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Synthesis and properties of 4′,5′-bis(methylthio)-4,5-bis(2-pyridylethynyl)tetrathiafulvalene and its copper complexes

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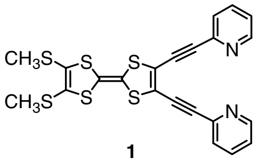
Abstract—Synthesis of redox-active bis-pyridine ligand, 4′,5′-bis(methylthio)-4,5-bis(2-pyridylethynyl)tetrathiafulvalene (**1**) has been carried out in moderate yield starting from the corresponding diiodide. Bis(pyridylethynyl)–TTF **1** forms 1:1 complexes with Cu(I) and Cu(II) salts. Occurrence of the charge transfer from the TTF moiety to the copper atom was found to depend on the environment of copper atom.

Tetrathiafulvalene (TTF) and its derivatives have received considerable attention because of the high electrical conductivities of their CT-complexes and cation radical salts,[1] and because of their applicability in molecular science as a strong π-donor to form stable cation radical species.[2] Thus, TTFs have been employed for the construction of functional molecular materials.[3,4] On the other hand, new compounds bearing both magnetic interactions and electrical conductivities are an attractive target molecule for synthetic chemists and molecular scientists.[5] An important requirement for these materials is a long-range magnetic coupling between localized spins of organic radicals (π-electron) and transition metals (d-electron) through mobile electrons of the conducting π–π networks. Although many TTF derivatives having metallic state coexisting with ferromagnetism via d–π interaction were reported,[6] the structure contains two completely independent metallic and magnetic sublattices.

To construct molecules having strong intramolecular d–π interaction, we designed a diad system composed of covalently linked TTF and copper–pyridine moieties, because the strong interactions between TTF moiety and copper(II) atom can be expected. Furthermore, this multi-functional system can be regarded as an ideal model to examine charge-transfer interaction between TTF and Cu(II) atom. We report here the synthesis and interesting electronic properties of 4′,5′-bis(methylthio)-4,5-bis(2-pyridylethynyl)tetrathiafulvalene (**1**) and



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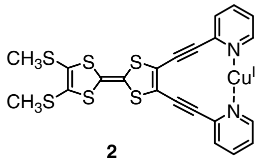

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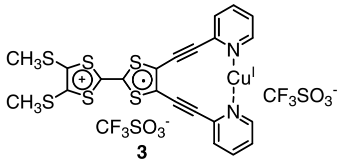

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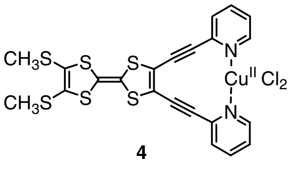

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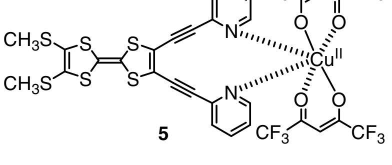

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Keywords: Tetrathiafulvalene; π-Conjugated system; d–π Interaction; Copper complex.

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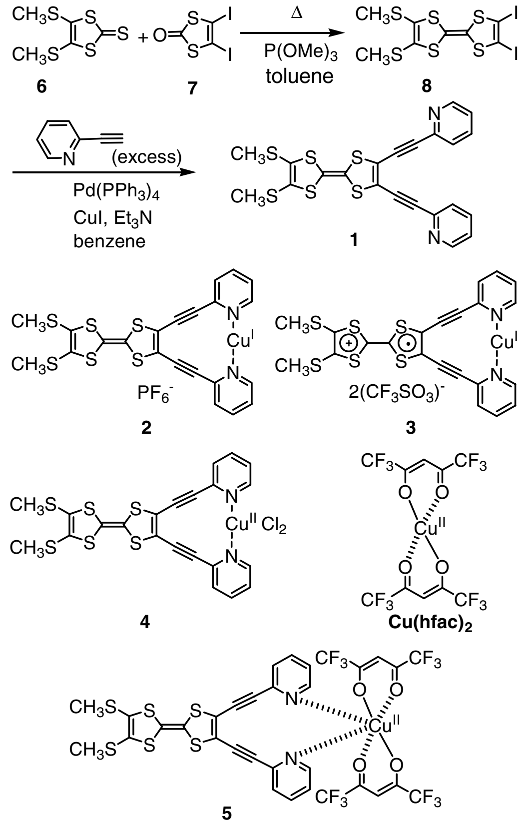
its copper(I) and copper (II) complexes **2**, **4**, and **5** together with their cation radical species **3**.

Synthesis of **1**–**5** was carried out using the reactions shown in Scheme 1. Thus, the phosphite-mediated cross-coupling of **6** with **7** formed **8** (48%).[7] Sonogashira coupling of **8** with 2-ethynylpyridine in the presence of $Pd(PPh_3)_4$ and CuI in Et_3N-benzene at room temperature produced **1** (66%).[8] Bis(pyridylethynyl)–TTF **1** is stable in the solid state but **1** in a solution gradually decomposes at room temperature. The cyclic voltammetric analysis shows that **1** possesses a moderate donor ability ($E_{1/2}^{\mathrm{ox1}} = 0.15$ V and $E_{1/2}^{\mathrm{ox2}} = 0.43$ V vs Fc/Fc^+), because the ethynylpyridine units act as electron-withdrawing substituents. Interestingly, **1** exhibits solvatochromism, and a solution **1** in CH_2Cl_2 or THF is reddish orange, whereas a solution of **1** in CS_2 is wine-red.[4a,b,9]

The molecular structure of **1** was determined by X-ray analysis (Fig. 1).[10] As shown in Figure 1a, each nitrogen atom in the pyridine ring is placed outside the molecular frame. The TTF moiety has a slightly bent boat form, and the dihedral angle of the two 1,3-dithiole ring is 18.69° (Fig. 1b). In contrast, the two pyridylethynyl units and C(1)–C(2) bond are coplanar, and the maximum atomic deviation from the least-squares plane is 0.0997 Å (Fig. 1b). As shown in Figure 1c and Supplementary data, **1** forms a dimer structure along the head-to-tail stacked pyridine–acetylene-1,3-dithiole units, and a pyridine ring of the perpendicularly located neighboring molecule occupies the inner space formed by the two pyridylethynyl units in **1**. There is an intermolecular CH···N short contact [C(7)···N(1) 3.384(7) Å] between SCH_3 and pyridine units.



Scheme 1. Synthesis of **1** and **2**–**5**.

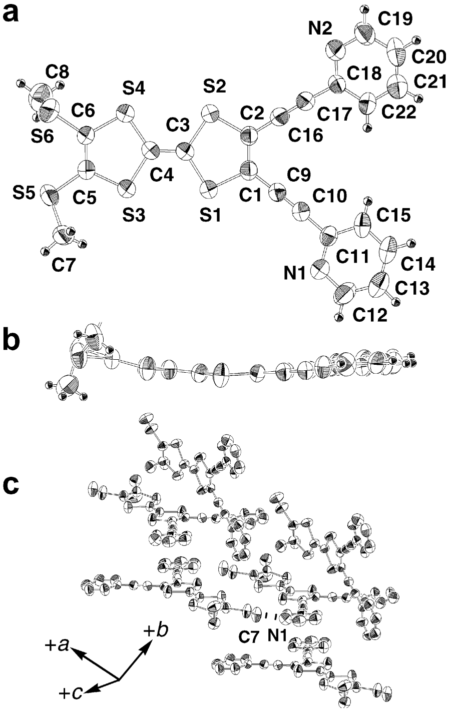


Figure 1. X-ray structure of **1**. (a) Top view; (b) side view; (c) packing structure. The selected bond lengths (Å) are as follows: S1–C1 1.753(4); S1–C3 1.741(6); C1–C2 1.350(8); C3–C4 1.336(6); C5–C6 1.344(8).

Copper(I) complex **2** was prepared in 95% yield by mixing **1** with $Cu^I(CH_3CN)_4PF_6$ in CH_2Cl_2, whereas **3** was

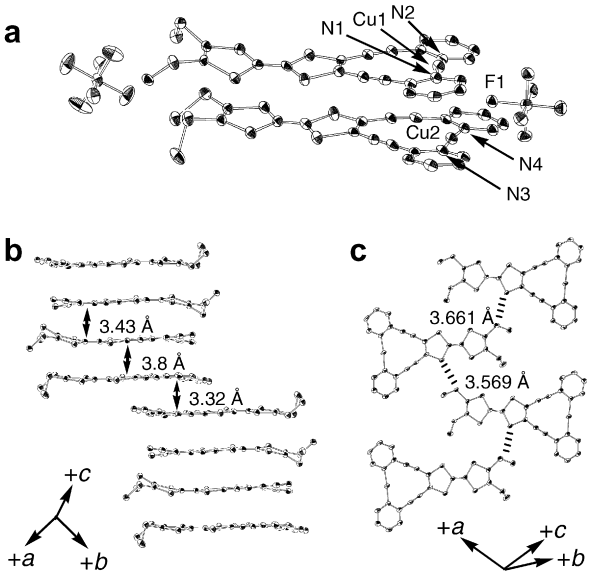


Figure 2. X-ray structure of **2**. (a) Molecular structure; (b) side view; (c) top view. Counter ions are omitted for clarity in (b) and (c). The selected bond lengths (Å) and angles (°) are as follows: Cu1–N1 1.915(2); Cu1–N2 1.902(2); Cu2–N3 1.887(2); Cu2–N4 1.886(2); Cu1–F1 2.954(2); Cu2–F1 2.935(3); N1–Cu1–N2 174.63(16); N3–Cu2–N4 174.52(16).

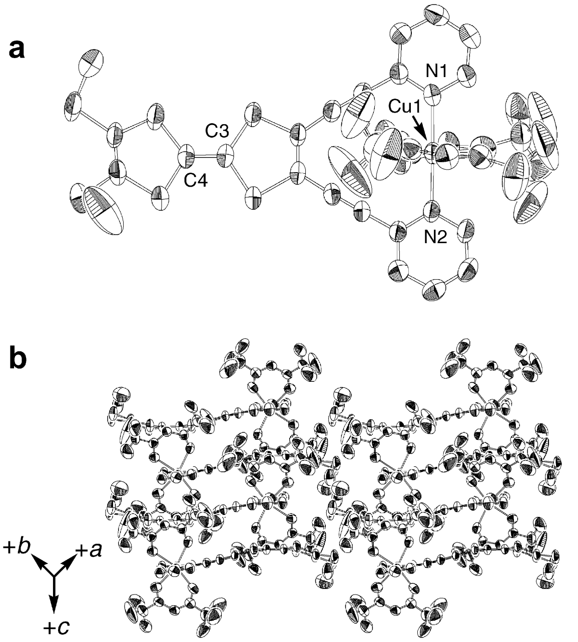


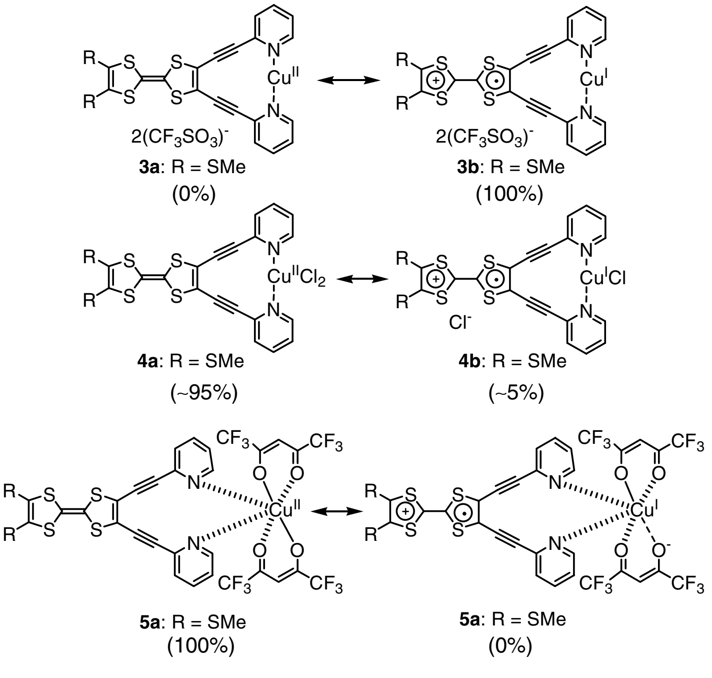
Figure 3. X-ray structure of **5**. (a) Molecular structure; (b) side view. The selected bond lengths (Å) and angles (°) are as follows: Cu1–N1 2.012(3); Cu1–N2 2.014(3); C3–C4 1.339(5); N1–Cu1–N2 177.52(15).

prepared in 74% yield by mixing **1** with $Cu^{II}(CF_3SO_3)_2$ in CH_2Cl_2–acetone. The copper(II) complex **4** was prepared in 84% yield by mixing **1** with $Cu^{II}Cl_2$ in THF–EtOH, and **5** was obtained in 87% yield by heating a solution of **1** with $Cu^{II}(hfac)_2$ in hexane–CH_2Cl_2.

Copper(I) complex **2** was crystallized from CH_2Cl_2–EtOH–AcOEt to yield single crystals. The molecular structure of the 1:1 complex **2** was proved by X-ray crystallographic analysis.[11] The crystal lattice includes head-to-head stacked two crystallographically independent molecules, which are found to have essentially the same structure except for the N(1)–Cu(1)–N(2) bonds [1.915(2) and 1.902(2) Å] and N(3)–Cu(2)–N(4) bonds [1.887(2) and 1.886(2) Å].[12] It is worth noting that the dihedral angles of N–Cu–N bonds are 174.52(13)° and 174.63(13)°, reflecting no ring strain (Fig. 2). As shown in Figure 2a, F(1) of the PF_6 anion interacts with the two copper(I) atoms, and another PF_6 anion is located near the methylthio groups of the head-to-head dimerized TTF moieties. Dimeric **2** stacks head-to-tail to form a layered structure, in which there are no short contacts in the head-to-head and head-to-tail dimeric pairs. However, the slide-stacked pair of **2** exhibits a short contact of 3.32 Å between the two dipyridylethynyl moieties (Fig. 2b). Interestingly, **2** forms a seat structure with the two S···S contacts of 3.569 and 3.661 Å (Fig. 2c). Although **2** forms a layered structure, **2** shows no electric conductivity due to its neutral TTF moiety.

The structure of copper(II) complex **5** was determined by X-ray analysis.[13] As shown in Figure 3, the hfac ligands in **5** are located perpendicular to the molecular plane of **1**, and the copper(II) atom is folded in the pyridine and hfac ligands. The distances of the Cu(1)–N(1) and Cu(1)–N(2) bonds are 2.012(3) and 2.014(3) Å (Fig. 3a), which are very close to the distances of known $Cu(hfac)(pyridine)_2$ complexes.[14] The Cu–O distances are also close to the known values. Interestingly, the dihedral angle of N(1)–Cu(1)–N(2) bond is 177.52(15)°. The complex **5** stacks head-to-tail to form a partially overlapped columnar structure to sidestep the bulky hfac groups (Fig. 3b).[15]

Although no X-ray structural data of **3** and **4** were obtained, the UV and ESR spectra of these compounds exhibit detailed information about their structures. The reaction of **1** with $Cu^{II}(CF_3SO_3)_2$ produces **3**, and the structure of **3** exhibits almost no contribution of



Scheme 2. Magnitude of electron transfer from TTF group to copper(II) metal.

TTF(neutral)–Cu^{II} form **3a**, because the ESR spectrum of **3** in CH_2Cl_2 shows a signal at $g = 2.0072$ based on TTF cation radical. Thus, **3** exists as $TTF^{\cdot+}$ (cation radical)–Cu^{I} form **3b** (Scheme 2). In contrast, the X-ray analysis of **5** clearly shows that **5** exists as TTF(neutral)–Cu^{II} form **5a**, for example, the C(3)–C(4) bond length of **5** (Fig. 3) is similar to that of **1** (Fig. 1). Furthermore, the ESR spectrum of **5** shows complex broad signals at the range from $g = 1.9830$ to 2.3730 based on a copper(II) species. In the case of **4**, the copper complex exhibits complex ESR signals in the range from 1.9653 to 2.3558, and hence **4** exists as TTF(neutral)–Cu^{II} form **4a**. However, UV–vis spectrum of **4** shows a weak charge-transfer absorption at 860 nm ($\varepsilon = 155$) typical to $TTF^{\cdot+}$(cation radical)–Cu^{I} form **4b**.[16] Therefore, we estimate a small contribution (~5%) of **4b** to **4** (Scheme 2). Compressed pellets of **3** and **4** show electric conductivities of $\sigma_{rt} = 1.08 \times 10^{-3}$ and 1.39×10^{-3} S cm^{-1}, respectively, presumably due to their $TTF^{\cdot+}$ (cation radical)–Cu^{I} structure. In contrast, **5** is an insulator due to TTF(neutral)–Cu^{II} structure.

In summary, we found an interesting intramolecular CT interaction between TTF moiety and copper(II) atom. Ligands of copper(II) atom play an important role for the intramolecular CT process. This intramolecular CT interaction is important for appearance of electric conductivity.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: doi:10.1016/j.tetlet.2007.06.048.

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8. All the new compounds reported here were fully characterized by spectroscopic methods and elemental analyses, see Supplementary data. [Compound **1**: mp 154 °C (decomp., DSC); LDI-TOF-MS (*m/z*) 498 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 6H), 7.28 (m, 2H), 7.57 (d, 2H, $J = 7.6$ Hz), 7.69 (m, 2H), 8.63 (d, 2H, $J = 6.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 79.9, 98.2, 109.8, 112.4, 121.8, 123.5, 127.6, 127.8, 136.2, 142.2, 150.2; Anal. Calcd for $C_{22}H_{14}N_2S_6$: C, 52.98; H, 2.83; N, 5.62. Found: C, 52.90; H, 2.98; N, 5.69].
9. For the solvatochromism of **1** in CH_2Cl_2 and CS_2, see Supplementary data.
10. *X-ray analysis for* **1**: $C_{22}H_{14}N_2S_6$, MW = 498.73, monoclinic, $P2_1/c$ (#14), $Z = 4$, $a = 12.401(8)$ Å, $b = 17.364(16)$ Å, $c = 11.231(5)$ Å, $\beta = 108.87(4)°$, $V = 2288.5(27)$ Å^3, $D_{calcd} = 1.447$ g cm^{-3}, $T = 298$ K, μ(Mo Kα) = 6.103 cm^{-3}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 272 parameters, $R_1 = 0.0548$, $R_W = 0.2056$, GOF = 1.277.
11. *X-ray analysis for* **2**: $C_{22}H_{14}N_2CuF_6PS_6$, MW = 707.24, triclinic, $P{-}1$ (#2), $Z = 4$, $a = 13.959(4)$ Å, $b = 16.214(10)$ Å, $c = 13.063(5)$ Å, $\alpha = 92.43(4)°$, $\beta = 116.86(2)°$, $\gamma = 81.39(4)°$, $V = 2606.9(20)$ Å^3, $D_{calcd} = 1.802$ g cm^{-3}, $T = 103$ K, μ(Mo Kα) = 14.409 cm^{-1}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 686 parameters, $R_1 = 0.0489$, $R_W = 0.1435$, GOF = 0.874.
12. The reported bond distance and dihedral angle of the N–Cu(I)–N linkage in 1,2-bis(2-pyridylethynyl)benzene–Cu(I) PF_6 complex are 1.935 Å and 170.28°, respectively, see: (a) Kawano, T.; Kuwana, J.; Shinomaru, T.; Du, C.-X.; Ueda, I. *Chem. Lett.* **2001**, 1230–1231; (b) Kuwano, T.; Kuwana, J.; Ueda, I. *Bull. Chem. Soc. Jpn.* **2002**, *76*, 789–797.
13. *X-ray analysis for* **5**: $C_{32}H_{16}CuF_{12}N_2O_4S_6$, MW = 976.38, triclinic, $P{-}1$ (#2), $Z = 2$, $a = 12.342(2)$ Å, $b = 13.419(3)$ Å, $c = 12.238(4)$ Å, $\alpha = 108.65(2)°$, $\beta = 95.659(19)°$, $\gamma = 85.637(18)°$, $V = 1908.8(8)$ Å^3, $D_{calcd} = 1.699$ g cm^{-3}, $T = 298$ K, μ(Mo Kα) = 9.991 cm^{-1}, Rigaku AFC7R, Mo Kα ($\lambda = 0.71069$ Å), 531 parameters, $R_1 = 0.0536$, $R_W = 0.1380$, GOF = 1.192.
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15. The intercolumnar shortest distance is 3.615 Å between the overlapped TTF and pyridine moieties.
16. For the UV–vis spectra of **3**–**5**, see: Supplementary data.