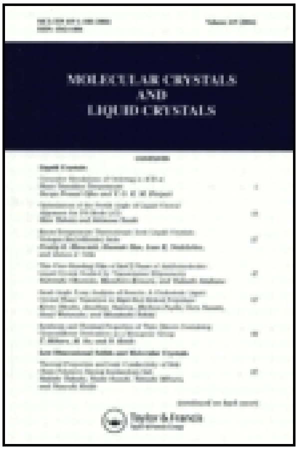


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Spectroscopic Investigations of Transformation Phenomena Exhibited by Metal-TCNQ Materials

E. I. Kamitsos [a] & W. M. Risen Jr. [b]

[a] The National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, Athens, 48 Vas. Constantinou Ave., 116/35, Greece

[b] Chemistry Department, Brown University, Providence R.I., 02912, U.S.A.

Version of record first published: 17 Oct 2011.

To cite this article: E. I. Kamitsos & W. M. Risen Jr. (1986): Spectroscopic Investigations of Transformation Phenomena Exhibited by Metal-TCNQ Materials, Molecular Crystals and Liquid Crystals, 134:1, 31-42

To link to this article: http://dx.doi.org/10.1080/00268948608079574

Mol. Cryst. Liq. Cryst., 1986, Vol. 134, pp. 31-42
0026-8941/86/1344-0031$20.00/0

Printed in the United States of America

SPECTROSCOPIC INVESTIGATIONS OF TRANSFORMATION PHENOMENA EXHIBITED BY METAL-TCNQ MATERIALS.

E.I.KAMITSOS[1] AND W.M.RISEN[2], Jr.

[1]Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, 48 Vas.Constantinou Ave., Athens 116/35, Greece.

[2]Chemistry Department, Brown University, Providence R.I. 02912, U.S.A.

Abstract The charge-transfer salts of TCNQ with copper and silver exhibit transformation and memory phenomena under the influence of an electric field, a laser beam or an electron beam. These phenomena have been studied in situ by Raman spectroscopy. The initial state was found to be fully ionic, M^+TCNQ^-, while the final one is a mixed-valence state containing neutral TCNQ, the untransformed M^+TCNQ^- and the corresponding metal. When the irradiation is carried out under controlled conditions continuous metallic regions or well dispersed metallic particles are formed. Various potential applications of these materials are also discussed.

INTRODUCTION

The synthesis of TCNQ(7,7,8,8-tetracyanoquinodimethane) and related electron acceptors has stimulated great interest in the field of low dimensional organic conductors (1).TCNQ is a strong π-electron acceptor and forms a great variety of charge-transfer compounds with inorganic and organic donors. These compounds have an important common structural characteristic; the face-to-face stacking of the TCNQ moieties to form pseudo-one-dimensional columns. This results in highly anisotropic properties of both fundamental and technological interest (2).

CuTCNQ and AgTCNQ have additional interest since it was shown that these materials undergo electrical switching as well as phototransformation phenomena under the influence of an electric field (3) or a laser beam (3-5). Such kinds of properties make these materials promising **candidates** for useful technological applications and thus it is important to understand the chemical changes taking place and the nature of the exhibited phenomena. In this paper we report the results of using Raman spectroscopy to systematically study the transformation phenomena exhibited by CuTCNQ and AgTCNQ. It is shown that Raman spectroscopy is a valuable tool to study in situ such phenomena. In addition we report on our observations of similar transformations under the action of an electron beam. Finally various potential applications are discussed.

ELECTRICAL SWITCHING

Polycrystalline films of CuTCNQ and AgTCNQ show reversible and rapid electrical switching from a high to a low impedance state, with characteristic memory effects and fast switching times (10nsec)(3). Raman spectra are very sensitive to the charge on the TCNQ moieties and thus they can be used to probe the changes **taking** place.

M^+TCNQ^- polycrystalline films were prepared by dipping clean metal foils in $TCNQ/CH_3CN$ solution (1). **A transparent** thin Cr electrode was then vapor deposited on the MTCNQ film and the Raman spectrum was measured through the Cr electrode. A typical spectrum is shown in Fig.1a for a CuTCNQ film. This spectrum is identical to that of Cu^+TCNQ^- powder prepared by the reaction of CuI and TCNQ(6), and thus it is concluded that the unswitched form of the film is Cu^+TCNQ^- .

Spectrum 1a is dominated by the totally symmetric, **Ag** modes of $TCNQ^-$, which are resonantly enhanced because the

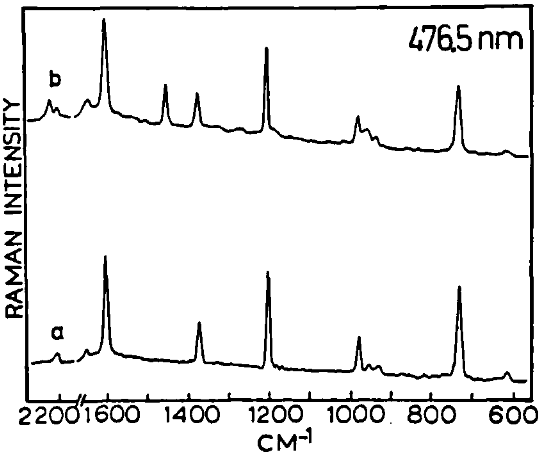


FIGURE 1. Raman spectra of CuTCNQ film through Cr electrode(a) and after electrical switching (b).

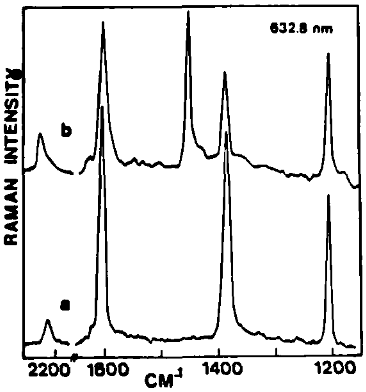
476.5nm laser line is within the high energy localized electronic transition of CuTCNQ(7). Reduction of $TCNQ^{o}$ to charged species causes substantial vibrational frequency shifts due to electronic structural changes. Specifically the frequency of the ν_4 mode (C=C wing stretch, 1375 cm^{-1} for CuTCNQ) shows an almost linear dependence on the degree of charge-transfer, ρ, on the TCNQ species (7). The ν_2 mode (C≡N stretch, 2205 cm^{-1} for CuTCNQ) is also sensitive to ρ, while other modes such as ν_3 (C=C ring stretch, 1603cm^{-1} for CuTCNQ) or ν_5 (C-H bent, 1203 cm^{-1} for CuTCNQ) show a very small dependence on ρ.

After spectrum 1a was measured electrical switching was performed and the Raman spectrum of switched film was immediately recorded through the Cr electrode and is illustrated in Fig.1b. Comparison with Fig.1a shows two new bands at 2223 and 1451 cm^{-1} after electrical switching, while the relative intensities of the 980,734 and 1375 cm^{-1} bands were reduced. The 2223 and 1451 cm^{-1} new bands correspond to ν_2 and ν_4 modes respectively of neutral TCNQ ($TCNQ^o$)(8) and so spectrum 1b clearly demonstrates the presence of $TCNQ^o$ after electrical switching. The amount of $TCNQ^o$ is estimated to be in the range 10-15% immediately after switching. Thus the switched form of the film is a mixed-valence state of $TCNQ^-$ and $TCNQ^o$ and this is consistent with its low impedance. This happens because the Coulombic repulsive forces are now reduced by allowing conduction electrons to occupy the empty molecular orbitals of $TCNQ^o$.Thus there are more available sites than there are unpaired electrons (9).

PHOTOTRANSFORMATIONS

Among the essential factors to obtaining the above results was the careful control of the irradiance by the laser beam. When it exceeded certain threshold values it was observed that CuTCNQ and AgTCNQ show light-induced transformation phenomena (4).

The materials studied include polycrystalline films, prepared as described above, powders prepared by the method of Melby et al (1) and homogeneous thin films prepared as follows. On a substrate (KBr, SiO_2, Si etc) a metal (Cu,Ag) film was vapor deposited under vacuum and then a layer of TCNQ was deposited followed by alternating layers of metal and TCNQ. The layer thicknesses were adjusted to obtain a 1:1 (M:TCNQ) mole ratio. The multilayer structure was then heated in situ or in an Ar atmosphere. The resulting thin film was found to be M^+TCNQ^- by Raman spectroscopy. This indicates that under these conditions the metal reacts with TCNQ, that is $M^o+TCNQ^o \rightarrow M^+TCNQ^-$.



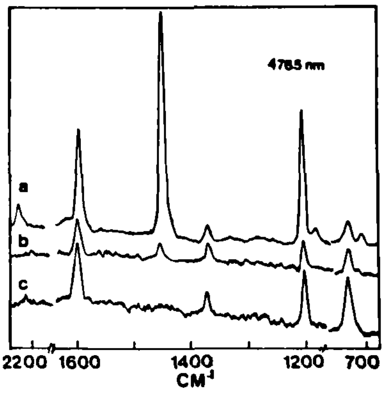


FIGURE 2. Raman spectra of AgTCNQ powder; untransformed (a) and partially transformed (b).

FIGURE 3. Memory effects in CuTCNQ powder; partially transformed (a), spectrum measured after 8h with low power (b), and 10h after transformation (c).

The phototransformations reported here were accomplished using laser beams from Ar and He-Ne lasers. Figure 2 shows such a transformation experiment. AgTCNQ powder measured at 632.8 nm with 1mW/mm^2 (Fig.2a) exhibits the ν_2,ν_3,ν_4 and ν_5 bands, in the 1200-2230cm^{-1} region. Measuring the same sample at 2.5 mW/mm^2 resulted in spectrum 2b, where the ν_4=1451 cm^{-1} and ν_2=2223 cm^{-1} bands of TCNQ^{o} are also present. The ν_4=1379 cm^{-1} band of AgTCNQ is reduced in intensity while the ν_3 and ν_5 bands appear for both TCNQ^{o} and AgTCNQ at about 1600 and 1203cm^{-1} respectively and so they do not show intensity reduction.

Thus higher laser power causes oxidation of TCNQ^{-} to TCNQ^{o}. This transformation requires that the laser irradiance exceeds certain threshold values.

Exposure at lower irradiance values, even for extended periods of time, does not cause phototransformation, indicating the non-linear nature of the materials studied. The threshold values depend on the specific material and its form. AgTCNQ is more sensitive than CuTCNQ, and highly reflective thin films require higher threshold values than polycrystalline films or powders. AgTCNQ powder has for example a threshold of 2.5 mW/mm^2 at 488.0 nm, while AgTCNQ thin film 150mW/mm^2 at 488.0nm. The threshold for a specific form of the same materials was found to be essentially independent on the wavelength of the laser beams used in this study.

The mixed-valence state obtained by phototransformation is spectroscopically the same as the low impedance form of the material, and returns to the M^+TCNQ^- form spontaneously but slowly at room temperature. This constitutes a memory effect and is demonstrated in Fig.3. The Raman spectrum of CuTCNQ powder, measured at 60mW/mm^2,(Fig.3a),shows the presence of $TCNQ^o$ (1451cm^{-1} band) and untransformed CuTCNQ. The laser was turned off. The spectrum obtained 8h later, with 10mW/mm^2, is shown in Fig.3b. $TCNQ^o$ is still present but in significantly reduced amounts. Two hours later the system had completerly returned to the thermodynamically more stable Cu^+TCNQ^-, as illustrated by spectrum 3c. This slow return to the M^+TCNQ^- form can be speeded up (shorter memory) upon heating, based on our observation that metal and $TCNQ^o$ react to form M^+TCNQ^-. A convenient heat source can be a defocused CO_2 laser.

The transformations described so far are partial transformations. When the laser irradiance is much higher than the threshold value then complete transformation is effected and macroscopic amounts of $TCNQ^o$ are formed, resulting in high-contrast patterns. At even higher irradiance and/or

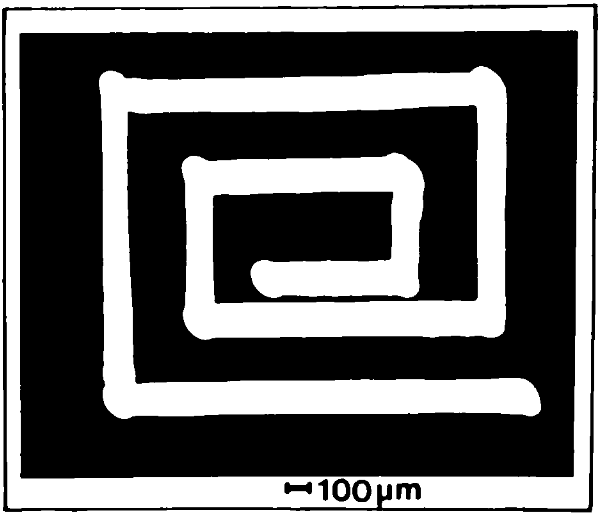


FIGURE 4. Optical writing on a 0.3µm AgTCNQ/SiO_2 thin film performed with a 488.0 nm laser beam of 120µm diameter and 250 mW power.

vacuum, $TCNQ^o$ sublimes off of the sample and the exposed region containes only the metal. Figure 4 shows an optical transmission microphotograph of a thin AgTCNQ film exposed to a high irradiance laser beam. The pattern was generated by moving the sample on an X-Y translation stage. Under a fixed laser beam $TCNQ^o$ is completely removed and Ag lines are formed in the exposed areas.

The light-induced transformation phenomena are similar to those of electric-fields and the following solid state equilibrium describes the process:

$$(M^+TCNQ^-)_x \underset{\Delta}{\overset{E,h\nu}{\rightleftharpoons}} M^o_y + TCNQ^o_y + (M^+TCNQ^-)_{x-y} \qquad (1)$$

where, $y<x$ for partial transformation and $x=y$ for complete transformation.

Since both electric field and laser beams cause the same process, eq.(1), it would be useful to compare their threshold values. For CuTCNQ polycrystalline film for example the effective electric field threshold is ca 1.7 x 10^5 V/m(7). A typical threshold value for phototransformation of the same material is 5 x 10^4 W/m^2. The electric field of the laser beam is given by:

$$E = (2P)^{1/2} (\mu_0/\varepsilon_0)^{1/4} \qquad (2)$$

where P is the beam irradiance and μ_0, ε_0 are the permeability and permittivity of empty space. Using P=5 x 10^4 W/m^2 a field value of 6 x 10^3 V/m is calculated, and is about 25 times weaker than the threshold for electrical switching.

Thermal effects could be excluded as the cause of the transformation on the basis that heat favors the reverse of reaction (1). The result that the threshold for optical transformation is much smaller than that for electrical transformation can be understood on the basis that the laser beams cause also an electronic excitation of $TCNQ^-$. Thus it becomes easier for an electron to leave $TCNQ^-$ and be captured by M^+. The electronic excitation seems to assist the electric field effect, resulting in a smaller threshold value.

ELECTRON BEAMS EFFECTS

There is currently a significant need for resist materials that can be patterned to yield submicron structures for microelectronics applications. The materials used for lithography are usually polymers which change their solubility upon exposure to radiation. It was recently reported that change-transfer salts of TTF with halogen acceptors (i.e.TTF-Br_x) can be used as electron beam resist materials (10). These observations along with the fact the M^+TCNQ^- materials exhibit phototransformation phenomena led to our investigating the effects of electron-beams on these materials.

Thin films of M^+TCNQ^- were prepared on the appropriate substrate by the vapor depositing techniques. In that way smooth homogeneous films of uniform thickness were prepared. This is important since for lithographic applications the resolution and sensitivity depend on the film uniformity. A CuTCNQ thin film (2000 A^o) was directly prepared on a Cu grid, used as substrate for the transmission electron microscope, and exposed for ca 0.5 sec to an electron beam of 40μm diameter and 1 x 10^{-7} A current. After exposure a transmission electron micrograph was obtained (Fig.5a),at a 5 x 10^{-9} A current. The central exposed area of the film was now characterized by the presence of small particles not present in the unexposed region. The particle size increases from the center towards the circumference of the exposed area, while the intensity of the beam having a Gaussian profile decreases in the same direction. Figure 5b shows an area of the exposed region under higher magnification.

To identify the particles formed under exposure to an electron-beam, electron microprobe analysis was used. A thin CuTCNQ film on SiO_2 was exposed to the electron beam and particles similar to those of Figure 5 were formed. A low energy beam was then focused on a single particle and the emitted X-rays were measured. The characteristic $CuLa_1$ line at 930 eV was observed indicating that Cu particles are formed under irradiation. Similar results were obtained for

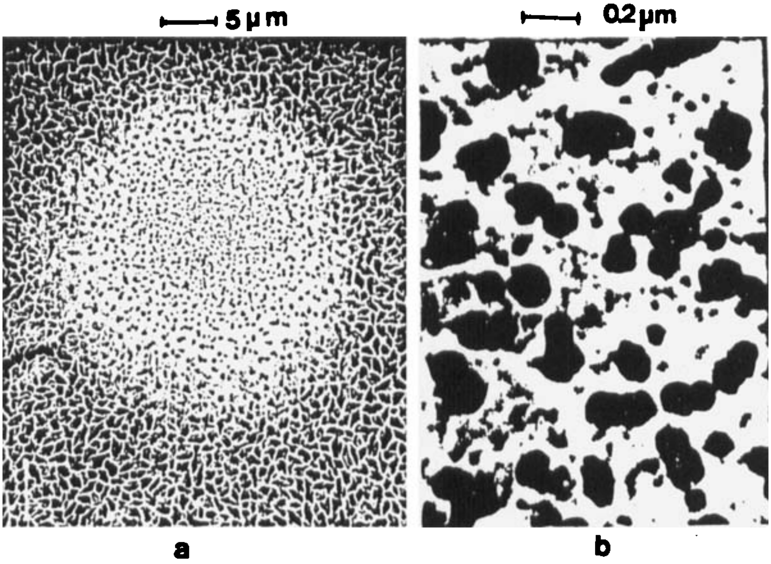


FIGURE 5. Transmission electron micrograph of CuTQ thin film exposed to a 1 x 10^{-7} A electron-beam for 0.5 sec.

AgTCNQ thin films.

The effects of the e-beams are similar to those of an electric field or laser beam, described by eq.(1). Due to local heating by the e-beam and the high vacuum (10^{-8} Torr) the $TCNQ^{o}$ formed by transformation sublimes off, leaving the metal particles on the substrate. For big diameter electron beams the transformation is not complete in the entire exposed area (Fig.5), and highly dispersed particles are formed. When a high current density e-beam is used then complete transformation is effected and continuous, conducting metal lines similar to those in Figure 4 are formed. In that way high contrast patterns can be generated *in situ*, without the need of additional developing steps (11). The sensitivity of CuTCNQ, that is the minimum electron dose required for transformation is ca 1×10^{-2} C/cm^2. This is about the same as that of some other useful e-beam resist materials (12).

CONCLUSIONS

It has been shown that CuTCNQ and AgTCNQ exhibit interesting transformation phenomena which can be studied and well understood by employing Raman spectroscopy. These properties combined with the ability of preparing the materials in the form of thin films give them a special technological importance. Some possible applications may include the following:

(a) Formation of high resolution conductive lines without developing steps, with useful application as resists for electronic device fabrication.

(b) Current controlled bistable threshold and memory switches

(c) Light activated switches and erasable memory elements, with applications in optical computers and optical communication systems.

(d) Electron-beam processing of thin films to generate high resolution holograms.

REFERENCES

1. L.R.Melby et al., J.Amer.Chem.Soc.84,3374(1962)
2. S.Yoshimura and M.Murakami, in "Synthesis and Properties of Low-Dimensional Materials",ed.by J.S.Miller and A.J. Epstein, Annals of New York Academy of Science,N.Y.(1978)
3. R.S.Potember, T.O.Poehler and D.D.Cowan, Appl.Phys.Lett. 34(6),405(1979); and R.Benson et al,Appl.Phys.Lett. 42, 855(1983)
4. W.M.Risen,Jr., and E.I.Kamitsos,Patent Submission,Brown University, March 1982
5. E.I.Kamitsos and W.M.Risen,Jr.,Solid State Commun.45, 165(1983)
6. E.I.Kamitsos,C.H.Tzinis and W.M.Risen,Jr.,Solid State

Commun., 42, 561 (1982)
7. E.I.Kamitsos and W.M.Risen,Jr.,J.Chem.Phys.79,5808(1983)
8. A.Girlando and C.Pecile,Spectrochim.Acta,A 29,1859(1973)
9. O.H.LeBlanc,Jr.J.Chem.Phys.42,4307(1965)
10. Y.Tomkiewicz et al, Appl.Phys.Lett.40, 90 (1982)
11. Details will be published elsewhere
12. P.Schmidt et al, Appl.Phys.Lett. 40, 93 (1982)