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Iron(II) Complexes Based on π -Conjugated Terpyridine Ligands with Tetrathiafulvalene or Its Radical Analogue

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Two tetrathiafulvalene (TTF) functionalized 2,2':6',2''-terpyridine derivatives, 4'-tetrathiafulvalene-2,2':6',2''-terpyridine (L¹) and 6,6''-dimethyl-4'-tetrathiafulvalene-2,2':6',2''-terpyridine (L²), were synthesized and characterized. Based on L¹ and L², four electrochemically active TTF-containing iron(II) complexes, [Fe^{II}(L¹)₂][ClO₄]₂ (**1**), [Fe^{II}(L¹⁺)₂][ClO₄]₄ (**2**), [Fe^{II}(L¹)₂][CF₃SO₃]₂ (**3**) and [Fe^{II}(L²)₂][ClO₄]₂ (**4**), were successfully obtained. The preparation, spectroscopic and electrochemical properties of these new compounds as well as the crystal structures of complexes **1**, **3** and **4** are described. Magnetic studies on **4** (with the ligand L²) suggest

Introduction

One of the current challenges in solid-state science is the synthesis and investigation of molecule-based materials involving interplay and synergy between multiple physical properties.^[1] In particular, due to the important applications in molecular spintronics, new bifunctional materials with both conductivity and magnetism have attracted increasing interest in the last few years.^[2] Among numerous organic building blocks exploited for the preparation of hybrid conducting and magnetic materials, tetrathiafulvalene (TTF) and its derivatives are of importance for their potential applications as versatile building blocks.^[3] One of the ways of attempting to obtain new TTF-based multi-functional molecular materials is to associate the electrochemically active TTF core with optical or magnetic properties of the metal ions bridged by various functional groups.^[4-6] To date, many TTF-substituted pyridine and bipyridine derivatives have been reported, and these compounds might enable electron transfer and communication between the localized spins and the mobile electrons.^[7-9] In 2011, Oshio

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that the Fe^{II} ion is in the high-spin state. Complex **2** was isolated as an interesting and stable open-shell substance, and the free spin is mainly associated with the TTF radicals, as indicated by EPR, UV/Vis spectra, electrochemical analysis, spectroelectrochemical measurements and XPS spectra. After the oxidation and the formation of the radical cation, the electrical conductivity of **2** is almost 3 orders of magnitude higher than that of **1**. DFT and TDDFT calculations provided insight into interpreting the electronic properties of complex **1** and its oxidized states.

and co-workers reported the new tridentate ligand dppTTF (TTF moieties are linked to the ligand through an ethylene unit) and its iron(II) complexes, [Fe(dppTTF)₂](BPh₄)₂· MeNO₂·0.5Et₂O and [Fe(dppTTF)₂][Ni(mnt)₂]₂(BF₄)· PhCN, which showed reversible redox behavior and thermal spin-crossover {dppTTF = 1-[2-(1,3-dithiol-2-ylidene)-1,3-dithiolyl]-2-[2,6-bis(1-pyrazolyl)pyridyl]ethylene}.^[10] For further enhancing the interaction of conducting and magnetic π -d systems, it is important to shorten the distance between the magnetic metal-ion and conducting TTF units by designing new π -conjugated ligands.

The compound 2,2':6',2''-terpyridine and its derivatives are classic tridentate ligands that have been widely utilized in supramolecular and materials chemistry.^[11,12] In the last decades, special attention has been paid to the attachment of functional groups to the terpyridine unit since the appended substituents may be utilized not only to tailor the electronic properties of the ligand and its metal complexes but also to incorporate new functionalities through further derivatisation reactions.

The association of the TTF unit with terpyridine is intriguing in coordination and materials chemistry because of the strong coordinating ability of terpyridine and the electron-donating ability of TTF. In 2013, El-Ghayoury and Sallé et al. successfully prepared the terpyridine ligand L¹ with TTF for the first time.^[5f] The TTF unit is directly connected to the terpyridine, which significantly decreases the distance between the magnetic metal-ion and conducting TTF units. In this work, we developed a simple and efficient synthetic route for the TTF-terpy derivatives, 4'-tetra-

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thiafulvalene-2,2':6',2''-terpyridine (L¹) and 6,6''-dimethyl-4'-tetrathiafulvalene-2,2':6',2''-terpyridine (L²). By using the above ligands, four typical iron(II) complexes [Fe^{II}-(L¹)₂][ClO₄]₂ (1), [Fe^{II}(L¹⁺)₂][ClO₄]₄ (2), [Fe^{II}(L¹)₂]-[CF₃SO₃]₂ (3) and [Fe^{II}(L²)₂][ClO₄]₂ (4) were synthesized and their spectroscopic, electrochemical and conductive properties were studied. The crystal structures of complexes 1, 3 and 4 are described, and XPS and DFT calculations were also performed for the characterization of some of the new compounds.

Results and Discussion

Synthesis

As shown in Scheme 1, the two versatile tetrathiafulvalene-based terpyridine derivatives L^1 and L^2 were prepared in a one-pot synthesis from formyltetrathiafulvalene, 2-acetylpyridine (or 2-acetyl-6-methylpyridine) and ammonia in the presence of *t*BuONa. The synthetic method for the ligands is simple, and the yield for L¹ (14%) is slightly higher than that reported in the literature (ca. 6%).^[5f] Complexes **1** and **3** were obtained from the reaction of L¹ with Fe(ClO₄)₂·*x*H₂O or Fe(CF₃SO₃)₂, whereas complex **4** was obtained from the reaction of L² with Fe(ClO₄)₂·*x*H₂O in methanol/dichloromethane. Interestingly, the iron(II) complex **2** with radical ligands was obtained from the reaction of L¹ with 1 equiv. Fe(ClO₄)₃·*x*H₂O in methanol/dichloromethane during which Fe³⁺ oxidized the TTF unit to TTF⁺⁺, itself being reduced to Fe²⁺ (Scheme 2). It will be important to isolate new iron(III) complexes with radical ligands, although attempts to oxidize **2** by using an excess of Fe(ClO₄)₃·*x*H₂O or other common oxidants were unsuccessful.

Cyclic Voltammetry

The electrochemical properties of L^1 and L^2 , and complexes 1, 3 and 4 were investigated by using cyclic voltam-



Scheme 2. Synthesis of complexes 1-4.





Figure 1. Cyclic voltammograms for L¹, L², 1, 3 and 4.

metry in CH₂Cl₂/CH₃CN (1:1 ratio, 0.1 mol L⁻¹ nBu₄-NClO₄). As shown in Figure 1, two reversible oxidation couples were observed at 0.45 and 0.85 V for L¹, 0.44 and 0.86 V for L², which are associated with the successive oxidation of neutral TTF (TTF⁰) to the radical cation (TTF⁺⁺) and then to the dication (TTF²⁺). Upon coordination, three quasi-reversible oxidation waves were observed at 0.48, 0.83 and 1.27 V for **1**, 0.49, 0.84 and 1.27 V for **3**, and 0.47, 0.84 and 1.25 V for **4**. Upon coordination, the first reversible oxidation works shift slightly to a positive position compared with the respective ligands. The first two oxidation waves correspond to two-electron oxidation of the TTF moieties, and the third oxidation waves can be assigned to the Fe^{II}-centered one-electron oxidation process.

Spectroscopic Properties

The absorption spectra of L¹ and L², and their iron(II) complexes 1–4 were recorded in CH₂Cl₂/CH₃CN (1:1 ratio) at room temperature (Figure 2). For L¹ and L², strong absorption bands at high energy ($\lambda < 360$ nm) can be assigned to the intraligand (IL) π – π * transition,^[5] and a weak absorption band (360–540 nm) at lower energy can be assigned to IL charge transfer (ILCT) from the highest occupied molecular orbital in TTF to the lowest unoccupied molecular orbital in the electron-accepting pyridyl unit.^[12] In comparison, complexes 1–3 all exhibit a broad and intense band in the visible region in addition to the slightly redshifted and more intense IL and ILCT transitions. The broad band in the visible region is attributable to an admix-

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ture of metal-to-ligand charge-transfer (MLCT) and ligandto-ligand charge-transfer (LLCT) transitions.^[12] In contrast, **4** exhibits more intense IL and ILCT transitions with a tailing into the visible region from a ligand π – π * absorption, the absence of the MLCT band for complex **4** in the visible region correlates nicely with the high-spin nature of the Fe^{II} center.^[13] The chemical oxidative titration of complex **1** with NOPF₆ was carried out in acetonitrile and monitored by absorption spectrophotometry (Figures S1 and S2). The oxidation leads to the appearance of new bands characteristic for the radical cation (440 and 665 nm), and these are in good agreement with the absorption spectra of complex **2**.



Figure 2. Absorption spectra of L¹, L², and 1–4 (1×10⁻⁵ M) in CH₂Cl₂/CH₃CN (1:1).

Spectroelectrochemical measurements were also carried out during the electrolysis of the solution of L^1 and complex 1 in CH₂Cl₂/CH₃CN (1:1) at suitable constant potentials corresponding to its redox processes (Figures 3 and 4). The first stage of the electrochemical oxidation leads to the



Figure 3. Spectroelectrochemistry of L^1 in CH_2Cl_2/CH_3CN (1:1) (0.1 M nBu_4NClO_4).

appearance of TTF radical cation bands around 446 nm. Upon application of a potential of 1.25 V for L¹ and 1.1 V for complex **1**, the electronic spectra show a decrease in the characteristic absorptions of the radical cation bands and the appearance of dication bands around 340–410 nm.



Figure 4. Spectroelectrochemistry of 1 in CH_2Cl_2/CH_3CN (1:1) (0.1 M nBu_4NClO_4).

At room temperature, only a signal at g = 2.012 can be observed in the EPR spectrum of powdered samples of complex **2** (Figure 5) suggesting the existence of L^{1.+} spins.^[7d] The absence of a signal at around 1500 G shows that there is no Fe³⁺ in **2** (Figure S3).^[14] We can therefore conclude that Fe³⁺ oxidizes the TTF unit to TTF^{.+}, itself being reduced to Fe²⁺.



Figure 5. EPR signal of complex 2.

Crystal Structures

The crystallographic and data collection parameters of compounds 1, 3 and 4 are given in Table 5. Selected bond lengths and angles are given in Tables 1, 2, and 3, respectively.

The ORTEP diagram of the complex 1 is depicted in Figure 6. Compound 1 crystallizes in the orthorhombic system (space group *Pccn*), and the asymmetric unit contains two $[Fe^{II}(L^1)_2]^{2+}$ cations, four ClO_4^- anions, one diethyl ether



Table 1. Selected bond lengths [Å] and angles [°] in complex 1.

Fe(1)–N(1)	1.984(4)	Fe(1)–N(2)	1.874(4)
Fe(1) - N(3)	1.971(4)	Fe(1)-N(4)	1.978(4)
Fe(1) - N(5)	1.880(4)	Fe(1)-N(6)	1.980(4)
N(1)-Fe(1)-N(2)	80.97(17)	N(1)-Fe(1)-N(4)	90.28(17)
N(2)-Fe(1)-N(4)	98.24(17)	N(2)-Fe(1)-N(5)	178.12(17)
N(3)-Fe(1)-N(5)	100.82(17)	N(3)-Fe(1)-N(6)	89.13(17)
N(1)-Fe(1)-N(2) N(2)-Fe(1)-N(4) N(3)-Fe(1)-N(5)	98.24(17) 100.82(17)	N(1) - Fe(1) - N(4) N(2) - Fe(1) - N(5) N(3) - Fe(1) - N(6)	178.12(17) 89.13(17)

Table 2. Selected bond lengths [Å] and angles [°] in complex 3.

Fe(1)–N(1) 1.8	69(4)	Fe(1)-N(2)	1.981(4)
Fe(1)–N(3) 1.9	77(4)	Fe(1)-N(4)	1.980(5)
Fe(1)–N(5) 1.8	77(4)	Fe(1)-N(6)	1.979(5)
N(1)-Fe(1)-N(2) 80.	13(17)	N(1) - Fe(1) - N(4)	95.88(18)
N(2)-Fe(1)-N(4) 91.	50(18)	N(1)-Fe(1)-N(5)	176.43(18)
N(3)-Fe(1)-N(5) 98.	24(18)	N(3) - Fe(1) - N(6)	91.12(18)

molecule and six H_2O molecules. In each $[Fe^{II}(L^1)_2]^{2+}$ cation, the central iron(II) ion is coordinated by six nitrogen atoms from two tridentate terpyridine units, which are directly linked to the TTF moieties. This results in a distorted

Table 3. Selected bond lengths [Å] and angles [°] in complex 4.

Fe(1)–N(1)	2.260(3)	Fe(1)–N(2)	2.103(3)
Fe(1)-N(3)	2.259(3)	Fe(1)-N(4)	2.310(3)
Fe(1)-N(5)	2.100(3)	Fe(1)-N(6)	2.237(3)
N(1)-Fe(1)-N(2)	74.06(12)	N(1)-Fe(1)-N(4)	93.15(12)
N(2)-Fe(1)-N(4)	101.01(12)	N(2)-Fe(1)-N(5)	174.53(12)
N(3) - Fe(1) - N(5)	108.49(12)	N(3)-Fe(1)-N(6)	92.31(12)

octahedral FeN6 coordination structure. The Fe–N bond lengths are in the range of 1.874(4)–1.984(4) Å, and this is characteristic of low-spin (LS) iron(II) ions. The two TTF units of the L¹ ligands containing the S1–S4 and S5–S8 atoms are twisted out of the plane of the central pyridyl ring by 12.6 and 21.7°, respectively. The closest interchain C_{terpy}–C_{TTF} (3.328 Å) and C_{terpy}–S_{TTF} distances (3.428 Å) between the TTF and terpy units are less than the sum of the van der Waals radii of these atoms (C–C 3.40 Å; C–S 3.55 Å). Through C···C and C···S interactions between terpy and TTF rings, a 2D network structure is formed as shown in Figure 7.



Figure 6. The 50% probability thermal ellipsoid plot of 1. Solvent molecules and anions are omitted for clarity.



Figure 7. Crystal-packing arrangement of 1 showing intermolecular C···C and C···S interactions.



Complex 3 crystallizes in the triclinic system (space group $P\overline{1}$), and the asymmetric unit contains one [Fe^{II}- $(L^{1})_{2}$ ²⁺ cation, two CF₃SO₃⁻ anions, one ethanol molecule and one H₂O molecule (Figure S4). In each $[Fe^{II}(L^1)_2]^{2+1}$ cation, the central iron(II) ion is coordinated by six nitrogen atoms from two tridentate terpyridine units, which are directly linked to the TTF moieties giving a distorted octahedral FeN6 coordination environment. The Fe-N bond lengths are in the range of 1.869(4)-1.981(4) Å, which is characteristic of low-spin iron(II) ions. The two TTF units containing the S1-S4 and S5-S8 atoms are twisted out of the plane of the central pyridyl ring by 8.6 and 14.5°, respectively. Two kinds of interchain C_{terpy}-C_{TTF} distances (3.338 and 3.383 Å) between TTF and terpy units are less than the sum of the van der Waals radii of 3.40 Å. Figure 8 illustrates the observation that face-to-face interactions between terpy and TTF rings leads to 1D chains.

As shown in Figure 9, complex 4 crystallizes in the triclinic system (space group $P\overline{1}$), and the asymmetric unit contains one [Fe^{II}(L²)₂]²⁺ cation, two ClO₄⁻ anions and three CH₃CN molecules. In each $[Fe^{II}(L^2)_2]^{2+}$ cation, the central iron(II) ion is coordinated by six nitrogen atoms from two tridentate terpyridine groups, which are directly linked to the TTF moieties giving a distorted octahedral FeN6 coordination structure. The Fe-N bond lengths are in the range of 2.100(3)-2.310(3) Å, and this is characteristic of high-spin iron(II) ions. The two TTF units of the L^2 ligands containing the S1-S4 and S5-S8 atoms are twisted out of the plane of the central pyridyl ring by 20.8 and 21.6°, respectively. Two kinds of closest interchain C_{terpy}-C_{TTF} distances (3.331 and 3.388 Å) between TTF and terpy units are less than the sum of the van der Waals radii of 3.40 Å. Through C···C interactions between terpy and TTF rings, a 1D chain structure is formed as shown in Figure 10.



Figure 8. Crystal-packing arrangement of 3 showing intermolecular C···C interactions.



Figure 9. The 50% thermal ellipsoid plot of 4. Solvent moolecules and anions are omitted for clarity.



Figure 10. Crystal-packing arrangement of 4 showing intermolecular C···C interactions.



Conductivity Measurements

Electrical conductivity measurements carried out by using compressed powder pellets and a four-probe method over the range 225–290 K (Figure 11) reveal conductivities of 3.9×10^{-10} and 1.3×10^{-7} S cm⁻¹ for **1** and **2** at 290 K, respectively. The conductivity value of pellets of **1** is much smaller than that of **2** due to the existence of the radical cation in the latter compound.



Figure 11. Temperature dependence of the conductivity in complexes 1 and 2.

XPS Spectra

To confirm the oxidation state of iron in complexes **1** and **2**, XPS measurements were carried out, and Fe 2p XPS core peaks were analyzed (Figure 12). The Fe 2p spectrum consists of two components due to spin-orbit coupling (Fe $2p_{3/2}$ and Fe $2p_{1/2}$) as described by Dedryvère.^[15] Each component consists of a main peak and a "shake-up" satellite. The binding energy position of the main peak is related to the oxidation state of iron. The Fe $2p_{3/2}$ and Fe $2p_{1/2}$ main peaks are centered at 707.6 and 720.4 eV for **1**, and 707.8 and 720.4 eV for **2**. These results further support the assertion that Fe in complex **2** is totally in the 2+ oxidation state.



Figure 12. XPS valence spectra of complexes 1 and 2.

Magnetic Properties

Variable-temperature (*T*) magnetic susceptibility (χ_M) measurements were performed on polycrystalline samples of complex **4** in the range 1.8–300 K. As shown in Figure 13, the $\chi_M T$ value is 3.52 emu K mol⁻¹ at 300 K, which is close to the Curie constant (3.00 emu K mol⁻¹ with g=2) for high-spin iron(II) ions. The high-spin nature of complex **4** is mainly because of the steric requirements created by the methyl substituents in the pyridyl rings. As the temperature decreases, the $\chi_M T$ value is almost constant until 60 K and then rapidly drops to 1.30 emu K mol⁻¹ at 2.0 K due to zero-field splitting of the octahedral high-spin Fe^{II} ion.^[13]



Figure 13. Temperature dependence of the $\chi_M T$ for complex 4 at 2 kOe.

Computational Studies

Quantum chemical calculations were carried out by using time-dependent DFT (TDDFT) for the dication of complex 1^{2+} and a series of its oxidized states (1^{4+} and 1^{6+}). The selected bond lengths and angles around metal ions in the optimized structure are comparable with those in the experimental crystal (Table S1), and the extended conjugated configuration of ligand L¹ is reproduced well. The calculated absolute values of the torsional angles (|a| = 6.98 and 7.20°) between TTF and terpy moieties is a little smaller than the experimental values (|a| = 15.13 and 26.26°). This may contribute to overestimation of the systematic delocalization in π -conjugated structures.^[16]

In order to provide insight into the experimentally observed optical transitions, TD-DFT calculations were performed for 1^{2+} and 1^{4+} . The excitations correlate well with observed absorption bands, in terms of both energy and strength. The results in terms of orbital contributions for the transitions with significant oscillator strengths (f >0.010 for 1^{2+} and 1^{4+}), as well as the experimental one are summarized in Tables 4 and S2. Predicted excitations are shown in Figures 14 and 15, and dominantly involved molecular orbitals are provided in Figures S5 and S6.



Orbital excitation	Composition	λ [nm] (calcd.)	<i>f</i> ^[a]	λ [nm] (exptl.)
236→239	0.51790	603	0.0653	596
235→239	0.50810	601	0.0118	
232→238	0.47714	473	0.2883	506 (sh)
233→237	0.47839			
230→237	0.47321	351	0.2917	368 (sh)
231→238	0.46633			
232→241	0.40392	319	0.3140	323
228→237	0.37390	313	0.1689	
233→245	0.36740	290	0.2862	284

Table 4. Main calculated optical transitions for 1^{2+} .

[a] Oscillator strength.



Figure 14. Superimposed experimental absorption spectrum (in grey) of 1^{2+} and corresponding calculated electronic transitions (in red, f 0.010).

Figure 16 shows a graphical representation of the frontier molecular orbitals for 1^{2+} . The experimental low-energy band at 596 nm for 1^{2+} corresponds to the estimated absorptions at 603 and 601 nm, which are related to an orbital mixing of the transitions $236\rightarrow 239$ and $235\rightarrow 239$. The involved occupied orbitals are composed of the iron-based t_{2g} orbital and $L^1 \pi$ contributions, while the unoccupied orbitals possess the π^* character of the terpy moiety. These transitions can therefore be ascribed to a mixed MLCT



Figure 15. Superimposed experimental absorption spectrum (in grey) of 1^{4+} and corresponding calculated electronic transitions (in red, f 0.010).

" $t_{2g}(Fe) \rightarrow \pi^*(terpy)$ " and " π (L¹) $\rightarrow \pi^*(terpy)$ " situation. The high-energy absorption (< 370 nm) originates mainly from $\pi \rightarrow \pi^*$ transitions due to the orbital characteristics of related starting and final states.

For the diradical cation 1⁴⁺, the new absorption band at 665 nm correlates with the experimental electronic transitions from the 230 β and 231 β to the 235 β and 236 β levels, which can be assigned to mixed MLCT [$t_{2g}(Fe) \rightarrow \pi^*(TTF)$] and $\pi \rightarrow \pi^*$ [" π (L¹) $\rightarrow \pi^*(TTF)$ "] transitions. The new peak at around 440 nm may come from combined excitations (233 $a \rightarrow 237a$, 234 $a \rightarrow 239a$, and 234 $\beta \rightarrow 239\beta$), which refers to a " $t_{2g}(Fe) \rightarrow \pi^*(terpy)$ " MLCT transition mixed with some " π (terpy) $\rightarrow \pi^*(terpy)$ " and " π (TTF) $\rightarrow \pi^*(terpy)$ " character.

The highest occupied molecular orbitals (HOMOs) for 1^{2+} , 1^{4+} and 1^{6+} are depicted in Figure 17 with proposed reversible electron oxidation processes shown in Scheme 3. Starting from 1^{2+} , two electrons are removed simultaneously from the two separated TTF moieties to afford 1^{4+} due to Coulombic repulsion.^[17] The spin density distribution for 1^{4+} is illustrated in Figure 18. It is clear that the spin density is essentially delocalized on two TTF moieties.



Figure 16. Molecular orbital energy diagram for 1^{2+} . Red bars represent unoccupied orbitals, and black bars represent occupied orbitals.



14+

16+

Figure 17. The highest single occupied molecular orbital (HOMO) for 1^{2+} and related oxidation states (1^{4+} and 1^{6+}).

12+



Scheme 3. Proposed reversible electron oxidation process of 1^{2+} .

For the oxidation state 1^{6+} , the HOMOs mainly consist of an Fe(terpy)₂ moiety suggesting that two-electron oxidations occur from two TTF segments for the second step.



Figure 18. Calculated spin density for 1^{4+} . The excess *a* and β spins are shown in blue and green, respectively. The isovalue of the surface is 0.0006 eÅ⁻³.

Conclusions

Versatile ligands L^1 and L^2 in which TTF is directly linked to the terpy moiety have been synthesized and four interesting iron(II) complexes $[Fe^{II}(L^1)_2][CIO_4]_2$ (1), $[Fe^{II}(L^{1++})_2][CIO_4]_4$ (2), $[Fe^{II}(L^1)_2][CF_3SO_3]_2$ (3) and $[Fe^{II}(L^2)_2][CIO_4]_2$ (4) derived from these ligands were also prepared. Electrochemical studies suggest that they all display rich redox processes. EPR, XPS and UV/Vis spectroscopic methods, electrochemical and spectroelectrochemical measurements and DFT calculations confirm that the oxidized complex 2 is isolable as a stable open-shell substance in which the low-spin Fe^{II} ions are six-coordinate due to two TTF radical ligands. The electrical conductivity of 2 is almost 3 orders of magnitude higher than that of 1. Magnetic susceptibility measurements of 4 suggest that high-



spin Fe^{II} is obtained based on the L² ligand. The results show that the versatile π -conjugated terpyridine ligands are useful for new multifunctional materials, and further work for exploring interesting conducting and magnetic materials is ongoing in our laboratory.

Experimental Section

Materials and Physical Measurements: Formyltetrathiafulvalene was synthesized according to a literature procedure.^[18] All solvents were purified by using standard techniques prior to use. Moistureor air-sensitive reactions were carried out under nitrogen. Elemental analyses for C, H and N were determined by using a Perkin-Elmer 240C analyzer. Infrared spectra were recorded in the 400-4000 cm⁻¹ region with a Bruker Vector22 spectrophotometer with KBr pellets. EPR spectra were obtained by using a Bruker EMX-10/12 variable-temperature apparatus. Conductivity measurements were measured by using a computer-controlled Keithley 2400 source meter. Spectroelectrochemical measurements were performed at the Beijing Institute of Chemistry, the Chinese Academy of Sciences. UV/Vis spectra were obtained with a UV-3100 spectrophotometer. Mass spectra were determined with an Autoflex II TM instrument for EI-MS. NMR spectra were recorded with a Bruker AM 500 instrument. Cyclic voltammetry was performed on an Im6eX electrochemical analytical instrument with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode; an Ag/AgCl electrode containing saturated KCl served as the reference electrode and 0.1 M nBu₄NClO₄ was used as the supporting electrolyte.

Preparation of 4'-Tetrathiafulvalene-2,2':6',2''-terpyridine (L¹): To a solution of 2-acetylpyridine (0.492 g, 3.92 mmol) in absolute ethanol (18 mL) were added formyltetrathiafulvalene (0.455 g, 1.96 mmol), sodium tert-butoxide (0.517 g, 5.4 mmol) and ammonia solution (7.1 mL). The reaction mixture was stirred at ambient temperature for 24 h. After this time, the precipitated impure product was filtered and successively washed with cold water and cold diethyl ether. The precipitate collected from the filtration was then purified by column chromatography on activated basic Al₂O₃ (hexane/CH₂Cl₂, 1:1) to give an orange powder (0.117 g, 14%). IR (KBr): $\tilde{v} = 3059$ (w), 2957 (s), 2923 (s), 2852 (s), 1743 (w), 1637 (w), 1583 (m), 1566 (m), 1466 (s), 1394 (m), 1180 (w), 991 (w), 783 (s), 633 (m) cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): δ = 8.71 (dd, J₁₂ = 1, $J_{13} = 4.5$ Hz, 2 H), 8.64 (d, J = 8.0 Hz, 2 H), 8.48 (s, 2 H), 7.90 (t, J_{12} = 8.0 Hz, 2 H), 7.39 (dd, J_{12} = 4.5, J_{13} = 7.5 Hz, 2 H), 7.20 (s, 1 H), 6.41 (d, J = 2.0 Hz, 2 H) ppm. EI-MS: m/z (%) = 435 (73) $[M]^+$, 290(100) $[M - C_4S_3H_2]^+$. $C_{21}H_{13}N_3S_4$ (435.59): calcd. C 57.90, H 3.01, N 9.65; found C 57.75, H 3.12, N 9.56.

Preparation of 6,6''-Dimethyl-4'-tetrathiafulvalene-2,2':6',2''-terpyridine (L²): To a solution of 2-acetyl-6-methylpyridine (0.529 g, 3.92 mmol) in absolute ethanol (18 mL) were added formyltetrathiafulvalene (0.455 g, 1.96 mmol), sodium *tert*-butoxide (0.517 g, 5.4 mmol) and ammonia solution (7.1 mL). The reaction mixture was stirred at ambient temperature for 24 h. After this time, the precipitated impure product was filtered and successively washed with cold water and cold diethyl ether. The precipitate collected from the filtration was then purified by column chromatography on activated basic Al₂O₃ (hexane/CH₂Cl₂, 1:1) to give an orange powder (0.104 g, 12%). IR (KBr): \tilde{v} = 3062 (w), 2922 (m), 2854 (w), 2359 (w), 1696 (w), 1646 (m), 1576 (s), 1458 (m), 1401 (m), 1153 (w), 1085 (w), 991 (w), 799 (m), 638 (m) cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): δ = 8.48 (s, 2 H), 8.45 (d, *J* = 7.5 Hz, 2 H), 7.80 (t, *J*₁₂ = 7.5 Hz, 2 H), 7.27 (d, J= 7.5 Hz, 2 H), 7.20 (s, 1 H), 6.45 (d, J= 1.5 Hz, 2 H), 2.70 (s, 6 H) ppm. EI-MS: m/z (%)= 462.8 (100) [M]⁺. C₂₃H₁₇N₃S₄ (463.65): calcd. C 59.58, H 3.70, N 9.06; found C 59.65, H 3.62, N 9.12.

Preparation of [Fe^{II}(L¹)₂][ClO₄]₂ (1): To a solution of L¹ (43.5 mg, 0.1 mmol) in CH₂Cl₂ (4 mL) was added a solution of Fe(ClO₄)₂· xH₂O(18.1 mg, 0.05 mmol) in methanol (5 mL). The color of the reaction solution turned to blue-violet immediately. After the mixture had been stirred at room temperature for 30 min, the resultant blue-violet precipitate was filtered and washed with methanol to give the product as a blue-violet solid (36 mg, 64%). Single crystals suitable for X-ray structure analysis were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of complex **1**. IR (KBr): $\tilde{v} = 3067$ (w), 2917 (w), 2847 (w), 1653 (m), 1608 (s), 1556 (w), 1535 (s), 1468 (w), 1428 (s), 1408 (m), 1247 (w), 1083 (s), 787 (s), 753 (m), 623 (s) cm⁻¹. C₄₂H₂₆Cl₂FeN₆O₈S₈ (1125.94): calcd. C 44.80, H 2.33, N 7.46; found C 44.65, H 2.42, N 7.36.

Preparation of [Fe^{II}(L¹⁺⁺)₂][CIO₄]₄ (2): To a solution of L¹ (43.5 mg, 0.1 mmol) in CH₂Cl₂ (4 mL) was added a solution of Fe(CIO₄)₃· xH₂O (51.3 mg, 0.1 mmol) in methanol (5 mL). The color of the reaction solution turned to blue-green immediately. After the mixture had been stirred at room temperature for 30 min, the resultant blue-violet precipitate was filtered and washed with methanol to give the product as a blue-green solid (29 mg, 44%). IR (KBr): \tilde{v} = 3069 (w), 2922 (w), 2849 (w), 1607 (m), 1540 (w), 1464 (w), 1428 (m), 1405 (m), 1345 (s), 1080 (s), 787 (m), 752 (w), 621 (s) cm⁻¹. C₄₂H₂₆Cl₄FeN₆O₁₆S₈ (1324.84): calcd. C 38.07, H 1.98, N 6.34; found C 37.95, H 1.92, N 6.51.

Preparation of [Fe^{II}(L¹)₂][CF₃SO₃]₂ (3): To a solution of L¹ (43.5 mg, 0.1 mmol) in CH₂Cl₂ (4 mL) was added a solution of Fe(CF₃SO₃)₂ (17.7 mg, 0.05 mmol) in methanol (5 mL). The color of the reaction solution turned to blue-violet immediately. After the mixture had been stirred at room temperature for 30 min, the resultant blue-violet precipitate was filtered and washed with methanol to give the product as a blue-violet solid (32 mg, 52%). Single crystals suitable for X-ray structure analysis were obtained by recrystallization from CH₂Cl₂/C₂H₅OH. IR (KBr): \tilde{v} = 3067 (w), 2918 (w), 2854 (w), 1608 (m), 1552 (w), 1534 (s), 1467 (m), 1429 (w), 1255 (s), 1223 (m), 1156 (s), 1029 (s), 787 (s), 754 (w), 636 (s) cm⁻¹. ESI-MS: *m*/*z* = 463.1 [(M - 2 CF₃SO₃)²⁺], 148.9 [CF₃SO₃⁻]. C₄₄H₂₆F₆FeN₆O₆S₁₀ (1225.16): calcd. C 43.13, H 2.14, N 6.86; found C 43.05, H 2.22, N 6.69.

Preparation of [Fe^{II}(L²)₂][ClO₄]₂ (4): To a solution of L² (46.3 mg, 0.1 mmol) in CH₂Cl₂ (4 mL) was added a solution of Fe(ClO₄)₂. xH₂O (18.1 mg, 0.05 mmol) in methanol (5 mL). The color of the reaction solution turned to blue-violet immediately. After the mixture had been stirred at room temperature for 30 min, the resultant blue-violet precipitate was filtered and washed with methanol to give the product as a blue-violet solid (35 mg, 59%). Single crystals suitable for X-ray structure analysis were obtained by recrystallization from CH₂Cl₂/CH₃CN. IR (KBr): \tilde{v} = 3068 (w), 2925 (w), 2848 (w), 2362 (w), 1635 (s), 1559 (m), 1458 (m), 1398 (m), 1251 (w), 1118 (s), 1085 (s), 802 (m), 754 (w), 628 (m) cm⁻¹. C₄₆H₃₄Cl₂FeN₆O₈S₈ (1182.04): calcd. C 46.74, H 2.90, N 7.11; found C 46.65, H 2.82, N 7.06.

Structure Determination: The X-ray diffraction data were collected with a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo- K_a ($\lambda = 0.71073$ Å) radiation (Table 5). The highly redundant data sets were reduced by using SAINT^[19] and corrected for Lorentz and polarization effects. Absorption corrections were applied by using SADABS^[20] supplied by Bruker. The structure was solved by direct methods and refined

	1	3	4
Empirical formula	C ₈₈ H ₇₄ Cl ₄ Fe ₂ N ₁₂ O ₂₃ S ₁₆	C46H34F6FeN6O8S10	C ₅₂ H ₄₃ Cl ₂ FeN ₉ O ₈ S ₈
Mr	2434.05	1289.24	1305.18
Crystal system	orthorhombic	triclinic	triclinic
Space group	Pccn	$P\bar{1}$	$P\overline{1}$
<i>a</i> [Å]	25.067(4)	11.818(3)	12.073(2)
<i>b</i> [Å]	20.189(3)	12.016(3)	12.365(2)
c [Å]	20.591(3)	21.170(6)	20.902(4)
a [°]	90	92.791(4)	77.535(3)
β [°]	90	105.637(4)	82.291(3)
γ [°]	90	110.377(4)	66.869(2)
V[Å ³]	10421(3)	2679.9(13)	2797.6(8)
Z	4	2	2
$\rho_{\text{calcd.}} [\text{g cm}^{-3}]$	1.551	1.598	1.549
F(000)	4984.0	1312.0	1340.0
<i>T</i> [K]	296	296	296
$\mu(Mo-K_a) [mm^{-1}]$	0.777	0.750	0.727
Index ranges	$-29 \le h \le 29$	$-14 \le h \le 13$	$-15 \le h \le 15$
	$-24 \le k \le 23$	$-14 \le k \le 14$	$-16 \le k \le 16$
	$-20 \le l \le 24$	$-25 \le l \le 24$	$-27 \le l \le 20$
GOF (F^2)	1.012	1.097	1.046
$R_1^{[a]}/wR_2^{[b]} [I > 2\sigma(I)]$	0.0592/0.1932	0.1095/0.2242	0.0595/0.1868

Table 5. Crystallographic data for complexes 1, 3 and 4.

[a] $R_1 = \Sigma ||C| - |F_c|| / \Sigma F_o|$. [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$.

by full-matrix least-squares methods on F^2 by using SHELXTL-97.^[21] All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} . CCDC-943093 (for 1), -943094 (for 3) and -943095 (for 4) contain 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.

Computational Details: All calculations were carried out with Gaussian $03^{[22]}$ Time-dependent density functional theory (TDDFT) with the three-parameter B3LYP hybrid functional were employed.^[23] The calculations were carried out by using a 6-31G* basis set for the C, H, N, S and Fe atoms. All geometries were characterized as minima by frequency analysis ($N_{imag} = 0$). For solvent modeling the integral equation formalism polarisable continuum model (IEFPCM) was employed.

Supporting Information (see footnote on the first page of this article): Additional UV/Vis and EPR spectra, structure and relevant DFT and TDDFT calculations data, and X-ray crystallographic files in CIF format for 1, 3 and 4.

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