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Research paper

Electrochemistry of $TCNQF_2$ in acetonitrile in the presence of $[Cu(CH_3CN)_4]^+$: Electrocrystallisation and characterisation of $CuTCNQF_2$

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Morphology

ABSTRACT

The bulk electrochemical reduction of $TCNQF_2$ (where $TCNQF_2$ = 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane) in acetonitrile (0.1 M Bu_4NPF_6) in the presence of $[Cu(CH_3CN)_4]^+$ leads to the electrocrystallisation of $TCNQF_2^{1-}$ and $TCNQF_2^{2-}$ materials, identified and proposed as $Cu^ITCNQF_2^{I-}$ and $Cu^I_2(TCNQF_2^{II-})(CH_3CN)_2$, respectively. The existence of two forms of each solid was established by cyclic voltammetry. The low solubility of both $Cu^ITCNQF_2^{I-}$ and $Cu^I_2(TCNQF_2^{II-})(CH_3CN)_2$ solids, facilitated detection of a solid-solid transformation in the presence of $[Cu(CH_3CN)_4]^+$. $Cu^ITCNQF_2^{I-}$ was synthesized chemically as a dark blue microcrystalline solid by reaction of $TCNQF_2$ and CuI in CH_3CN, as well as electrochemically. Electronic and vibrational spectroscopic methods confirmed the $Cu^ITCNQF_2^{I-}$ product obtained by either method was structurally identical. Powder X-ray diffraction studies of $Cu^ITCNQF_2^{I-}$ gave a closely related pattern to that for the thermodynamically stable Cu^ITCNQ^{I-} phase II (a coordination polymer) rather than the kinetically favoured Cu^ITCNQ^{I-} phase I. Scanning electron microscopy established the dominant morphology, derived from both electrocrystallized and chemically synthesised samples, were the same. The conductivity of $Cu^ITCNQF_2^{I-}$ as a film on FTO glass was 6.0×10^{-6} S cm^{-1}, which lies in the semiconducting range.

1. Introduction

Organic charge-transfer materials derived from TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane, Fig. 1) have been widely investigated and exhibit a range of practically important properties [1,2]. For example, TCNQ charge-transfer complexes with transition metals ions, such as copper (I) or silver (I) are semi-conductors, and have been utilised in optical, electrical and magnetic devices [3–7]. $TCNQF_4$-based materials ($TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, Fig. 1) have also been studied recently [8,9]. The presence of four fluorine atoms enhances the electron affinity of $TCNQF_4$, which facilitates reduction to $TCNQF_4^{1-}$ and $TCNQF_4^{2-}$ and increases the stability of derived anions, especially the dianionic, two electron reduced form. This property allows $TCNQF_4^{2-}$-based materials to be generated in the air [10–13], while those of the dianionic parent compound, $TCNQ^{2-}$ usually need to be synthesized anaerobically [14–16]. The enhanced stability of the $TCNQF_4$ derivative therefore offers the exciting prospect of new dianionic materials. A family of dihalogenated dibromo-, dichloro- and difluoro-TCNQ complexes also have been reported [1,17–19]. However examples of the difluorinated, $TCNQF_2$ ($TCNQF_2$ = 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane, Fig. 1) derivatives are relatively rare.

$TCNQF_2$-based materials are expected to possess intermediate electronic properties between TCNQ and $TCNQF_4$.[20] For example, its electron affinity is 3.02 eV, which lies midway between 2.85 and 3.20 eV for TCNQ and $TCNQF_4$, respectively [21,22]. $TCNQF_2^{1-}$ salts of TTF^+ (TTF = tetrathiafulvalene) and its derivatives have been reported [17–19] and a $TCNQF_2$-nucleobase, cytosine material was synthesized and shown to be a fully ionic material derived from the $TCNQF_2^{1-}$ monoanion and the cytosine cation [23]. However, studies on the interaction between reduced forms $TCNQF_2$ and transition metals have yet to be reported. In this study, the reductive electrochemistry of $TCNQF_2$, in the presence of $[Cu(CH_3CN)_4]^+$ is reported in acetonitrile. The formation of $Cu^ITCNQF_2^{I-}$ based on the electrochemical investigation is described along with the its synthesis, electronic and vibrational spectroscopy and structural characterization. In addition, the electrocrystallisation of $Cu^I_2(TCNQF_2^{II-})(CH_3CN)_2$ is also described.

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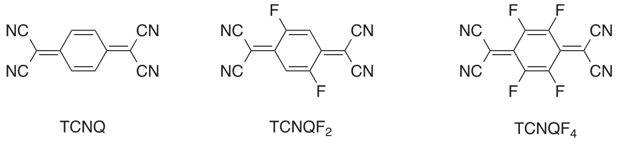


Fig. 1. Molecular structures of TCNQ, $TCNQF_2$ and $TCNQF_4$.

2. Experimental[1]

2.1.Chemicals

$TCNQF_2$ (98%, TCI Tokyo), $[Cu(CH_3CN)_4]PF_6$ (98%, Aldrich), acetonitrile (CH_3CN or alternatively MeCN; HPLC grade, Omnisolv), isopropanol (BHD) and acetone (suprasolv, Merck KGaA) were used as received from the manufacturer. Bu_4NPF_6 (Aldrich), used as the supporting electrolyte in electrochemical studies, was recrystallized twice from 96% ethanol (Merck) and then dried at 100 °C under vacuum for 24 h prior to use. Copper iodide (CuI) was obtained from Strem Chemicals (98%, Newburyport). Microanalysis was carried out at the Campbell Microanalytical Laboratories, University of Otago, New Zealand.

2.2. Electrochemistry

Voltammetric experiments were undertaken at room temperature (22 ± 1 °C) using a Bioanalytical Systems (BAS) 100 W workstation. A standard three electrode cell configuration, comprising a glassy carbon (GC, 1 or 3 mm diameter) working electrode, an Ag/Ag^+ (1.0 mM Ag^+) reference electrode (RE) and a 1.0 mm diameter platinum wire counter electrode, was employed in most experiments. For some experiments, working electrodes were BAS gold or platinum (Au or Pt, 1.6 mm or Au 10 µm diameter), indium tin oxide (ITO)- or fluorine tin oxide (FTO)-coated glass plates (0.1–0.2 cm^2) with a resistance of 10 Ω/sq, as specified by the manufacturer (Prazisions Glas and Optik GmbH). The data reported in detail on GC are almost independent of electrode material; GC, Au, Pt and FTO. Prior to each experiment, the working electrode was polished with an aqueous 0.3 µm Al_2O_3 slurry using a polishing cloth, rinsed with water followed by sonication in an ultrasonic bath for 30 s and dried under a stream of nitrogen. The RE was constructed from Ag wire in contact with acetonitrile solution (0.1 M Bu_4NPF_6) containing 1.0 mM $AgNO_3$ and separated from the test solution using a salt bridge. The potential of this reference electrode was −124 mV vs the ferrocene/ferrocenium ($Fc^{0/1+}$) couple. All solutions were purged with nitrogen gas for at least 10 min prior to each experiment and a stream of nitrogen was maintained above the solutions during the course of the voltammetric experiments. In bulk electrolysis experiments, a three-compartments cell was used with a large area Pt mesh working electrode, a Ag/Ag^+ (1.0 mM Ag^+) reference electrode and a Pt mesh counter electrode. In this case, each compartment was separated by a glass frit.

2.3. Synthesis of $Cu^{I}TCNQF_2^{I-}$

$Cu^{I}TCNQF_2^{I-}$ was prepared electrochemically as follows. Initially a 5.0 mM solution of $TCNQF_2^{1-}$ was prepared quantitatively by the reductive bulk electrolysis of 10 ml of 5.0 mM $TCNQF_2$ in acetonitrile (0.1 M Bu_4NPF_6). The potential of the Pt, ITO or FTO working electrode was held at −100 mV vs Ag/Ag^+ until the current reached 1% of its initial value. A dark blue precipitate formed immediately upon addition of 0.75 ml of 100 mM $[Cu(CH_3CN)_4]^+$. After stirring for 10 min, the solid was collected by filtration and washed several times with CH_3CN. Finally, the solid was dried under vacuum overnight before further characterisation.

Solid $Cu^{I}TCNQF_2^{I-}$ was also chemically synthesized by a redox reaction between $TCNQF_2$ and CuI (in a 1:1.5 stoichiometric ratio) in acetonitrile with stirring for 3 h. CuI acts as the reductant and the resulting dark blue solid, formed by the reaction given in Eq. (1), was filtered, washed with CH_3CN and dried as described above, prior to further characterisation.

$$3CuI + 2TCNQF_2 \rightarrow 2Cu^{I}TCNQF_2^{I-} + 3CuI_3 \qquad (1)$$

2.4. Conductivity of $CuTCNQF_2$

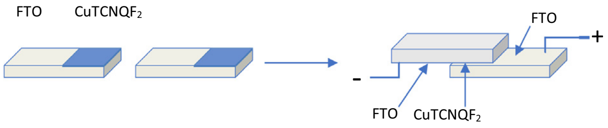
The conductivity was measured on a $Cu^{I}TCNQF_2^{I-}$ film. A $Cu_{(metal)}$ film was firstly sputter-coated using a Quorum Q150TS sputter coater instrument over a 1.0 cm × 1.0 cm area of FTO-coated glass (1.0 cm × 3.0 cm). The modified FTO glass was then soaked in an acetonitrile solution containing 10 mM $TCNQF_2$ for 12 h, resulting in the $Cu^{I}TCNQF_2^{I-}$ film as describe in Eq. (2).

$$Cu_{(metal)} + TCNQF_{2(MeCN)} \rightarrow Cu^{I}TCNQF^{I-}_{2(s)} \qquad (2)$$

Films on the FTO glasses were rinsed briefly with acetonitrile, to remove excess $TCNQF_2$, followed by a further rinsing step using copious amounts of water, before being dried under a stream of nitrogen and stored under vacuum. For conductivity measurements, two $Cu^{I}TCNQF_2^{I-}$-coated FTO glass pieces were stacked together so that the two $Cu^{I}TCNQF_2^{I-}$ films were in contact. The FTO glasses were then clamped carefully to minimize the contact force as shown in Scheme 1. Constant potential measurements were performed for 60 s at potentials from 50 to 500 mV with 50 mV intervals. The resistance (R) was calculated as R = U/I (where U (V) is the applied potential and I (A) is the measured current). The DC conductivity, σ, was calculated from the relationship σ = t/R.S where t (cm) is the thickness of the layer formed by two $Cu^{I}TCNQF_2^{I-}$ films, and S (cm^2) is the cross-sectional area. A VMP3 multi-channel potentiostat from BioLogic Instruments was used for the resistance measurements. The thickness of the $Cu^{I}TCNQF_2^{I-}$ films was measured using a VeeCo Dektak 150 profilometer. All of these measurements were performed in triplicate on two different thicknesses of FTO, at the same temperature, humidity and light conditions and corrected for the background conductivity contribution from FTO.

2.5. Other instrumentation

UV–Vis spectra were recorded with a Varian Cary 5000 UV–Vis NIR spectrophotometer with a 1.0 cm path length quartz cuvette. A Varian UMA600 IR microscope and FTS7000 optics bench with 128 scans and a resolution of 8 cm^{-1} was used for IR spectra measurements. Raman spectra were recorded on a Renishaw Invia Raman spectrograph with an Argon ion laser with excitation at 633 nm. After being coated with iridium, SEM images were collected with FEI Nova NanoSEM 450 FEGSEM instrumentation using an accelerating voltage of 5.0 kV. The X-ray powder diffraction (XRD) pattern was collected using an Oxford Diffraction Supernova diffractome-



Scheme 1. Experimental configuration used for conductivity measurements.

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[1] In equations, acetonitrile soluble species are designated by use of the subscript (MeCN), whereas solids use the subscript (s).