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Conducting Materials

Highly Conducting Coordination Polymers Based on Infinite M(4,4′-bpy) Chains Flanked by Regular Stacks of Non-Integer TCNQ Radicals**

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Porous coordination polymers, often referred to as metal-organic framework solids (MOFs), hold great promise for the separation and storage of gases and for catalytic applications.[1] The wealth of knowledge in this area notwithstanding, there is considerable untapped potential for the study of polymeric coordination compounds in the area of functional materials composed of redox-active molecules and metal ions that bear unpaired spins.[2] In this vein, an important current goal of many molecular materials research programs is to synthesize "hybrid" inorganic–organic architectures, in which the physical properties of individual components act synergistically in a single material. Specifically, there is a quest for systems that exhibit coexistence of conductivity and magnetism, research that represents forefront topics in terms of both fundamental knowledge and applications.[3]

With respect to our current interests in coordination polymers, we are focusing on compounds of 7,7,8,8-tetracyanoquinodimethane (TCNQ), which, in its reduced form, leads to materials with fascinating physical properties.[4,5] The prototype example in the field is the seminal charge-transfer material TTF–TCNQ (TTF = tetrathiafulvalene) in which the TCNQ molecules are partially reduced to $\rho = -0.59$ (ρ = calculated charge). Crystals of this compound exhibit remarkably high metallic conductivity with σ values of $10^4\,\mathrm{S\,cm^{-1}}$. Numerous other, mostly semiconducting, TCNQ materials have been prepared over the ensuing years since this discovery, a majority of which are based on organic cations.[4,5] In addition to conducting charge-transfer salts, TCNQ radical anions are also known to coordinate to open-shell metal ions to produce binary phases such as $\mathrm{M^{II}(TCNQ)_2}$ (M = Mn, Fe, Co, Ni), which undergo long-range magnetic ordering.[6] It should be noted, however, by way of distinguishing the two aforementioned cases, that the magnetism of the TTF–TCNQ material is derived solely from the conduction π electrons of TTF–TCNQ[4] and that the $\mathrm{M^{II}(TCNQ)_2}$ magnets possess localized radicals.[6] In fact, these examples represent two different paradigms and there is no unusual coexistence of properties in either case.

One approach to straddling the disparate areas of conductors and magnets is to depart from a 3D metal-containing phase in favor of a lower dimensional architecture that involves TCNQ–TCNQ stacking reminiscent of organic charge-transfer salts. Such a situation is expected to occur if a rodlike co-ligand is incorporated into the paramagnetic metal coordination polymer backbone.[2,7] This strategy has met with some success over the years, but there remains a general lack of such compounds with interesting properties.[7]

In a recent study that is relevant to the present work, Kitagawa and co-workers reported 3D MOFs composed of $\mathrm{Zn^{II}}$ ions coordinated to 4,4′-bipyridine (4,4′-bpy) as well as the dianion or the σ dimer form of TCNQ, namely $\mathrm{[Zn(4,4'\text{-}bpy)(TCNQ^{2-})]\cdot 6\,CH_3OH}$ and $\mathrm{[Zn(4,4'\text{-}bpy)(\mu_4\text{-}TCNQ\text{-}TCNQ)]\cdot 1.5\,C_6H_6}$.[8] These materials are noteworthy because the former material participates in charge-transfer interactions with guest molecules[7a] and the latter compound adopts a channel structure that allows for selective guest adsorption.[8b,c,d] In terms of other physical properties, however, the materials are limited because they contain the diamagnetic dianion and σ dimer forms of TCNQ. In the course of our studies involving reactions of $\mathrm{Mn^{II}}$ and $\mathrm{Zn^{II}}$ ions with 4,4′-bpy in the presence of TCNQ anions we isolated products that are completely different than the aforementioned materials. The conditions that we employed lead to 1D chains in which partially reduced TCNQ molecules are incorporated into the framework of the paramagnetic metal ions along with the 4,4′-bpy co-ligands.

Samples of Li(TCNQ) and 4,4′-bpy were dissolved in methanol and layered on a methanol solution of $\mathrm{M(NO_3)_2\cdot 6H_2O}$ (M = Mn for **1** and Zn for **2**). After 24 h, black platelike crystals of $\mathrm{\{[Mn(4,4'\text{-}bpy)(\eta^1\text{-}TCNQ)_2(CH_3OH)_2]TCNQ\}\cdot 0.5\,H_2O}$ (**1**) and $\mathrm{\{[Zn(4,4'\text{-}bpy)(\eta^1\text{-}TCNQ)_2(CH_3OH)_2]TCNQ\}}$ (**2**) were harvested. The synthesis is similar to the previously reported one,[8] except that the concentrations of the reagents are much higher.[8]

Given that compounds **1** and **2** are isostructural,[9] only the details of the Mn derivative **1** will be provided. The crystal system and space group for both compounds is triclinic $P\bar{1}$

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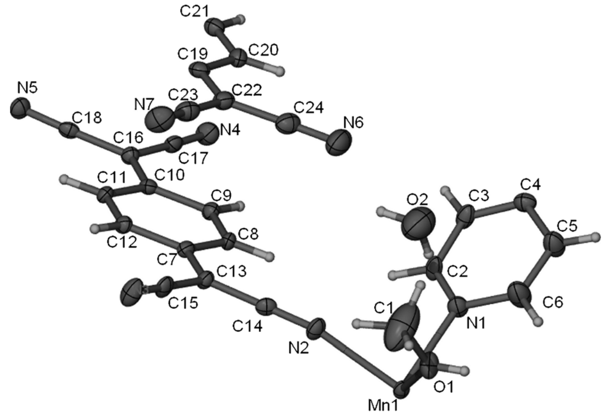


Figure 1. The asymmetric unit of **1** with the atom-labeling scheme.

with the unique metal ion being located on a center of inversion (Figure 1). Each Mn^{II} ion is bound to two *trans*-disposed 4,4′-bpy nitrogen atoms, two cyano groups from independent TCNQ ligands, and two CH_3OH solvent groups all of which are mutually *trans* in an octahedral arrangement.

The metrical parameters are summarized in Table 1. The bridging 4,4′-bpy ligands lead to the formation of a one-dimensional motif (Figure 2), in which neighboring chains are aligned parallel along the $a+b$ direction; interdigitated chains create a layered structure in the *ab* plane. Two TCNQ molecules are present, one of which is coordinated (C) to a Mn^{II} ion and the other of which is uncoordinated TCNQ (U). The TCNQ of the C type is η^1 with a Mn−N bond length of 2.22 Å, which is in a typical range. The TCNQ units in **1** and **2** form stacked columns along the *b* direction with the repeat sequence −C−C−U−. The M(4,4′-bpy) chains that run along the $a+b$ direction and the TCNQ stacks along the *b* direction are twisted by 48° with respect to each other. The molecular planes of the neighboring C−U and C−C units exhibit ring-over-bond π–π stacking (Figure 1b). The ring slippage of the overlapping molecular planes is more pronounced for C−C, since the positions of C are fixed by their interactions with the metal ions. The distance between the neighboring molecular planes of TCNQ (D) is approximately 3.23 Å for U−C or C−U (D_{U-C}), and approximately 3.03 Å for C−C (D_{C-C}) in the stacks. Both D_{U-C} and D_{C-C} are unusually short, and, in fact, are among the shortest contacts reported for conducting TCNQ materials.[4,6a,9] Such contracted distances are rendered possible by the confinement of the TCNQ molecules, which is achieved by their association with the M(4,4′-bpy) chain. The π–π interaction would be predicted as being stronger for the C−C pair, given the shorter D_{C-C} as compared to D_{U-C} but it must be pointed out that the greater slippage of the rings in the C−C pair serves to reduce the interaction.

Table 1: Pertinent bond lengths and angles in **1** and **2**.[a]

Bond length [Å]	Bond angle [°]
Mn-N2 2.221(2)	N2-Mn-N2[b] 180
Mn-N1 2.271(2)	N1-Mn-N1[b] 180
Mn-O1 2.180(19)	C14-N2-Mn 166.3(19)
Zn-N2 2.140(18)	N2-Mn-N1 90.3(7)
Zn-N1 2.160(18)	C14-N3-Zn 168.8(15)
Zn-O1 2.128(5)	N2-Zn-N1 90.1(7)

[a] The numbering Scheme is shown in Figure 1; [b] Symmetry operators: −x, −y, −z.

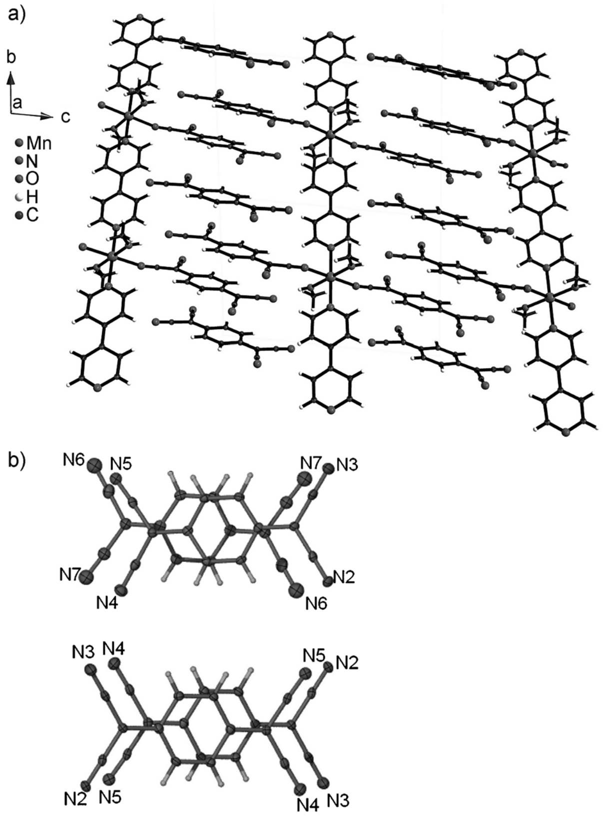
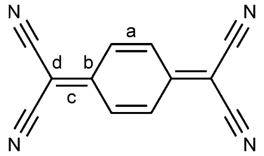


Figure 2. Packing diagrams of **1**; a) in the *bc* plane, b) thermal ellipsoid plots of the neighboring TCNQ units viewed perpendicular to the molecular plane in **1**; U−C (top), C−C (bottom).

A knowledge of the charge on TCNQ is essential for understanding the properties of these complexes because a partially reduced stack is necessary for high conductivity, whereas the localized or delocalized nature of the spin is decisive for the magnetic behavior.[3,4] The parameter ζ can be used as an indicator of charge for TCNQ molecules and is estimated from the bond lengths in **1** and **2** by the Kistenmacher relationship as $\zeta = A[c/(b+d)] + B$ ($A = -41.667$, $B = 19.833$, c, b, and d are the bond lengths of TCNQ shown in Scheme 1).[11] The ζ values of U are estimated as being −0.71 for **1** and −0.74 for **2**. The estimated



Scheme 1. The TCNQ molecule with the notation used for the Kistenmacher relationship.

ζ is close to −2/3 for U in **1** and **2**, which indicates the delocalization of the charge over the TCNQ columns. An estimation of ζ for C is less reliable because of the asymmetric molecular shape, although C still maintains its planarity. The ζ values for C vary from −0.68 to −1.25 for **1** and from −0.71 to −1.11 for **2**, depending on the selected combination of the bond lengths. The distortion of C is ascribed to the unusually short distance for C−C and the asymmetric bonding of C to the metal ions. Given that the crystallographically independent TCNQ units are exactly one C and one half of a U in the repeat unit, the ζ value for C is taken to be approximately −2/3 based on the calculated value of U, although we are aware that a small degree of disproportionate charge distribution between U and C is possible, given the averaged empirical analysis provided by this method. The main point of this exercise is that the charge of three TCNQ molecules must compensate for the M^{2+} ions in {[M(4,4′-bpy)(η^1-TCNQ)$_2$-(CH_3OH)$_2$]TCNQ}, given the innocence of 4,4′-bipyridine and MeOH ligands, a situation that leads to an average charge of −2/3 for each of them based on the metrical parameter analysis described above.

Infrared spectroscopy is another excellent method for evaluating charge on the TCNQ units (Table 2).[6] The ν_{C-N} absorptions for **1** and **2** occur at lower energies than the stretches for $TCNQ^0$ and are closer to that of fully reduced $TCNQ^{-1}$, supporting evidence that the TCNQ units in **1** and **2** are reduced to a value that is not far from −1. An analysis of the bond distances taken together with the ν_{C-N} data support the conclusion that the TCNQ molecules are equally charged, that is, −2/3, regardless of whether they are coordinated (C) or uncoordinated (U) in **1** and **2**. Although the starting material Li(TCNQ) contains TCNQ in the −1 state, disproportionation of TCNQ (namely, $2\,TCNQ^- \rightleftarrows TCNQ^0 + TCNQ^{2-}$) is fairly common and leads to the current situation, in which the reagents $TCNQ^-$, $TCNQ^0$, M^{II}, and 4,4′-bpy are all present in solution; these building blocks self-assemble into the products **1** and **2** with an average oxidation state for TCNQ that is between 0 and −1.[11]

Table 2: Infrared spectral data for TCNQ compounds (ν_{C-N}).

Compound	ν_{C-N} [cm^{-1}]
TCNQ[5]	2222 s
Mn(TCNQ)$_2$[5]	2205 s, 2187 s, 2137 sh
[(C_4H_9)$_4$N](TCNQ)[5]	2188 sh, 2180 s, 2162 s, 2157 s
Li(TCNQ)[5]	2211 s, 2196 s, 2180 sh, 2154 s
1	2214 s, 2196 s, 2186 s, 2169 s
2	2210 s, 2193 s, 2183 s, 2169 s

The structures of the compounds in this study raise an obvious question as to whether there is an interaction between the conduction electrons associated with the TCNQ stacks and the d orbital spins on the Mn^{II} ions mediated by the coordinated TCNQ. The closest distance between Mn ions (D_{Mn-Mn}) is 7.67 Å associated with neighboring chains. Along the stacking direction of TCNQ, the shortest D_{Mn-Mn} is 9.72 Å and between the neighboring layers of the bpy chain the value is 14.93 Å. These separations are more than ample for the suppression of magnetic interactions between Mn^{II} ions other than through the intervening TCNQ radicals.[12]

The conductivities of **1** and **2** were measured on pressed pellets by the conventional four-probe method (Figure 3). The values of σ, for **1** and **2** at 300 K, are 3.8 and 1.4 S cm^{-1} respectively. It is noted that σ increases with cooling from 330 K to 300 K both in **1** and **2**, a behavior that hints at "metallic" conductivity. These results are reproducible with additional heating and cooling cycles. To the best of our knowledge, the conductivities at 300 K for **1** and **2** are the highest values ever reported for coordination compounds of TCNQ.[7a,13,14] As a point of reference, we note that, although there are many other "all-organic" TCNQ-based charge-transfer materials with excellent conducting properties, for example NMP–TCNQ (NMP = N-methylphenzenium) with $\sigma = 200\,S\,cm^{-1}$), there are very few highly conducting TCNQ materials based on inorganic donors. Two leading examples are [Cu(dpa)$_2$(TCNQ)$_2$] (dpa = dipyridylamine) and Pd-(CNMe)$_4$(TCNQ)$_4$·2 CH_3CN, which have conductivity values of 50 and 3.5 S cm^{-1}, respectively.[5] No structural data for the Cu material is available, however, and the Pd compound is a salt rather than a coordination polymer of TCNQ.

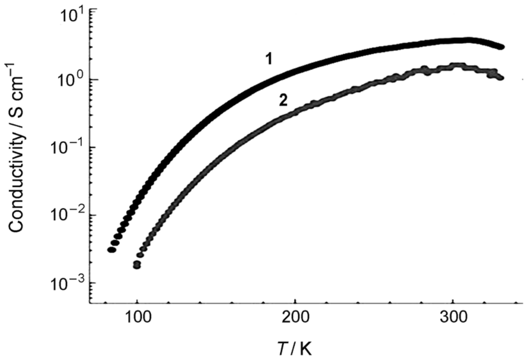


Figure 3. Temperature dependence of the conductivity of **1** and **2**.

Below 300 K, semiconducting behavior is observed for both new materials; the energy gap (E_g) is 73 meV for **1** and 84 meV for **2**. The exceptionally high conductivities in **1** and **2** are derived from the excellent conducting path of the regularly spaced partially reduced TCNQ radicals, a situation that is difficult to achieve in metal complexes of TCNQ.

The temperature dependence of the dc magnetic susceptibility for **1** exhibits Curie–Weiss behavior as indicated in the plot of χT versus T (Figure 4) The Curie constant is 4.33 emu K mol^{-1} and the Weiss temperature (θ) is −1.7 K. The negative θ value is taken as an indication of a weak antiferromagnetic interaction but this is unlikely to be due to superexchange interactions between the $S = 5/2$ Mn^{II} ions through the very long 4,4′-bpy bridging ligand or through space. It is assumed, therefore, that the interaction occurs through the TCNQ stacks involving C and U. To clarify the contribution of TCNQ to the magnetism of **1**, the dc susceptibility data for **2** were measured. In this material, the only spin-bearing units are the TCNQ molecules with $2 \times S =$

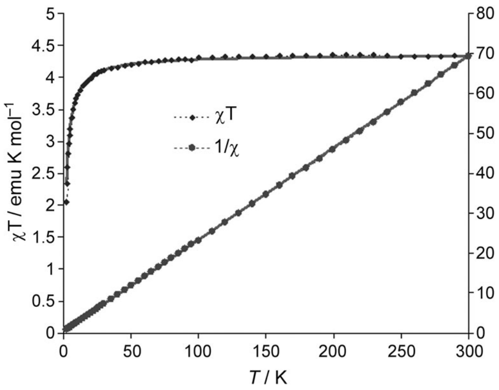


Figure 4. Temperature dependence of χT for **1** (diamonds) and $1/\chi T$ (circles). The solid lines are the best fit to the Curie–Weiss law.

1/2 spins being formally located on the −C−U−C− trimer repeat unit. It was found, however, that the Zn compound is diamagnetic, therefore the magnetism of the Mn derivative **1** is due solely to contributions from weakly coupled $S = 5/2$ Mn^{II} ions.[7a]

Compound **1** is the first example of a polymer with partially reduced radical anions of TCNQ coordinated to Mn^{II} ions; the closest previously reported examples is a compound containing $TCNQ^{-1}$ and four $Mn^{I/II}$ centers and a 1D Mn^{III} complex with coordinated TCNQ radical anions.[12,15] For example in the case of $[Mn(5\text{-TMAMsaltmen})TCNQ](ClO_4)_2$ (5-TMAMsaltmen = *N*,*N*′-(1,1,2,2-tetramethylethylene)bis(5-trimethylamminiomethylsalicylideneiminato)), the radical anion of TCNQ bridges Mn^{III} centers through two of the four cyano groups to form a 1D structure that gives rise to single-chain magnetism.[11] In this material, the coupling constant for the Mn^{III}/TCNQ interaction was evaluated to be much stronger at $J_{\pi d}/k_B = -96$ K. The Mn–N distance is 2.380(4) Å and the angle Mn–N–C is 123.8(3)°. In the case of the present compound, the corresponding values are 2.221(3) and 166.4(3)°. The Mn–N distance is much shorter in the present Mn^{II} compound as compared to the compound $[Mn(5\text{-TMAMsaltmen})TCNQ](ClO_4)_2$, which would lead one to predict that the $J_{\pi d}$ for **1** should be larger, a situation that is clearly not the case. In another material, namely the binary $Mn^{II}(TCNQ)_2$ magnet with coordinated TCNQ radicals, the θ value is reported to be 44 K[6], which supports that strong coupling is possible between Mn^{II} and TCNQ radicals although it has not been observed in the present case. The lack of contribution of TCNQ spins to the magnetism of **1** indicates that $J_{\pi\pi}$ is sufficiently large so as to reduce any appreciable contribution to the susceptibility from the organic spins as noted for other TCNQ polymeric materials with strongly correlated spins, that is, Cu(TCNQ) phase I.[10]

In summary, we have isolated new highly conducting coordination polymers with TCNQ radicals. The one-dimensional structures of **1** and **2** enhance the rigidity, hence regularity, of the conducting stacks by the direct bonding of the TCNQ groups to the metal ions. The conductivities of $\{[Mn(4,4'\text{-bpy})(\eta^1\text{-TCNQ})_2(CH_3OH)_2]TCNQ\}\cdot 0.5\,H_2O$ (**1**) and $\{[Zn(4,4'\text{-bpy})(\eta^1\text{-TCNQ})_2(CH_3OH)_2]TCNQ\}$ (**2**) are exceptionally high and hint at the potential for unprecedented metallic conductivity for TCNQ framework solids. An analysis of the magnetic properties of **1** and **2** revealed that the spins on the TCNQ stacked radicals are strongly correlated and that there is no appreciable interaction between the localized Mn^{II} spins as one may have expected. We are currently attempting to prepare analogous materials with Ni^{II}, Co^{II}, and Fe^{II} to test their magnetic and conducting properties and compare them to the Mn derivative.

Experimental Section

The reactions were performed in air. Synthesis of **1**: A sample of 4,4′-bipyridine (0.016 g, 0.1 mmol) was dissolved in CH_3OH (3 mL) and added to a solution of LiTCNQ (0.021 g, 0.1 mmol) in CH_3OH (7 mL) and was stirred for 5 min. The mixture was carefully layered on a solution of $Mn(NO_3)_2\cdot 6\,H_2O$ (0.018 g, 0.1 mmol) in methanol (3 mL) in a 5 dram vial. Black platelet crystals of **1** appeared after 24 h. The macroscopically large crystals were separated from impurities using a glass capillary and were washed with methanol. (Yield: 0.015 g, ca. 50%). Synthesis of **2**: A sample of 4,4′-bipyridine (0.016 g, 0.1 mmol) was dissolved in methanol (1 mL) and was added to a solution of LiTCNQ (0.0105 g, 0.05 mmol) in CH_3OH (4 mL) and was stirred for 5 min. The mixed solution was layered on a solution of $Zn(NO_3)_2\cdot 6\,H_2O$ (0.018 g, 0.1 mmol) in CH_3OH (3 mL) in 6 mm diameter glass tubes. Black platelet crystals of **1** appeared after 24 h. The sample crystals were filtered and were washed with CH_3OH. (Yield: 0.018 g, ca. 60%). After being dried in air, unit cells of numerous crystals from batches of **1** and **2** were measured by X-ray diffraction to verify the purity before performing properties measurements.

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[9] Crystal data for **1**: triclinic, $P\bar{1}$, $C_{48}H_{29}N_{14}O_{2.5}Mn$, $a = 7.674(5)$, $b = 9.719(5)$, $c = 14.936(5)$ Å; $\alpha = 95.724(5)$, $\beta = 90.34(5)$, $\gamma = 96.66(5)°$; $V = 1100.8(10)$ Å^3; $Z = 1$, $T = 110$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.7106$ Å). $R_1 = 0.0536$ for 295 parameters and 2928 unique reflections with $(I > 2\sigma(I))$ and $\omega R_2 = 0.166$ for all 3627 reflections with GOF = 1.100; Crystal data for **2**: triclinic, $P\bar{1}$, $C_{48}H_{28}N_{14}O_2Zn$, $a = 7.631(5)$, $b = 9.653(5)$, $c = 14.908(5)$ Å; $\alpha = 95.559(5)$, $\beta = 90.729(5)$, $\gamma = 97.844(5)°$; $V = 1082.4(10)$ Å^3; $Z = 1$, $T = 110$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $R_1 = 0.033$ for 295 parameters and 2982 unique reflections with $(I > 2\sigma(I))$ and $\omega R_2 = 0.093$ for all 3249 reflections with GOF = 1.02 CCDC 789652 and CCDC 789653 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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