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Article

Tetrathiafulvalene−Tetracarboxylate: An Intriguing Building Block with Versatility in Coordination Structures and Redox Properties

Yu-Rong Qin,[†] Qin-Yu Zhu,*[,†,‡] Li-Bin Huo,[†] Zheng Shi,[†] Guo-Qing Bian,[†] and Jie Dai*[,†,‡]

[†] *Department of Chemistry & Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, P. R. China, and* [‡] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

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The synthesis of the transition metal coordination polymers containing a tetrathiafulvalene (TTF) moiety substituted with a tetracarboxylate group of the formulas $[Mn(L)_{0.5}(phen)(H_2O)_2]_n \cdot nH_2O$ (**1**), $[Mn(L)_{0.5}(bpy)]_n \cdot nH_2O$ (**2**), $[Mn(L)_{0.5}(bpy)(CH_3OH)]_n \cdot 2nH_2O$ (**3**), and $[Cu(L)_{0.5}(bpy)(DMF)]_n \cdot n(DMF)$ (**4**) (L^{4-} = TTF-tetracarboxylate; phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine) is reported. Complex **1** is a two-dimensional (2-D) coordination polymer constructed of infinite carboxylate bridged Mn(II) chains and TTF moiety linkages. Complex **2** possesses a 3-D polymeric structure formed by infinite $-Mn-(O-C-O)_2-Mn-$ bridged one-dimensional (1-D) chains, which are further coordinated by TTF-tetracarboxylate ligands of two different orientations. Both complexes **3** and **4** show 1-D extended chain structures but are constituted by different dinuclear metal(II) units with a $-Mn-(O-C-O)_2-Mn-$ bridge in **3** and a $-Cu-(O)_2-Cu-$ bridge in **4**. Electrochemical study of the solid-state compounds attests to the redox activity of the coordination system. Magnetic investigations reveal the existence of antiferromagnetic interactions between magnetic centers in complexes **3** and **4**, while in **1**, the paramagnetic metallic centers are isolated, in agreement with the solid-state structure.

Introduction

Metal coordination polymers have attracted significant attention in recent years not only due to their intriguing structural topologies but also because of their potential applications in a variety of areas.[1] As a kind of versatile ligand, carboxylate ligands have been widely used in the construction of coordination polymers with desired structures and properties.[2] Among the reported works of metal carboxylate polymers, various carboxylate ligands have been used, for example, rigid polycarboxylate ligands, such as benzenepolycarboxylates and pyridinepolycarboxylates,[3] and flexible polycarboxylate ligands like cycloalkane−polycarboxylates and tetrahydrofurantetracarboxylates.[4] However, to the best of our knowledge, relatively few studies of the carboxylates with redox activity have been conducted.[5]

Tetrathiafulvalene (TTF) has been used as an excellent redox-active moiety for the construction of multifunctional materials because it can be oxidized to the corresponding

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*To whom correspondence should be addressed. E-mail: zhuqinyu@suda.edu.cn (Q.Y. Z.); daijie@suda.edu.cn (J. D.).

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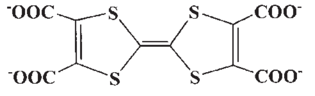
Scheme 1. Structure of the Ligand L^{4-}



radical cation and dication species sequentially by organic or inorganic oxidizing reagents[6] or through electrochemical techniques.[7] Functionalization of the TTF fragment bearing a coordination group is efficient because of its ability to coordinate to transition metal ions and to offer a novel perspective on the modulation of architecture and multifunctional molecular materials. Although a large number of coordination complexes involving redox-active TTF ligands have been prepared and characterized,[8-10] only a few mono- or dinuclear coordination compounds of TTF-carboxylate have been reported.[11] The Beer group studied the TTF-tetracarboxylate compound (Scheme 1) in 1998 and reported excitedly a hydrogen-bond-assembled clathrate compound, $[Co^{II}(H_2O)_6]H_2(TC\text{-}TTF)\cdot 2H_2O$ (**A**, hexaaquacobalt(II) 1,3-dihydrogen-tetra(carboxy)tetrathiafulvalene dihydrate).[12] Heating **A** obtained a proposed polymeric compound $[Co(H_2O)_2H_2(TC\text{-}TTF)]$, in which the carboxyl groups of the anion were thought to coordinate directly to the cobalt atom, but which was not characterized crystallographically. Unbelievably, since then, after more than a decade, no progress has been made in the coordination chemistry of the TTF-tetracarboxylate compound, though it has been well-known that the introduction of a redox-active TTF moiety into the coordination framework might lead to interesting structures and properties of the final product.

Recently, we successfully isolated metal organic frameworks of paramagnetic Mn(II) and Cu(II) with building block of TTF-tetracarboxylate. Three different structural Mn(II) coordination polymers and one Cu(II) coordination polymer, formulated as $[Mn(L)_{0.5}(phen)(H_2O)_2]_n\cdot nH_2O$ (**1**), $[Mn(L)_{0.5}(bpy)]_n\cdot nH_2O$ (**2**), $[Mn(L)_{0.5}(bpy)(CH_3OH)]_n\cdot 2nH_2O$ (**3**), and $[Cu(L)_{0.5}(bpy)(DMF)]_n\cdot n(DMF)$ (**4**), are reported herein. All four compounds have been characterized by single-crystal X-ray diffraction. Their electrochemical and magnetic properties are also investigated.

Experimental Section

General Remarks. The precursor, tetrathiafulvalene−tetracarboxylic ester, was prepared according to a reported method.[13] The compound, tetrathiafulvalene−tetracarboxylate sodium salt (Na_4L), was obtained by hydrolization of tetrathiafulvalene−tetracarboxylic ester in a NaOH aqueous solution. Standard deionized water was used for syntheses of the complexes. HPLC grade solvents (Alfa Aesar) and doubly distilled water were used for measurements of electrochemistry and spectra. All other reagents or solvents for syntheses and analyses were of analytical grade and used as received. The IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. Electronic absorption spectra were measured on a Shimadzu UV-3150 spectrometer. Thermal analysis was conducted on a SDT 2960 TGA-DCS microanalyzer. The samples were heated under a nitrogen stream of 100 mL/min with a heating rate of 20 °C/min. Cyclic voltammetry (CV) of the solid-state compounds was investigated on a CHI600 electrochemistry workstation in a three-electrode system, using a surface-modified Pt-plate working electrode,[14] a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference. As a typical technique for the surface-modified electrode, a slurry was prepared using a well-powdered solid-state sample dropped with some acetonitrile, and then the slurry was layed uniformly on the electrode. The surface-modified working electrode was obtained after evaporation of the solvent. The temperature dependence of the magnetic susceptibility of a powdered sample was measured by a Quantum Design SQUID magnetometer on the MPMS-7 system.

Preparation of Complexes. ***CAUTION!*** *All metal perchlorates must be regarded as potentially explosive. Only a small amount of compound should be prepared, and it should be handled with caution.*

$[Mn(L)_{0.5}(phen)(H_2O)_2]_n\cdot nH_2O$ (1). To a solution of $Mn(ClO_4)_2\cdot 6H_2O$ (7.2 mg, 0.02 mmol) or $MnCl_2\cdot 4H_2O$ (4.0 mg, 0.02 mmol) in methanol (2 mL) was added a solution of phen (4.0 mg, 0.02 mmol) in methanol (2 mL). Then, the mixture was added to an aqueous solution (2 mL) of Na_4L (9.4 mg, 0.02 mmol). The final mixed solution was stirred for 30 min at room temperature and filtered into a glass tube; then red needle single crystals of **1** were obtained for 10 days from the filtrate by controlled evaporation of the solvent and were used for all measurements (4.1 mg, yield: 43.2%). Anal. Calcd. for $C_{17}H_{14}MnN_2O_7S_2$: C, 42.77; H, 2.96; N, 5.87%. Found: C, 42.56; H, 2.89; N, 5.78%. IR data (cm^{-1}): 3435(m), 1662(m), 1608(s), 1516(w), 1424(w), 1356(m), 1097(m), 850(m), 725(m).

$[Mn(L)_{0.5}(bpy)]_n\cdot nH_2O$ (2). Complex **2** was obtained by following a similar procedure to that of **1**, but bpy (3.1 mg, 0.02 mmol) was used instead of phen. Single crystals of **2** as dark red rods appeared for 5 days by slow evaporation at room

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Table 1. Crystal Data and Structural Refinement Parameters for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{17}H_{14}MnN_2O_7S_2$	$C_{15}H_{10}MnN_2O_5S_2$	$C_{16}H_{16}MnN_2O_7S_2$	$C_{21}H_{22}CuN_4O_6S_2$
fw	477.36	417.29	467.37	554.09
cryst size (mm^3)	0.10 × 0.10 × 0.30	0.05 × 0.12 × 0.20	0.15 × 0.17 × 0.20	0.15 × 0.18 × 0.20
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.8823(11)	24.472(4)	7.6041(5)	10.2150(3)
b (Å)	21.903(3)	10.4173(14)	11.2211(8)	10.4799(4)
c (Å)	10.1255(13)	16.127(3)	12.2046(5)	12.6602(4)
α (deg)	90.00	90.00	70.409(7)	71.072(10)
β (deg)	109.547(3)	125.049(3)	73.137(8)	68.047(10)
γ (deg)	90.00	90.00	80.350(9)	69.032(10)
V (Å^3)	1856.3(4)	3365.8(9)	936.04(10)	1145.01(12)
Z	4	8	2	2
ρ_{calcd} (g cm^{-3})	1.708	1.576	1.658	1.607
$F(000)$	972	1608	478	570
μ (mm^{-1})	0.981	1.053	0.971	1.183
T (K)	223(2)	223(2)	223(2)	223(2)
reflns collected	10641	6630	4037	4961
unique reflns	4206	2948	4194	5156
observed reflns	3023	2155	3189	3852
no. params	288	210	249	308
GOF on F^2	1.079	1.090	1.065	1.024
R_1 [I > 2σ(I)]	0.0527	0.0685	0.0647	0.0504
wR_2 [I > 2σ(I)]	0.1135	0.1300	0.1627	0.1248

temperature and were used for all measurements (yield: 1.7 mg, 20.4%). Anal. Calcd. for $C_{15}H_{10}MnN_2O_5S_2$: C, 43.17; H, 2.42; N, 6.71%. Found: C, 43.09; H, 2.38; N, 6.73%. IR (cm^{-1}): 3430(m), 1644(m), 1626(s), 1590(s), 1549(m), 1474(w), 1439(m), 1354(s), 1017(m), 761(m), 736(m).

[Mn(L)$_{0.5}$(bpy)(CH$_3$OH)]$_n$·2nH$_2$O (3). An aqueous solution (2 mL) of Na$_4$L (9.4 mg, 0.02 mmol) was placed into the underlayer of a glass tube. A mixed solution of Mn(ClO$_4$)$_2$·6H$_2$O (7.2 mg, 0.02 mmol) or MnCl$_2$·4H$_2$O (4.0 mg, 0.02 mmol) in methanol (2 mL) and bpy (3.1 mg, 0.02 mmol) in methanol (2 mL) was carefully put into the superstratum dropwise. The dark red block single crystals of **3** were obtained for 5 days by slow diffusion at room temperature and were used for all measurements (yield: 4.6 mg, 48.7%). Anal. Calcd. for $C_{16}H_{16}MnN_2O_7S_2$: C, 41.12; H, 3.45; N, 5.99%. Found: C, 41.04; H, 3.39; N, 5.90%. IR (cm^{-1}): 3427(m), 1662(s), 1590(s), 1552(m), 1473(w), 1440(m), 1353(m), 1087(w), 1018(m), 767(m), 737(w).

[Cu(L)$_{0.5}$(bpy)(DMF)]$_n$·n(DMF) (4). Complex **4** was prepared in the same way as **3**. An aqueous solution (2 mL) of Na$_4$L (9.4 mg, 0.02 mmol) was placed into the underlayer of a glass tube. A mixed solution of Cu(ClO$_4$)$_2$·6H$_2$O (7.4 mg, 0.02 mmol) or CuCl$_2$ (2.7 mg, 0.02 mmol) in DMF (2 mL) and bpy (3.1 mg, 0.02 mmol) in DMF (2 mL) was carefully put into the superstratum dropwise. The yellow-green block single crystals of **4** were obtained for 15 days by slow diffusion at room temperature and were used for all measurements (yield: 2.7 mg, 24.5%). Anal. Calcd. for $C_{21}H_{22}CuN_4O_6S_2$: C, 45.52; H, 4.00; N, 10.11%. Found: C, 45.47; H, 3.87; N, 10.02%. IR (cm^{-1}): 3436(s), 2924(w), 1659(m), 1622(s), 1610(s), 1576(m), 1473(w), 1439(m), 1354(s), 1088(w), 1017(w), 761(m), 737(w).

X-Ray Crystallographic Study. The measurement was carried out on a Rigaku Mercury CCD diffractometer at a low temperature with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. X-ray crystallographic data for all compounds were collected and processed using CrystalClear (Rigaku).[15] The structure was solved by direct methods using SHELXS-97,[16] and the refinement against all reflections of the compound was performed using SHELXL-97.[17] All of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added theoretically, except that the H atoms of O−H were located from the map. Relevant crystal data, collection parameters, and refinement results can be found in Table 1. Selected bond lengths and bond angles for complexes **1**−**4** are listed in Table 2.

Result and Discussion

Synthesis. Generally, many factors can affect the structures of the final products, such as counteranions,[18] the pH values of the reaction solutions,[19] the temperature,[20] the molar ratio between reactants,[21] and the solvent system.[22] In our experiment, all four compounds were prepared by mixing an aqueous solution of Na$_4$L with a solution of metal salts in organic solvents under ambient conditions. We found that powdered precipitates were obtained if ancillary ligands were not added. The reactions of Mn(ClO$_4$)$_2$·6H$_2$O with Na$_4$L under the same conditions yielded two different structural coordination polymers if different ancillary ligands were added, phen or bpy. Adding

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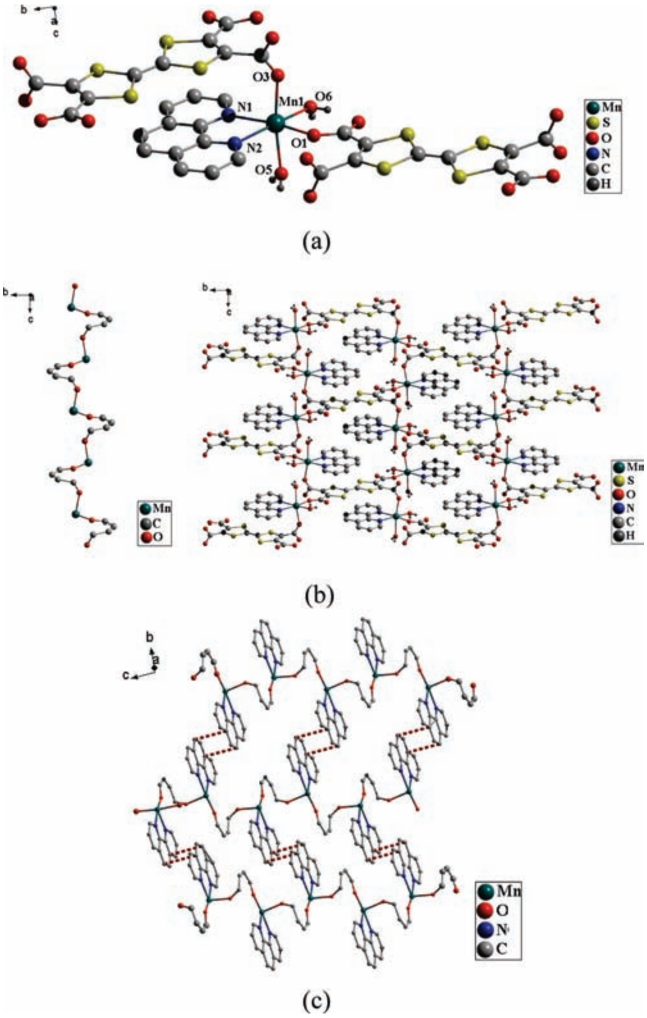
Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**−**4**[a]

	1		
Mn1−O1	2.122(2)	Mn1−O6	2.239(2)
Mn1−O3#1	2.145(2)	Mn1−N1	2.270(3)
Mn1−O5	2.208(3)	Mn1−N2	2.247(3)
O1−Mn1−O3#1	85.08(9)	N2−Mn1−O5	86.01(11)
O1−Mn1−O5	86.26(11)	N2−Mn1−O6	168.53(10)
O5−Mn1−O3#1	170.91(10)	N1−Mn1−O1	169.18(9)
O1−Mn1−O6	93.65(8)	N1−Mn1−O3#1	96.95(9)
O6−Mn1−O3#1	90.37(9)	N1−Mn1−O5	92.08(11)
O5−Mn1−O6	87.43(10)	N1−Mn1−O6	96.95(9)
N2−Mn1−O1	95.30(9)	N1−Mn1−N2	73.92(9)
N2−Mn1−O3#1	97.53(9)		
	2		
Mn1−O1	2.138(4)	Mn1−O4#3	2.131(4)
Mn1−O2#2	2.165(4)	Mn1−N1	2.281(6)
Mn1−O3	2.175(4)	Mn1−N2	2.250(6)
O1−Mn1−O4#3	88.25(16)	N2−Mn1−O2#2	94.15(19)
O2#2−Mn1−O4#3	89.37(16)	N2−Mn1−O3	88.20(19)
O1−Mn1−O2#2	95.73(15)	N1−Mn1−O4#3	168.59(19)
O3−Mn1−O4#3	97.01(15)	N1−Mn1−O1	101.94(19)
O1−Mn1−O3	81.43(15)	N1−Mn1−O2#2	94.64(18)
O3−Mn1−O2#2	172.91(16)	N1−Mn1−O3	79.67(18)
N2−Mn1−O4#3	96.7(2)	N1−Mn1−N2	72.4(2)
N2−Mn1−O1	169.0(2)		
	3		
Mn1−O1	2.128(3)	Mn1−O5	2.182(4)
Mn1−O2#4	2.177(3)	Mn1−N1	2.247(4)
Mn1−O3	2.165(3)	Mn1−N2	2.240(4)
O1−Mn1−O3	84.96(12)	O2#4−Mn1−N2	82.44(14)
O1−Mn1−O2#4	94.59(12)	O5−Mn1−N2	163.12(15)
O3−Mn1−O2#4	177.24(12)	O1−Mn1−N1	160.33(15)
O1−Mn1−O5	103.46(14)	O3−Mn1−N1	88.11(13)
O3−Mn1−O5	90.72(13)	O2#4−Mn1−N1	93.17(13)
O2#4−Mn1−O5	86.74(13)	O5−Mn1−N1	95.00(16)
O1−Mn1−N2	90.33(15)	N1−Mn1−N2	72.81(17)
O3−Mn1−N2	100.27(14)		
	4		
Cu1−O1	1.941(2)	Cu1−N1	1.999(3)
Cu1−O3	1.962(2)	Cu1−N2	2.015(3)
Cu1−O5	2.356(3)	N1−Cu1−N2	80.75(10)
O1−Cu1−O3	92.67(9)	O1−Cu1−O5	91.86(9)
O1−Cu1−N1	173.79(9)	O3−Cu1−O5	104.37(9)
O3−Cu1−N1	92.33(10)	N1−Cu1−O5	90.48(10)
O1−Cu1−N2	93.66(10)	N2−Cu1−O5	86.16(10)
O3−Cu1−N2	167.53(10)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-0.5 + x, 0.5 - y, -0.5 + z$; (#2) $1 - x, 1 - y, 1 - z$; (#3) $1 - x, y, 1.5 - z$; (#4) $-x, 1 - y, -z$.

phen as the starting material resulted in a 2-D structure of **1**. The use of bpy as a replacement for phen generates a 3-D coordination polymer of **2**. Also, the methods of crystal growth affect the final structures of coordination polymers. In comparison with the 3-D structure of **2**, the 1-D structure of **3** was obtained with slow diffusion, while **2** was obtained with slow evaporation. By using $MCl_2 \cdot 4H_2O$ to replace $M(ClO_4)_2 \cdot 6H_2O$ (M = Mn, Cu) as the starting material under the same reaction conditions, the same crystal structures of **1**−**4** were obtained. All of the compounds are insoluble, even in DMF solvent.

Description of Crystal Structures. Complex $[Mn(L)_{0.5}(phen)(H_2O)_2]_n \cdot nH_2O$ (1). Single-crystal X-ray structural analysis shows that complex **1** is a two-dimensional (2-D) coordination polymer crystallized in the monoclinic $P2_1/n$ space group, and the asymmetric unit consists of one manganese atom, a half ligand L^{4-}, one chelating phen, two coordinated water molecules, and one cocrystallized water molecule. The Mn(II) ion is six-coordinated by a chelating phen, two water oxygen atoms, and two carboxylate oxygen atoms from two different L^{4-} ligands, thereby forming a slightly distorted octahedral coordination geometry. The structure is depicted in Figure 1a. The bond distances between the metal ions and the coordinated water molecules are slightly longer [average 2.224(3) Å] than those related to the oxygen atoms of the carboxylate groups [average 2.134(2) Å], and the Mn−N bond lengths are 2.247(3) and 2.270(3) Å, which are consistent with the reported manganese(II) complexes of similar coordination environments.[23]



(a)

(b)

(c)

Figure 1. (a) Coordination environment of Mn(II) in **1**. (b) Left: The infinite −Mn−O−C−C−C−C−O−Mn− chain. Right: The 2-D network constructed by the chains and L^{4-} ligands. In a and b, the uncoordinated water molecules and hydrogen atoms except those of coordinated water molecules were omitted for clarity. (c) The $\pi \cdots \pi$ stacking in **1**, only phen molecules and the atoms consisting of the −Mn−O−C−C−C−C−O−Mn− chains are denoted.

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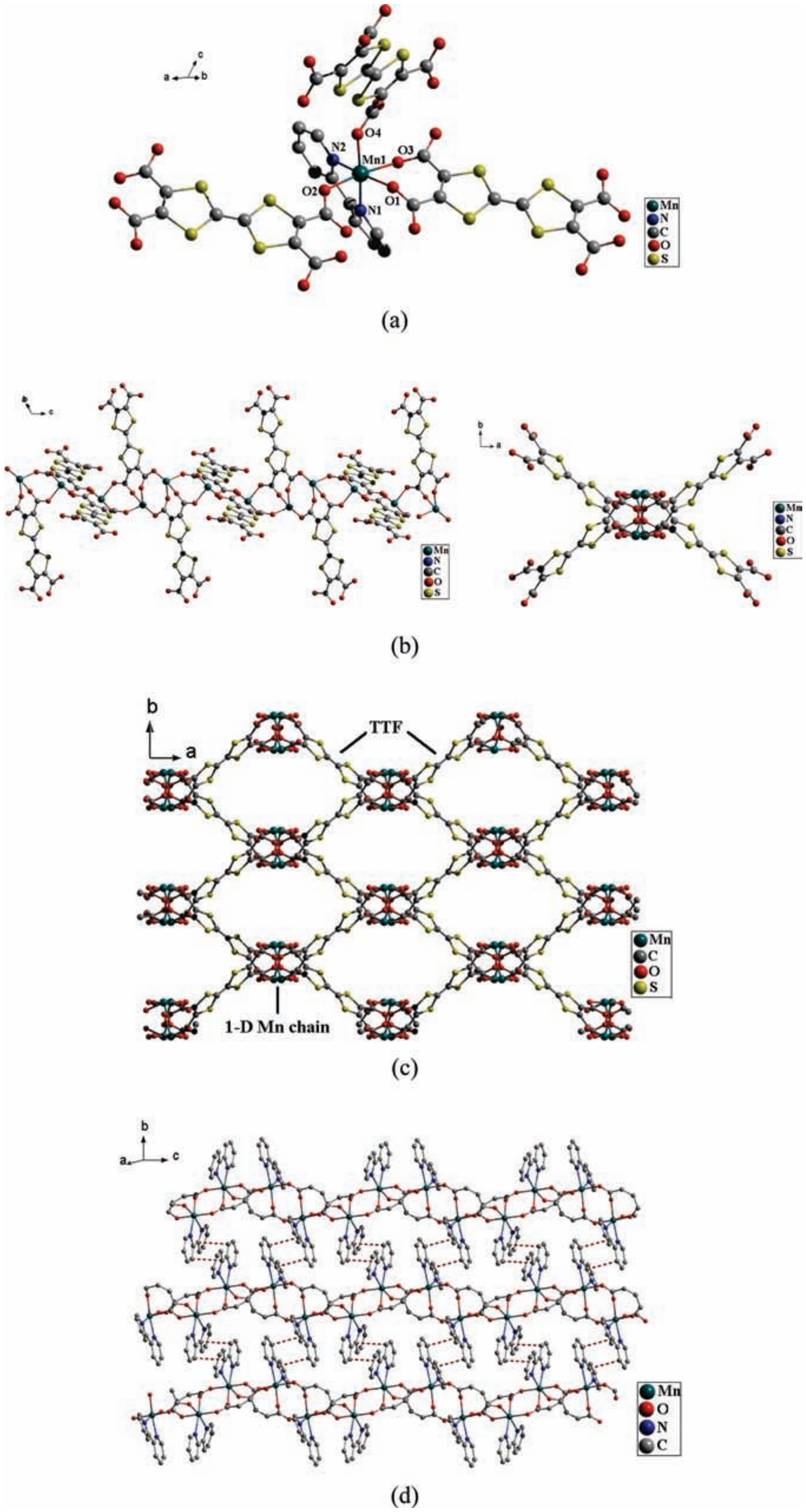
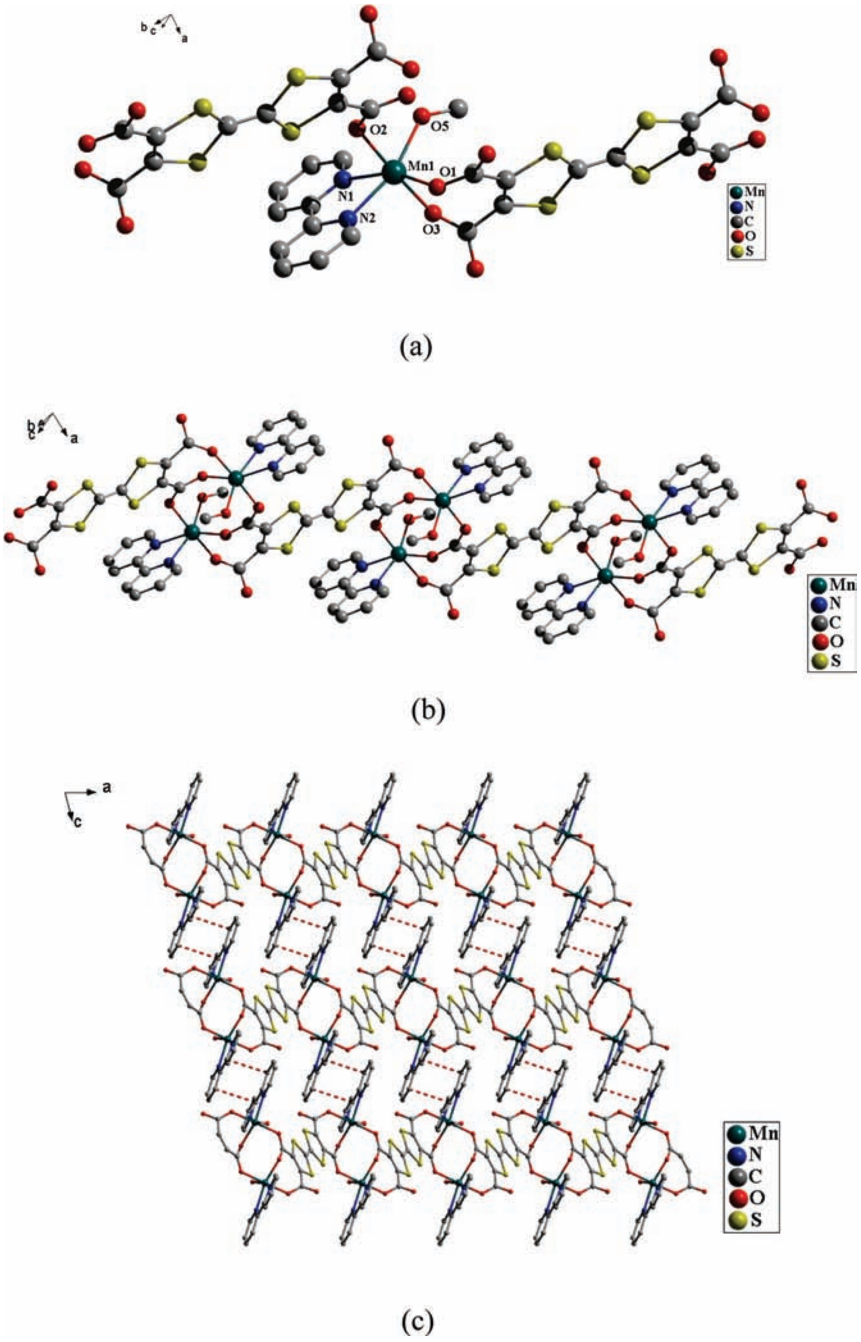


Figure 2. (a) Coordination environment of Mn(II) in **2**. The uncoordinated water molecules and hydrogen atoms were omitted for clarity. (b) Left: Infinite −Mn−(O−C−O)$_2$−Mn− bridged chain showing the different orientation of the TTF moieties. Right: The chain viewed along the *c* axis. (c) The 3-D network constructed by L^{4-} ligands. The bpy molecules were omitted for clarity in b and c. (d) The $\pi\cdots\pi$ interactions among the 3-D structure. Only bpy molecules and the atoms consisting of the infinite chains were denoted.

The Mn(II) atoms in **1** are linked together by carboxylate bridges to form an infinite O−Mn−O−C−C−C−C−O−Mn− one-dimensional (1-D) chain with a Mn−Mn(#1) (#1 = $-0.5 + x$, $0.5 - y$, $-0.5 + z$) distance of 5.65 Å



(a)

(b)

(c)

Figure 3. (a) Coordination environment of Mn(II) in **3**. (b) The infinite chain constructed by −Mn−(O−C−O)$_2$−Mn− and TTF moieties. (c) The $\pi\cdots\pi$ interactions link the chains to generate a 2-D structure. Hydrogen atoms and uncoordinated water molecules were omitted for clarity in a, b, and c.

(Figure 1b, left). The chelating phen ligands attached to the chain alternately on opposite sides. The 2-D network structure of **1** is achieved by bridging adjacent 1-D chains with the coordination of carboxylate groups on two sides of the TTF moiety (Figure 1b, right). On the other hand, the phen ligands from neighboring 2-D networks are arranged in a face-to-face pairwise fashion to facilitate relatively strong $\pi\cdots\pi$ stacking interactions (3.33 Å), which link the 2-D networks into a three-dimensional (3-D) supramolecular structure. Figure 1c only shows the 2-D linkage (carboxylate bridge and $\pi\cdots\pi$ stacking), and the TTF linkages are omitted for clarity.

Complex [Mn(L)$_{0.5}$(bpy)]$_n$·nH$_2$O (2). The use of bpy as a replacement for phen generates a 3-D coordination polymer **2**. Polymer **2** is crystallized in the monoclinic $C2/c$ space group. It includes one manganese atom, a half ligand L^{4-}, one chelating bpy, and one cocrystallized water molecule in the asymmetric unit. The manganese(II) atom is surrounded by two nitrogen atoms from chelating bpy and four oxygen atoms from three different L^{4-} ligands in a somewhat distorted octahedral environment (Figure 2a). The Mn−O bond lengths are in the range of 2.131(4)−2.175(4) Å, and the Mn−N bond lengths are somewhat longer, ranging from 2.250(6) to 2.281(6) Å.

The Mn(II) atoms in **2** are linked together by carboxylate bridges to form an infinite −Mn−(O−C−O)$_2$−Mn− 1-D chain (Figure 2b). Each chain links four adjacent

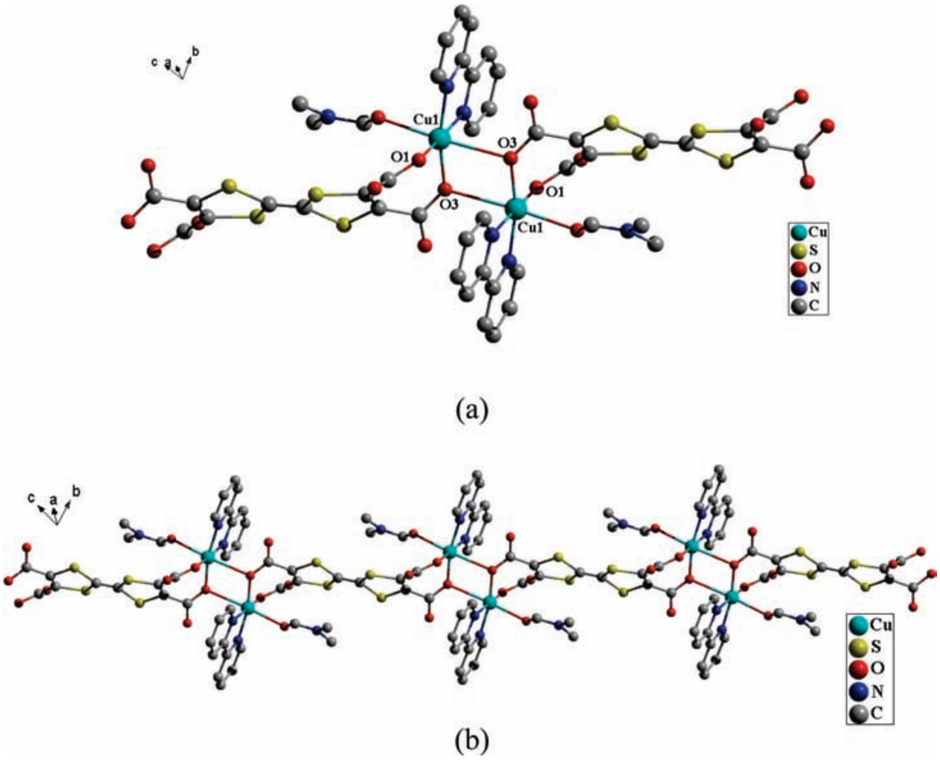


Figure 4. (a) Coordination environment of Cu(II) in **4** with a $-\mathrm{Cu}-(\mathrm{O})_2-\mathrm{Cu}-$ unit. (b) The infinite chain constructed by L^{4-} ligands. Hydrogen atoms and uncoordinated DMF molecules were omitted for clarity in a and b.

chains of two different orientations, $\{1, 1, 0\}$ and $\{1, -1, 0\}$, by means of the coordination of carboxylate groups on two sides of the TTF moieties, and then 3-D coordination polymer of **2** is formed (Figure 2c). The $\pi\cdots\pi$ interactions between the bpy molecules from neighboring chains further steady the 3-D structure (Figure 2d).

Complex $[\mathrm{Mn(L)_{0.5}(bpy)(CH_3OH)}]_n\cdot 2n\mathrm{H_2O}$ (3). The structure of **3** is composed of 1-D coordination chains with dinuclear manganese(II) units crystallized in the triclinic $P\bar{1}$ space group, and the asymmetric unit consists of one manganese atom, a half ligand L^{4-}, one chelating bpy, one coordinated methanol molecule, and two cocrystallized water molecules. The Mn(II) ion exhibits a distorted octahedral coordination geometry completed by two nitrogen atoms from chelating bpy, one oxygen atom from solvent methanol, and three oxygen atoms from two different L^{4-} ligands (Figure 3a). The bond distance between the metal ion and the coordinated methanol molecule is slightly longer [2.182(4) Å] than those related to the oxygen atoms of the carboxylate groups [mean values of 2.157(3) Å]. The Mn−O bond distances range from 2.128(3) to 2.182(4) Å, and the Mn−N bond distances are 2.240(4) and 2.247(4) Å, respectively.

Two crystallographically equivalent Mn(II) atoms in **3** are linked together by carboxylate into a dinuclear unit $(-\mathrm{Mn}-(\mathrm{O}-\mathrm{C}-\mathrm{O})_2-\mathrm{Mn}-)$ with a Mn−Mn(#5) (#5 = $-x, 1-y, -z$) distance of 4.75 Å. The dimers are further joined to each other by carboxylate groups on two sides of the TTF moieties into an infinite one-dimensional (1-D) coordination chain (Figure 3b), and such 1-D chains are linked by $\pi\cdots\pi$ interactions between the bpy molecules to generate a 2-D supramolecular network structure (Figure 3c).

Complex $[\mathrm{Cu(L)_{0.5}(bpy)(DMF)}]_n\cdot n\mathrm{(DMF)}$ (4). Complex **4** also has a 1-D extended chain structure with dinuclear copper(II) units crystallized in the triclinic $P\bar{1}$ space group, and the asymmetric unit consists of one copper atom, a half ligand L^{4-}, one chelating bpy, one coordinated DMF molecule, and one cocrystallized DMF molecule. The coordination environment around the Cu(II) ion in **4** is similar to that in **3** except that the coordinated DMF molecule replaces the methanol (Figure 4a).

Two crystallographically equivalent Cu(II) atoms in **4** are linked together by the O3 atom (different from the bridge in **3**) of the carboxylate group to a dinuclear unit $(-\mathrm{Cu}-(\mathrm{O})_2-\mathrm{Cu}-)$ with a Cu−Cu(#6) (#6 = $2-x, 1-y, 1-z$) distance of 3.62 Å, a value which is much shorter than those in the above three complexes. The dimers are further joined by carboxylate groups on two sides of the TTF moieties into an infinite one-dimensional (1-D) coordination chain (Figure 4b).

Coordination Modes of the Tetrathiafulvalene−Tetracarboxylate Ligand. The results of the present study show that there are a variety of coordination modes for the ligand L^{4-} that can be seen clearly in Scheme 2. In summary, each L^{4-} in **1**, **3**, and **4** coordinates with four metal atoms, but the coordination mode is dissimilar. The ligand L^{4-} exhibits tetra-monodentate binding in **1** and **4** and has a μ_2-η^2:η^0 bridging mode in **4**, while in **3**, there are two types of carboxyl groups: one acts as a μ_2-η^1:η^1 coordination mode, and the other serves as a monodentate. In **2**, each L^{4-} also has a syn−syn μ_2-η^1:η^1 coordination mode but links six metal atoms that are different from those in **1**, **3**, and **4**. The differences in the coordination modes of the ligand L^{4-} directly lead to the different coordination polymers as described above. The C−O bonds with μ_2-η^1:η^1 carboxylate bridges are in a resonance

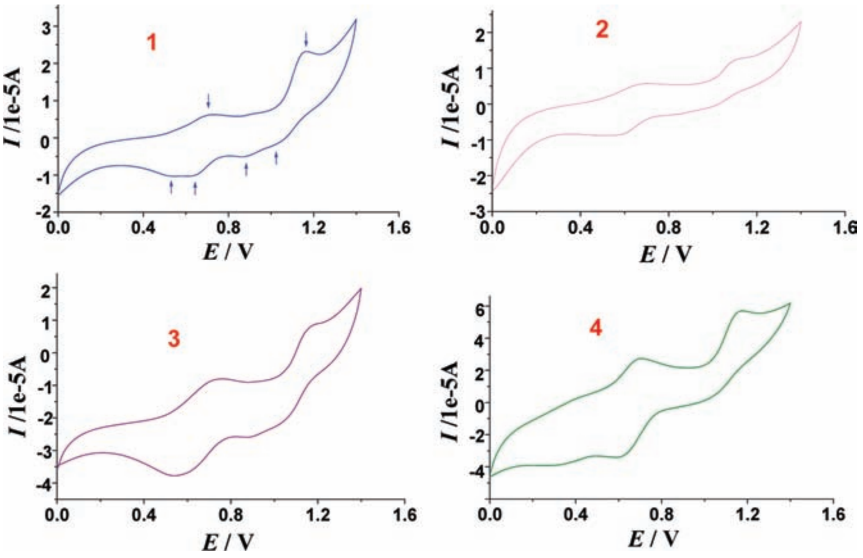
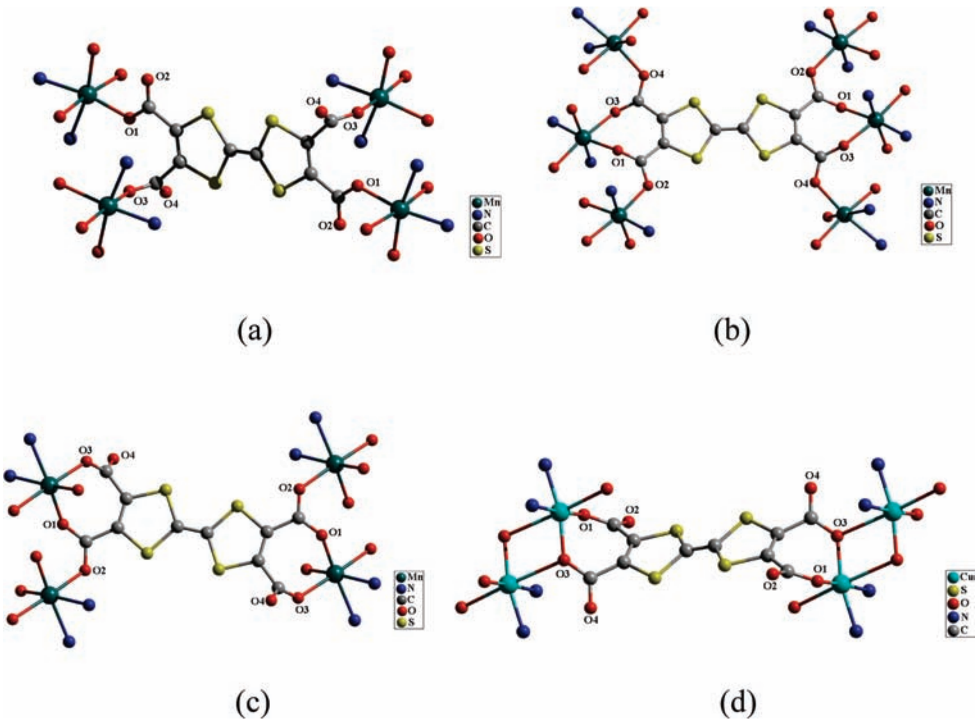


Figure 5. Solid-state cyclic voltammogram of complexes **1**−**4** (CH_3CN, 0.1 mol·L^{-1} Bu_4NClO_4, 100 mV s^{-1}).

Scheme 2. Coordination Modes of the Ligand L^{4-} in Complexes **1**−**4**



(a)

(b)

(c)

(d)

state, while the C−O's with those noncoordinated oxygen atoms are carbonyl groups (C=O). It is impossible to predict the coordination mode of the carboxyl group or rationalize the formation of the structure, because the results of the assembly are not only dependent upon many factors such as the subtle interplay between the metal ion and the ligand or the solvent system but also influenced by synthetic conditions such as temperatures and molar ratios. However, it is doubtless that the tetrathiafulvalene−tetracarboxylate ligand L^{4-} is an intriguing building block for coordination polymers with a versatility in structure.

Electrochemical Properties. As mentioned above, the TTF moiety can be oxidized to its radical cation ($TTF^{+\bullet}$) and dication (TTF^{2+}) sequentially and reversibly at low potentials. A large number of coordination complexes involving TTF redox active ligands have been electrochemically characterized, but little is known about the redox properties of the coordination polymers with TTF ligands for their insolubility. Surface modified electrodes of **1**−**4** were used to study their redox properties in the solid state by cyclic voltammetry (CV), and the result obtained is shown in Figure 5. The CV curves of the modified electrodes are similar to those of the solution, because the electrochemical reaction occurs at the solid/liquid interface (liquid phase: acetonitrile with 0.10 mol·L^{-1} tetrabutylamonium perchloride).

The ligand Na_4L exhibits two one-electron redox couples (Supporting Information, SI-Figure 2), the first one at 0.45 V and the second one at 0.82 V. Compared with the ligand, the redox waves for complexes **1**−**4** are

Table 3. Cyclic Voltammetry Data (/V) for Compounds Na_4L and **1**−**4**

compound	E_{ox}^{1}	E_{re}^{1}	E_{ox}^{2}	E_{re}^{2}
Na_4L	0.478	0.424	0.833	0.798
1	0.722 (broad)	0.544, 0.625	1.166	0.877, 1.001
2	0.689 (broad)	0.563 (broad)	1.119	0.848, 0.997
3	0.747 (broad)	0.546 (broad)	1.183	0.883, 1.013
4	0.701	0.596	1.173	1.003

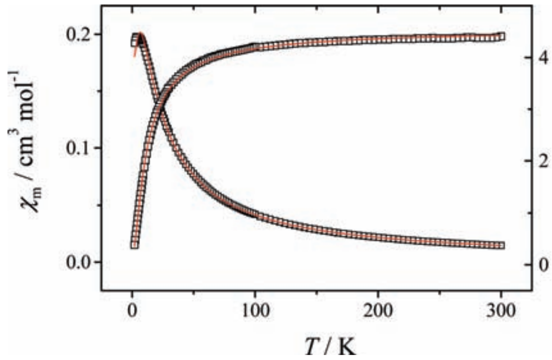


Figure 6. Experimental χ_m versus T and $\chi_m T$ versus T curves for complex **3**. The red lines were plotted according to the best fitting parameters given in the text.

ligand-centered as expected, and the redox potentials after complexation of carboxylate groups with M^{2+} are shifted to higher potentials (Table 3). This result of the inductive effect has been seen by multiple groups who have prepared coordination compounds with TTF-based ligands.[8,9a] With **1** as a representative, splitting of the redox waves (especially the reductive waves) can be observed. There are two possible reasons for the phenomenon: one might be because of the presence of a metastable mixed oxidized state, involving $TTF/TTF^{+\cdot}$ interaction,[24] and the other might be due to the surface effect. However, these explanations need to be further studied. This electrochemical study confirms the redox activity of the polymeric system. Repetitive scans show no decomposition or further evolution that confirms the stability of the metal complexes bearing radical cation ligands.

Magnetic Properties. The temperature dependence of χ_m and $\chi_m T$ of compound **3** (Figure 6) can be interpreted in terms of the dipolar coupling approach for a Mn(II) dimer. Below 30 K, the value of $\chi_m T$ drops down sharply, reaching 0.35 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K, which can be attributed to the weak antiferromagnetic interaction of the manganese(II) dimer. The expression for the magnetic susceptibility of the manganese(II) dimer was derived from Van Vleck's eq 1[25] based on the spin Hamiltonian $H = -JS_1S_2$. The dimer model reproduces quite satisfactorily the magnetic behavior of **3** in the whole temperature range with the following parameters $J = -0.80\ cm^{-1}$, $g = 1.99$, and $R = 1.0 \times 10^{-5}$. This result indicates that the long distance magnetic interactions through the TTF ligand are negligible. Also for this reason, no significant magnetic interactions were found between the Mn(II) ions for compound **1**.

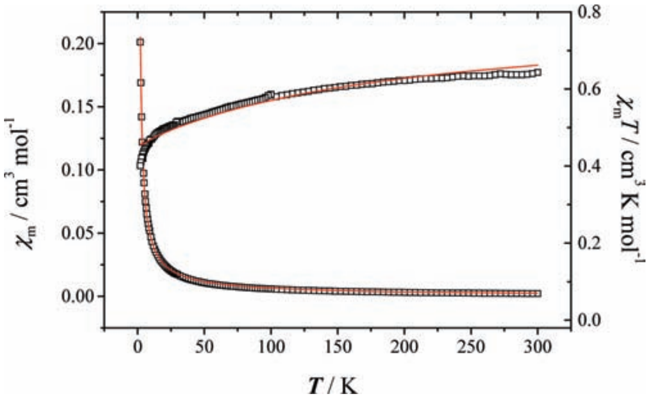


Figure 7. Experimental χ_m versus T and $\chi_m T$ versus T curves for complex **4**. The red lines were plotted according to the best fitting parameters given in the text.

$$\chi_m = \frac{2Ng^2\beta^2}{kT}\left(\frac{A}{B}\right) \qquad (1)$$

where $A = 55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)$ and $B = 11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$.

The temperature dependence of the magnetic susceptibility data in the form of χ_m versus T and $\chi_m T$ versus T plots for complex **4** are shown in Figure 7. The $\chi_m T$ value at 300 K is 0.65 $cm^3\ K\ mol^{-1}$, which is lower than the expected for two magnetically quasi-isolated spin doublets (0.75 $cm^3\ K\ mol^{-1}$). When the system is cooled down, the $\chi_m T$ value decreases, slowly reaching the value of 0.42 $cm^3\ K\ mol^{-1}$ at 2 K due to the partial depopulation of the $S = 1$ level in this exchange-coupled system. The profile of the curve indicates the presence of antiferromagnetic exchange interactions between the Cu(II) ions. The magnetic data were fitted to eq 2 given in the literature[26] for dinuclear copper cores with intercore interaction in which the parameter ρ denotes the fraction of the paramagnetic part and zJ' the interaction between neighboring dinuclear identities. The best fit parameters are $g = 2.06$, $J = -11.3$, $zJ' = -247.6$, $\rho = 0.52\%$, and $R = 6.96 \times 10^{-7}$. This result indicates that there are weak antiferromagnetic exchanges within the 1-D polymeric compound, carboxylate bridged interaction, and TTF bridged interaction.

$$\chi_m = \frac{2Ng^2\beta^2}{(kT - (2zj'/(3 + \exp(J/kT))))} \cdot \frac{(1-\rho)}{(1 + 3\exp(J/kT))} + \chi_p\rho \qquad (2)$$

Conclusion

In summary, four transition metal coordination polymers with the TTF-tetracarboxylate ligand have been successfully

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prepared for the first time. The structures of the compounds are distinct from one another. In compound **1**, the ligand exhibits tetra-monodentate binding to link Mn ions into a 2-D network structure. Compound **2** is a 3-D coordination polymer in which the ligand takes tetra-bidentate coordination modes. Compounds **3** and **4** are both 1-D coordination polymers but constituted by different dinuclear metal(II) units with double carboxylate bridges in **3** and double oxo bridges in **4**. The results indicate that the TTF-tetracarboxylate ligand is a useful and intriguing building block for the construction of metal organic polymers or frameworks. The redox-active properties of the new coordination polymeric system have been evidenced by electrochemical studies. The magnetic properties reveal the existence of antiferromagnetic interactions between magnetic centers. The coexistence of redox and magnetic properties in the polymeric solid state paves the way to multifunctional materials, a trend of much interest in contemporary TTF-based material science.

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Supporting Information Available: Crystallographic data of **1**−**4** in CIF format. Figures of CV of Na_4L, solid-state UV−vis spectra of **2** and **3**, and thermal analysis data of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.