Solvent-, Cation- and Anion-Induced Structure Variations in Manganese-Based TCNQF₄ Complexes: Synthesis, Crystal Structures, Electrochemistry and Their Catalytic Properties**


The reaction of Mn(BF₄)₂·xH₂O with (Pr₆N)₂TCNQF₄ (TCNQF₄₂⁻ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in a mixture of CH₃OH/CH₂Cl₂ gives a 2:3 stoichiometric complex of (Pr₆N)[Mn₂(TCNQF₄)₂(CH₃OH)] (1). If the solvent system used for the crystallisation of 1 is changed to CH₃OH/DMF, then a different product, [Mn(TCNQF₄)(DMF)]₃(CH₃OH)₂ (2), is obtained. The use of Li₂TCNQF₄ instead of (Pr₆N)₂TCNQF₄ leads to the generation of [Mn(TCNQF₄)(DMF)]₃DMF (3). An unexpected mixed oxidation state network with a composition of [Mnⁿ⁺₁M₄⁺O₈(μ₂-OH)₂(μ₂-OCCH₃)₂(μ₃-TCNQF₄)](NO₃)₂·4CH₃OH (4), is formed if Mn(NO₃)₂·xH₂O is used in place of Mn(BF₄)₂·xH₂O in the reaction that leads to the formation of 3. Compounds 1–3 have been characterised by X-ray crystallography; FTIR, Raman and UV/Vis spectroscopy; and electrochemistry. Compound 4 has only been analysed by X-ray crystallography and vibrational spectroscopy (Raman, FTIR), owing to rapid deterioration of the compound upon exposure to air. These results indicate that relatively minor changes in reaction conditions have the potential to yield products with vastly different structures. Compound 1 adopts an anionic 2D network with unusual π-stacked dimers of the TCNQF₄₂⁻ dianion, whereas 2 and 3 are composed of similar neutral sheets of [Mn(TCNQF₄)(DMF)]₃. Interestingly, the solvent has a significant influence on the stacking of the sheets in the structures of 2 and 3. In compound 4, clusters with a composition of [Mnⁿ⁺₁M₄⁺O₈(μ₂-OH)₂(μ₂-OCCH₃)₂(μ₃-TCNQF₄)]₆⁺ serve as eight-connecting nodes, whereas TCNQF₄₂⁻ ligands act as four-connecting nodes in a 3D network that has the same topology as fluorite. Compound 3 exhibits an exceptionally high super-catalytic activity for the electron-transfer reaction between ferricyanide and thiocyanate ions in aqueous media.

Introduction

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄⁻) has attracted considerable interest because it is a stronger electron acceptor than that of the parent compound 7,7,8,8-tetracyanoquinodimethane (TCNQ)⁻ and easily generates the stable TCNQF₄⁺⁻ radical monoanion. Many charge-transfer complexes based on TCNQF₄⁻ have been prepared and have shown interesting and practical magnetic/electronic properties.[8–11] Copper derivatives have recently demonstrated practical applications, as illustrated by their super-hydrophobicity.[12,13] In contrast, studies of the TCNQF₄⁺⁻ dianion with metal or organic cations are limited because the TCNQF₄⁺⁻ dianion is less stable than that of the TCNQF₄⁺⁻ monoanion in solution.[14,15] Furthermore, stable metal salts/organic precursors of the TCNQF₄⁺⁻ dianions, if used as starting materials, are difficult to synthesise on a large scale. However, recently, Bond and co-workers synthesised pure Li₂TCNQF₄ and (Pr₆N)₂TCNQF₄ as starting materials on a large scale by both chemical and electrochemical methods.[14] Robson et al. successfully used H₂TCNQF₄ with a weak base, such as LiOAc, to produce organic TCNQF₄⁺⁻ salts and metal-coordination polymers.[16–18] Coordination polymers incorporating the TCNQF₄⁺⁻ anion commonly form networks with channels that may permit the intercalation of either oxidants or electron-acceptor molecules. The incorporation of such guest molecules into the voids inside the framework has the potential to modify the physical properties of the solid, which results in interesting and potentially useful electronic and magnetic behaviour. Herein, we report the synthesis of four new Mn–TCNQF₄ dianion complexes; the composition and structure of the compounds depend upon the choice of solvent and/or counter-ions employed. These new compounds have been investigated by X-ray crystallography; Raman, FTIR and UV/Vis spectroscopy; and electrochemistry. One of the compounds (3) has been used as a heterogeneous catalyst in the electron-transfer reaction between ferricyanide and thiocyanate ions.
fate in aqueous solution and shows 100% reduction efficiency, even after 50 cycles, with no degradation of the catalyst. This represents exceptional, super-catalytic activity compared with that of most other catalysts used for this reaction, \(^{20-24}\) although we have observed similar high activity for [Pr(NH\(_3\))\(_4\)](TCNQF\(_4\)) under comparable reaction conditions.\(^{24}\)

Results and Discussion

Synthesis

In the synthesis of the compounds described herein, TCNQF\(_2\)^{2-} was introduced as the tetrabutylammonium salt, the lithium salt or as its acid form, H\(_3\)TCNQF\(_4\). For compounds 1–4, the 2-oxidation state of the ligand is retained in the product. When a solution of (Pr\(_2\)N)\(_2\)TCNQF\(_4\) in methanol is slowly diffused into a solution of Mn(BF\(_4\))\(_2\)-H\(_2\)O in CH\(_2\)OH/CH\(_2\)Cl\(_2\), colourless single crystals with a composition of [Pr\(_2\)N\(_2\)]\([\text{Mn(TCNQF}_3\text{(CH}_2\text{OH)}_2\text{)}]\) (1) are formed in 42% yield. If the solvent system used for the crystallisation of 1 is changed to CH\(_2\)OH/DMF, a different product, (Mn(TCNQF\(_4\))(DMF))\(_2\)(CH\(_2\)OH\(_2\)) (2), is isolated in excellent yield. Compound 2 can also be prepared starting from H\(_3\)TCNQF\(_4\) with LiOAc as a base. The use of Li\(_2\)TCNQF\(_4\) instead of (Pr\(_2\)N)\(_2\)TCNQF\(_4\) yields a compound with a composition of [Mn\(_2\)(TCNQF\(_4\))(DMF)]\(_3\)DMF (3) in good yield. Surprisingly, when the nitrate salt, Mn(NO\(_3\))\(_2\)-6H\(_2\)O, is used instead of Mn(BF\(_4\))\(_2\)-H\(_2\)O, in a similar synthetic procedure to that which resulted in the formation of 3, blue square prisms form with a remarkable composition of [Mn\(_n\)Mn\(_m\)O\(_n\)OH\(_n\)OC\(_\text{H}_3\)]\(_n\)(TCNQF\(_3\))\(_n\)(NO\(_3\))\(_n\)24CH\(_2\)OH (4). Although crystals of 4 were only very weakly diffracting, it was possible to determine the connectivity of the structure by means of single-crystal XRD. These crystals were unstable outside the mother liquor and quickly deteriorated upon direct exposure to air. As a consequence, analysis of the bulk material was not possible. Full details relating to the syntheses are presented in the Experimental Section. Colourless compounds 1, 2 and 3 have been structurally characterised by single-crystal XRD and investigated by FTIR, Raman and UV/Vis spectroscopy, as well as electrochemistry. Although both 1 and 2 are unstable in water, compound 3 is stable in aqueous solution. Details of an investigation into 3 as a heterogeneous catalyst for the reduction of ferricyanide to ferrocyanide in the presence of thiosulfate in aqueous solution is also presented.

Crystal structures

(Pr\(_2\)N)\(_2\)[Mn\(_3\)(TCNQF\(_4\))(CH\(_2\)OH\(_2\))](1)

Compound 1 is triclinic and adopts the space group P1. The asymmetric unit of 1 contains one and a half TCNQF\(_4\) anions (designated as TCNQF\(_4\)-A and TCNQF\(_4\)-B, respectively), one Mn\(^{3+}\) centre, one Pr\(_{2}\)N\(^{2+}\) cation and a single coordinated methanol molecule (Figure 1a and Figure S1 in the Supporting Information). The structure consists of a 2D network in which the Mn\(^{3+}\) centres are linked by the two crystallographically distinct TCNQF\(_4\)^{2-} ligands. The Mn\(^{3+}\) centre is in an approximately octahedral coordination environment, which is formed by the oxygen atom of the coordinated methanol molecules and five cyano nitrogen atoms; three from three TCNQF\(_4\)-A dianions and two from a pair of TCNQF\(_4\)-B dianions.

The TCNQF\(_4\)-A dianion is close to planar and displays only a slight bowing of the CN groups away from the phenyl plane, whereas in TCNQF\(_4\)-B the dihedral angle formed between the phenyl ring and the pair of C(CN) planes is 34°. Each TCNQF\(_4\)-B is bound to four Mn\(^{3+}\) centres that are located at the corners of a rectangle with dimensions of 7.516 and 11.212 Å. These Mn\(_n\)(TCNQF\(_4\)-B) rectangular units share an edge along the short edge to create an infinite strip that runs parallel to the b axis. In contrast to the TCNQF\(_4\)-B dianions, the TCNQF\(_4\)-A dianions are only bound to three Mn\(^{3+}\) centres, with the non-coordinated cyano group forming an N–H–O interaction with the
coordinated methanol molecule. Surprisingly, given the formal charge associated with TCNQF$_4^-$ in the 2– oxidation state, the TCNQF$_2$-A ligands are present as pairs in which the individual anions, which are crystallographically related to each other across a centre of inversion, are slightly offset from each other, as indicated in Figure 1a. The separation between the mean planes of the dianions is 3.4 Å. Each TCNQF$_2$-A dianion within a pair is bound to the same four Mn$^{II}$ centres through either direct coordination of a cyano group or a hydrogen-bond interaction involving the coordinated methanol. The combination of a pair of TCNQF$_2$-A dianions bound to a quartet of Mn$^{II}$ centres, located at the vertices of a rectangle, forms part of an infinite strip within a 2D network that runs parallel to the b axis. The Mn$^{II}$ centres of these strips are shared with the aforementioned strips involving the TCNQF$_2$-B dianions. Within the 2D network, these two types of parallel strips alternate (Figure 1a). The anionic 2D networks with an overall composition of [Mn$_4$(TCNQF$_2$)$_4$(DMF)$_8$]- are separated by parallel layers of Pr$_3$N$^+$ cation, as indicated in Figure 1b.

$$\text{[Mn(TCNQF$_2$)$_4$(DMF)$_8$]}_2\text{CH}_3\text{OH (2)}$$

Colourless or pale crystals of 2 prepared by either methods A or B (see the Experimental Section) crystallise in the monoclinic space group C2/m. The asymmetric unit consists of one quarter of the formula unit; the Mn$^{II}$ centres and TCNQF$_4^{2-}$ ligands are located on sites of 2/m symmetry. The TCNQF$_4^{2-}$ ligands are almost planar, with a maximum dihedral angle between the phenyl and C(CN)$_2$ planes of 2.2°.

Compound 2 is composed of a 2D sheet, in which each TCNQF$_4^{2-}$ ligand is bound to four Mn$^{II}$ centres located at the corners of a rectangle. In turn, each Mn$^{II}$ centre is bound to four TCNQF$_4^{2-}$ ligands, with the four nitrogen atoms occupying four coplanar sites around the metal centre. An octahedral coordination geometry is completed by the oxygen atoms of a pair of trans-DMF molecules (Figure 2a). This type of network is very similar to a series of sheet-like structures, in which trans-pyridyl-based ligands complete an octahedral geometry of divalent metal centres linked by TCNQF$_4^{2-}$ ligands.\(^{[10]}\) As with the TCNQ-based structures described in the literature, tetradeinate TCNQF$_4^{2-}$ is inclined to the plane of the four central metal centres to which it is bound. As a consequence, the dianions within a sheet are not co-planar, although the 1,4-axes (passing through the 1,4-positions of the aromatic rings) of all dianions are all parallel. The trans-coordinated DMF molecules extend above and below the sheet, as indicated in Figure 2a. Parallel networks stack with the interdigitation of coordinated DMF molecules (Figure 2b). The stacking arrangement leads to the generation of narrow channels between the sheets. Methanol molecules occupy these channels and each forms a hydrogen bond with the oxygen atom of a coordinated DMF molecule.

$$\text{[Mn(TCNQF$_2$)$_4$(DMF)$_8$]}_3\text{DMF (3)}$$

Colourless crystals of 3 are monoclinic and adopt the space group P2$_1$/c. The asymmetric unit consists of two crystallographically distinct Mn$^{II}$ centres (Mn1 and Mn2), one full and two half TCNQF$_4^{2-}$ ligands, four coordinated DMF molecules, and three uncoordinated DMF molecules (Figure 3a). The structure provides a remarkable contrast with that of the methanol solvate, 2. The connectivity of the network is identical to that of 2, with Mn$^{II}$ centres bound to a pair of trans-DMF molecules and linked by tetradeinate TCNQF$_4^{2-}$ ligands; however, as indicated by a comparison of Figures 2a with 3a, the sheets are far less regular in 3. Figure 3b shows the stacking of sheets in a manner that once again produces narrow channels; however, as revealed by a comparison of Figures 2b and 3b, the channel cross section has a distinctly different shape. It seems likely that the ability of the methanol molecule to form hydrogen bonds with coordinated DMF in 2 contributes towards a regular arrangement for the coordinated DMF molecules. In contrast, the uncoordinated DMF molecules are unable to form significant hydrogen-bonding interactions with the coordinated DMF molecules in 3.
the edge of the tetrahedron); a tetrahedral \( \mu_4 \)-oxo anion within the core of the cluster; and a pair of N atoms, which belong to two distinct TCNQF \(_2^+\) ligands. The Mn\(^{III}\) assignment is based upon the Mn–N/O bond lengths, which are in the range of 2.13–2.46 Å. The manganese(III) centre located in the middle of each face is in an octahedral environment formed by a trio of \( \mu_3 \)-methoxy anions, with the methyl groups extending out almost normal to the triangular face of the tetrahedron; three core \( \mu_4 \)-oxo anions complete the coordination sphere. The 12 manganese(III) centres that occupy the tetrahedron edges (two on each edge) represent two distinct crystallographic centres; however, both types are in similar octahedral environments. Each of these manganese(III) centres is bound to a pair of \( \mu_2 \)-methoxy groups, two \( \mu_2 \)-methoxy groups, and \( \mu_2 \)-hydroxo groups that are \( \mu_2 \) to each other. As indicated in Figure 4a, the \( \mu_2 \)-methoxy and \( \mu_2 \)-hydroxo groups are located on each edge of the tetrahedron, with the \( \mu_2 \)-hydroxo group located halfway along the edge. The incorporation of the hydroxide ion instead of a third methoxide ion along the edge is most likely a consequence of the steric effect of the flanking methyl groups.

As indicated in Figure 4b, each TCNQF \(_2^-\) dianion is bound to four Mn\(^{III}\) clusters, the centres of which form a distorted tetrahedral arrangement around the TCNQF \(_2^-\) ligand. From a topological perspective, the TCNQF \(_2^-\) dianion may be considered as a tetrahedral node. With each of the four Mn\(^{III}\) centres of the cluster linking to a pair of TCNQF \(_2^-\) ligands, the Mn\(^{III}\) cluster, in turn, serves as an eight-connecting node. The resulting network, therefore, consists of 8-connecting Mn\(^{III}\) clusters and 4-connecting TCNQF \(_2^-\) ligands in a 1:2 ratio. The topology of the network, schematically represented in Figure 4c, is the same as that of fluorite (CaF\(_2\)). The network is relatively open and, according to calculations performed using the program PLATON, the framework occupies only 53% of the crystal volume. The intrawork space is occupied by highly disordered solvent.

As indicated in the Introduction, compound 4 was obtained by means of a synthetic procedure similar to that employed to produce 3, except that Mn\(^{II}\) was introduced as the nitrate salt, rather than as the tetrafluoroborate salt. This highly unusual network material consists of clusters each with a composition of \([\text{Mn}^{IV}_{14}\text{Mn}^{II}_{16}O_{10}(\text{OH})_8(\text{OCH}_3)_{24} \text{(CH}_2\text{OH})_4\text{TCNQF}_4\text{J}]\) (NO\(_3\))\(_2\)\(24\text{CH}_2\text{OH}\) (4)

As indicated above, compound 4 was obtained by means of a synthetic procedure similar to that employed to produce 3, except that Mn\(^{II}\) was introduced as the nitrate salt, rather than as the tetrafluoroborate salt. This highly unusual network material consists of clusters each with a composition of \([\text{Mn}^{IV}_{14}\text{Mn}^{II}_{16}O_{10}(\text{OH})_8(\text{OCH}_3)_{24} \text{(CH}_2\text{OH})_4\text{TCNQF}_4\text{J}]\) (NO\(_3\))\(_2\)\(24\text{CH}_2\text{OH}\) (4)

As indicated above, compound 4 was obtained by means of a synthetic procedure similar to that employed to produce 3, except that Mn\(^{II}\) was introduced as the nitrate salt, rather than as the tetrafluoroborate salt. This highly unusual network material consists of clusters each with a composition of \([\text{Mn}^{IV}_{14}\text{Mn}^{II}_{16}O_{10}(\text{OH})_8(\text{OCH}_3)_{24} \text{(CH}_2\text{OH})_4\text{TCNQF}_4\text{J}]\) (NO\(_3\))\(_2\)\(24\text{CH}_2\text{OH}\) (4)

As indicated above, compound 4 was obtained by means of a synthetic procedure similar to that employed to produce 3, except that Mn\(^{II}\) was introduced as the nitrate salt, rather than as the tetrafluoroborate salt. This highly unusual network material consists of clusters each with a composition of \([\text{Mn}^{IV}_{14}\text{Mn}^{II}_{16}O_{10}(\text{OH})_8(\text{OCH}_3)_{24} \text{(CH}_2\text{OH})_4\text{TCNQF}_4\text{J}]\) (NO\(_3\))\(_2\)\(24\text{CH}_2\text{OH}\) (4)

As indicated above, compound 4 was obtained by means of a synthetic procedure similar to that employed to produce 3, except that Mn\(^{II}\) was introduced as the nitrate salt, rather than as the tetrafluoroborate salt. This highly unusual network material consists of clusters each with a composition of \([\text{Mn}^{IV}_{14}\text{Mn}^{II}_{16}O_{10}(\text{OH})_8(\text{OCH}_3)_{24} \text{(CH}_2\text{OH})_4\text{TCNQF}_4\text{J}]\) (NO\(_3\))\(_2\)\(24\text{CH}_2\text{OH}\) (4)
Vibrational (Raman and FTIR) spectroscopy

Raman and IR spectroscopic studies have been used widely to determine the redox state of TCNQF₄ in its complexes. The Raman spectra of compounds 1–3 are presented in Figure S5, and exhibit diagnostic bands for TCNQF₄⁻⁻ ions. The C≡N stretches are observed at slightly lower frequencies (2110 to 2221 cm⁻¹), compared with those for neutral TCNQF₄ (2226 cm⁻¹) and monovalent TCNQF₄⁻ (2205 to 2223 cm⁻¹), showing a) the C≡N stretching vibration of TCNQF₄⁻⁻ ions are observed, similar to those for neutral TCNQF₄.

The Ramans of compound 1 are similar to those found for the C≡N stretching vibration of TCNQF₄⁻⁻ ions, and show different splitting modes, which can be explained by assuming that the cyano groups are inequivalent, owing to different coordination environments. The C≡N stretching vibration of compound 3 is shown in Figure 5c. Although the C≡N bands show a similar splitting pattern to those for 1, we note that the ratios of intensities of the three bands are significantly different, possibly owing to differences in the structures of 1 and 3. Furthermore, two extra, small bands at 1290 and 1017 cm⁻¹ are observed.

The FTIR spectra for compounds 1–3 are shown in Figure S4 in the Supporting Information and exhibit typical characteristics of the TCNQF₄⁻⁻ dianion. By comparison, the C≡N stretches for 1–3 shift to lower frequency, compared with that of the neutral TCNQF₄ and exhibit different splitting patterns of these modes, owing to different coordination environments in the crystal structures. The five C≡N bands at ν = 2205, 2179, 2161, 2136 and 2109 cm⁻¹ for compound 1 are detected, whereas compound 2 shows four strong C≡N bands at ν = 2195, 2149 and 2125 cm⁻¹, with a shoulder at ν = 2094 cm⁻¹. In the case of compound 3, there are three bands at ν = 2198, 2125 and 2094 cm⁻¹ associated with the C≡N group. The ring C–C stretch also gives diagnostic bands for the TCNQF₄⁻⁻ dianion. The bands at ν = 1479 cm⁻¹, with a shoulder at ν = 1488 cm⁻¹, for compound 1; the bands at ν = 1480 cm⁻¹, with a shoulder at ν = 1488 cm⁻¹, for 2; and the bands at ν = 1480 cm⁻¹, with a shoulder at ν = 1493 cm⁻¹, for 3 are observed; these bands are associated with the ring C=C stretches and are all at lower frequencies than those found in TCNQF₄ (ν = 1599 cm⁻¹) and TCNQF₄⁻⁻ (ν = 1534 cm⁻¹). FTIR spectra are consistent with the results obtained by Raman spectroscopy, and indicate that the TCNQF₄ moieties in compounds 1–3 exist in the fully reduced dianion form, TCNQF₄⁻⁻.

Figure 4. The crystal structure of 4 showing a) the [Mn₄⁺Mn₃⁻O₃(OH)₉(OCH₃)₆(CH₃OH)]₄⁺⁺ cluster with connections (indicated in green) to eight coordinating N atoms belonging to TCNQF₄⁻⁻ ligands; b) a single TCNQF₄⁻⁻ ligand linked to four Mn₃⁺ clusters; the clusters with pink connections are in the foreground, whereas clusters with light-blue connections are in the background; and c) a schematic representation of the network connectivity; the large blue spheres represent Mn₃⁺ clusters. Colour code: C, black; H, pale pink; N, light blue; O, red; F, green; Mn⁺, blue; Mn³⁺, purple. Except for the µ₂-OH⁻ ions, hydrogen atoms have been omitted for clarity.
Electrochemistry and UV/Vis studies

Transient voltammetry

In spite of the compositional and structural differences of compounds 1–3, their electrochemical behaviour in solution is identical (Figure 6 and Figures S5 and S6 in the Supporting Information). A transient cyclic voltammogram of 1 dissolved in DMF (containing 0.1 M Bu₄NPF₆) at a glassy carbon macro-electrode is shown in Figure 6. It exhibits two reversible, diffusion-controlled, one-electron oxidation processes over a scan rate range of 5 to 500 mV s⁻¹ that correspond to the TCNQF⁺₂ → TCNQF⁺₁⁻ [Eq. (1)] and TCNQF⁺₁⁻ → TCNQF⁺₀ [Eq. (2)] processes. The mid-point potentials are $E_{m1} = -0.17$ mV and $E_{m2} = 0.524$ mV (vs. Ag/Ag⁺), in which $E_{m}$ is the average of the reduction ($E_{p}^{red}$) and oxidation ($E_{p}^{ox}$) peak potentials and represents a close approximation of the reversible formal potential, $E^\circ$. The separation in the potentials for the two processes is 541 mV, and is consistent with data reported in the literature under similar conditions.²⁴ These voltammetric data imply that, upon dissolution of 1 in DMF, TCNQF⁺₂ and Mn⁺⁺⁺ are formed. In this scan range, no other higher oxidation species are observed (e.g., Mn⁺⁺⁴⁺).

To confirm the stability of the reactants and products in Equations (1) and (2), transient cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹ for 30 cycles over the potential range (Figure S6 in the Supporting Information). The small decrease in current observed on cycling potential is predicted by theory, and the behaviour confirms that TCNQF⁺₂, TCNQF⁺₁⁻ and TCNQF⁺₀ are stable in DMF on this cyclic voltammetric timescale.

Steady-state voltammetry

Steady-state voltammetry can be used to determine the redox level of TCNQF⁺ in compounds 1–3.²⁴ In principle, the one-electron oxidation of either TCNQF⁺₂ → TCNQF⁺₁⁻, or TCNQF⁺₁⁻ → TCNQF⁺₀, will give a positive current in the steady-state voltammogram. Figure 7 and Figure S7 in the Supporting Information show near-steady-state voltammograms for a solution of compounds 1–3 in DMF (0.1 M Bu₄NPF₆) by using a 10 μm Pt micro-electrode.

Figure 5. Raman spectra for compounds a) 1, b) 2 and c) 3.

Figure 6. The transient cyclic voltammogram of 1 at variable scan rate with a glassy carbon macro-electrode.

Figure 7. Steady-state voltammogram of 1 at 5 mV s⁻¹ with a 10 μm Pt micro-electrode.
10 μm Pt micro-electrode. The position of zero current reveals that 1 (and 2 and 3) contains only TCNQF$_2^{–}$ species because only the oxidation current associated with the TCNQF$_2^{–}$ and TCNQF$_4^{–}$ processes is present (Figure 7). These electrochemical studies on compound 1 in solution are consistent with the results obtained from FTIR and Raman spectroscopy, and X-ray structural data, and confirm that the dissolution of 1 provides only TCNQF$_4^{–}$ species.

Electronic (UV/Vis) spectroscopy

UV/Vis spectra for compounds 1–3 dissolved in CH$_2$CN are shown in Figure S8 in the Supporting Information. These spectra in CH$_2$CN are dominated by two intense absorption bands at $\lambda_{max} = 333$ and 219 nm, assigned to the TCNQF$_2^{–}$ dianion, which are consistent with our previous reports$^{[14,27]}$ and confirm the results obtained from electrochemical studies.

Formation of [Mn(TCNQF)$_4$(DMF)$_2$] (5) in aqueous media

As part of an investigation into the potential of Mn-TCNQF$_4$ networks to serve as heterogeneous catalysts, we were interested in determining the stability of 3 upon immersion in water. Although 3 was insoluble in water, it was considered likely that the non-coordinated DMF molecules could be lost from the channels, but it was uncertain whether the coordinated DMF would remain bound to the Mn$^{II}$ centres. To investigate the stability in water, crystals of 3 were placed in D$_2$O, and the solution phase was examined by $^1$H NMR spectroscopy. The spectrum clearly revealed the presence of DMF in the aqueous solution (Figure S9 in the Supporting Information). The solid material was filtered from the solution in D$_2$O, washed with water and dried under vacuum, over P$_2$O$_5$, for 1 day prior to FTIR spectroscopy analysis. The FTIR spectrum of the solid material was similar to that found for 3, although the uncoordinated DMF bands were absent, which suggested that 3 lost only the uncoordinated DMF molecules in water to form [Mn(TCNQF)$_4$(DMF)$_2$] (5).

Heterogeneous catalytic studies on the reduction of [Fe(CN)$_6^{3–}$ by [S$_2$O$_3^{2–}$ in aqueous solution by compounds 3 and 5

Metal–TCNQ materials, and their tetra-fluorinated analogues have been widely investigated for applications in electronic switching and field-emission devices; however, the catalytic properties of these materials are rarely explored. O’Mullane et al. used films derived from MTCNQ or MTCNQF$_4$ (M=Cu$^{I}$, Ag$^{I}$) to catalyse the otherwise very slow redox reaction of ferricyanide and thiosulfate ions in aqueous solution,$^{[21]}$ and, more recently, Bond and co-workers discovered that blue crystalline [(NH$_4$)$_2$Pt(TCNQF)$_4$] displayed super-catalytic activity and reusability, with respect to the above reaction under the same conditions.$^{[24]}$ This encouraged us to explore whether the manganese-based networks 1–3 were capable of exhibiting similar catalytic behaviour with respect to this redox reaction. Unfortunately, neither 1 nor 2 were stable in aqueous solution containing K$_3$[Fe(CN)$_6$] and Na$_2$S$_2$O$_3$. By contrast, compound 3 was stable in water and was employed as a heterogeneous catalyst for the reaction indicated in Equation (3).

$$2[Fe(CN)_6]^{3–} + 2S_2O_3^{2–} \rightarrow 2[Fe(CN)_6]^{4–} + S_2O_6^{2–}$$ (3)

The catalytic reaction process can be monitored by UV/Vis spectroscopy by recording changes in the intensity of the band at $\lambda_{max} = 420$ nm during the reaction in the presence and absence of 3 (or 5).

As compound 3 (5 mg) was added to the above reaction mixture without stirring, the yellow solution immediately turned colourless. Analysis of the UV/Vis spectrum indicated that the absorption band at $\lambda = 420$ nm, and the other bands corresponding to the [Fe(CN)$_6$]$_{3–}$ ion, completely disappeared; this suggested that the reduction was completed immediately upon the addition of compound 3 (or 5; Figure 8). The performance of 3 for this redox reaction is similar to that found for the blue crystalline material [(NH$_4$)$_2$Pt(TCNQF)$_4$] recently reported by Lu et al.$^{[24]}$

The UV/Vis spectra in the regions of $\lambda = 600–800$ and 400–450 nm were examined to determine whether any reaction occurred between dissolved 5 and K$_3$[Fe(CN)$_6$] during the catalytic reduction process. No absorptions are apparent in these regions, which indicates the absence of TCNQF$_4^{–}$ in solution. The presence of the radical anion would be indicated by characteristic absorptions at $\lambda = 750$ and 412 nm.$^{[27]}$ Thus, there is no evidence that compound 5 dissolves and produces TCNQF$_4^{–}$ in solution. This result supports the view that compound 5 is acting as a heterogeneous catalyst in the reduction of [Fe(CN)$_6$]$_{3–}$ to [Fe(CN)$_6$]$_{4–}$ by S$_2$O$_3^{2–}$.

Compound 5 can be easily separated from the aqueous reaction mixture by means of a syringe. Upon rinsing several times with ultrapure water, it may then be re-used in another catalytic experiment. To test the reusability of 5, the same reaction was repeated multiple times in fresh 10 mL solutions, for which 5 was washed with ultrapure water between each run.
A UV/Vis spectrum was recorded for each run to determine if the reduction of the [Fe(CN)]$_3^{3-}$ to [Fe(CN)]$_6^{3-}$ had occurred. Surprisingly, even in the 50th experiment, the yellow solution turned colourless again as 5 was introduced; the UV/Vis spectrum showed the absence of the [Fe(CN)]$_6^{3-}$ ion, which indicated that 100% reduction was still achieved. This result indicates that 5 has maintained a remarkable level of catalytic activity over 50 runs, in which it facilitates electron transfer between [S$_2$O$_7$]$_2^{-}$ and [Fe(CN)]$_6^{3-}$ ions in aqueous solution (Figure 8).

Stability of compound 5 during the catalytic reaction

**Thermogravimetric analysis of compounds 3 and 5**

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of compound 3 before, and compound 5 after, catalytic reaction over the range 40 to 400 °C under N$_2$. The TGA curve of compound 3 is shown in Figure S10a in the Supporting Information, and reveals a weight loss of approximately 18% before 150 °C, which corresponds to the loss of three uncoordinated DMF molecules (calcld: 18.6%). This is consistent with the crystal structure, in which there are three uncoordinated DMF solvate molecules per formula unit of 5, as shown in Figure S3 in the Supporting Information. Upon continued heating, decomposition commences. The TGA data for 5 following its use in the catalytic reaction is presented in Figure S10b in the Supporting Information. The mass loss before 150 °C is only 1%, which confirms the absence of uncoordinated DMF in 5.

Raman and FTIR spectra of compound 3 before, and compound 5 after, catalytic reaction

To assess the stability of compounds 3 and 5 during the catalytic reaction, Raman and FTIR spectra were recorded after the 50th catalytic cycle. In this case, compound 5 was collected, washed with water and dried under high vacuum over P$_2$O$_5$ for 24 h. Raman and FTIR spectra of 5 were recorded (Figure 9), and indicated that 5 was stable during the catalytic reduction process. As expected, minor differences existed in the both the Raman and FTIR spectra of compounds 3 (before) and 5 (after) in the catalytic reaction. FTIR spectra of 3 (before) and 5 (after) in the catalytic reaction (Figure 9a) are similar, except that the uncoordinated DMF bands are absent after the catalytic reaction. In the Raman spectra (Figure 9b), the bands assigned to the CN groups in 5 shifted to slightly higher energy (ca. 3–5 cm$^{-1}$) after the catalytic reactions. This shift is attributed to the loss of uncoordinated DMF molecules. The fact that splitting modes of CN group do not change is expected, if 5 has the proposed chemical composition of [Mn$_6$(TCNQ)$_4$(DMF)$_6$].

Catalytic cycle involving compounds 3 and 5

In their studies on films of CuTCNQ(F$_2$)$_2$/AgTCNQ(F$_2$)$_2$, which were used to catalyse the electron-transfer reaction between ferricyanide and thiosulfate ions, O’Mullane et al. assumed that a balance existed between electron injection into the catalyst surface and ejection from the surface.$^{[21]}$ They also reported that fluorinated TCNQ$_4^-$ exhibited higher catalytic activity than that of TCNQ.$^{[20]}$ In the case of [Ni(CN)$_6$]$_{2-}$/AgTCNQ(F$_2$)$_2$, Bond et al. proposed that the thiosulfate ions injected one or two electrons into the solid surface of [Ni(CN)$_6$]$_{2-}$/AgTCNQ(F$_2$)$_2$, and, as a consequence, the TCNQ$_4^-$ radical anions could be reduced to TCNQ$_2^-$ dianions.$^{[24]}$ Finally, TCNQ$_2^-$ dianions could be oxidised back to the TCNQ$_4^-$ radical anions through reactions with [Fe(CN)]$_6^{3-}$ and release of an electron to give [Fe(CN)]$_6^{4-}$ to complete the reduction cycle.

If 5 acts as a heterogeneous catalyst, we propose that coordinated TCNQ$_2^-$ dianions reduce [Fe(CN)]$_6^{3-}$ to [Fe(CN)]$_6^{4-}$ (Scheme 1). The tetradeutate TCNQ$_2^-$ ligands are, in turn, oxidised within the network to the radical monoanion form (TCNQ$_2^{-}$). The thiosulfate dianion is then able to reduce the coordinated monoanion back to its original TCNQ$_2^-$ form. In this final step, S$_2$O$_7^{2-}$ is then oxidised to S$_2$O$_5^{2-}$.

Raman and FTIR spectra for 4

The Raman spectrum of compound 4 is shown in Figure S11 in the Supporting Information. Four diagnostic bands at 2128, 1654, 1440 and 1239 cm$^{-1}$ are attributed to the C=N, the ring C=C, exo-ring C=C stretches, and a mix of C–F bending and –
C–C– stretching, respectively, which is consistent with the presence of the reduced TCNQF$_2$ dianion. The FTIR spectrum of the crystals also exhibits typical characteristics of the TCNQF$_2$ dianion, for example, $\tilde{\nu} = 2186$ and 2113 cm$^{-1}$ for the CN stretch, $\tilde{\nu} = 1488$ cm$^{-1}$ for the ring C=C stretch, and the exo-ring C=C stretch $\tilde{\nu} = 1377$ cm$^{-1}$ (Figure S12 in the Supporting Information). These spectral data are consistent with those reported for TCNQF$_2$ in the literature.$^{[14,27]}$

**Conclusion**

The reaction of Mn(BF$_4$)$_2$·H$_2$O with (Pr$_2$N)$_2$TCNQF$_4$ in different solvent systems resulted in two different Mn-based TCNQF$_2$ dianion compounds, 1 and 2. X-ray crystallographic studies on single crystals of 1 and 2 showed 2D network that consisted of an unusual TCNQF$_2$ dianion π-stacked dimer for 1, and a sheet structure involving the TCNQF$_2$ dianion and DMF solvent molecules for 2. Interestingly, if the organic precursor of (Pr$_2$N)$_2$TCNQF$_4$ was replaced by Li$_2$TCNQF$_4$, as the starting material, a new compound, 3, formed. Although both 2 and 3 have a 2D sheet structure, significant differences exist. Compound 3 exhibited an exceptionally high catalytic activity with respect to the electron-transfer reaction between ferricyanide and thiosulfate ions in aqueous solution. Spectroscopic analyses implied that 3 converted to 5, losing only the uncoordinated DMF solvent molecules during the catalytic process. Surprisingly, an unexpected Mn$_{10}$ cluster, 4, which contained TCNQF$_2$ dianions, formed if Mn(NO$_3$)$_2$·H$_2$O was used instead of Mn(BF$_4$)$_2$·H$_2$O in the reaction used to form compound 3.

**Experimental Section**

**Chemicals**

All reactions were performed under a N$_2$ atmosphere. Mn(BF$_4$)$_2$·H$_2$O, Mn(NO$_3$)$_2$·H$_2$O, Li$_2$Pr,Nb,$\beta$[Fe(CN)$_6$], Na$_2$S$_2$O$_3$, ferrocene (Fc), AgNO$_3$, MeOH, CH$_3$CN, CH$_3$ClO$_2$, diethyl ether and DMF were used as received from Sigma Aldrich. TCNQF$_4$ was used as received (Aldrich). Bu$_4$NP$_F$ was purchased from GFS and recrystallised twice from ethanol prior to use. All aqueous solutions were prepared from high-purity water (resistivity of 18.2 MΩcm) purified by means of a Sartorius Arium 611 system (Sartorius). Li$_2$TCNQF$_4$ and [(Pr$_2$N)$_2$TCNQF$_4$] were synthesised by following procedures reported in the literature.$^{[46]}$

**Synthesis of 1**

A solution of (Pr$_2$N)$_2$TCNQF$_4$ (56.7 mg, 0.09 mmol) in CH$_3$OH (8 mL) was layered over a solution of Mn(BF$_4$)$_2$·H$_2$O (19.6 mg, 0.06 mmol) in CH$_3$OH/CH$_2$Cl$_2$ (5:1, 6 mL). Colourless crystals of 1 formed after 3 days at room temperature (48 mg, 42 %). FTIR: $\tilde{\nu} = 3196$ (w), 2957 (w), 2942 (w), 2886 (w), 2203 (s, CN), 2182 (s, CN), 2162 (s, CN), 2135 (s, CN), 2108 (s, CN), 1634 (w), 1480 (s), 1387 (w), 1318 (w), 1238 (m), 1151 (m), 1114 (w), 1028 (m), 963 (s), 842 (w), 792 (s), 758 cm$^{-1}$ (m); UV/Vis (CH$_3$CN): $\lambda = 219$ (TCNQF$_2^-$), 333 nm (TCNQF$_4^-$); elemental analysis calc (%) for C$_{64}$H$_{64}$N$_{25}$Fe$_2$O$_3$Mn$_2$: C 54.15, H 4.69, N 14.26; found: C 54.32, H 4.54, N 14.01.

**Synthesis of 2**

**Method A**

A solution of (Pr$_2$N)$_2$TCNQF$_4$ (58.4 mg, 0.09 mmol) in CH$_3$OH (10 mL) was layered over a solution of Mn(BF$_4$)$_2$·H$_2$O (30.3 mg, 0.09 mmol) in DMF (6 mL). Colourless or pale crystals of 2 were formed after a week at room temperature (28 mg, 94 % based on (Pr$_2$N)$_2$TCNQF$_4$). FTIR: $\tilde{\nu} = 2938$ (w), 2194 (s, CN), 2150 (s, CN), 2121 (s, CN), 1645 (s), 1481 (s), 1437 (m), 1434 (w), 1413 (w), 1380 (m), 1315 (w), 1243 (m), 1152 (m), 1110 (m), 1061 (w), 966 (s), 898 (w), 793 (s), 673 cm$^{-1}$ (m); UV/Vis (CH$_3$CN): $\lambda = 333$ (TCNQF$_2^-$), 220 nm (TCNQF$_4^-$); elemental analysis calc (%) for C$_{64}$H$_{64}$N$_{25}$Fe$_2$O$_3$Mn$_2$: C 44.37, H 4.10, N 15.52; found: C 44.02, H 4.09, N 15.48.

**Method B**

A solution of Mn(NO$_3$)$_2$·H$_2$O (13.5 mg, 0.047 mmol) and Li$_2$O$_2$C$_2$H$_4$ (7.9 mg, 0.078 mmol) in methanol (6 mL) was layered over a solution of H$_2$TCNQF$_4$ (13 mg, 0.047 mmol) in DMF (1 mL). Pale crystals, with a yellow tinge formed, which were filtered and air-dried (10.7 mg, 0.020 mmol, 42 %).

**Synthesis of 3**

A solution of Li$_2$TCNQF$_4$ (43.4 mg, 0.15 mmol) in CH$_3$OH (15 mL) was layered over a solution of Mn(BF$_4$)$_2$·H$_2$O (50.4 mg, 0.15 mmol) in DMF (10 mL). Colourless crystals of 3 formed after 2 days at room temperature (31 mg, 63 % based on Li$_2$TCNQF$_4$). FTIR: $\tilde{\nu} = 2976$ (w), 2941 (w), 2842 (w), 2766 (bw), 2568 (bw), 2197 (s, CN), 2152 (s, CN), 2124 (s, CN), 1654 (m), 1599 (m), 1536 (w), 1493 (s), 1480 (s), 1413 (m), 1383 (w), 1321 (w), 1241 (s), 1222 (m), 1155 (w), 1129 (w), 1112 (w), 1065 (w), 1007 (s), 1000 (s), 963 (s), 872 (m), 807 (s), 793 (s), 731 (w), 674 cm$^{-1}$ (w); UV/Vis (CH$_3$CN): $\lambda = 333$ (TCNQF$_2^-$), 220 nm (TCNQF$_4^-$); elemental analysis calc (%) for C$_{64}$H$_{64}$N$_{25}$Fe$_2$O$_3$Mn$_2$: C 46.04, H 4.21, N 17.90; found: C 46.24, H 4.51, N 17.82.

**Synthesis of 4**

A solution of Li$_2$TCNQF$_4$ (22.9 mg, 0.08 mmol) in CH$_3$OH (1.5 mL) was layered over a solution of Mn(NO$_3$)$_2$·H$_2$O (19.8 mg, 0.08 mmol) in a mixture of methanol and dichloromethane (1.3 mL/0.2 mL).
Table 1. Crystallographic details and refinements for compounds 1–4.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C₈H₈F₆MnN₂O₁₀</td>
<td>C₈H₈F₆MnN₂O₁₀</td>
<td>C₈H₈F₆MnN₂O₁₀</td>
<td>C₈H₈F₆MnN₂O₁₀</td>
</tr>
<tr>
<td>a [Å]</td>
<td>10.8258(4)</td>
<td>15.0913(10)</td>
<td>9.1870(3)</td>
<td>16.2905(13)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>8.1816(4)</td>
<td>7.3799(5)</td>
<td>23.2435(6)</td>
<td>16.2905(13)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>7.2389(5)</td>
<td>11.3463(7)</td>
<td>25.8661(7)</td>
<td>27.4773(3)</td>
</tr>
<tr>
<td>α [°]</td>
<td>84.2973(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>69.206(3)</td>
<td>115.541(2)</td>
<td>99.540(2)</td>
<td>90</td>
</tr>
<tr>
<td>γ [°]</td>
<td>79.038(3)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>1595.23(10)</td>
<td>1201.37(13)</td>
<td>5447.03(3)</td>
<td>7291.8(14)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Mr.</td>
<td>687.57</td>
<td>541.37</td>
<td>1173.67</td>
<td>3679.17</td>
</tr>
<tr>
<td>space group</td>
<td>P1</td>
<td>C2/m</td>
<td>P2₁/c</td>
<td>P4₁/nmm</td>
</tr>
<tr>
<td>T [°C]</td>
<td>−150(1)</td>
<td>−150(1)</td>
<td>−150(1)</td>
<td>−143(1)</td>
</tr>
<tr>
<td>ρ [g cm⁻³]</td>
<td>1.431</td>
<td>1.497</td>
<td>1.431</td>
<td>1.676</td>
</tr>
<tr>
<td>μ [cm⁻¹]</td>
<td>0.486</td>
<td>0.619</td>
<td>0.552</td>
<td>14.459</td>
</tr>
<tr>
<td>R (F &gt; 2σ(F))</td>
<td>0.0266</td>
<td>0.0418</td>
<td>0.0045</td>
<td>0.1163</td>
</tr>
<tr>
<td>Rw (P²)</td>
<td>0.0640</td>
<td>0.1116</td>
<td>0.0890</td>
<td>0.4059</td>
</tr>
</tbody>
</table>

After two weeks, blue square crystals suitable for X-ray crystallographic analysis were obtained. FTIR: ν = 2186 (s, CN), 2113 with a shoulder at 2138 (s, CN), 1736 (w), 1631 (m), 1488 (s, ring C = O), 792 cm⁻¹ (m).

**Catalytic reaction**

Crystalline compound 3 (5 mg) was added to a mixture of an aqueous solution of Na₂S₂O₃ (5 mL, 10 mm) and an aqueous solution of K₂[Fe(CN)]₆ (5 mL, 1 mm). The resultant reaction mixture was analysed by UV/Vis spectroscopy (Cary 50 Bio spectrophotometer). In the re-usability tests, the same reaction with UV/Vis monitoring was repeated multiple times in fresh 10 mL solutions, for which 5 was separated by removing the reaction mixture with syringe, washing with ultrapure water several times between each run and recording a UV/Vis spectrum for each run.

**Electrochemical procedures and instrumentation**

Voltammetric experiments were conducted in a standard three-electrode cell, at (22 ± 2) °C, with a Bioanalytical Systems BAS100B electrochemical workstation. The working electrode was either a glassy carbon macro-electrode (1 mm diameter, Bioanalytical Systems) or a Pt micro-electrode (10 μm, Cypress). A platinum wire was used as the counter electrode. A silver wire immersed in a solution containing 1.0 mM AgNO₃ and 0.1 M Bu₄PF₆ in acetonitrile was used as an Ag/Ag⁺ reference electrode (the potential was 0.366 V versus the Fe/C₆ CF⁻ couple). Potentials were reported versus the Ag/Ag⁺ reference electrode. All solutions were degassed with nitrogen for 10 min prior to electrochemical experiments.

**Physical characterisation procedures and instrumentation**

Microanalyses were performed at the Campbell Microanalytical Laboratories, University of Otago, New Zealand. FTIR spectra were recorded by using a Spectrac Diamond ATR instrument. Raman spectra were acquired with a Renishaw Raman RM2000 spectrometer and microscope by using a laser strength of 18 mW at a wavelength of λ = 514 nm. TGA was performed by using a Mettler Toledo thermogravimetric analyser over the temperature range of 40 to 400 °C at a heating rate of 2 °C min⁻¹ under a N₂ atmosphere.

In the X-ray crystallographic studies, single crystals were transferred directly from the mother liquor to a viscous hydrocarbon oil before being mounted on a goniometer in a stream of cold nitrogen. For compounds 2 and 3, data were collected by using a Bruker X8 ApexII diffractometer equipped with graphite monochromated MoKα radiation. Data for 1 were measured on an Oxford Diffraction Xcalibur, Gemini Ultra diffractometer. Data were measured for 4 by using CuKα radiation on a SuperNova diffractometer. The structures were solved by direct methods with the SHELXL-97 program.[29] Least-squares refinements against F² were performed by using the SHELXL-2014/6 program.[30] All data are collected in Table 1.

CCDC 874491 (1), 1560435 (2), 1560436 (3), and 1560437 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Acknowledgements**

Financial support from the Australian Research Council (ARC) to B.F.A, R.R., A.M.B and L.L.M is gratefully acknowledged.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** cluster compounds · electron transfer · heterogeneous catalysis · manganese · structure elucidation


Manuscript received: October 10, 2017
Revised manuscript received: November 1, 2017
Accepted manuscript online: November 2, 2017
Version of record online: December 12, 2017