Semiconducting Tellurium−Iron−Copper Carbonyl Polymers

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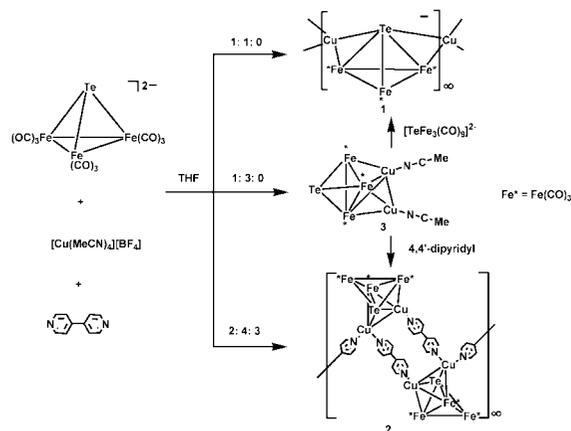
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The self-assembly approach to the construction of supramolecules or extended frameworks based on coordination complexes is currently a major research area[1] because of their potential application in semiconductors, photoluminescence materials, chemical sensors, and molecular magnets.[2,3] Self-assembled nanomaterials based on metal carbonyl complexes have been reported in the field of metal carbonyl chemistry.[4,5] However, molecular metal wires assembled by metal in zero or negative oxidation states with carbonyl groups as only ligands are rare.[5] To the best of our knowledge, the first structurally characterized example of metal-bridged metal carbonyl polymers was $[CuCo(CO)_4]_\infty$, which was derived from the self-assembly of $[Co(CO)_4]^-$ and Cu^+ ions.[5a] More recently, an interesting silver-bridged metal wire, $[\{AgRu_6C(CO)_{16}\}^-]_\infty$, has been reported from the reaction of $[Ru_6C(CO)_{16}]^{2-}$ with Ag^+ ions.[5b] An infinite ⋯Bi−Fe⋯ metal carbonyl chain has also been prepared in the Bi−Fe−CO system.[5c] Nevertheless, the physical properties of such metal-bridged metal carbonyl frameworks have remained unexplored. Therefore, the rational synthesis of metal- or metal-ligand-bridged metal carbonyl-based frameworks, with the opportunity to probe and evaluate the effect of bridges on their special properties, is an interesting challenge. In addition, ternary $CuFeE_2$ (E = S, Se) have long been known as semiconducting materials,[6] while the Te−Fe−Cu phase has never been prepared. However, to date, no polymeric Te−Fe carbonyl complexes of any type have been reported.[7,8] Herein, we wish to report the self-assembly, X-ray structure, and optical properties of two novel Cu- and Cu-dipyridyl-linked Te−Fe carbonyl cluster polymers, namely $[\{TeFe_3(CO)_9Cu\}^-]_\infty$ (1) and $[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_\infty$ (2), which represent the first examples of ternary semiconducting Te−Fe−Cu polymers with small energy gaps.

When $[Et_4N]_2[TeFe_3(CO)_9]$[8a−c] was treated with $[Cu(MeCN)_4][BF_4]$[9] in a 1:1 molar ratio in THF at 0 °C, a novel polymeric complex $[\{Et_4N\}\{TeFe_3(CO)_9Cu\}]_\infty$ ($[Et_4N]_\infty[1]$) was readily produced in 76% yield (Scheme 1). X-ray analysis reveals that the anionic polymer, $[\{TeFe_3(CO)_9Cu\}^-]_\infty$ (1) (Figure S1), consists of the $[TeFe_3(CO)_9]^{2-}$ units with two of the Te−Fe edges asymmetrically linked by two different Cu^+ ions to form a one-dimensional zigzag-like chain in which each Cu^+ ion resides on a crystallographic inversion center with a site-occupation factor of 0.5. The Cu^+ ion bridges the Te−Fe edge of $TeFe_3(CO)_9$, which is in contrast to those in the Fe−Fe edge-bridged complexes[8b,d] $[TeFe_3(CO)_9(\mu\text{-AuPPh}_3)]^-$ and $[TeFe_3(CO)_9(\mu\text{-CuCl})]^{2-}$. Alternatively, the anionic polymer 1 can be viewed as consisting of two cross-linked metal chains composed of the zigzag ⋯−Te−Cu−⋯ and ⋯−Fe−Fe−Cu−⋯ wires that intersect at the Cu centers (Figure 1a). Polymer 1 represents an unprecedented example of

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Scheme 1

double metal chains in the ternary Te−Fe−Cu system. Noteworthy in 1 is that the ⋯−Te−Cu−⋯ chain possesses alternating two long (2.8001(3) Å) and two short (2.6572(3) Å) Te−Cu bonds with a Cu−Te−Cu angle of 111.72(1)° while the ⋯−Fe−Fe−Cu−⋯ chain has alternating two short (2.4476(6) Å) and two long (2.4923(6) Å) Fe−Cu bonds that are spaced by an Fe−Fe bond (2.6556(9) Å) with Cu−Fe−Fe angles of 119.05(3)° and 99.81(3)°.

On the other hand, when $[Et_4N]_2[TeFe_3(CO)_9]$ was treated with $[Cu(MeCN)_4][BF_4]$ and 4,4′-dipyridyl in a molar ratio of 2:4:3 in THF, the 4,4′-dipyridyl-bridged $TeFe_3Cu_2$-based cluster polymer, $[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_\infty$ (2) (Figure S2), was obtained in 50% yield (Scheme 1). X-ray analysis shows that polymer 2 consists of the $TeFe_3(CO)_9Cu_2$ units alternately linked by single

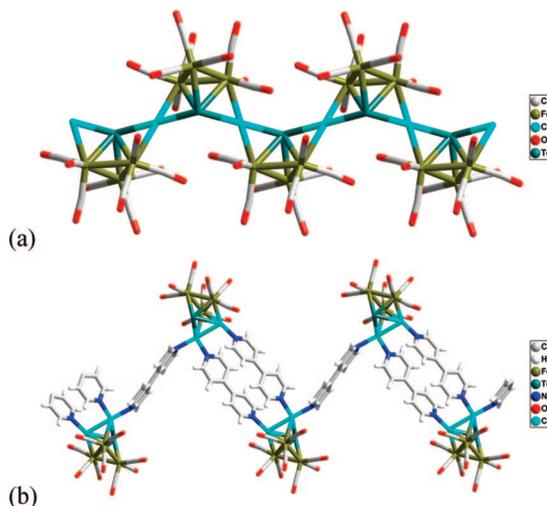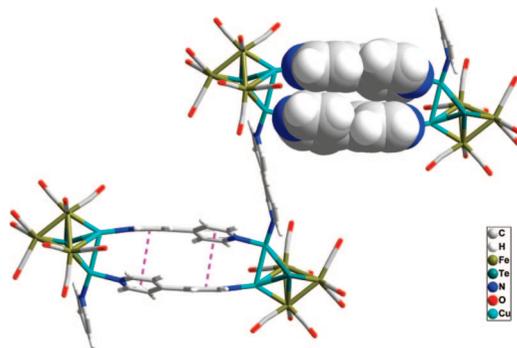**Figure 1.** Portion of the zigzag chains of polymers (a) 1 and (b) 2.

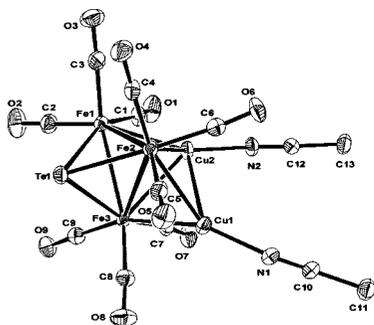**Figure 2.** Intramolecular $\pi-\pi$ interactions of polymer **2**.

Figure 3. ORTEP diagram of **3**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Te(1)−Fe(1) 2.485(1), Te(1)−Fe(2) 2.4831(9), Te(1)−Fe(3) 2.489(1), Fe(1)−Fe(2) 2.742(1), Fe(1)−Fe(3) 2.695(1), Fe(2)−Fe(3) 2.801(1), Cu(2)−Fe(1) 2.471(1), Cu(2)−Fe(2) 2.529(1), Cu(2)−Fe(3) 2.595(1), Cu(1)−Fe(2) 2.535(1), Cu(1)−Fe(3) 2.487(1), Cu(1)−Cu(2) 2.605(1), Cu(1)−N(1) 1.918(7), Cu(2)−N(2) 1.940(6), N(1)−C(10)−C(11) 179.4(8), N(2)−C(12)−C(13) 178.3(7).

and double 4,4′-dipyridyl ligands to form a one-dimensional zigzag-like framework (Figure 1b). The TeFe$_3$(CO)$_9$Cu$_2$ core unit of **2** can be seen to exhibit an Fe-capped TeFe$_2$Cu$_2$ trigonal bipyramidal geometry, in which the mono-4,4′-dipyridyl-coordinated Cu atom sits in the equatorial position, while the bis-4,4′-dipyridyl-coordinated Cu atom occupies the axial position. The two axial dipyridyl ligands are almost perpendicular to each other, while the dihedral angle between the nearly parallel axial and equatorial dipyridyl bridges is 20.4(4)° and the interplanar distance is 3.7127(2) Å, as calculated from the distance between the central atoms on the two pyridyl planes. This suggests the presence of weak intramolecular $\pi-\pi$ interactions (Figure 2). Although high-nuclearity carbonyl clusters linked by bidentate ligands have been reported, polymer **2** represents a rare example of an infinite ternary metal carbonyl cluster-based framework with the use of a N,N′-donating ligand as the linker.[10]

Furthermore, when [Et$_4$N]$_2$[TeFe$_3$(CO)$_9$] was treated with [Cu(MeCN)$_4$][BF$_4$] in a 1:3 molar ratio in THF at 0 °C, a neutral cluster TeFe$_3$(CO)$_9$Cu$_2$(MeCN)$_2$ (**3**) was produced. Cluster **3** consists of an TeFe$_3$(CO)$_9$ core which is further capped by a Cu$_2$(MeCN)$_2$ fragment with a Cu−Cu bond of 2.605(1) Å (Figure 3). It is noteworthy that neutral cluster **3** is a precursor complex for the rationalized construction of polymers **1** and **2** (Scheme 1). It was found that **3** could readily transform to **1** and **2** upon the addition of 1 equiv of [Et$_4$N]$_2$[TeFe$_3$(CO)$_9$] or 1.5 equiv of 4,4′-dipyridyl in THF, respectively. Polymer **1** can be seen as the result of the polymerization of a rearrangement product of the reduced **3** involving the Cu−Cu and Cu−Fe bond cleavage, which was substantiated by a controlled experiment wherein **3** could be reduced by 1 equiv of Na/benzophenone/THF to form polymer **1**. On the

other hand, polymer **2** can be considered to be a polymerized product of the acid−base adduct of **3** and 4,4′-dipyridyl, accompanied by Cu−Fe bond breakage and Te−Cu bond formation.

To understand the nature of the species in solutions, ESI-MS measurements of polymers **1** and **2** in MeCN were performed. ESI-MS of [Et$_4$N]$_\infty$[**1**] displays peaks corresponding to [TeFe$_3$(CO)$_9$Cu]$^-$ (613.1) and [{Et$_4$N}{TeFe$_3$(CO)$_9$Cu}$_2$]$^-$ (1353.0), and that of polymer **2** displays peaks corresponding to [TeFe$_3$(CO)$_9$Cu]$^-$ (612.9) and [{TeFe$_3$(CO)$_9$}$_2$Cu$_3$]$^-$ (1285.9), which is indicative of the degradation of polymers **1** and **2** in solutions. Therefore, the electronic spectra of [Et$_4$N]$_2$[TeFe$_3$(CO)$_9$] and polymers [Et$_4$N]$_\infty$[**1**] and **2** in the solid state were measured. In general, the spectra exhibit continuous and featureless absorptions between 240 and 1100 nm. Compared with the spectrum of [Et$_4$N]$_2$[TeFe$_3$(CO)$_9$], polymers [Et$_4$N]$_\infty$[**1**] and **2** have wider absorption ranges by extending the absorptions to the lower-energy region. To reduce the computation time, two units of polymer **1** ([TeFe$_3$(CO)$_9$Cu]$_2^{2-}$, **1a**) and two units of polymer **2** (H$_2$[{TeFe$_3$(CO)$_9$Cu$_2$}(μ-4,4′-dipyridyl)$_{1.5}$]$_2$, **2a**) were used to compute their respective singlet−singlet transitions to understand the absorption spectra (Figure S3). The calculations show that the absorption patterns of polymers [Et$_4$N]$_\infty$[**1**] and **2** also extend to a redder region compared to [Et$_4$N]$_2$[TeFe$_3$(CO)$_9$], in which the low-energy transitions of **1a** and **2a** are involved in the transitions contributed from the Cu and dipyridyl. This result suggests that the incorporation of Cu and dipyridyl into the TeFe$_3$ skeleton can contribute to the low-energy absorption of polymers [Et$_4$N]$_\infty$[**1**] and **2**, which can be used to account for the small energy gaps of these polymers obtained from the onset frequencies of the frequency-dependent conductivity addressed below.

To fully elucidate their electronic transitions, room-temperature optical reflectance was measured over the entire frequency range (no polarization dependence in the data was detected) of [Et$_4$N]$_\infty$[**1**] and **2** in solids (Figure S4a). Each spectrum displays a series of narrow structures associated with molecular vibrations at low frequencies. The real part of the conductivity $\sigma_1(\omega)$ of [Et$_4$N]$_\infty$[**1**] and **2** was calculated (Figure S4b). Overall, the two polymers exhibit a semiconducting character, with small residual conductivity (but no Drude-like response) in the far-infrared region. By extrapolating the frequency-dependent conductivity to zero frequency, the dc conductivities of polymers [Et$_4$N]$_\infty$[**1**] and **2** were estimated to be 2×10^{-2} and 5×10^{-2} Ω^{-1} cm^{-1}, respectively. The conductivity of [Et$_4$N]$_\infty$[**1**] and **2** is clearly seen to increase for frequencies above 4771 and 3298 cm^{-1}, respectively, and the onset frequencies roughly correspond to the energy gap ($E_g \approx 0.59$ and 0.41 eV).

Two to six units of polymers **1** and **2** were calculated to understand why they show surprising semiconducting properties. For **1** and **2**, when the chain lengths increase, the HOMO−LUMO energy gaps decrease. In addition, the density of states near the HOMO for these two polymers increases more than 3-fold when the numbers of chain units are increased from two to six. Both effects would be expected to enhance conductivity when units of **1** and **2** are polymerized. If the Et$_4$N$^+$ cations are taken into consideration, the HOMO−LUMO energy gaps of the two and four units of **1** would increase. This suggests that anion **1** can be further stabilized by the Et$_4$N$^+$ salts when [TeFe$_3$(CO)$_9$]$^{2-}$ units are polymerized by Cu$^+$ ions, which would result in a conductivity that is lower than expected from calculations. Moreover, for polymer **2**, the substitution of two nearly parallel 4,4′-dipyridyl ligands of **2a** with four NH$_3$ ligands, H$_2$[{TeFe$_3$(CO)$_9$Cu$_2$(NH$_3$)$_2$}(μ-4,4′-dipyridyl)$_{0.5}$]$_2$ (**2a′**), was calculated to understand the bridging effect of 4,4′-dipyridyl. Comparing **2a** with **2a′**, we found that when the two TeFe$_3$(CO)$_9$Cu$_2$ units were coordinated with four NH$_3$ ligands, the HOMO−LUMO energy gaps would significantly increase and

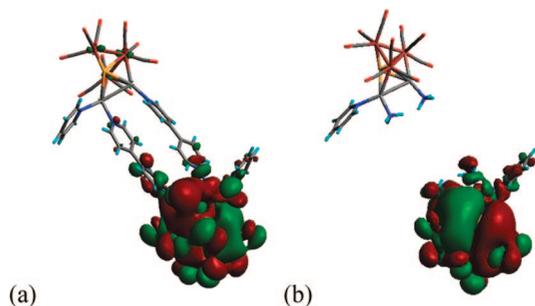**Figure 4.** Spatial plots of HOMO of (a) $H_2[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_2$ (**2a**) and (b) $H_2[\{TeFe_3(CO)_9Cu_2(NH_3)_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{0.5}]_2$ (**2a′**) (isovalue = 0.004).

the density of states near the HOMO decreased as well. Furthermore, the HOMO of **2a** also reveals that a portion of the probability density is shifted to the adjacent units via 4,4′-dipyridyl ligands when the 4,4′-dipyridyl ligands bridge two $TeFe_3(CO)_9Cu_2$ units but not in the case of NH_3-coordinated **2a′** (Figure 4). Both effects indicate that the 4,4′-dipyridyl linker plays an important role in enhancing conductivity, while the $TeFe_3(CO)_9Cu_2$ units are polymerized by the 4,4′-dipyridyl ligand. To further explore the $\pi-\pi$ interactions between two 4,4′-dipyridyl ligands, one of two 4,4′-dipyridyl linkers is removed to calculate the electronic structure of the single-linker species. It is found that although the HOMO−LUMO energy gap of the single linker species is larger than that of the original double linker species **2a** (1.84 vs 1.47 eV), it may be still small enough to have semiconducting properties. In fact, the conductivity of polymer **2** (5×10^{-2} Ω^{-1} cm^{-1}) is much higher than that reported for other singly 4,4′-dipyridyl-linked transition metal polymers ($\sim 10^{-5}-10^{-10}$ Ω^{-1} cm^{-1}),[11] which further illustrates the importance of the $\pi-\pi$ interactions between the two 4,4′-dipyridyl linker pairs in polymer **2**. In addition, the effects of the relative orientation between two linkers on electronic properties are also studied. The HOMO−LUMO energy gaps for species with $\sim 0°$ and $\sim 90°$ of the dihedral angles between two adjacent pyridine rings on different linkers are 1.27 and 0.95 eV, respectively, which is lower than that for the original double linker species **2a**. This result suggests that even though **2a** is not a species of the configuration with the lowest energy gap, this configuration is adopted in the polymer crystal probably due to the constrains of lattice forces and other factors imposed on the relative orientation between two linkers.

In summary, we have prepared the first examples of Te−Fe−Cu-based polymers, $[\{Et_4N\}\{TeFe_3(CO)_9Cu\}]_\infty$ and $[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_\infty$, from the self-assembly of $[Et_4N]_2[TeFe_3(CO)_9]$ with $[Cu(MeCN)_4][BF_4]$ in THF or in the presence of 4,4′-dipyridyl in THF. In addition, $TeFe_3(CO)_9Cu_2(MeCN)_2$ has proven to be an effective synthon for the construction of these two novel Cu- and Cu-dipyridyl-linked $TeFe_3$-based chain polymers which display surprising semiconducting properties with small band gaps of ~ 0.59 and ~ 0.41 eV, respectively. Their conductivity and the effect of the bridging ligand are further elucidated by theoretical calculations. This study paves a new avenue to the construction of semiconducting metal- or metal-organo-bridged Te−Fe-based polymers via both synthetic and theoretical approaches. Further investigation into the bridging effect of other linkers is underway.

Supporting Information Available: Experimental details for the synthesis and characterization of $[Et_4N]_\infty[\mathbf{1}]$, **2**, and **3**. Details of the X-ray structure determinations for $[Et_4N]_\infty[\mathbf{1}]$, **2**, and **3** in CIF format. Electronic spectra for $[Et_4N]_2[TeFe_3(CO)_9]$, $[Et_4N]_\infty[\mathbf{1}]$, and **2** and optical measurement for $[Et_4N]_\infty[\mathbf{1}]$ and **2**. Computational details for $[TeFe_3(CO)_9]^{2-}$, **1a**, **2a**, **2a′**, single linker species $H_2[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})]_2$, and $H_2[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_2$ with $\sim 0°$ and $\sim 90°$ of the dihedral angle between two adjacent pyridine rings on different linkers. This material is available free of charge via the Internet at http://pubs.acs.org.

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