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# Preparation of Metal−TCNQ Charge-Transfer Complexes on Conducting and Insulating Surfaces by Photocrystallization

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***Abstract:*** A generic method for the synthesis of metal-7,7,8,8-tetracyanoquinodimethane (TCNQ) charge-transfer complexes on both conducting and nonconducting substrates is achieved by photoexcitation of TCNQ in acetonitrile in the presence of a sacrificial electron donor and the relevant metal cation. The photochemical reaction leads to reduction of TCNQ to the $TCNQ^-$ monoanion. In the presence of $M^{x+}{}_{(MeCN)}$, reaction with $TCNQ^-{}_{(MeCN)}$ leads to deposition of $M^{x+}[TCNQ]_x$ crystals onto a solid substrate with morphologies that are dependent on the metal cation. Thus, CuTCNQ phase I photocrystallizes as uniform microrods, KTCNQ as microrods with a random size distribution, AgTCNQ as very long nanowires up to 30 $\mu$m in length and with diameters of less than 180 nm, and $Co[TCNQ]_2(H_2O)_2$ as nanorods and wires. The described charge-transfer complexes have been characterized by optical and scanning electron microscopy and IR and Raman spectroscopy. The CuTCNQ and AgTCNQ complexes are of particular interest for use in memory storage and switching devices. In principle, this simple technique can be employed to generate all classes of metal−TCNQ complexes and opens up the possibility to pattern them in a controlled manner on any type of substrate.

## Introduction

Metal 7,7,8,8-tetracyanoquinodimethane (TCNQ) complexes have been the focus of intensive research for the last 40 years.[1−14] CuTCNQ and AgTCNQ, in particular, have recently received renewed interest due to their interesting structural, optical, electronic, and switching properties.[15−30] The latter phenomenon has seen the development of a CuTCNQ nonvolatile-based memory device,[16] which has been downscaled to an area of 0.25 $\mu m^2$. Crucial to this type of development is the ability to control crystal growth using a facile method of synthesis. The traditional method of Cu and Ag TCNQ preparation is the reaction between dissolved TCNQ in acetonitrile and copper or silver metal.[7,9,11,13,23,24,26] Several different approaches using this spontaneous electrolysis technique have been employed to yield a host of different morphologies such as microwires,[22,25,30] films of needle shaped crystals,[16,23,26] and even dendritic AgTCNQ.[24] Other techniques like chemical vapor deposition of TCNQ on metal surfaces and synthetic procedures involving TCNQ and metal salt precursors also have been widely employed.[7−10,13,27,31,32] Recent work from this laboratory has

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focused on electrochemical methods for the controlled synthesis of either large isolated CuTCNQ crystals[21] or densely packed films of small micron sized needles of CuTCNQ.[19]

TCNQ also has been used as an electron-accepting sensitizer in photoinduced electron-transfer processes because of its low reduction potential (0.21 V vs SCE in acetonitrile[21]) and an excitation energy that lies within the visible region.[33] In this paper, the development of a simple technique is described that takes advantage of these properties of TCNQ in acetonitrile to fabricate, in principle, any $M^{x+}TCNQ_x$ charge-transfer complex. This approach involves photochemical doping of TCNQ dissolved in acetonitrile with visible light in the presence of a sacrificial electron donor (benzyl alcohol). Generation of $TCNQ^-$ via this method, in the presence of $Cu^+_{(MeCN)}$, $Ag^+_{(MeCN)}$, $K^+_{(MeCN)}$, and $Co^{2+}_{(MeCN)}$ cations results in photocrystallization of the relevant metal−TCNQ charge-transfer complex onto a solid substrate. Photochemical doping of TCNQ in solution and the solid state has been reported previously[33−36] but has not been directed toward crystallization of potentially technologically important charge-transfer complexes such as CuTCNQ or AgTCNQ.

Photoinduced crystallization in the more general context has been used to generate metal nanoparticles in solution[37,38] and polymer films[39] and also for the formation of metal nanowires[40,41] within mesoporous materials. Photodeposition of metals at the semiconductor-solution interface[42−45] and photoinduced phase changes of semiconducting materials[46,47] also have been described. This work details for the first time how $M^{x+}[TCNQ]_x$ compounds can be photocrystallized onto both conducting and nonconducting substrates and subsequently characterized by optical imaging, scanning electron microscopy and various forms of spectroscopy. This photochemical based approach opens up the possibility of fabricating not only highly conducting MTCNQ compounds such as CuTCNQ and AgTCNQ, but also magnetic materials like $Co[TCNQ]_2$. The synthesis of magnetic $M^{2+}[TCNQ]_2(S)$ compounds, where S is a co-ordinating solvent, often require the use of highly reactive precursors and hence use of extremely pure solvents and a dry box atmosphere.[48−50] This new method can, for example, be used to synthesize $Co[TCNQ]_2(H_2O)_2$ under normal laboratory conditions.

## Experimental

**Materials and Chemicals.** Tetrakis(acetonitrile) copper(I) hexafluorophosphate ($[Cu(MeCN)_4]PF_6$), tetrakis(acetonitrile) silver(I) tetrafluoroborate ($[Ag(MeCN)_4]BF_4$), potassium hexafluorophosphate ($KPF_6$), hydrated cobalt perchlorate ($Co(ClO_4)_2{\cdot}6H_2O$), and TCNQ from Aldrich were used as supplied from the manufacturer. Analytical grade acetonitrile (Merck), tetrafluoroboric acid (Aldrich), benzyl alcohol (BDH), propan-2-ol (BDH), and acetone (Merck) also were used as received.

**Procedures.** Glass and ITO (Prazisions Glas and Optik GmbH) covered glass substrates onto which $M^{x+}[TCNQ]_x$ samples (M = Cu, Ag, K, and Co) were crystallized were cleaned by sonication in acetone for 10 min, then in propan-2-ol. Finally, they were dried by blowing with a stream of high purity nitrogen.

**Irradiation Procedure.** Acetonitrile solutions containing the metal salt precursor ($[Cu(MeCN)_4]PF_6$, $[Ag(MeCN)_4]BF_4$, $Co(ClO_4)_2.6H_2O$, or $KPF_6$) with TCNQ at an equimolar concentration were sonicated for 2 min. Benzyl alcohol was then added at a 10% v/v concentration and sonication was continued for an additional minute. The final equimolar concentration of metal salt and TCNQ after addition of benzyl alcohol was 8.33 mM.

The solution as prepared above was drop cast onto glass or ITO substrates (ca. 0.5 $cm^2$) and spread (still in a liquid state) over the entire substrate to give a thin film. This liquid thin film was then irradiated from above the substrate for 3 min at a distance of 0.5 cm. Use of an optical fiber attachment to the light source (Newport Scientific, Model 6292 200 W Hg(Xe) lamp with fused silica fiber optic bundle) produced a 3.2 mm diameter spot size for these irradiation experiments. Finally, the irradiated sample was allowed to dry overnight in the dark. A slight variation on this procedure was also used in which pyrex vessels, filled with solution, were irradiated from below, as shown in Figure S2.

**Sample Preparation Prior to Imaging Experiments.** The $M^{x+}TCNQ_x$ samples adhered to ITO or glass substrates were gently rinsed with acetonitrile to remove any unreacted TCNQ or metal salt precursor that may be present. This was achieved by adding drops of acetonitrile onto the solid sample and then removing the solvent with a tissue (Kimwipe). This sample preparation procedure was repeated three times.

**Instrumentation.** Electronic spectra were obtained in a 1 cm path length cell with a Varian Cary 5 UV−visible spectrophotometer (Varian OS2 software). Optical images were captured with an Olympus BX-51M optical microscope (10, 20, 50, and 100× magnification) and a DM-12 digital camera. Scanning electron microscopy (SEM) measurements employed a Philips XL30 Field Emission Gun Scanning Electron Microscope with an Oxford Link energy dispersive X-ray (EDAX) system. ITO was used as the substrate for sample preparation for SEM experiments to minimize background charging. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) data were obtained with an inverted Praying Mantis (Harrick Scientific) diffuse reflectance optical accessory. Raman spectra were obtained with a Renishaw RM 2000 Raman spectrograph and microscope using a 18 mW, 780 nm excitation source. Raman spectra from individual crystals were obtained using a 150X objective with the microscope. The course of benzaldehyde generation from benzyl alcohol was monitored by gas chromatography employing a 6′ × 1/4″ Carbowax 20M column using a Varion 3700 GC and HP3396 integrator. Its identity was confirmed by comparison of the retention time of the peak with that found using an authentic sample.

Voltammetric experiments were performed with an Autolab PGSTAT100 (ECO-Chemie) electrochemical workstation using a standard 4-necked electrochemical cell that allowed reproducible positioning of the working, reference and auxiliary electrodes and a nitrogen inlet tube. A 3 mm diameter glassy carbon (GC) was used as the working electrode and polished with a 0.3 $\mu$m alumina slurry on Microcloth

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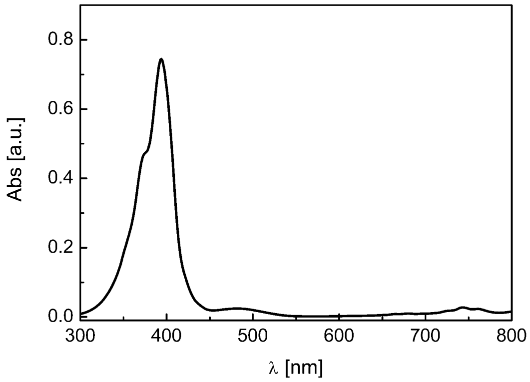

***Figure 1.*** UV−visible absorption spectrum of 1 × $10^{-5}$ M TCNQ in acetonitrile.

polishing cloth, rinsed in deionized water and dried (Kimwipe) prior to use. The Ag/AgCl (aqueous 3 M KCl) reference electrode was separated from the test solution by a salt bridge containing acetonitrile (0.1 M $Bu_4NPF_6$). The auxiliary electrode was made from platinum mesh. Voltammetric experiments were commenced after degassing the acetonitrile (0.1 M $Bu_4NPF_6$) electrolyte solutions with solvent saturated nitrogen for at least 10 min.

## Results and Discussion

For crystallization of a metal-TCNQ complex to occur its solubility must be exceeded. For example, the solubility product[21] for CuTCNQ in acetonitrile is 1.96 × $10^{-8}$ $M^2$ and studies of the electrocrystallization of CuTCNQ[21] confirm that large CuTCNQ crystals could be formed via reduction of TCNQ when equimolar concentrations (3−10 mM) of $[Cu(MeCN)_4]PF_6$ and TCNQ were used. In the present study the presence of equimolar concentrations (8.33 mM) of TCNQ and the metal salt precursor allowed the solubility of $M^{x+}[TCNQ]_x$ to be exceeded and crystallization of $M^{x+}[TCNQ]_x$ (M = Cu, Ag, K, and Co) to occur upon generation of $TCNQ^-$ by irradiation with light.

**UV−Visible Spectroscopy.** The UV−visible absorption spectrum for 10 $\mu$M TCNQ in acetonitrile exhibits a strong absorption band with $\lambda_{max}$ at 394 nm (Figure 1) with a molar absorption coefficient of 7.5 × $10^4$ $M^{-1}$ $cm^{-1}$. The band is associated with the well-known $^1A_g \rightarrow {}^1B_{3u}$ transition for TCNQ in acetonitrile.[51,52] A slight amount of absorbance is detected at 700−800 nm which may be attributed to a trace amount of $TCNQ^-$ in the solution.[53] Dilution of the equimolar solutions (8.33 mM) of TCNQ and metal salt containing 10% v/v benzyl alcohol to obtain a final TCNQ concentration of 10 $\mu$M did not lead to detection of new bands in the UV−visible spectrum. This result implies the absence of any charge transfer interactions in the ground state. In contrast, previous studies with TCNQ and xylenol in acetonitrile did lead to the detection of a ground state charge-transfer complex in the 400−450 nm region for $\mu$M TCNQ concentrations but with xylenol present at the 0.1−0.3 M concentration level[35] and hence in a large concentration excess. Ground state charge-transfer complexes have also been observed for TCNQ dissolved in *p*-xylene and mesitylene solvents.[54] A wavelength of 369 nm, which is close to the $\lambda_{max}$ value of 394 nm, was chosen for the excitation of TCNQ for all experiments involving the photoinduced crystallization of $M^{x+}[TCNQ]_x$ (M = Cu, Ag, K, and Co) compounds.

**Irradiation Experiments in the Absence of Benzyl Alcohol.** Control experiments in the absence of benzyl alcohol involved irradiation ($\lambda$ = 369 nm) of a liquid thin film comprised of an equimolar solution (8.33 mM) of TCNQ and $[Cu(MeCN)_4]PF_6$. The thin film completely absorbed the light (no evidence was found of light penetrating the film to the other side) and turned very-pale green indicating possible $TCNQ^-$ formation upon prolonged exposure to light. This procedure resulted in complete drying out of the film at which stage the light easily penetrated the underlying substrate. The dried out film both with and without washing with acetonitrile to remove unreacted TCNQ and $[Cu(MeCN)_4]PF_6$ (see Experimental section) did not show any evidence for CuTCNQ formation. However, wire like filaments with even finer microstructures growing from them in a perpendicular direction were observed when the sample was treated with acetonitrile (Figure 2). Analogous growth of TCNQ microcrystals[55] has been observed for TCNQ films grown on substrates held at 80 °C from chlorobenzene solutions containing small amounts of ethanol or carbon tetrachloride. Interestingly ca. 2 min is required for complete dissolution of these microstructures in acetonitrile.

Control experiments repeated using either $[Ag(MeCN)_4]BF_4$ or $KPF_6$ again resulted in microwire structures as shown in Figure 2a instead of AgTCNQ and KTCNQ respectively. These microwire structures are attributed to the washing procedure that induces dissolution and reprecipitation of TCNQ. Figure 2b contains optical micrographs of a TCNQ film on glass formed by allowing a liquid thin film of TCNQ in acetonitrile to evaporate, and produces cube shaped TCNQ crystals. After washing, the cube shaped crystals are converted into wire like structures (Figure 2c). TCNQ morphologies including rods (Figure 2d), wires (Figure 2e) and dendritic structures (Figure 2f) also can be generated by spin coating different concentrations of TCNQ solutions at different spin rates.

Further control experiments were carried out in which a thin liquid film of $M^{x+}_{(MeCN)}$ solution on ITO and glass substrates was irradiated at $\lambda$ = 369 nm to ensure that Cu and Ag metal in particular was not formed which would spontaneously react with neutral TCNQ. Equimolar solutions of $M^{x+}_{(MeCN)}$ and $TCNQ_{(MeCN)}$ were cast as thin films and allowed to dry both in the dark and under normal laboratory light conditions. These experiments were repeated on a hotplate (50 °C) to rule out any thermal effects. No evidence of $M^{x+}[TCNQ]_x$ formation was observed in these controls.

**Photocrystallization of $M^{x+}[TCNQ]_x$ (M = Cu, Ag, K, and Co) in the Presence of Benzyl Alcohol.** The control experiments suggest that TCNQ dissolved in acetonitrile cannot be photoreduced to generate a stable TCNQ anion and hence $M^{x+}[TCNQ]_x$ charge-transfer salts. However, the very-pale green color of the solution after irradiation suggested that formation of an unstable TCNQ-acetonitrile charge-transfer exciplex may have occurred as reported in photochemical studies of TCNQ in acetonitrile[36] and toluene.[54] The likely counter reaction if photoreduction of TCNQ occurred under these conditions would be oxidation of $Cu^+_{(MeCN)}$, $Ag^+_{(MeCN)}$, $K^+_{(MeCN)}$, acetonitrile itself, or impurities such as water. The voltammetric oxidation

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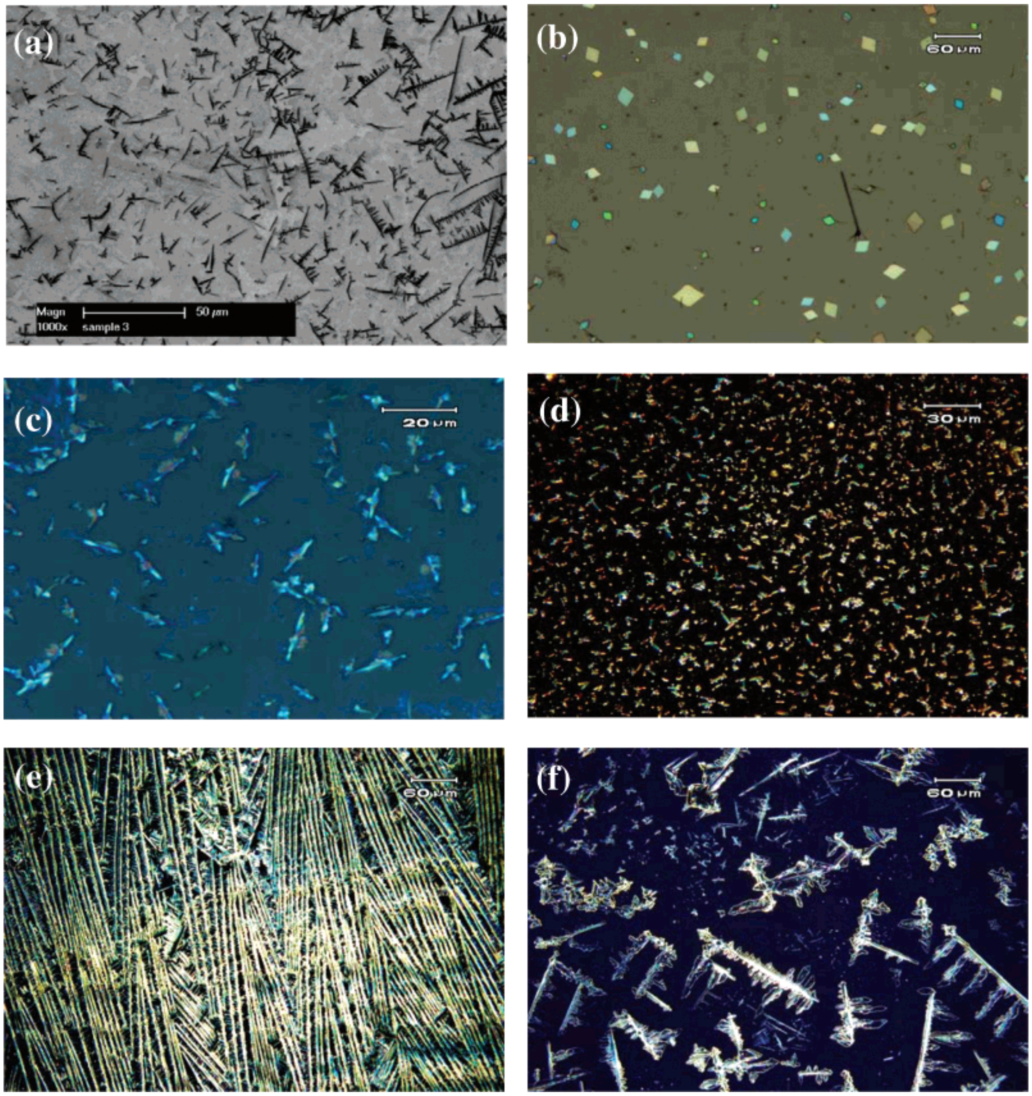

***Figure 2.*** SEM micrograph images of TCNQ microstructures formed by (a) irradiation ($\lambda = 369$ nm) of a liquid thin film of 1:1 [Cu(MeCN)$_4$]PF$_6$/TCNQ in acetonitrile. Optical micrographs of (b) 8.33 mM TCNQ in acetonitrile allowed to dry, (c) sample as in (b) washed with acetonitrile (see Experimental section) and spin cast films of TCNQ dissolved in acetontrile (d) 0.2 mg/mL at 1500 rpm, (e) 1 mg/mL at 1250 rpm, and (f) 1 mg/mL at 750 rpm.

peak potential for $Cu^+_{(MeCN)}$ at a glassy carbon electrode with a scan rate of 100 mV s$^{-1}$ was found to be 1.2 V and for $Ag^+_{(MeCN)}$ a broad ill-defined peak at about 1.9 V vs Ag/AgCl was observed. Thus, these reactions are highly unlikely. K$^+$ cannot be oxidized and the oxidation of acetonitrile under these conditions is also unlikely. Therefore to achieve significant $M^{x+}$-[TCNQ]$_x$ formation, a sacrificial electron donor was introduced. Benzyl alcohol was chosen for this purpose because it can be oxidized to benzaldehyde when irradiated by solar light in the presence of electron acceptors such as polyoxometalates.[56]

**CuTCNQ Formation.** Irradiation at $\lambda = 369$ nm of a liquid thin film of an equimolar solution (8.33 mM) of TCNQ and [Cu(MeCN)$_4$]PF$_6$ containing 10% v/v benzyl alcohol led to the immediate formation of a deep-green color (indicative of TCNQ$^-$ formation) which gradually became even darker green on increasing the irradiation time. Illustrated in Figure 3 are SEM images of rod shaped crystals formed on the ITO substrate (ITO was used to minimize charging effects) after the irradiated film has been washed with acetonitrile. The rod shaped crystals now present over the entire substrate were shown by EDAX analysis to contain Cu, C, and N which implies CuTCNQ formation. IR data confirm this assignment by the presence of bands at 2199, 2172, 1909, and 825 cm$^{-1}$ that are characteristic of CuTCNQ phase I formation[13] only (no evidence for phase II formation[13]). The uniformity in size of the microrods (4.5 × 0.5 $\mu$m) is striking. Even in areas where clusters are observed (Figure 3b−c) the rods appear to merely stack on top of each other (Figure 3c−d) as opposed to twinning or clustering in which crystals grow out from each other, as often observed in chemical and electrochemical syntheses.[15,21] Optical images taken after sample preparation on glass substrates also revealed rod shaped CuTCNQ formation.

Irradiation of the thin liquid film was also undertaken at 600 nm (well removed from the excitation wavelength of TCNQ in acetonitrile). At this wavelength, the light penetrates a large volume of TCNQ solution (2 cm path length). SEM images taken of samples prepared at this wavelength produced more sparsely spaced and unusually shaped crystals (Figure S1, Supporting Information). Raman spectra from a crystal such as that shown in Figure S1b showed the presence of bands at 2202, 1602, 1372, and 1204 cm$^{-1}$ which are indicative of phase I

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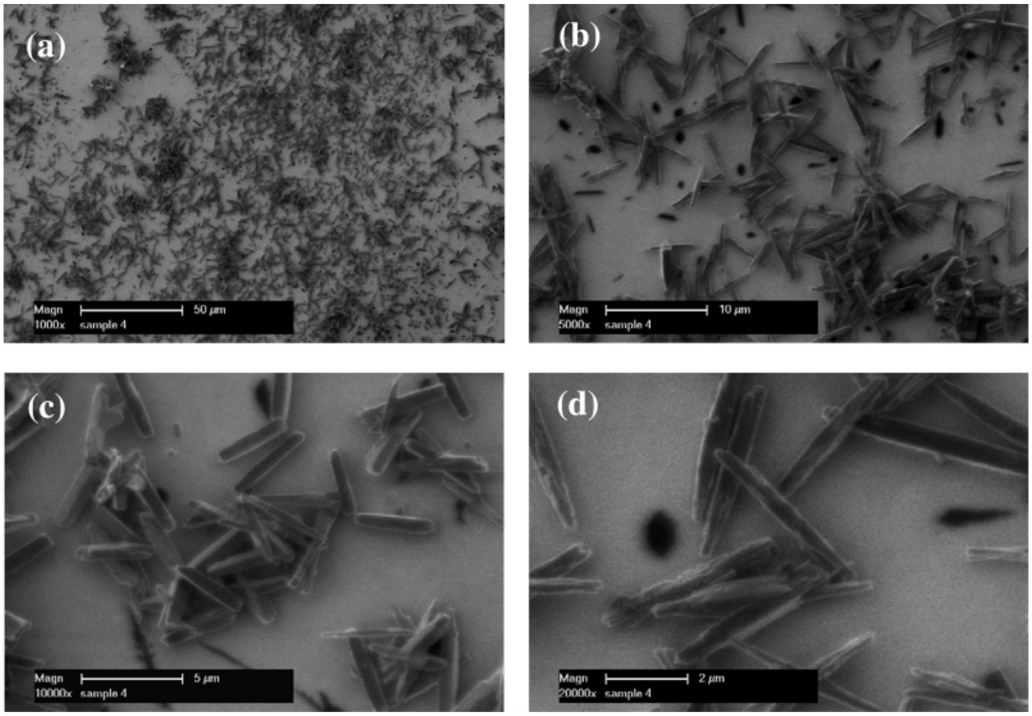

***Figure 3.*** SEM micrograph images of CuTCNQ formed by irradiation ($\lambda = 369$ nm) of a liquid thin film of 1:1 $[Cu(MeCN)_4]PF_6$/TCNQ (8.33 mM) in acetonitrile containing 10% v/v benzylalcohol.

CuTCNQ.[57] Photocrystallization of a sparse amount of CuTCNQ at this wavelength suggests that TCNQ in acetonitrile does absorb a certain amount of radiation and can be seen from the UV−visible spectrum in the wavelength range of 600−800 nm in Figure 1. However, the rod shaped crystals in particular (Figure S1b) are not as uniformly shaped as those produced when an irradiation wavelength of 369 nm was used. This suggests possible dissolution or incomplete formation of rod shaped CuTCNQ crystals under these conditions.

**AgTCNQ Formation.** The photocrystallization of AgTCNQ was attempted using $[Ag(MeCN)_4]BF_4$ and TCNQ in a 1:1 ratio (8.33 mM). The thin film again initially turned green but then green/blue with longer irradiation times, as expected if $TCNQ^-$ formation followed by AgTCNQ formation had occurred. SEM images of crystals formed in this case after the washing procedure reveal an extensive network of interconnecting nanowires (Figure 4a−d). Elemental analysis using SEM (EDAX) indicated that AgTCNQ formation had occurred. The nanowires were confirmed to be AgTCNQ by IR spectroscopy which showed bands indicative of reduced TCNQ[14] at 2200, 2161, 1506, and 824 $cm^{-1}$.

Some of these photocrystallized nanowires are up to 30 $\mu$m in length with diameters less than 180 nm. In some cases, the nanowires simply lie on top of each other, but do not grow from each other (Figure 4c). Nanowires of AgTCNQ have previously been fabricated via the spontaneous electrolysis reaction between silver metal and TCNQ dissolved in acetonitrile[24,25] and by vapor deposition of TCNQ onto silver foil.[20,30] A few isolated areas of rod shaped AgTCNQ crystals were observed, and as in the case of CuTCNQ, each of the individual rods were stacked on top of each other (Figure 4e).

**KTCNQ Formation.** Photocrystallization with $KPF_6$ as the metal salt produced less intense color changes during the course of the irradiation than detected during CuTCNQ and AgTCNQ formation. However, the film did turn pale green, indicating $TCNQ^-$ formation. IR spectroscopy after treating the sample with acetonitrile indicated KTCNQ formation by the presence of characteristic bands[58] at 2198, 2169, and 823 $cm^{-1}$. SEM images (Figure 5) show the extent of KTCNQ formation is less than for CuTCNQ and AgTCNQ. Rod shaped crystals are formed, but they exhibit a much larger size distribution than the case of CuTCNQ. Typical sizes range from 2.3 × 0.5 $\mu$m to 10.5 × 1 $\mu$m.

**$Co[TCNQ]_2(H_2O)_2$ Formation.** The cobalt precursor compound used for these experiments was $Co(ClO_4)_2.6H_2O$, which exhibits a pink-red color when dissolved in acetonitrile. This is in contrast to the Cu, Ag, and K salts used previously which give colorless acetonitrile solutions. However, a UV−visible spectrum measured after diluting a 1:1 (8.33 mM) TCNQ : $Co(ClO_4)_2.6H_2O$ solution containing 10% v/v benzyl alcohol to the 10 $\mu$M level showed no evidence of spectral changes in the TCNQ absorption region when compared to the absorption spectrum recorded for TCNQ alone (Figure 1).

Irradiation of a liquid thin film of an equimolar solution (8.33 mM) of TCNQ and $Co(ClO_4)_2{\cdot}6H_2O$ in the absence of benzyl alcohol resulted in detection of TCNQ structures like those shown in Figure 2a. The introduction of benzyl alcohol into the experiment resulted in successful photocrystallization of $Co[TCNQ]_2$ based material. This was confirmed by EDAX elemental analysis which indicated the presence of Co, N and C. SEM images in Figure 6 reveal that the extent of crystal formation is not as extensive as for CuTCNQ and AgTCNQ

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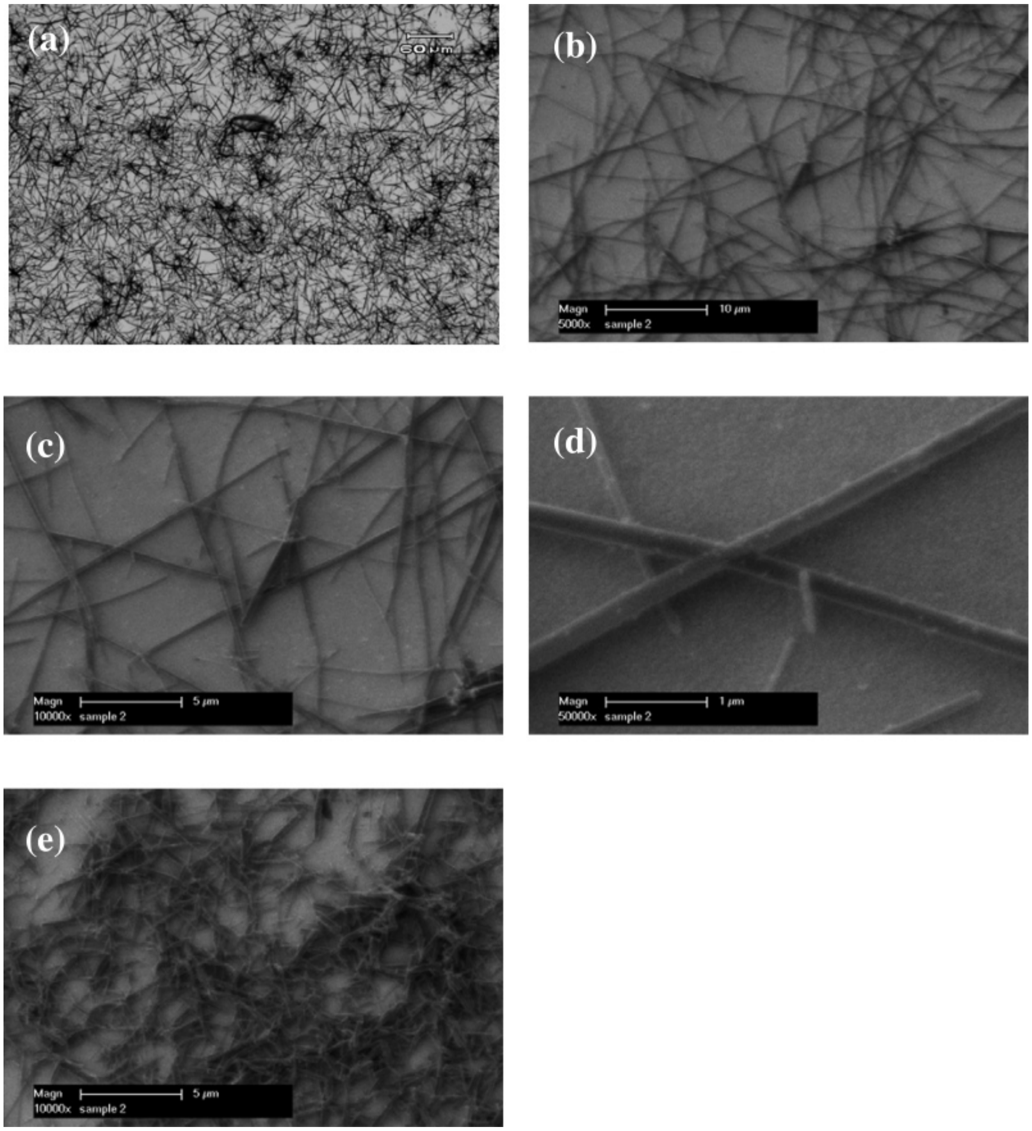

***Figure 4.*** Optical (a) and SEM (b−e) micrograph images of AgTCNQ formed by irradiation ($\lambda = 369$ nm) of a liquid thin film of 1:1 $[Ag(MeCN)_4]BF_4$/TCNQ (8.33 mM) in acetonitrile containing 10% v/v benzylalcohol.

and is more akin to the KTCNQ case. $Co[TCNQ]_2$ based material crystallized in two different morphologies. Needle shaped crystals are clearly evident in Figure 6a,b and rhombus shaped crystals in Figure 6c. Raman spectra showed the presence of bands at 1606, 1387, and 1200 $cm^{-1}$, indicative of $Co[TCNQ]_2(H_2O)_2$ formation. Raman spectra were compared to authentic samples prepared by the electrochemical solid−solid conversion[59] of TCNQ into $Co[TCNQ]_2(H_2O)_2$. The hydrated form is expected given that the cobalt precursor used was $Co(ClO_4)_2{\cdot}6H_2O$.

**Mechanism.** The mechanism for metal−TCNQ photocrystallization involves photoexcitation of TCNQ followed by oxidation of benzyl alcohol to benzaldehyde (confirmed by GC experiments), which leads to $TCNQ^-$ formation. The benzyl alcohol oxidation process contributes to the reaction in eq 1 and leads to $H^+$ formation as well as benzaldehyde. An analogous photochemical process involving TCNQ and benzyl ether in acetonitrile gave a quantum yield of 0.02.[34] This relatively low quantum yield was attributed to the presence of dicyanomethylene units in TCNQ, which are capable of dissipating excited-state energy through a free-rotor effect.[60] Thus, TCNQ has an extremely short excited-state lifetime and it is assumed that interaction with benzyl alcohol and benzyl ether in the photoexcited state would be comparable. Complex formation between $TCNQ^-$ and the cation is followed by crystallization of the metal complex at the solid substrate−solution interface when the solubility of $M^{x+}[TCNQ]_x$ is exceeded in acetonitrile.

The mechanism is supported by results obtained via a modification to the experimental arrangement. Taking CuTCNQ as an example, instead of synthesising crystals within a liquid thin film, a pyrex beaker containing an equimolar solution (8.33 mM) of TCNQ and $[Cu(MeCN)_4]PF_6$ with 10% v/v benzyl alcohol (total volume 2.2 mL) was irradiated at $\lambda = 369$ nm from underneath the beaker (see Figure S2). After ca. 20 min, evidence of a very dark colored precipitate was observed which intensified with time. Figure S3a−b (1 h irradiation time, see Supporting Information) provides images of disks of CuTCNQ

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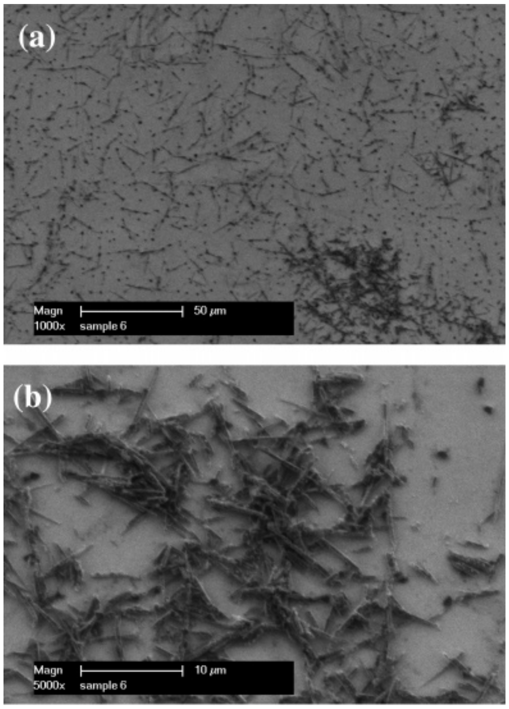

***Figure 5.*** SEM micrograph images of KTCNQ formed by irradiation ($\lambda = 369$ nm) of a liquid thin film of 1:1 $KPF_6$/TCNQ (8.33 mM) in acetonitrile containing 10% v/v benzylalcohol.

formed at the bottom of the beaker still containing the reaction solution. The solid disks diameter corresponds to that of the irradiation spot size (as shown in Figure S3c, white paper was placed between the light source and beaker to allow the spot to be observed). However, the amount of CuTCNQ formed increases with time (compare Figure S4 with 4 h irradiation time to S3a). This experiment was again repeated with an irradiation wavelength of 600 nm. However, in this case, no evidence of CuTCNQ formation was found after 2 h which suggests that the amount of CuTCNQ formed at this wavelength is minimal and most likely dissolves in such a large volume of TCNQ in acetonitrile solution.

The influence of protons present in acetonitrile solutions (derived from benzyl alcohol oxidation) was investigated by measuring the voltammetric response obtained for the electrocrystallization of CuTCNQ[21] in acetonitrile (0.1 M $TBAPF_6$) in the presence of tetrafluoroboric acid. The presence of protons was found to inhibit electrocrystallization of CuTCNQ via formation of TCNQ and $H_2$TCNQ via disproportionation of HTCNQ.[53,61] Thus, generation of protons under photosynthesis conditions also may decrease the extent of $M^{x+}[TCNQ]_x$ formation.

In summary, all data suggest that the mechanism of $M^{x+}[TCNQ]_x$ formation can be summarized by the following reaction scheme

$$2\mathrm{TCNQ}_{\mathrm{MeCN}} + \mathrm{C_6H_5CH_2OH} \xrightarrow{h\nu} 2\mathrm{TCNQ}^{-}_{\mathrm{MeCN}} + \mathrm{C_6H_5CHO} + 2\mathrm{H}^{+} \quad (1)$$

$$x\mathrm{TCNQ}^{-}_{\mathrm{MeCN}} + \mathrm{M}^{x+}_{\mathrm{MeCN}} \rightarrow \mathrm{M}^{x+}[\mathrm{TCNQ}^{-}]_x \quad (2)$$

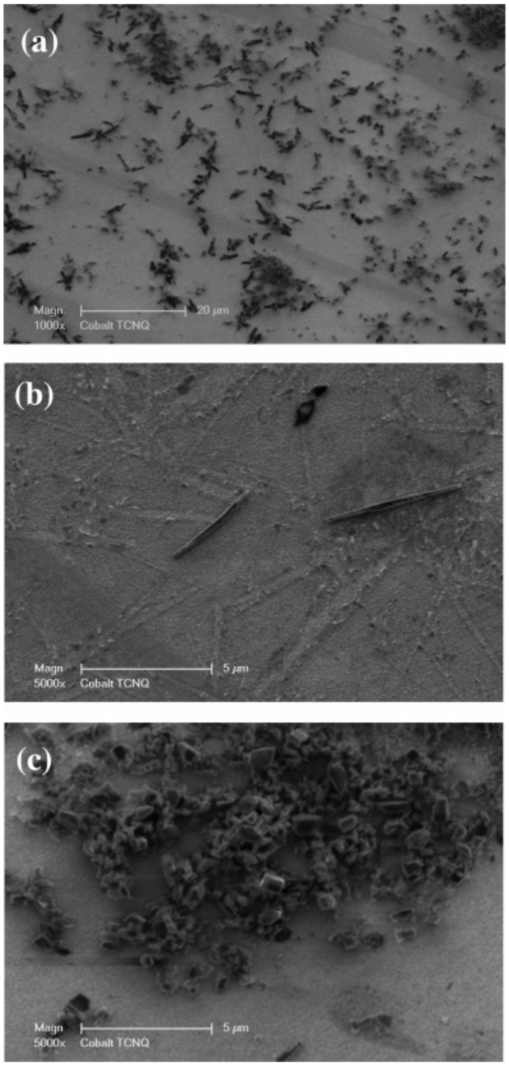

***Figure 6.*** SEM micrograph images of $Co[TCNQ]_2(H_2O)_2$ formed by irradiation ($\lambda = 369$ nm) of a liquid thin film of 1:1 $Co(ClO_4)_2{\cdot}6H_2O$/TCNQ (8.33 mM) in acetonitrile containing 10% v/v benzylalcohol.

However, the morphology of the $M^{x+}[TCNQ]_x$ charge-transfer complexes formed differ substantially when variation occurs with the cation present in solution. CuTCNQ and KTCNQ crystallize as rod shaped needles. $Co[TCNQ]_2(H_2O)_2$ also crystallizes as rod shaped needles but there is evidence of a more rhombus shaped morphology. In contrast, AgTCNQ is deposited as extremely long and thin nanowires. The rod and wire shaped morphologies are not too surprising given that TCNQ itself can adopt these crystal shapes.[55] This was confirmed by noting that the washing procedure employed in the present investigation gives rise to a random distribution of rod shaped TCNQ crystals (Figure 2c). The spin casting technique can generate microwires several mm in length. However, the nature of the cation must control the extent and direction of growth since $Ag^+$ based nanostructures are significantly different to the rods formed with the other cations studied.

This simple solution based approach for synthesis of $M^{x+}[TCNQ]_x$ charge-transfer complexes detailed in this paper may offer a convenient method of patterning flexible substrates with $M^{x+}[TCNQ]_x$ material in a controllable manner as is the case with photolithographic type procedures. Vacuum deposition or electroplating of metallic films is thereby avoided for production of spatially defined $M^{x+}[TCNQ]_x$ surfaces.

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## Conclusions

In the presence of metal cations, the photochemical reduction of TCNQ in acetonitrile, assisted by the presence of benzyl alcohol as a sacrificial electron donor, results in the deposition of sparingly soluble metal−TCNQ charge-transfer complexes onto both conducting or insulating solid substrates. The morphology of the resultant photoinduced crystallized products is dependent on the cation present in acetonitrile solution. Thus, a uniform distribution of phase I CuTCNQ microrods, a random size distribution of KTCNQ microrods and extremely long AgTCNQ nanowires up to 30 micrometres in length can be formed. This simple generic technique also can be employed to generate $Co[TCNQ]_2(H_2O)_2$, confirming that in principle, any metal-TCNQ complex that has limited solubility in acetonitrile could be synthesized via this strategy. The photocrystallization approach may provide a convenient alternative to the synthesis of $M^{x+}[TCNQ]_x$ compounds that commonly require extremely reactive and difficult to handle precursors. The nature of the procedure, also opens up the possibility to pattern insulating or flexible substrates with CuTCNQ or AgTCNQ materials without the need for vacuum deposition or electroplating of Cu and Ag metal films. This may be advantageous in fabrication of memory storage or switching devices.

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**Supporting Information Available:** Figures S1−S4 containing SEM images of unusual CuTCNQ microcrystals formed with an irradiation wavelength of 600 nm and optical images of CuTCNQ formation within pyrex vessels (illustrating the experimental setup) at various irradiation times. This material is available free of charge via the Internet at http://pubs.acs.org.

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