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Role of Water in the Dynamic Disproportionation of Zn-Based TCNQ(F_4) Coordination Polymers (TCNQ = Tetracyanoquinodimethane)

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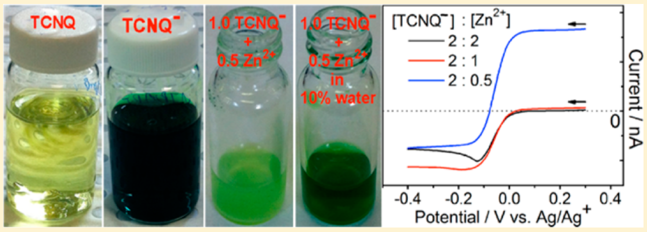
Supporting Information

ABSTRACT: Intriguingly, coordination polymers containing $TCNQ^{2-}$ and $TCNQF_4{}^{2-}$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane, $TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, both designated as $TCNQ(F_4)^{2-}$) may be generated from reaction of metal ions with $TCNQ(F_4)^{\bullet-}$. An explanation is now provided in terms of a solvent-dependent dynamic disproportionation reaction. A systematic study of reactions associated with TCNQ(F_4) and electrochemically generated $TCNQ(F_4)^{\bullet-}_{MeCN}$ and $TCNQ(F_4)^{2-}_{MeCN}$ revealed that disproportionation of $TCNQ(F_4)^{\bullet-}_{MeCN}$ radical anions in acetonitrile containing a low concentration of water is facilitated by the presence of Zn^{2+}_{MeCN}. Thus, while the disproportionation reaction $2TCNQ(F_4)^{\bullet-}_{MeCN} \rightleftharpoons TCNQ(F_4)_{MeCN} + TCNQ(F_4)^{2-}_{MeCN}$ is thermodynamically very unfavorable in this medium ($K_{eq} \approx 9 \times 10^{-10}$; $TCNQF_4$), the preferential precipitation of $ZnTCNQ(F_4)_{(s)}$ drives the reaction: $Zn^{2+}_{MeCN} + 2\ TCNQ(F_4)^{\bullet-}_{MeCN} \rightleftharpoons ZnTCNQ(F_4)_{(s)} + TCNQ(F_4)_{MeCN}$. The concomitant formation of soluble $TCNQ(F_4)_{MeCN}$ and insoluble $ZnTCNQ(F_4)_{(s)}$ and the loss of $TCNQ(F_4)^{\bullet-}_{MeCN}$ were verified by UV−visible and infrared spectroscopy and steady-state voltammetry. Importantly, the reverse reaction of comproportionation rather than disproportionation becomes the favored process in the presence of ≥3% (v/v) water, due to the increased solubility of solid $ZnTCNQ(F_4)_{(s)}$. Thus, in this "wet" environment, Zn^{2+}_{MeCN} and $TCNQ(F_4)^{\bullet-}_{MeCN}$ are produced from a mixture of $ZnTCNQ(F_4)_{(s)}$ and $TCNQ(F_4)_{MeCN}$ and with the addition of water provides a medium for synthesis of $[Zn(TCNQ(F_4))_2(H_2O)_2]$. An important conclusion from this work is that the redox level of TCNQ(F_4)-based materials, synthesized from a mixture of metal cations and $TCNQ(F_4)^{\bullet-}$, is controlled by a solvent-dependent disproportionation/comproportionation reaction that may be tuned to favor formation of solids containing the monoanion radical, the dianion, or even a mixture of both.



1. INTRODUCTION

Coordination polymers based on the $TCNQ^{\bullet-}$ radical monoanion and its fluorinated derivative $TCNQF_4{}^{\bullet-}$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane, $TCNQF_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) are of significant interest because of their fascinating structural architectures and intriguing conductivity, magnetic, and electronic properties.[1−7] Although there has been an emphasis on possible applications of CuTCNQ and AgTCNQ, recent research has been directed toward the fluorinated analogues $CuTCNQF_4$ and $AgTCNQF_4$.[8−10]

Advances in industrial applications of TCNQ and $TCNQF_4$ materials requires a fundamental understanding of rational methods for their synthesis along with mechanistic details associated with their formation and reactivity. Metal−TCNQ(F_4) derivatives (where TCNQ(F_4) designates both TCNQ and $TCNQF_4$) are readily accessible because of the availability of highly stable $TCNQ^{\bullet-}$ and $TCNQF_4{}^{\bullet-}$ radical anion sources. Thus, in addition to the 1:1 stoichiometries associated with materials such as CuTCNQ(F_4) and AgTCNQ(F_4), 1:2 materials, $M(TCNQ)_2$ (where M^{II} = V, Mn, Fe, Co, Ni, Zn)[11−14] have been synthesized from a range of $TCNQ^{\bullet-}$ sources. These include both nonsolvated $M(TCNQ)_2$ (M^{II} = Mn, Fe, Co, Ni) "glassy magnets"[12,13] and solvated $[M(TCNQ)_2(S)_2]$ (S = MeOH, H_2O)[14] congeners. Similarly, $TCNQF_4{}^{\bullet-}$ radical anion sources have been successfully utilized to synthesize $[Ni(TCNQF_4)_2(H_2O)_2]$,[15] as well as a homologous series of mononuclear $[M(TCNQF_4)_2(H_2O)_x]\cdot(TCNQF_4)\cdot 3H_2O$ (x = 6, 7) complexes with trivalent lanthanides (M^{III} = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb).[5]

Although the majority of the aforementioned transition-metal compounds were chemically synthesized using well-established methods that gave the expected materials containing the monoanion, the detection of solids containing $TCNQ(F_4)^{2-}$ dianions has been reported less often.[12,16] For example, methanolic solutions of $[Mn(CH_3CN)_4](BF_4)_2$ and $LiTCNQF_4$, allowed to react in a 1:1 ratio, formed dark blue

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crystals of the "glassy magnet" $\{[Mn_2(TCNQF_4)(CH_3OH)_{7.5}(H_2O)_{0.5}](TCNQF_4)_2{\cdot}7.5CH_3OH\}_\infty$.[16] Structural analysis by single-crystal X-ray diffraction revealed the presence of μ_4-$TCNQF_4^{2-}$ dianions in a 2D honeycomb-like net lying along with the $TCNQF_4^{\bullet-}$ radical anions residing between the layers. The presence of $TCNQF_4^{2-}$ in the product was postulated to be a consequence of disproportionation of the $TCNQF_4^{\bullet-}$ radical anion.[16] A related finding also has been reported using acetonitrile solutions of $[Mn(CH_3CN)_6](SbF_6)_2$ or $[Ni(CH_3CN)_6](SbF_6)_2$ (1 equiv) mixed with a slight excess of $(Bu_4N)TCNQ$. This afforded $M(TCNQ)_x$-based materials (M^{II} = Mn, Ni) with $1 < x < 2$ and is hence indicative of the presence of the $TCNQ^{2-}$ dianion along with the $TCNQ^{\bullet-}$ monoanion in the isolated products.[12]

Clearly, the synthesis of purely $TCNQ^{2-}$-containing materials is more likely when the starting material is the dianion, although this approach is relatively rare. Thus, Kitagawa et al. synthesized the 3D coordination polymer $[Zn(TCNQ)bpy]{\cdot}6CH_3OH$ (bpy = 4,4′-bipyridine) by reacting hydrated $Zn(NO_3)_2$ with LiTCNQ and bpy in methanol. Generation of the $TCNQ^{2-}$ dianion under these conditions was unexpected but assumed to arise from the disproportionation of $TCNQ^{\bullet-}$.[3] However, no experimental evidence for disproportionation was provided. The same group, again using LiTCNQ as a reagent, was able to obtain $TCNQ^{2-}$-containing [M(TCNQ)bpy] (M = Fe, Zn, Mn, Co, Cd) porous coordination polymers having 3D pillared layer structures.[6]

In this study, a quantitative investigation of a disproportionation reaction in which $TCNQ(F_4)^{\bullet-}_{MeCN}$ radical anions are converted into neutral $TCNQ(F_4)_{MeCN}$ and solid dianionic $TCNQ(F_4)^{2-}$ material in acetonitrile upon addition of $Zn(ClO_4)_2{\cdot}6H_2O$ is reported. The disproportionation/comproportionation reaction is sensitive to the reaction conditions and in the presence of a low concentration of water gives rise to precipitation of $ZnTCNQ(F_4)_{(s)}$ (s = solid), which has been isolated and characterized by elemental analysis and ultraviolet−visible (UV−vis) and Fourier transform infrared (FT-IR) spectroscopy. The concomitant formation of neutral $TCNQ(F_4)_{MeCN}$ was quantitatively demonstrated by UV−vis spectroscopy and electrochemistry. The fact that the disproportionation of dissolved $TCNQ(F_4)^{\bullet-}_{MeCN}$ to $TCNQ(F_4)_{MeCN}$ and $TCNQ(F_4)^{2-}_{MeCN}$ is highly unfavorable thermodynamically highlights the crucial role of the metal cation in facilitating the formation of insoluble coordination polymers. A mechanism that incorporates the reaction of Zn^{2+}_{MeCN} with $TCNQ(F_4)^{2-}_{MeCN}$, available from a dynamic disproportionation reaction to form Zn^{2+}-$TCNQ(F_4)^{2-}{}_{(s)}$, is proposed. Intriguingly, addition of ≥3% (v/v) water to the reaction medium reverses the disproportionation reaction, so that comproportionation to generate $TCNQ(F_4)^{\bullet-}_{MeCN}$ becomes the favored pathway. Thus, results presented in this investigation offer insight into the role of the concentration of water in controlling the direction of disproportionation/comproportionation reactions, thereby determining whether dianions (low concentration of water) or monoanions (in the presence of high concentration of water) are present in the ultimate Zn-TCNQ(F_4) coordination polymer based materials.

2. EXPERIMENTAL SECTION

2.1. Chemicals. $Zn(ClO_4)_2{\cdot}6H_2O$ (Aldrich), ferrocene (98%, EGA-Chemie), acetonitrile (HPLC grade, Omnisolv), isopropyl alcohol (BHD), and acetone (Suprasolv, Merck) were used as received by the manufacturer. TCNQ (98%, Aldrich) and $TCNQF_4$ (98%, Beijing Health) were recrystallized twice from boiling acetonitrile and dichloromethane (Suprasolv, Merck), respectively, prior to use. Bu_4NPF_6 (Wako) was recrystallized twice from 96% ethanol (Merck) and then dried at 100 °C under vacuum for 24 h before being used as the supporting electrolyte in the electrochemical experiments. The HPLC grade acetonitrile has 0.3% water by analysis. In this paper the percentage of water refers only to added water to the reaction mixtures, not the total amount of water present.

2.2. Procedures. Acetonitrile solutions containing either 10.0 mM $TCNQF_{4\,MeCN}^{\bullet-}$ or 10.0 mM $TCNQ^{\bullet-}_{MeCN}$ were quantitatively prepared by exhaustive electrochemical reduction of 10.0 mM $TCNQF_{4\,MeCN}$ or $TCNQ_{MeCN}$ in acetonitrile (0.1 M Bu_4NPF_6) at a Pt-mesh working electrode using applied potentials (E_{appl}) of 100 mV vs Ag/Ag^+ for the former and −300 mV (vs Ag/Ag^+) for the latter. Nitrogen degassing, to remove oxygen, was used for the duration of these experiments. An analogous protocol was applied to prepare a 10.0 mM solution of $TCNQF_{4\,MeCN}^{2-}$ in which, after quantitative generation of the monoanion, E_{appl} was set to −400 mV to convert $TCNQF_{4\,MeCN}^{\bullet-}$ to $TCNQF_{4\,MeCN}^{2-}$. $TCNQ^{2-}$ was too reactive to be prepared electrochemically under these benchtop conditions. Controlled potentials were maintained until the current decreased to 0.1% of its initial value. UV−vis spectroscopy was utilized to confirm that all the starting material was reduced to the required product in these bulk electrolysis experiments.

Zn-$TCNQF_{4(s)}$ material, characterized by elemental analysis and spectroscopy, was obtained by mixing 10.0 mL solutions of the electrochemically generated $TCNQF_{4\,MeCN}^{\bullet-}$ or $TCNQF_{4\,MeCN}^{2-}$ (10.0 mM) in acetonitrile (0.1 M Bu_4NPF_6) with 5.0 mL (2:1 ratio) or 10.0 mL (1:1 ratio) acetonitrile solutions containing 10.0 mM Zn^{2+}_{MeCN}, followed by stirring for 5 min. The rapidly formed precipitates were collected by centrifugation, washed with 5 × 2 mL of acetonitrile, and dried overnight under vacuum. No single crystals suitable for structural analysis by X-ray diffraction could be obtained.

2.3. Electrochemistry. Voltammetric experiments were undertaken with a Bioanalytical Systems (BAS) Epsilon electrochemical workstation at room temperature (22 ± 2 °C) using a standard three-electrode cell configuration. The working electrode was a BAS carbon fiber microelectrode (11 ± 2 μm diameter). The counter electrode was 1.0 mm diameter Pt wire. The reference electrode consisted of a Ag wire placed in acetonitrile solution containing 1.0 mM $AgNO_3$ and 0.1 M Bu_4NPF_6 and separated from the test solution by a glass frit. Conversion to the Fc/Fc^+ reference scale can be achieved by addition of −135 mV. In the case of bulk electrolysis experiments, a three-compartment "H-type" cell configuration with Pt-mesh working and counter electrodes and the same Ag/Ag^+ reference electrode employed in voltammetric studies were used. Solutions for electrochemical measurements were purged with nitrogen gas for 10 min before commencing the experiments.

2.4. Other Instrumentation. Elemental (C, H, N, Zn) analysis was carried out at the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, Otago, New Zealand. UV−vis and FT-IR instrumentation are as detailed elsewhere.[17]

3. RESULTS AND DISCUSSION

3.1. Electrochemical and UV−Vis Monitoring of the Reactions between Zn^{2+}_{MeCN} and $TCNQ(F_4)^{\bullet-}_{MeCN}$ Radical Anions.

As described above, 10.0 mM solutions of $TCNQ(F_4)^{\bullet-}_{MeCN}$ in acetonitrile (0.1 M Bu_4NPF_6) were generated electrochemically, using bulk electrolysis. The change in location of the zero current position was used as evidence for quantitative conversion of $TCNQ(F_4)^{\bullet-}_{MeCN}$ to $TCNQ(F_4)_{MeCN}$, (parts (a) and (b) of Figure 1, respectively). Further proof was obtained by noting that UV−vis spectral bands characteristic for neutral $TCNQF_{4\,MeCN}$ (λ_{max} 365 and 386 nm) and $TCNQ_{MeCN}$ (λ_{max} 374 and 393 nm) completely disappeared after the exhaustive one-electron reductive electrolysis and were replaced by new ones at λ_{max} 411 and 752 nm for $TCNQF_{4\,MeCN}^{\bullet-}$ and 420 and 743 nm for $TCNQ^{\bullet-}_{MeCN}$[17−20]

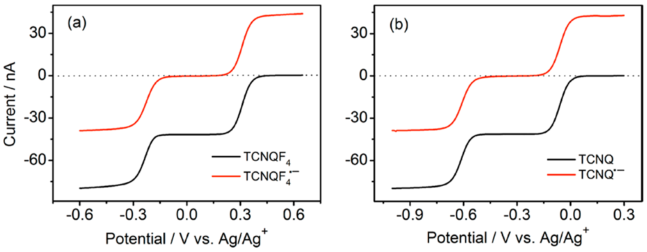


Figure 1. Near steady-state voltammograms obtained with a 11 μm diameter carbon-fiber microelectrode at a scan rate of 20 mV s^{-1} for (a) 10.0 mM $\mathrm{TCNQF_{4\,MeCN}}$ and (b) 10.0 mM $\mathrm{TCNQ_{MeCN}}$ in acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$) before (black) and after (red) bulk electrolysis.

(Figure 2). The color change associated with this electrochemical reduction in solution, TCNQ → $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$, is shown in Figure 3.

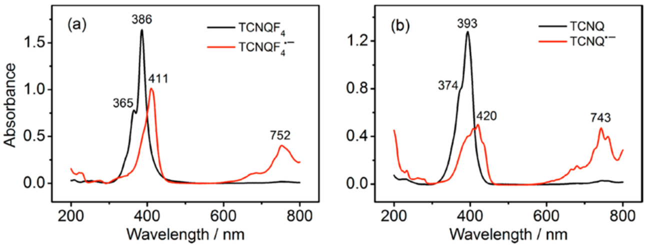


Figure 2. UV–vis spectra for (a) 0.02 mM $\mathrm{TCNQF_{4\,MeCN}}$ and (b) 0.02 mM $\mathrm{TCNQ_{MeCN}}$ in acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$) recorded before (black) and after (red) bulk electrolysis.

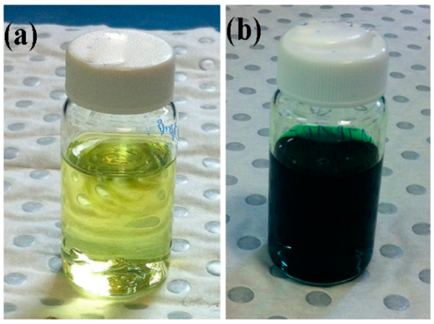


Figure 3. Photographs of solutions of 10.0 mM $\mathrm{TCNQ_{MeCN}}$ in acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$) before (a) and after (b) exhaustive bulk electrolysis was undertaken to reduce $\mathrm{TCNQ_{MeCN}}$ to $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$.

Interestingly, when 2.0 mL of the electrochemically prepared 10.0 mM $\mathrm{TCNQ(F_4)}^{\bullet-}_{\mathrm{MeCN}}$ in acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$) was mixed with 2.0, 1.0, or 0.5 mL of 10.0 mM $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ in acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$) to give 2:2, 2:1, and 2:0.5 $\mathrm{TCNQ(F_4)}^{\bullet-}_{\mathrm{MeCN}}$:$\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ stoichiometric ratios, pale green precipitates formed immediately upon addition of $\mathrm{TCNQF_4}^{\bullet-}_{\mathrm{MeCN}}$, whereas for $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$, ~5 min was required to convert the brown precipitate that formed immediately on mixing the solutions, to a pale green precipitate (Figure 4). Centrifugation was used to separate the solids, and the supernatant solutions were examined by UV–vis spectroscopy, following a 100-fold dilution. Remarkably, the UV–vis spectra (Figure 5) contain the characteristic absorption bands for neutral dissolved $\mathrm{TCNQF_{4\,MeCN}}$ (λ_{max} 386 and 365 nm) or dissolved $\mathrm{TCNQ_{MeCN}}$ (λ_{max} 374 and 393 nm), thereby implying the generation of the neutral forms as a result of the reaction of the monoanionic radicals with MeCN. The concentration of $\mathrm{TCNQ(F_4)_{MeCN}}$ and remaining (unreacted) $\mathrm{TCNQ(F_4)}^{\bullet-}_{\mathrm{MeCN}}$ radical anions was quantitatively determined via UV–vis spectroscopy, by measuring the absorbance at 386 and 752 nm for $\mathrm{TCNQF_{4\,MeCN}}$ and $\mathrm{TCNQF_4}^{\bullet-}_{\mathrm{MeCN}}$, respectively, or at 393 and 743 nm for $\mathrm{TCNQ_{MeCN}}$ and $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$, respectively, by reference to the appropriate calibration curves for these species. The results are summarized in Table 1. From these data, it can be concluded that both $\mathrm{TCNQF_4}^{\bullet-}_{\mathrm{MeCN}}$ and $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$ radical monoanions react with $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ in a 2:1 stoichiometric ratio to afford ~50% of the neutral $\mathrm{TCNQ(F_4)_{MeCN}}$ species together with a $\mathrm{ZnTCNQ(F_4)_{(s)}}$-based solid material.

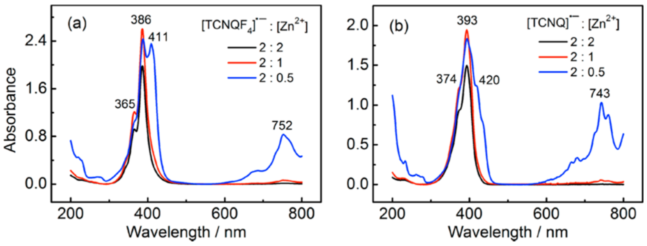


Figure 5. UV–vis spectra obtained after mixing acetonitrile solutions of (a) $\mathrm{TCNQF_4}^{\bullet-}_{\mathrm{MeCN}}$ or (b) $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$ and $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ with designated ratios of initial concentrations (the solutions were diluted 100-fold before recording the spectra).

Steady-state voltammetry was also used to assess the redox level and concentration of $\mathrm{TCNQ(F_4)}$ species formed after mixing the $\mathrm{TCNQ(F_4)}^{\bullet-}_{\mathrm{MeCN}}$ monoanions with $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ in

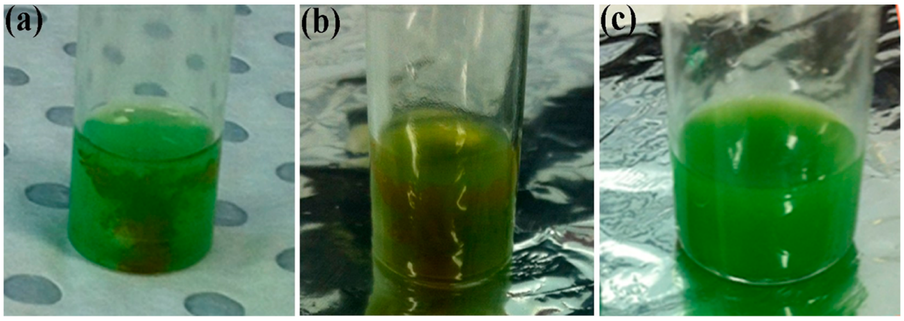


Figure 4. Photographs showing changes that take place when 0.5 equivalence of $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ in acetonitrile is added dropwise into 1.0 equivalence of $\mathrm{TCNQ}^{\bullet-}_{\mathrm{MeCN}}$ acetonitrile solution: (a) just after addition of a few drops of $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ solution; (b) just after addition of all the $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ solution; (c) 5 min after addition of all of the $\mathrm{Zn}^{2+}_{\mathrm{MeCN}}$ solution.

Table 1. Dependence of $\mathrm{TCNQ(F_4)_{MeCN}}$ and Unreacted $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ Concentrations on the Volumes of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$ Solutions Mixed Together

experiment	10.0 mM $\mathrm{TCNQ(F_4)^{\bullet-}}$ (mL)	10.0 mM $\mathrm{Zn^{2+}}$ (mL)	initial $\mathrm{TCNQ(F_4)^{\bullet-}}$ (mM)	initial $\mathrm{Zn^{2+}}$ (mM)	produced $\mathrm{TCNQ(F_4)}$ (mM)[a]	unreacted $\mathrm{TCNQ(F_4)^{\bullet-}}$ (mM)[a]
1	2.0	2.0	5.0	5.0	2.3 (2.4)	0.05 (0.05)
2	2.0	1.0	6.7	3.3	3.0 (3.1)	0.3 (0.3)
3	2.0	0.5	8.0	2.0	1.8 (1.8)	4.3 (4.2)

[a] Values in parentheses are for $\mathrm{TCNQF_4}$ species.

acetonitrile (0.1 M $\mathrm{Bu_4NPF_6}$). In this case, after removal of the solids, the supernatant solutions could be studied without dilution. Figure 6 shows near-steady-state voltammograms obtained with designated concentration ratios of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$. When the concentration ratios $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$:$\mathrm{Zn^{2+}_{MeCN}}$ were 2:2 and 2:1, the residual $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ concentration remaining after reaction with $\mathrm{Zn^{2+}_{MeCN}}$ was very small. This conclusion was based on the fact the anodic (positive) currents associated with the oxidation of the radical anions back to neutral forms were small relative to the negative currents for the reduction of the $\mathrm{TCNQ(F_4)_{MeCN}}$ reaction products. In contrast, when the concentration ratio of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ to $\mathrm{Zn^{2+}_{MeCN}}$ was 2:0.5, the oxidation currents for the $\mathrm{TCNQ(F_4)^{\bullet-/0}_{MeCN}}$ processes were almost twice those of the reduction currents for the $\mathrm{TCNQ(F_4)^{0/\bullet-}}_{\mathrm{MeCN}}$ processes, implying that after reaction with $\mathrm{Zn^{2+}_{MeCN}}$ the concentrations of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ remaining are about twice those of their neutral forms. These steady-state voltammetric results confirm the conclusions drawn from UV−vis data and clearly show that the reactions between the $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ anionic radicals and $\mathrm{Zn^{2+}_{MeCN}}$ cation occur via a 2:1 $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$:$\mathrm{Zn^{2+}_{MeCN}}$ stoichiometric ratio to generate ∼50% of neutral $\mathrm{TCNQ(F_4)_{MeCN}}$ dissolved in acetonitrile along with pale green $\mathrm{ZnTCNQ(F_4)_{(s)}}$-based solids.

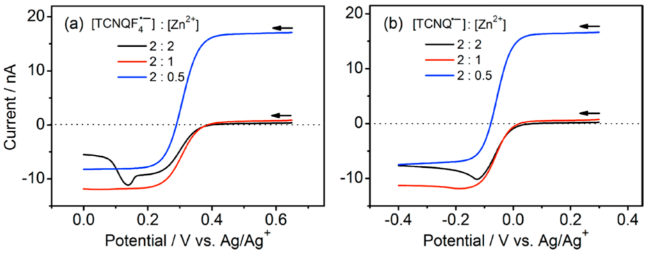


Figure 6. Near-steady-state voltammograms obtained after mixing (a) $\mathrm{TCNQF_4{}^{\bullet-}_{MeCN}}$ or (b) $\mathrm{TCNQ^{\bullet-}_{MeCN}}$ with $\mathrm{Zn^{2+}_{MeCN}}$ at designated concentration ratios when using a carbon-fiber microelectrode (11 μm diameter) at a scan rate of 20 mV $\mathrm{s^{-1}}$.

In the case of 2:2 $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$:$\mathrm{Zn^{2+}_{MeCN}}$ stoichiometry, voltammograms containing peaks were observed. The voltammetric features are attributed to the disproportionation of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$, generated by reduction of $\mathrm{TCNQ(F_4)_{MeCN}}$ when the potential is scanned to more negative values, accompanied by precipitation of solid $\mathrm{ZnTCNQ(F_4)}$ (see further details below). Deposition of the solid onto the electrode surface may cause a decrease in active area of the electrode and/or in diffusion of $\mathrm{TCNQ(F_4)_{MeCN}}$ from the bulk solution to the electrode surface, and hence a decrease in the current.

3.2. Characterization of the Solid Products. IR spectroscopy allows the redox level of $\mathrm{TCNQ(F_4)}$ in the solids to be established, since the vibrational modes for the C≡N and π(C=C) ring stretches are strongly sensitive to the degree of charge transfer.[6,15−17,21] The IR spectra for all solids obtained from mixing $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$ solutions at different ratios were found to be identical within experimental error.

Figure 7 shows the IR spectra for solids derived from a 2:1 ratio. The IR spectrum for the Zn-$\mathrm{TCNQF_{4(s)}}$-based solid (Figure 7a) contains two ν(C≡N) bands at 2165 and 2137 $\mathrm{cm^{-1}}$ that agree well with those reported for $\mathrm{[Co(C_5Me_5)_2]_2(TCNQF_4)}$ (ν(C≡N) 2168 and 2133 $\mathrm{cm^{-1}}$)[19] and $\mathrm{[Ni(C_5Me_5)_2]_2(TCNQF_4)}$ (ν(C≡N) 2167 and 2131 $\mathrm{cm^{-1}}$).[22] Therefore, they are assigned to the presence of the $\mathrm{TCNQF_4{}^{2-}}$ dianion. Furthermore, these frequencies are close to those obtained for the $\mathrm{ZnTCNQF_4}$ material (2161 and 2136 $\mathrm{cm^{-1}}$; Figure S1, Supporting Information) formed by reaction with $\mathrm{TCNQF_4{}^{2-}_{MeCN}}$, generated electrochemically, and $\mathrm{Zn^{2+}_{MeCN}}$ in a 1:1 concentration ratio (see below). A further two ν(C≡N) bands are found at 2181 and 2238 $\mathrm{cm^{-1}}$. Although the second of these frequencies is in the general region of neutral $\mathrm{TCNQF_4}$ (ν(C≡N) 2225 $\mathrm{cm^{-1}}$; Figure S2, Supporting Information), the band is very weak for the neutral form, in contrast with the strong 2238 $\mathrm{cm^{-1}}$ band observed for $\mathrm{Zn(TCNQF_4)}$. Furthermore, neutral $\mathrm{TCNQF_4}$ has strong bands at 1593 and 1338 $\mathrm{cm^{-1}}$ that are absent in the $\mathrm{Zn(TCNQF_4)}$ material. Hence, this band does not result from contamination of the sample with neutral $\mathrm{TCNQF_4}$. As noted by Meneghetti, the C≡N stretching frequencies are very sensitive to intermolecular interactions.[23] Density functional theory calculations (see Figure S3, Supporting Information) for complexes of $\mathrm{TCNQF_4{}^{2-}}$ with $\mathrm{Zn^{2+}}$ cations predict that ν(C≡N) bands at frequencies over 2200 $\mathrm{cm^{-1}}$ (and even over 2220 $\mathrm{cm^{-1}}$) can be produced by $\mathrm{TCNQF_4{}^{2-}}$. The weak and broad IR absorption band located at ∼3450 $\mathrm{cm^{-1}}$ is indicative of the presence of a small amount of water.[21,24] Three very weak bands at 2874, 2930, and 2968 $\mathrm{cm^{-1}}$ are indicative of traces of $\mathrm{Bu_4N^+}$ from the electrolyte (0.1 M $\mathrm{Bu_4NPF_6}$), as IR bands for $\mathrm{Bu_4NPF_{6(s)}}$ are located at 2878, 2938, and 2966 $\mathrm{cm^{-1}}$ (data not shown). No IR bands for the C≡N stretch of coordinated $\mathrm{CH_3CN}$, expected at 2286−2314 $\mathrm{cm^{-1}}$,[12,25] were detected.

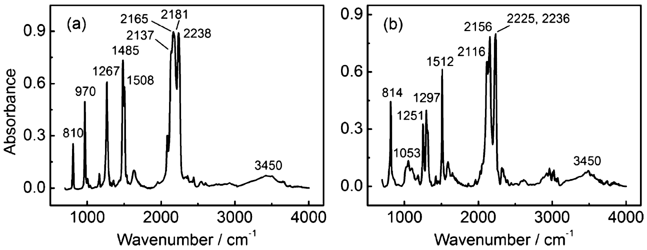


Figure 7. IR spectra for the solids obtained by mixing 5.0 mL of 10.0 mM $\mathrm{Zn^{2+}_{MeCN}}$ and 10.0 mL of (a) 10.0 mM $\mathrm{TCNQF_4{}^{\bullet-}_{MeCN}}$ and (b) 10.0 mM $\mathrm{TCNQ^{\bullet-}_{MeCN}}$.

In the case of the Zn-TCNQ-based solid, IR data (Figure 7b) contain two characteristic bands at 2156 and 2116 cm^{-1}, confirming the presence of TCNQ^{2-}.[3,26,27] These frequencies are in good agreement with those reported for Na_2TCNQ (2164 and 2096 cm^{-1}),[26] [Zn(TCNQ)bpy]·6CH_3OH (2194 and 2121 cm^{-1})[3] and the newly synthesized series of TCNQ^{2-}-based compounds by Robson et al. (2152−2194 and 2100−2166 cm^{-1}).[27] By analogy with arguments presented above for the $TCNQF_4$ solid, the bands at 2225 and 2236 cm^{-1} are also assigned to the presence of TCNQ^{2-}. Detection of the broad band at ∼3450 cm^{-1} implies the presence of water.[21,24] The three weak characteristic bands for Bu_4N^+ (as mentioned above) are also detected, indicating the presence of a small amount of this cation, probably in the form of Bu_4NPF_6, in the solid.

In summary, the IR data imply that the solids contain the dianions $TCNQ(F_4)^{2-}$ as ZnTCNQ(F_4) and Bu_4NPF_6 from the electrolyte.

Elemental analysis data for a well-washed solid obtained by reacting $TCNQF_4{}^{\bullet-}_{MeCN}$ with Zn^{2+}_{MeCN} in a 2:1 ratio has been used to determine the empirical formula of the solid. Accordingly, the solid analyzed well for [$ZnTCNQF_4$]·0.5H_2O, since experimental (calculated) data are as follows: C, 41.38 (41.11); H, 0.37 (0.29); N, 15.97 (16.30); Zn, 18.66 (18.40). Thus, the elemental analysis also is consistent with the solid being the $TCNQF_4{}^{2-}$ dianion derivative.

In summary, all the above evidence from elemental analysis results, UV−vis spectroscopy, and steady-state voltammetric experiments implies that, in the presence of Zn^{2+}_{MeCN} cations, the $TCNQ(F_4)^{\bullet-}_{MeCN}$ radical anion disproportionates to $TCNQ(F_4)^{2-}$ dianion (in the form of $ZnTCNQ(F_4)_{(s)}$) and neutral $TCNQ(F_4)_{MeCN}$.

In the majority of cases, reaction of $TCNQF_4{}^{\bullet-}$ or $TCNQ^{\bullet-}$ with a transition-metal cation leads to formation of a coordination polymer containing the monoanion. Nevertheless, as noted in the Introduction, detection of both the monoanions and dianions in chemically synthesized products has been also reported. For instance, Dunbar et al. showed that when methanol solutions of $LiTCNQF_4$ and $[Mn(CH_3CN)_4](BF_4)_2$ were reacted in a 1:1 ratio for 2 weeks, a compound containing both $TCNQF_4{}^{\bullet-}$ and $TCNQF_4{}^{2-}$ was isolated.[16] Similarly, Miller et al. reported that upon mixing acetonitrile solutions of Bu_4NTCNQ and $[M(CH_3CN)_6]SbF_6$ (M^{II} = Mn, Ni), solids having the empirical formulas $[Mn(TCNQ)_{1.38}(Bu_4N)_{0.1}(SbF_6)_{0.34}]$·1.32$CH_3CN$ and $[Ni(TCNQ)_{1.32}(Bu_4N)_{0.04}(SbF_6)_{0.24}]$·0.54$CH_3CN$ were produced,[12] although no rationalization of these stoichiometries was proposed.

3.3. Mechanistic Aspects of the Dianion Generation. A mechanism that accounts for the disproportionation of the $TCNQ(F_4)^{\bullet-}_{MeCN}$ monoanionic radicals in acetonitrile solution containing Zn^{2+}_{MeCN} is represented via eqs 1 and 2, where $K_{eq\,1}$ =

$$2\,TCNQ(F_4)^{\bullet-}_{MeCN} \overset{K_{eq\,1}}{\rightleftharpoons} TCNQ(F_4)_{MeCN} + TCNQ(F_4)^{2-}_{MeCN} \qquad (1)$$

$$TCNQ(F_4)^{2-}_{MeCN} + Zn^{2+}_{MeCN} \overset{K_{eq\,2}}{\rightleftharpoons} ZnTCNQ(F_4)_{(s)} \qquad (2)$$

$10^{-(F/2.303RT)(E_1^0-E_2^0)}$[28] or $10^{-(E_1^0-E_2^0)/0.0585}$ at 295 K (22 °C), F = Faraday constant, R = universal gas constant, T = temperature (K), E_1^0 and E_2^0 are the reversible formal potentials for the $TCNQ(F_4)^{0/\bullet-}{}_{MeCN}$ and $TCNQ(F_4)^{\bullet-/2-}{}_{MeCN}$ processes, respectively, and $K_{eq\,2} = K_{sp}{}^{-1}$ (K_{sp} = solubility product of $ZnTCNQ(F_4)_{(s)}$).

The equilibrium constants for the disproportionation reaction in eq 1 ($K_{eq\,1} = 9 \times 10^{-10}$ for $TCNQF_4$ as $E_1^0 - E_2^0$ = 0.53 V[17] or 4×10^{-10} for TCNQ as $E_1^0 - E_2^0$ = 0.55 V[29,30]) are both very small. Since the disproportionation is not favored in the absence of process 2, K_{sp} has to be sufficiently small in order to facilitate the formation of $ZnTCNQ(F_4)_{(s)}$. Combining eqs 1 and 2 yields eq 3, the net reaction that leads to the formation of $ZnTCNQ(F_4)_{(s)}$ and neutral $TCNQ(F_4)_{MeCN}$.

$$2TCNQ(F_4)^{\bullet-}_{MeCN} + Zn^{2+}_{MeCN} \overset{K_{eq\,3}}{\rightleftharpoons} TCNQ(F_4)_{MeCN} + ZnTCNQ(F_4)_{(s)} \qquad (3)$$

In principle, the solid $Zn(TCNQ(F_4))_2(H_2O)_2$ would be predicted to be formed due to the reaction given in eq 4, where

$$Zn^{2+}_{MeCN} + 2\,TCNQ(F_4)^{\bullet-}_{MeCN} + 2H_2O \overset{K_{eq\,4}}{\rightleftharpoons} Zn(TCNQ(F_4))_2(H_2O)_{2\,(s)} \qquad (4)$$

the water comes from the $[Zn(H_2O)_6]^{2+}$ salt.[31] However, this compound is slightly soluble in acetonitrile, and is certainly much more soluble than $ZnTCNQF_{4(s)}$ (see evidence below).

The insolubility of $ZnTCNQF_{4(s)}$ in acetonitrile has been verified by mixing 10.0 mM acetonitrile solutions of Zn^{2+}_{MeCN} and the air-stable dianion[18] $TCNQF_4{}^{2-}_{MeCN}$ generated electrochemically in acetonitrile (0.1 M Bu_4NPF_6), in a molar ratio of 1:1. A precipitate formed immediately when the two solutions were mixed together. The solid was collected and washed five times with acetonitrile and then shaken vigorously in acetonitrile for several minutes. The solution obtained after centrifugation was studied by UV−vis spectroscopy. No characteristic absorption bands for $TCNQF_4{}^{2-}_{MeCN}$ dianion could be detected, confirming that the solubility of $ZnTCNQF_{4(s)}$ is extremely low in acetonitrile.

The IR spectrum for the $ZnTCNQF_{4(s)}$ material, which was "chemically" synthesized by addition of 10.0 mM Zn^{2+}_{MeCN} to 10.0 mM electrochemically generated $TCNQF_4{}^{2-}_{MeCN}$ solution in a 1:1 molar ratio, exhibits the two characteristic ν(C≡N) bands for the $TCNQF_4{}^{2-}$ dianion[19,22] at 2161 and 2136 cm^{-1} as well as one at 2233 cm^{-1}, along with a shoulder at about 2180 cm^{-1} (Figure S1, Supporting Information). Within experimental uncertainty this spectrum is considered to be the same as that for the solid obtained by disproportionation (Figure 7). Thus, this solid is a $TCNQF_4{}^{2-}$ derivative devoid of any $TCNQF_4$ or $TCNQF_4{}^{\bullet-}$ and elemental analysis again agreed with the empirical formula $ZnTCNQF_4$·0.5H_2O.

Although monoanion disproportionation (eq 1) is facilitated by the presence of Zn^{2+}_{MeCN} in acetonitrile, the extent to which this reaction occurs is strongly dependent upon the concentration of water present. Consistent with this hypothesis, it was established that, upon deliberate addition of water, the disproportionation of $TCNQ(F_4)^{\bullet-}_{MeCN}$ in the presence of Zn^{2+}_{MeCN} (eq 3) becomes disfavored, while the reverse (comproportionation) reaction is now favored. Consequently, the concentration of the $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ monoanions remaining in solution increases upon increasing the concentration of water. This is supported by the increase in absorbances at 411 and 752 nm or 420 and 743 nm (Figure 8), which are characteristic $\lambda_{\max}$ values for $\mathrm{TCNQF_4{}^{\bullet-}_{MeCN}}$ or $\mathrm{TCNQ^{\bullet-}_{MeCN}}$, respectively. Importantly, when the added water content is ≥3% (v/v), no precipitation of $\mathrm{ZnTCNQ(F_4)_{(s)}}$ or any other solid is observed and the concentrations of the $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ monoanion in solutions in the presence or absence of both $\mathrm{Zn^{2+}_{MeCN}}$ and ≥3% H_2O are the same, as evidenced by UV–vis spectroscopic data (see Figure S4, Supporting Information).

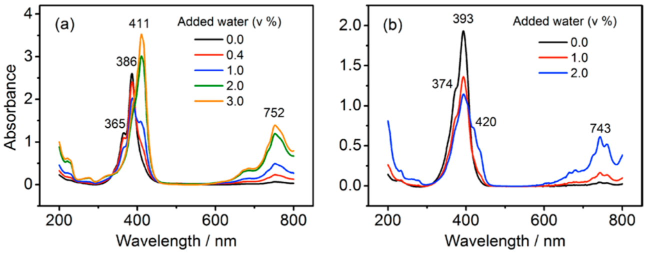


Figure 8. UV–vis spectra for solutions obtained after mixing (a) $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ and (b) $\mathrm{TCNQ^{\bullet-}_{MeCN}}$ solutions with $\mathrm{Zn^{2+}_{MeCN}}$ solution using a molar ratio of 2:1 in the presence of the designated percentage of added water.

The fact that the disproportionation of the $\mathrm{TCNQ(F_4)^{\bullet-}}$ monoanions can be inhibited by addition of water is attributed to the enhanced solubility of $\mathrm{ZnTCNQF_{4(s)}}$, which probably partially reflects the stronger solvation of $\mathrm{Zn^{2+}}$ in water in comparison to that found in acetonitrile: i.e., $\mathrm{Zn^{2+}_{aq}}$ is more strongly solvated than $\mathrm{Zn^{2+}_{MeCN}}$. This conclusion is further supported by the series of experiments described below.

(i) Mixing $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ radical anions with $\mathrm{Zn^{2+}_{MeCN}}$ in a 2:1 molar ratio yields soluble $\mathrm{TCNQ(F_4)_{MeCN}}$ and solid $\mathrm{ZnTCNQ(F_4)_{(s)}}$, in principle via disproportionation. The suspensions were diluted 100-fold, and then UV–vis spectra were recorded before and after addition of water (Figure 9). Clearly, increasing the water content results in a marked increase in the concentration of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ with a concomitant decrease in $\mathrm{TCNQ(F_4)_{MeCN}}$ concentration. This observation is supported visually by the inspection of photographs in Figure 10. Thus, addition of 10% (v/v) water gives rise to a change from a green suspension of $\mathrm{ZnTCNQ_s}$ and dissolved $\mathrm{TCNQ_{MeCN}}$ to a clear solution of the monoanion.

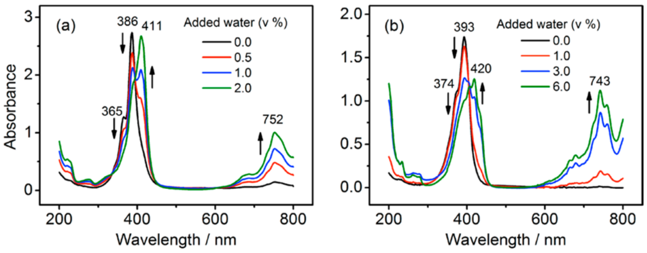


Figure 9. (a) UV–vis spectra for diluted (100-fold) suspension containing soluble $\mathrm{TCNQF_{4\,MeCN}}$ and solid $\mathrm{ZnTCNQF_{4(s)}}$, obtained by mixing acetonitrile solutions of $\mathrm{TCNQF_4{}^{\bullet-}{}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$ in a 2:1 molar ratio, followed by addition of the designated amount of water. (b) As for (a), but with TCNQ-based instead of $\mathrm{TCNQF_4}$-based compounds.

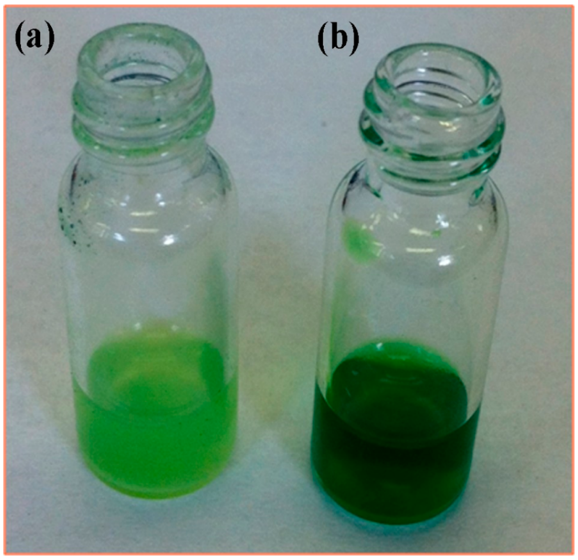


Figure 10. Color change of the suspension (a) obtained from mixing acetonitrile solutions of 1.0 equivalent of $\mathrm{TCNQ^{\bullet-}_{MeCN}}$ and 0.5 equivalent of $\mathrm{Zn^{2+}_{MeCN}}$ and (b) after addition of 10% (v/v) water.

(ii) $\mathrm{ZnTCNQ(F_4)}$ solid prepared from $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$ acetonitrile solutions in a 2:1 molar ratio was washed with 5 × 2 mL of acetonitrile and then added to neat acetonitrile to give a suspension. After addition of 3% (v/v) water and shaking for 2 min, no prominent UV–vis bands were detected in the solution phase (Figure 11, black curves). Known concentrations of $\mathrm{TCNQ(F_4)_{MeCN}}$ were then added. After the suspensions were shaken for a further 2 min, UV–vis spectra were recorded (Figure 11, red, blue, and green curves) and confirmed that the addition of $\mathrm{TCNQ(F_4)_{MeCN}}$ led to the formation of $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ in solution, as evidenced by the increase in the absorbance at 752 (743) nm.

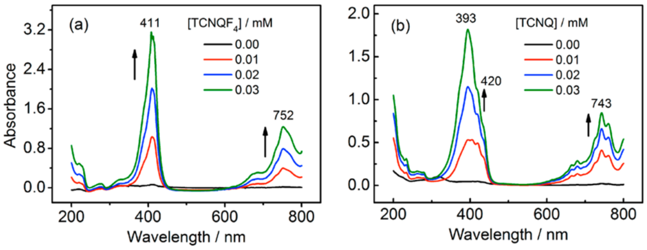


Figure 11. (a) UV–vis spectra derived from a suspension of $\mathrm{ZnTCNQF_{4(s)}}$, formed from mixing $\mathrm{TCNQF_4{}^{\bullet-}_{MeCN}}$ and $\mathrm{Zn^{2+}_{MeCN}}$ acetonitrile solutions, in acetonitrile containing 3.0% (v/v) water before and after addition of $\mathrm{TCNQF_{4\,MeCN}}$ at the designated concentrations. (b) As for (a) but with addition of $\mathrm{TCNQ_{MeCN}}$.

(iii) Suspensions of $\mathrm{ZnTCNQ(F_4)}$ solids were prepared in acetonitrile as in (ii). However, this time, water was added after the addition of $\mathrm{TCNQ(F_4)_{MeCN}}$. Prior to the addition of water, only UV–vis absorption bands for neutral $\mathrm{TCNQ(F_4)_{MeCN}}$ were detected. Upon addition of water, the absorbance from neutral $\mathrm{TCNQ(F_4)_{MeCN}}$ decreased, while that for $\mathrm{TCNQ(F_4)^{\bullet-}_{MeCN}}$ increased (data not shown).

(iv) In acetonitrile solutions containing a suspension of $\mathrm{ZnTCNQF_{4(s)}}$ in the presence (3% v/v) or absence of water, no UV–vis spectrum for the $\mathrm{TCNQF_4{}^{2-}_{MeCN}}$ dianion could be detected. This result attests to the very low solubility of $\mathrm{ZnTCNQF_{4(s)}}$ in acetonitrile, even following the addition of 3%

(v/v) water. However, when neutral $TCNQF_{4\ MeCN}$ was added to the 3% water/acetonitrile $ZnTCNQF_{4(s)}$ suspension, absorbance bands due to the presence of dissolved $TCNQF_{4\ MeCN}^{\bullet-}$ were observed, thereby again confirming that the comproportionation reaction is favored under these conditions.

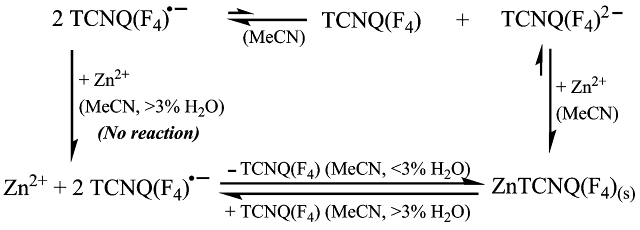
The combination of observations from experiments (i)−(iv) attests to the fact that the solubility of solid $ZnTCNQ(F_4)$ increases on addition of water, thereby disfavoring the disproportionation reaction and regenerating $TCNQ(F_4)_{MeCN}^{\bullet-}$ via the comproportionation reaction.

The significant outcome of this study is a new understanding and rationalization of how to control and quantitatively probe the role of the disproportionation reactions involving the $TCNQ(F_4)_{solvent}^{\bullet-}$, neutral $TCNQ(F_4)_{solvent}$, and $TCNQ(F_4)_{solvent}^{2-}$ dianions. The disproportionation of $TCNQ(F_4)_{solvent}^{\bullet-}$ is promoted by the precipitation of insoluble metal−$TCNQ(F_4)^{2-}$ coordination polymers. Solvent-dependent disproportionation−comproportionation reactions in combination with solubility issues can explain why different redox levels are detected in the synthesis of $TCNQ(F_4)$-based materials when the preparative methods involve the reaction of the radical anions with metal cation precursors.

4. CONCLUSIONS

This study highlights the crucial role that metal ions and water have on promoting and controlling the extent of the disproportionation reactions associated with the $TCNQ(F_4)_{solvent}^{\bullet-}$ monoanionic radicals and ultimately the solid products isolated from reactions with the radical anions (Scheme 1).

Scheme 1. Summary of the Interrelationship between Components in the Zn-Based $TCNQ(F_4)$ Reactions Emphasizing the Role of Water



In the absence of a precipitation reaction, e.g. when the species is generated electrochemically in acetonitrile (0.1 M Bu_4NPF_6), the radical anions are thermodynamically very stable with respect to disproportionation. In the absence of water, addition of Zn_{MeCN}^{2+} promotes the disproportionation of $TCNQ(F_4)_{MeCN}^{\bullet-}$ radicals, leading to generation of the neutral $TCNQ(F_4)_{MeCN}$ and precipitation of $ZnTCNQ(F_4)_{(s)}$. However, deliberate addition of water can be used to prevent the disproportionation reaction, since the reverse (comproportionation) reaction is now favored, giving rise to a soluble mixture of Zn_{MeCN}^{2+} and $TCNQ(F_4)_{MeCN}^{\bullet-}$. This study clarifies the interplay between the identity of the metal ion and the presence of water in controlling the disproportionation/comproportionation reactions encountered in many $TCNQ(F_4)$ chemical syntheses and provides a rationale for the control of products. Importantly, this work has not only resolved the ambiguity arising from formation of $TCNQ(F_4)$-based materials at different redox levels when mixing solutions of Zn^{2+} ions and $TCNQ(F_4)^{\bullet-}$ but also opened up the possibility to tune the composition of the final products. The possibility that other metal cations could exhibit these characteristics seems likely: cf. the Introduction. Rational rather than empirical methods of synthesis could be attractive in developing targeted strategies for the generation of new $TCNQ(F_4)$-based materials, which may form the basis for molecular electronic, sensing, or other devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, providing an FT-IR spectrum for a solid synthesized from $TCNQF_{4\ MeCN}^{2-}$ and Zn_{MeCN}^{2+} acetonitrile solutions, Figure S2, presenting the experimental IR spectrum of neutral $TCNQF_4$, Figure S3, showing some results for the nitrile regions of IR spectra for Zn^{2+}-$TCNQF_4^{2-}$ complexes calculated using density functional theory, Figure S4, providing a comparison of UV−vis spectra for a $TCNQ(F_4)_{MeCN}^{\bullet-}$ acetonitrile solution and a solution obtained by mixing $TCNQ(F_4)_{MeCN}^{\bullet-}$ and Zn_{MeCN}^{2+} acetonitrile solutions at a 2:1 molar ratio in the presence of 3% water, and text giving the full reference for Gaussian 09, Revision A.02. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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