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Synthesis and Optically Induced Transformation of Metal $TCNQF_4$ Thin Films

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Thin films of the composition Ag_2TCNQF_4 and Cu_2TCNQF_4, made with the tetrafluorinated derivative of TCNQ, have been prepared and characterized. These charge transfer compounds of $TCNQF_4^{2-}$ do no absorb strongly in the visible, but absorbed light at low power causes an electron transfer reaction resulting in formation of the highly absorbant $TCNQF_4^-$. This optical record is formed with low power and is erasable thermally .

Introduction

Films of metal-organic charge transfer compounds formed between Ag or Cu and TCNQ in 1:1 ratio have been investigated previously for optical storage and other optoelectronic applications (1-7). Thin films prepared by vapor deposition methods, in particular, have been shown to exhibit interesting properties, including photo-induced transformations. Thus, AgTCNQ and CuTCNQ have been transformed by light to compositions represented by [MTCNQ + (1-x) TCNQ + (1-x)M]. The result of the transformation is a change in the visible appearance of the exposed area due either to the yellow color of the TCNQ replacing the blue-green color of the film or to the metallic appearance of this area after sublimation of TCNQ.

These changes can be used as an optical record. If experimental conditions, such as application of an overlayer, prevent sublimation of the neutral TCNQ formed in the phototransformation, the overall composition of the transformed region is unchanged and the MTCNQ can be reformed thermally for erasing the record. However, even when this composition is maintained in the exposed region, the reformation of MTCNQ is rate-limited by the required dissociation of TCNQ and M crystallites and diffusion of the atoms and molecules to the reaction site.

Development of improved metal-organic charge transfer materials for this type of application will require synthesis of new compounds in which sublimation and resegregation of any components in the transformed regions is prevented. At the same time, higher optical density contrast between transformed and untransformed regions is required and the transformation should be achieved faster and at lower threshold power. Optimally, one phase would be nearly transparent and the other would have high absorbance. We have achieved these conditions through the synthesis of thin films of Ag_2TCNQF_4. The preparation and transformation are reported here.

We employed the tetrafluorinated derivative of TCNQ, abbreviated $TCNQF_4$, as the electron acceptor because the reaction $TCNQF_4^- + e \rightarrow TCNQF_4^{2-}$ has a sufficiently high electron affinity to form materials with the Ag_2TCNQF_4 stoichiometry. This means, first, that the phototransformation reaction can yield the non-volatile $TCNQF_4^-$ ion as the oxidized form rather than a sublimable neutral molecule. Moreover, the lowest energy strong intramolecular electronic transition of the $TCNQF_4^{2-}$ ion is at much higher energies (λmax = 310 nm) than the main bands of either $TCNQF_4^-$ (λmax = 350, 625, 1150 nm) or $TCNQF_4$ (solid) (λmax = 342, 410, 450 nm), including intermolecular charge-transfer absorptions. The Ag_2TCNQF_4 thin films are nearly transparent in the visible region, although they have low absorptivity tails extending from the 310 nm maximum throughout the visible range.

With the synthesis of nearly transparent thin films which should undergo phototransformation to a phase containing the highly colored but non-volatile $TCNQF_4^-$ species and return thermally to the thermodynamically stable Ag_2TCNQF_4 material, the occurence of phototransformation remains to be established and investigated. It may be expected to occur at comparatively low threshold power, since $TCNQF_4^{2-}$ is less stable relative to $TCNQF_4^-$ than the latter is relative to $TCNQF_4$, ignoring effects due to interionic (Madelung) and neutral $TCNQF_4$ selfassociation effects. On the other hand, the Ag_2TCNQF_4 absorption is low in the region where transformations would be attempted (450-950 nm), and the contributions of intermolecular charge-transfer to absorbance in this region is unknown. The phototransformation observations are reported below and compared, insofaras possible, to those of MTCNQ films.

Experimental

Thin films of Ag_2TCNQF_4 were prepared by vapor deposition, thermal treatment and overcoating as follows (8). A circular (1.3 cm diameter) thin film of $TCNQF_4$, prepared by the method of Wheland and Martin (9), was deposited by evaporation under high vacuum on a polished KBr substrate at ca 3×10^{-10} ms^{-1} to a thickness of $1\text{-}2 \times 10^{-7}$m. Then a larger circular (1.9 cm diameter) film of Ag was deposited in the thickness required to make the stoichiometry $Ag:TCNQF_4::2:1$. Finally, a $3\text{-}5 \times 10^{-7}$ m thick layer of KBr 1.9 cm diameter was deposited, and the multilayer structure was heated in vacuo for ca 100 sec. at 100°C. The inner circular area appeared nearly colorless and transparent, and it was surrounded by a ring of unreacted Ag. Thin films of composition Cu_2TCNQF_4, containing $TCNQF_4^{2-}$, and of $AgTCNQF_4$ and $CuTCNQF_4$ also have been prepared and characterized (8). Most work on this will be reported separately, although spectra of $AgTCNQF_4$ are presented to identify the phototransformed phase of Ag_2TCNQF_4. The infrared

(IBM98 FTIR) and ultraviolet-visible (Cary 15) spectra were measured on these films as prepared and after subsequent treatments described below.

Measurement of the Raman spectrum of Ag_2TCNQF_4 was not possible because exposed regions of the film undergo photo transformation under all conditions attempted, including defocusing the source beam, lowering the power, and spinning the sample.

The phototransformation was studied on the Spex Raman Micromate system with the sample on a microscope stage where it was exposed to a laser beam that was incident through the microscope by reflecting off a 45° beam splitter. The sample image is observed throughout with a videcon camera recording the image passing back through this beamsplitter. The incident power was measured at the focal point for a number of laser powers, for calibration of laser power versus power incident on the sample and then reduced by insertion of calibrated neutral density filters and beam splitters. The exposure time was controlled by a mechanical shutter with opening timers controllable to 0.01 s.

Transformations are reported on $4x10^{-5}$ m diameter spots formed at times in the range $1x10^{-2}$-5s with powers of $7x10^{-4}$-$2x10^{-1}$ mW. With 457.9 and 488.0 mm radiation, the power densities for transformation varied from 160 Wm^{-2} to $5.60x10^3$ Wm^{-2}, while with 632.8 nm they were $6.20x10^3$ to $1.87x10^5$ Wm^{-2}. The criterion for transformation was the appearance of a perceptible blue-green spot against the nearly transparent background on the video display.

Reversal of the transformation was achieved thermally at 150°C, and confirmed by the infrared and uv-visible spectra of the films.

Results and Discussion

The infrared spectrum of a typical Ag_2TCNQF_4 thin film shows major bands at 1477 and 1495 cm^{-1} (Fig. 1a) which are characteristic for $TCNQF_4^{2-}$ (8), while $AgTCNQF_4$ shows analogous bands at 1499 and 1532 cm^{-1} (Fig. 1b). This and its ultraviolet-visible spectrum (Fig. 2a), which contains the characteristic 310 nm band of $TCNQF_4^{2-}$ (8), together with the disappearance of Ag in the reacted region, demonstrated that the nearly transparent thin film is Ag_2TCNQF_4.

When such a film was exposed to low power visible laser radiation, the exposed regions were transformed to a blue-green phase. Exposure of about 35% of the film area resulted in a partially transformed film whose spectra are shown in Figs. 1b and 2b. The spectra of $AgTCNQF_4$, which contains $TCNQF_4^{-}$, are shown in Figs 1c and 1d for comparison. After thermal treatment the film gave the spectra of Figs 1d and 2d, showing the reversability of the process, which was repeated 10-20 times without spectral degradation Thus, the phototransformation and its thermal reverse maybe represented by:

$$Ag_2TCNQF_4 \rightleftarrows xAg_2TCNQF_4 + (1\text{-}x)\ AgTCNQF_4 + xAg$$

The threshold for transformation was measured by the appearance of a visually distinct spot displayed on a video monitor displaying a microscopic spot of $4x10^{-5}$m diameter. Although transformation of nearly circular $2x10^{-6}$m diameter spots also was recorded, power-time relationships were measured more readily with the power densities of the larger spots. Figure 3a shows the time required for transformation of such as a function of power

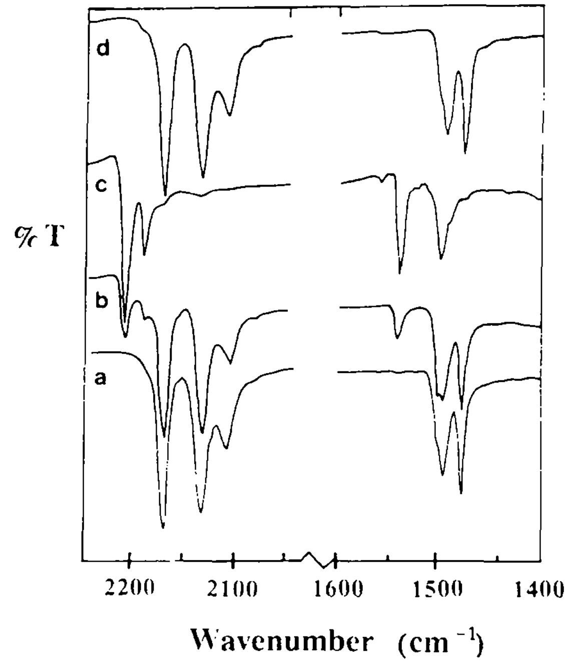

Figure **1** Infrared spectra in the 2250-2050 and 1600-1400cm^{-1} regions; **a** Ag_2TCNQF_4 film on KBr, **b** film of **a** after optical transformation of part (ca 35%) of the surface area, **c** $AgTCNQF_4$ thin film, and **d** film of spectrum **b** after thermal treatment to erase transformed regions. Spectra are offset for clarity.

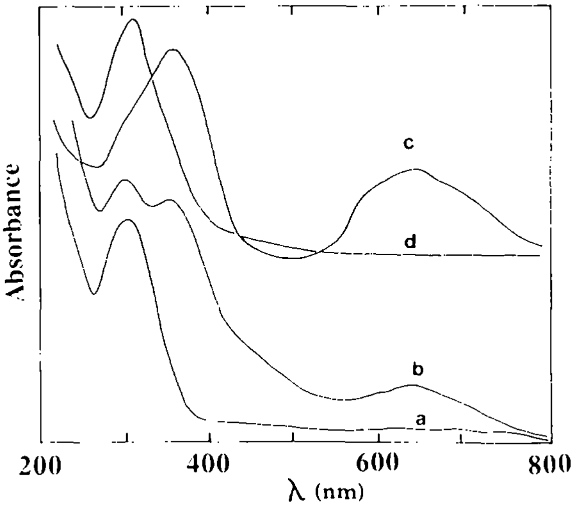

Figure **2** Visible-ultraviolet absorption spectra (200-800nm) of: **a** Ag_2TCNQF_4 film on KBr, **b** film of **a** after partial optical transformation, **c** $AgTCNQF_4$ film on KBr, and **d** film of spectrum **b** after thermal treatment to erase transformed regions. Spectra are offset for clarity.

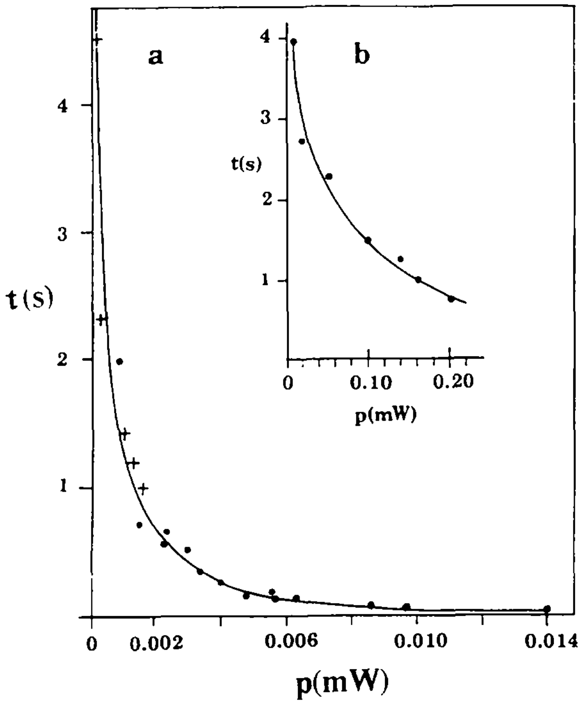

Figure 3 Plots of threshold time for observation of transformation of a $4x10^{-5}$m diameter spot on Ag2TCNQF4 thin film on KBr versus power for: **a** transformation with 488.0 nm (●) and 457.9nm (+) light; and **b** transformation with 632.8nm light.

at several wavelengths near 480 nm (457.9 and 488.0 nm). Additional points, off the scale shown here, were obtained at $p = 2x10^{-5}$mW, $t = 43$s and $p = 7x10^{-5}$ mW, $t = 31$s. The power densities range from $1.60x10^2$ to $5.60x10^3$ Wm^{-2}.

The data fit reasonably well to expressions of the form $t = B \exp(-Dp)$, where t(s) is the threshold time, p(mW) the power incident on a $1.257x10^{-9}m^2$ spot ($4x10^{-5}$m diameter spot.) At 632.8 nm, B= 3.0 and D = 6.7, while for 488.0 and 457.9 nm B = 2.9 and D = 610. Of course, it is not known how far they can be extrapolated, especially toward higher power and shorter times. While it seems unlikely they give very accurate predictions, extrapolation indicates that transformation of a $4x10^{-5}$m diameter spot would occur in about 20μs with $2x10^{-5}$W of 488.0nm radiation focussed on this spot. The analogous result for 632.8nm radiation is $1.77x10^{-3}$W or $1.4x10^6Wm^{-2}$.

For comparison, Hoshimo, et al, (7) found that a CuTCNQ thin film, made by the method of references (1-4), transformed in 20μs at $3x10^8Wm^{-2}$ at 810nm. Thus it appears that Ag$_2$TCNQF$_4$ is transformed with red light at about 200 times lower power density than CuTCNQ. However, such comparisons must be done with great caution because the wavelength dependence is so strong that the difference between 810 and 633nm is important and because numerous other effects, such as sample reflectivity, have not been considered. Nonetheless, the result must be qualitatively correct, because it is easy to obtain a Raman spectrum of CuTCNQ while Ag$_2$TCNQF$_4$ transforms under all such conditions.

The preparation and spectral analysis of a range of MTCNQF$_4$ thin films in 1:1 and 2:1 stoichiometries will be reported in detail separately.

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References

1. E. I. Kamitsos, C. H. Tzinis and W. M. Risen, Jr., Solid State Comm. **42**, 561 (1982).
2. E. I. Kamitsos and W. M. Risen, Jr., Solid State Comm. **45**, 165 (1983).
3. E. I. Kamitsos and W. M. Risen, Jr., J. Chem Phys. **79**, 5808 (1983).
4. E. I. Kamitsos and W. M. Risen, Jr., J. Chem. Phys. **79**, 477 (1983).
5. R. S. Potember, T. O. Poehler and D. O. Cowan, Appl. Phys. Lett. **34**, 405 (1979).
6. R. C. Benson, R. C. Hoffman, R. S. Potember, E. Bourkoff and T. O. Poehler, Appl. Phys. Lett. **42**, 855 (1983).
7. H. Hoshino, S. Matsushita and H. Samura, J. Appl. Phys. (Japan), **25**, L341 (1986).
8. A. Kotsiliou, Ph.D. Thesis, Brown University (1988).
9. R. C. Wheland and E. L. Martin, J. Org. Chem. **40**, 3101 (1975).