetic coupling of the unpaired electrons, which renders the sample essentially diamagnetic. This is consistent with earlier studies on the magnetism of chemically prepared Cu(TCNQ).³³ In phase II, on the other hand, the TCNQ^- radicals behave like isolated paramagnets in the high-temperature regime; in fact the μ_{eff} of $1.58 \mu_{\text{B}}$ at 320 K is very close to that of the spin-

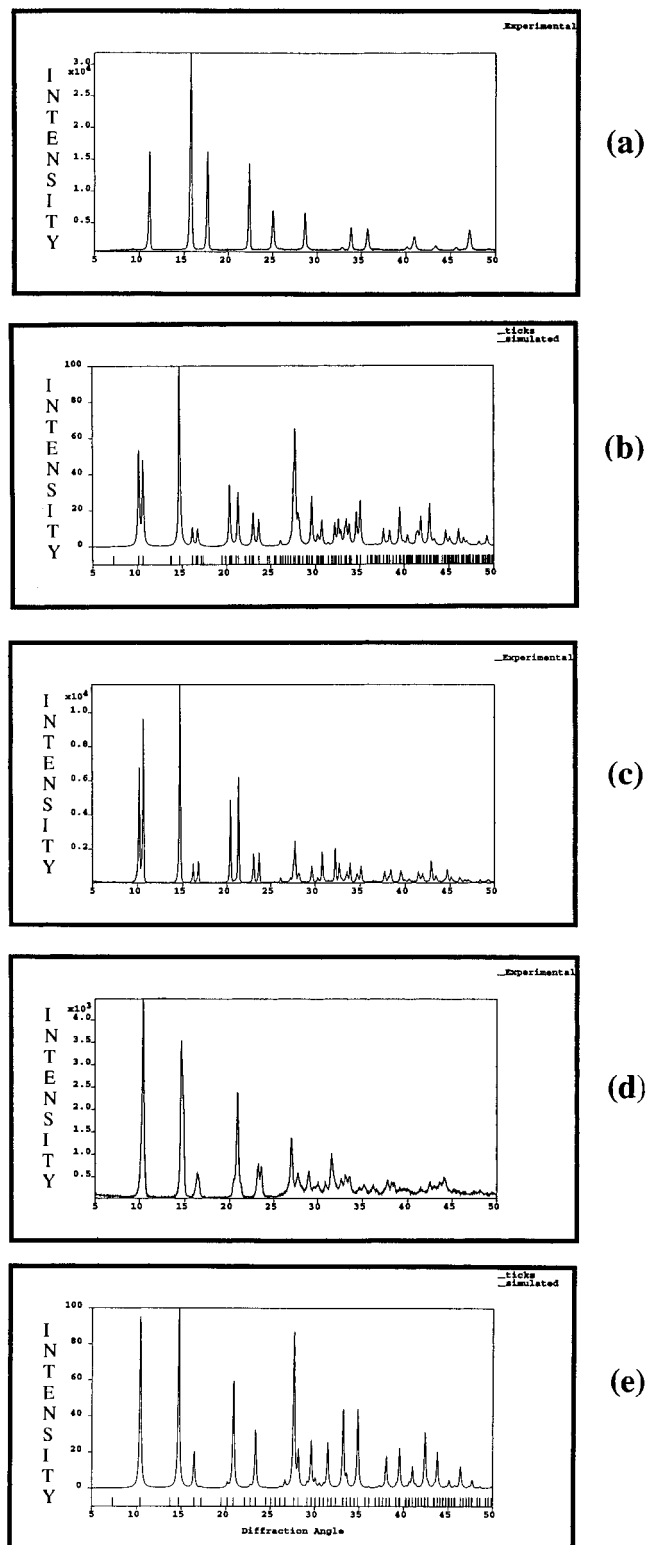


Figure 14. (a) Experimental XRD powder pattern for phase I Cu(TCNQ). (b) Simulated XRD powder pattern for orthorhombic Ag(TCNQ) from X-ray coordinates. (c) Experimental XRD powder pattern for the stable bulk phase of Ag(TCNQ). (d) Experimental XRD powder pattern for the new kinetic phase of Ag(TCNQ). (e) Simulated XRD powder pattern for an imposed tetragonal symmetry for Ag(TCNQ).

(33) (a) Kommandeur, J. In *Low-Dimensional Cooperative Phenomena*; Keller, H. J., Ed.; Plenum Press: New York, 1975; p 65. (b) Schwertfeger, C. F. *Solid State Commun.* **1977**, *23*, 621. (c) Siratori, K.; Kondow, T. *J. Phys. Chem. Solids* **1978**, *39*, 225. (d) Kommandeur, J. In *The Physics and Chemistry of Low Dimensional Solids*; Alcácer, L., Ed.; D. Reidel Publishing: Dordrecht, Holland, 1980; p 197. (e) Gossel, M. C.; Weston, S. C. *Chem. Mater.* **1996**, *8* (5), 977. (f) Gossel, M. C.; Weston, S. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1510. (g) Hynes, R. C.; Morton, J. R.; Preston, K. F.; Williams, A. J.; Evans, F.; Gossel, M. C.; Sutcliffe, L. H.; Weston, S. C. *J. Chem. Soc., Faraday Trans.* **1991**, *87* (14), 2229. (h) Iida, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 71.

only value for an isolated $S = 1/2$ system (Figure 15b). At low temperatures the effective magnetic moment for phase II begins to slowly decrease, indicating the onset of weak antiferromagnetic interactions between the unpaired spins which at 10 K abruptly changes to an ordering of the ferromagnetic type. In

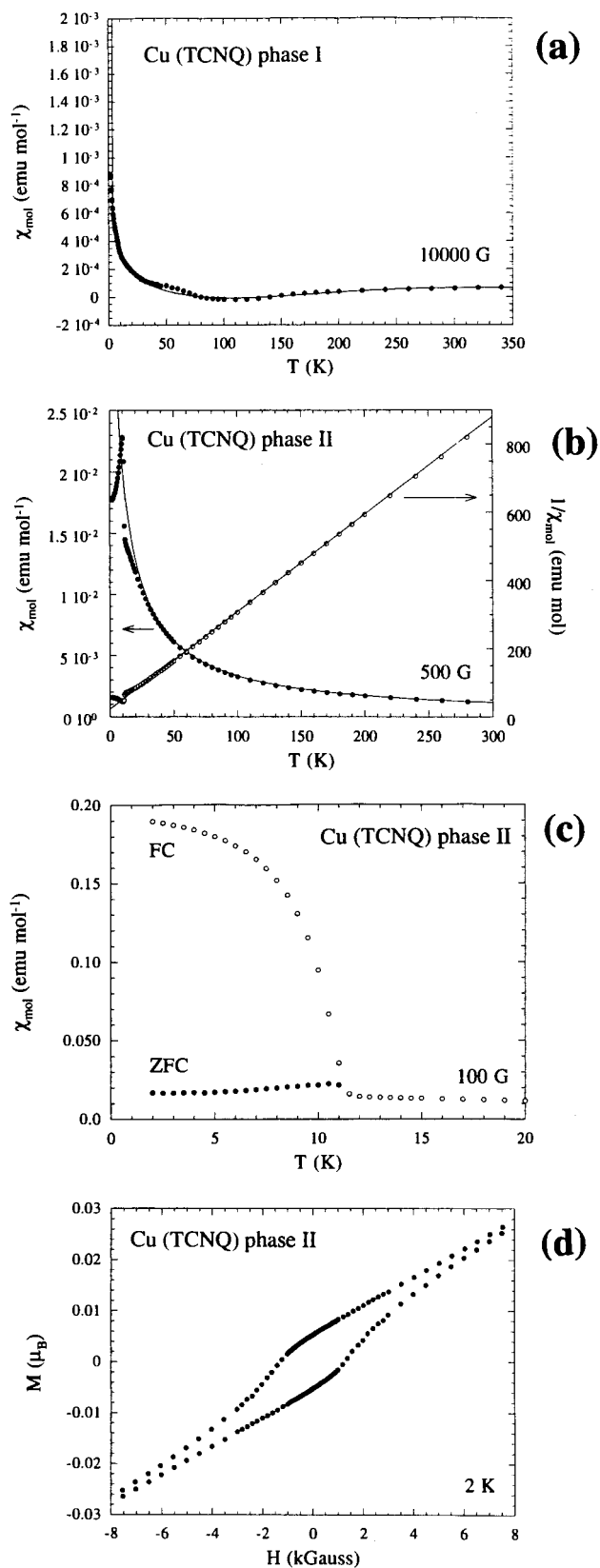


Figure 15. Variable temperature susceptibility data for Cu(TCNQ): (a) χ and μ_{eff} versus T for phase I, (b) χ and μ_{eff} versus T for phase II, (c) zero-field cooled and field-cooled χ versus T for phase II, and (d) hysteresis of phase II.

support of the ordering are the results of the zero-field cooled and field-cooled experiments (Figure 15c) and the hysteresis loop observed at 2 K with a coercive field of 500 G (Figure 15d).

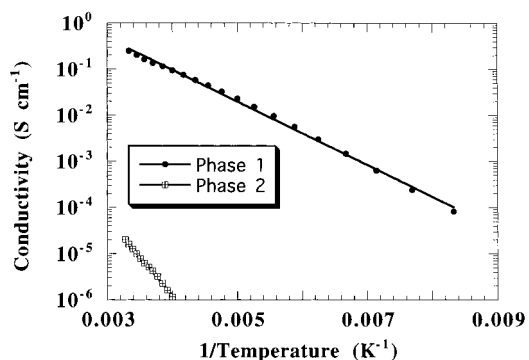


Figure 16. Plots of conductivity σ (S cm^{-1}) versus temperature for bulk Cu(TCNQ) phases I and II measured on pressed pellets.

(b) Conductivity. The two structural forms of Cu(TCNQ) were subjected to pressed pellet conductivity measurements, and it was found that they exhibit quite different charge-transport properties, as illustrated in the plots provided in Figure 16. Both behave as semiconductors, but **1** has a room-temperature conductivity of $2.5 \times 10^{-1} \text{ S cm}^{-1}$ whereas **2** is nearly insulating with a room-temperature conductivity of only $1.3 \times 10^{-5} \text{ S cm}^{-1}$. The band gaps are 0.137 and 0.332 eV for phases I and II, respectively. It is interesting to note that these values are very close to the corresponding electrical properties of the “unswitched” and “switched” forms of Cu(TCNQ) in the devices. Two separate studies of the conductivity of Cu(TCNQ) prepared by the method of Melby et. al. reported values of $\sigma(\text{rt}) = 1.6 \times 10^{-2} \text{ S cm}^{-1}$ and $\sigma(23^\circ\text{C}) = 1 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ and band gaps of 0.11 eV^{31a} and $E_{\text{gap}} = 0.16 \text{ eV}$.³⁴ These data are similar to what was found for phase I in this study. Clearly they exhibit a much higher conductivity than phase II, which was not recognized as a distinctly different phase prior to the present investigation.

F. Concluding Remarks. The results of this study establish the existence of two markedly different polymorphs of Cu(TCNQ) by X-ray photoelectron spectroscopy, infrared spectroscopy, powder X-ray diffraction techniques, and single-crystal X-ray methods. The key to this discovery was the recognition that the kinetic product (phase I) is soluble in acetonitrile and slowly converts to a more thermodynamically stable material (phase II). Both phases are dark purple, crystalline materials, and without the use of scanning electron microscopy and powder X-ray methods, it is not trivial to distinguish between the two samples. Unfortunately, the physical similarity in the two materials led many researchers to assume that the rapidly formed, kinetic product prepared from CuI and TCNQ (phase I) was the same material as the films used for switching (primarily phase II). We have incontrovertible evidence that this is not the case. Spectroscopic data collected on the bulk *kinetic* phase I, therefore, are not meaningful for understanding the switching mechanism of films of phase II.

The chemical composition and electronic characteristics of the two phases of Cu(TCNQ) are identical, but the structures and properties are quite different. Powder XRD studies revealed that both phases are present in thin films of Cu(TCNQ) grown on copper substrates, but that even subtle differences in reaction conditions can lead to variable quantities of the two phases. This is undoubtedly the cause of the reported inconsistencies in the properties of Cu(TCNQ) devices.^{8,17–20} Thin films prepared at short reaction times (ca. 2 min)¹⁹ contain only the kinetic form of Cu(TCNQ), whose conductivity is much higher

(34) Siemons, W. J.; Bierstedt, P. E.; Kepler, R. G. *J. Chem. Phys.* **1963**, *39*, 3523.

than that of the thicker films of phase II that appear after longer reaction times; consequently no switching is observed. Conductivity data on pressed pellets of bulk samples of the two phases support the conclusion that the material responsible for switching in the films is phase II, which is a very poor semiconductor. Phase I is a much better conductor; in fact its conductivity is basically the same as that of the Cu(TCNQ) films in the switched state. In our studies, no evidence for switching was observed for the pressed pellets, but this is not unexpected given that the sample thickness is much greater than one can achieve with the films. While the X-ray structures of Cu(TCNQ) do not, by themselves, explain the apparent switching, they provide convincing evidence that the structural motif dictates the magnetic and electrical properties of the material. If the electronic switching of Cu(TCNQ) thin film devices is an intrinsic property of the phase II material, and not merely a consequence of the contact of the aluminum electrode with the rough Cu(TCNQ) surface, it may involve a phase transition from a three-dimensional structure that does not allow for TCNQ⁻ stacking to a phase that brings parallel TCNQ radicals into close

proximity. The fact that the resting state of the film, phase II, is a centrosymmetric structure and that Phase I appears to be a non-centrosymmetric structure bodes well for a piezoelectrically driven transition, if, in fact, a phase change is occurring. The role of the electric field in the proposed structural transition is under current investigation in our laboratories, efforts that may ultimately lead to a resolution of this long-standing issue.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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