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An asymmetric TTF derivative bearing a phenyl β -diketone group as an efficient ligand towards functional materials[†]

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A novel asymmetric tetrathiafulvalene (TTF) derivative bearing a conjugated phenyl β -diketone moiety 1-(4-tetrathiafulvalyphenyl)-4,4,4-trifluorobutane-1,3-dione (TTF-ph-tfacH) has been synthesized using feasible methods and fully characterized. The chelating ability of its enolate anion (TTF-ph-tfac) has been investigated with [M^{II}Cl₂·xH₂O] (M = Zn and Co) leading to complexes [Zn(TTF-ph-tfac)₂(CH₃OH)₂] (**2a**) and [Co(TTF-ph-tfac)₂(CH₃OH)₂] (**2b**), where the metal center is coordinated with two TTF-ph-tfac ligands and two methanol molecules. This redox active ligand shows promising features for the elaboration of hybrid organic–inorganic building blocks. The magnetic analysis for **2b** reveals very weak antiferromagnetic interactions between spin centers, which would be a precursor for magnetic conductors. The herein reported mono-substituted TTF derivative interconnected *via* the phenyl group, which is of extended conjugation, enhanced planarity, and asymmetric geometry, shows a great promise to multifunctional (conducting, non-linear optical, and magnetic) materials.

Introduction

For more than three decades, tetrathiafulvalene (TTF) and its derivatives have been attracting continuous attention as precursors of molecular conductors.^{1,2} The research interest is further kindled when the conducting building blocks (TTFs with π electrons) collaborate with the magnetic building blocks (transition metal ions with d electrons) towards the multifunctional molecule-based material that is one of the most challenging issues in solid-state chemistry.³⁻⁶ Consequently, various electroactive TTF based ligands have been synthesized targeting at, via their coordination to a transition metal, novel hybrid organic-inorganic building blocks.^{7,8} Among lots of coordination groups, the acetylacetonate ion formed in a basic medium from the acetylacetone always presents powerful chelating capability and forms complexes with various transition metals and main group elements.⁹ For this reason, two types of acetylacetone substituted TTF derivatives either connected through a sulfur $atom^{2,7,8,10-14}$ to the donor core or directly linked^{13,14} to the TTF moiety have been reported thus far. Accordingly, the herein reported novel acetylacetone substituted TTF derivative interlinked by the phenyl group should be categorized as a new type to enlarge the acetylacetone

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substituted TTF family. Moreover, the deliberate introduction of the phenyl group enhances the coplanarity and extends the conjugation of the whole molecule, which facilitates the π -d interaction between the conducting core and the magnetic center beneficial to multifunctional materials. From another point of view, the mono-substituted TTF aiming at grafting the non-linear optical (NLO) property into the multifunctional materials with conductivity and magnetism should be a rational design but its multi-functionalized materials are difficult to obtain, which is restricted by the molecular organization.

Recently, we have employed an efficient synthetic strategy to covalently append binding sites onto TTF donors, targeting at dual-property electronic and magnetic materials.¹⁵ In continuation of our researches on TTF based coordination complexes, we prepared a novel TTF derivative bearing a conjugated phenyl β-diketone functional group (Scheme 1) and its coordination counterparts with metal(II) centers $(M = Zn^{II}, Co^{II})$ and systemically investigated the electrochemical variation of this redox-active ligand in the absence and presence of different metal centers. The detailed electrochemical analysis indicates that upon coordination, the observed shifts always move toward more cathodic potentials and only $E_{1/2}(1)$ values are affected significantly, whereas $E_{1/2}(2)$ values remain almost unchanged. The downshift of the potentials can be explained by the formation of the negative enolate ion, which coordinates to the M(II) ions. As far as our knowledge goes, no affiliation concerning such TTF derivative and its complexes has been reported so far.

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Scheme 1 Synthesis routes of 1, 2, 2a and 2b: (i) *n*-butyllithium, THF, -78 °C; (ii) ClSnBu₃, -78 °C, then room temperature; (iii) 4-bromophenylethanone, Pd(PPh₃)₄, toluene, reflux; (iv) NaH, THF, 0.5 h, 0 °C; (v) ethyl trifluoroacetate, 6 h; (vi) the M^{II}Cl₂·*x*H₂O (M = Zn (2a) and Co (2b)) methanol solution layered on the ligand CH₂Cl₂ solution.

Experimental

Materials

All chemicals used for the syntheses were of reagent grade quality. THF and methanol were distilled from sodium/ benzophenone and MeOH/Mg(OMe)₂, respectively. TTF was synthesized according to the previous literature.¹⁶

Syntheses

1-(4-(Tetrathiafulvaleneyl)phenyl)ethanone (1). To a stirred solution of TTF (2.04 g) in anhydr. THF (50 mL) at -78 °C under an atmosphere of Ar was syringed n-butyl lithium (6.9 mL, 2.93 M) over a period of 5 min. Then, after stirring was continued for a further 30 min at -78 °C, tributyltin chloride (2.9 mL) was added dropwise over 10 min at -78 °C. The mixture was then slowly allowed to warm to the room temperature over 3 h. The solvent was evaporated under vacuum. The mixture was treated by Pd(PPh₃)₄ (0.113 g) and 4-bromophenylethanone in the dry toluene solution (60 mL), and the temperature was raised to 130 °C for 12 h. After removal of the solvents, column chromatography of the crude product on silica gel with hexane/ CH_2Cl_2 (1:1, v/v) afforded compound 1 as a red solid. Compound 1 was a deep red solid; yield: 2.2 g (68%). Mp 159-160 °C, ¹H NMR (DMSO, 500 MHz): 2.592 (s, 3H), 6.785 (s, 2H), 7.526 (s, 1H), 7.614 (d, 2H, J = 8.4 Hz), 7.987 (d, 2H, J = 8.4 Hz). ¹³C NMR (DMSO, 125 MHz): 27.3, 119.8, 120.3, 120.7, 126.6, 127.3, 128.6, 129.9, 133.9, 136.2, 136.6, 197.6. MS (m/z): C₁₄H₁₀OS₄ calcd: 322.0. Found: 322.0 [M]⁺. Anal. calcd for C14H10OS4: C, 52.14; H, 3.13; S, 39.77%. Found: C, 52.17; H, 3.10; S. 39.76%.

1-(4-Tetrathiafulvalyphenyl)-4,4,4-trifluorobutane-1,3-dione (2). Compound 1 (0.644 g) was dissolved in 30 mL of dry THF under an argon atmosphere and 60% NaH (0.1 g) was added in three batches maintaining the temperature between -5 and 0 °C. After stirring at this temperature for 0.5 h, ethyl trifluoroacetate (0.7 mL) was injected and the reaction mixture was allowed to stir at ambient temperature for 4–5 h. The mixture was poured into ice water, acidified with 2N HCl and extracted with ethyl acetate. The combined organic layer was washed with water, dried, and evaporated leaving a residue which was washed with pet-ether. Recrystallization from toluene gave dark blue crystals; yield: 0.4 g (48%). Mp 189–193 °C, ¹H NMR (DMSO, 500 MHz): 6.784 (s, 2H), 7.020 (s, 1H), 7.651 (d, 3H, J = 8.4 Hz), 8.156 (d, 2H, J = 8.4 Hz). ¹³C NMR (DMSO, 125 MHz): 93.0, 105.7, 112.9, 120.0, 120.1, 120.3, 126.2, 128.7, 131.8, 133.1, 136.5, 174.5, 184.0. MS (m/z): C₁₆H₉F₃O₂S₄ calcd: 417.9. Found: 417.9 [M]⁺. Anal. calcd for C₁₄H₁₀OS₄: C, 45.92; H, 2.17; S, 30.65%. Found: C, 45.90; H, 2.17; S, 30.63%.

 $[M(TTF-ph-tfac)_2(CH_3OH)_2]$ (M = Zn^{II} (2a) and Co^{II} (2b)). Above a solution of ligand 2 (64 mg, 0.1 mmol) and triethylamine (10 mmol) in CH₂Cl₂ (2 mL) was gently layered a CH₃OH solvent (1 mL), and furthermore above the CH₃OH solvent was gently layered a solution of $M^{II}Cl_2 \cdot xH_2O$ (M = Zn and Co) (30 mg) in CH₃OH (3 mL). When this three-phase solution was kept at RT for about 1 week, orange-colored crystals, M(TTF-ph-tfac)₂(CH₃OH)₂, appeared at the interface between the upper two phases. [Zn(TTF-ph-tfac)₂(CH₃OH)₂], 2a yield: 61%, mp: 143-144 °C. Maldi MS: calcd for $C_{32}H_{16}F_6O_4S_8Zn [M-CH_3OH]^+$, 897.8; found, 897.8. Anal. calcd for C₃₂H₁₆F₆O₄S₈Zn: C, 42.69; H, 1.79; S, 28.49%. Found: C, 42.65; H, 1.81; S, 28.49%. [Co(TTF-ph-tfac)₂(CH₃OH)₂], **2b** yield: 71%, mp: 135–136 °C. Maldi MS: calcd for $C_{32}H_{16}CoF_6O_4S_8$ [M-CH₃OH]⁺, 892.8; found, 892.8. Anal. calcd for C₃₂H₁₆CoF₆O₄S₈: C, 43.00; H, 1.80; S, 28.70%. Found: C, 43.01; H, 1.80; S, 28.72%.

Physical measurements

¹H and ¹³C NMR spectra were recorded on an Inova-500 instrument. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane. X-Ray powder diffraction data were collected with a Philips X'Pert MPD system with Cu-Ka radiation. The simulated powder XRD patterns of 2a were obtained from the single-crystal X-ray data using the Mercury program.¹⁷ Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. The mass spectrum was acquired in the positive ion mode on an Autoflex III MALDI-TOF/TOF mass spectrometer. The electrochemical properties were measured by an LK98B electrochemistry system. The magnetic susceptibility measurement on complex 2b was obtained on a polycrystalline sample with a Quantum Design SQUID magnetometer MPMS-XL. The dc measurements were collected from 2.0 to 300 K under 1000 Oe. Experimental data were also corrected for the sample holder and for the diamagnetic contribution calculated from Pascal constants.¹⁸

Results and discussion

Synthesis and structures

There are some kinds of similar reactions to result in the TTF derivatives with aryl groups.^{19,20} To prevent the observed decomposition of this tributylstannyl-TTF, we only evaporated the solvent under vacuum without further purification like other literature. Compound **1** was synthesized in a satisfactory yield (68%). Compound **2** was synthesized by Claisen condensation²¹ using compound **1** and ethyl trifluoroacetate

Complex	2a
Empirical formula	$C_{34}H_{24}F_6O_6S_8Zn_1$
$FW/g mol^{-1}$	964.38
T/K	298(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	5.2175(5)
b/Å	10.5765(10)
c/Å	34.092(3)
$\alpha/^{\circ}$	90
$\dot{\beta}/^{\circ}$	90.726(2)
γ /°	90
$V/Å^3$	1881.1(3)
Z	2
ρ (calcd)/g cm ⁻³	1.703
GOF	1.048
$R_1 [I > 2\sigma(I)], wR_2$	0.0559, 0.1275

under slightly modified conditions involving sodium hydride in dry THF at the temperature of -5 °C.

The X-ray data were collected at 298(2) K from a single crystal. Complex **2a** crystallizes in the monoclinic $P2_1/n$ space group (Table 1). The crystal structure analysis reveals that 2a is a mononuclear complex and the Zn atom lies on an inversion centre. The ligands connect the Zn^{II} centre in trans conformations through their O atoms of two TTF-ph-tfac anions in the equatorial plane. The octahedral coordination geometry around the metal is completed by two axial CH₃OH ligands, as shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The axial Zn–O(3) distance of 2.160(3) Å is slightly longer than the equatorial Zn-O distances that range from 2.020(3) to 2.086(3) Å, as a result of the negative charge and the chelating coordination mode of the trifluoroacetone part. The bond angles around the equatorial plane are in the range of 89.3° – 90.7° . The central C=C bond length of the TTF cores (1.338(7) Å) is in the average range for neutral donor cores.



Fig. 1 ORTEP drawing of **2a** at the 50% probability level (#1 represents the symmetry transformation used to generate equivalent atoms: 1 - x, -y, -z).

Table 2Selected bond lengths [Å] and angles [°] for complex $2a^a$

Zn-O(1) Zn-O(2)	2.086(3)	$O(1)$ -Zn- $O(2)^{\#1}$	90.7(1)
Zn-O(2) Zn-O(3)	2.160(3)	$O(1)=Zn=O(3)^{m}$ O(2)=Zn=O(3)	90.5(1)
O(1)-Zn-O(2) O(1)-Zn-O(3)	89.3(1) 91.4(1)	$O(2)-Zn-O(2)^{rr}$ $O(2)-Zn-O(3)^{\#1}$	180 89.5(1)
$O(1)-Zn-O(1)^{\#1}$	180	$O(3)$ -Zn- $O(3)^{\#1}$	180

^{*a*} #1 represents the symmetry transformation used to generate equivalent atoms by (1 - x, -y, -z).



Fig. 2 The plot of the H-bonding interactions of 2a.



Fig. 3 The plot of the main $S \cdots H$ interactions to construct the threedimensional structure of 2a.

As shown in Fig. 2, TTF-ph-tfac ligands in **2a** interact with methanol molecules through H-bonds $O(3)-H(18)\cdots O(1)^{\#2}$ (1.910(3) Å, symmetry code: -x + 2, -y, -z) to form columns along the *a*-axis. Then, the TTF cores of the columns are stacked *via* the S···H interactions to obtain the 3 dimensional (3D) structure. The distances of S···H are 2.99–3.00 Å (Fig. 3).

The analysis by Maldi mass spectrometry of **2a** and **2b** confirmed that the metal(II) center is chelated by two TTF-ph-tfac units. Unfortunately, the growth of **2b** single crystals suitable for the structure determination failed, although great efforts have been made. To verify whether **2b** is structurally similar to **2a**, powder XRD patterns were recorded for **2a** and **2b**, which are compared with the ones obtained from the single crystal X-ray data of **2a** by simulation. Unit cell parameters from powder XRD data of **2b** are obtained using the XRD analysis software MDI jade 7 (Materials Data Inc., Liverpool, CA), giving a = 5.20(1) Å, b = 10.51(1) Å, c = 34.10(3) Å, $\beta = 90.59(7)^{\circ}$, and Z = 2. The close similarity of XRD results (Fig. 4) let us to conclude that **2a** and **2b** are isomorphous complexes.²²



Fig. 4 Experimental powder XRD data of 2a and 2b vs. XRD patterns simulated from the single-crystal X-ray data of 2a.

Table 3 Cyclic voltammetric data ^a						
Compd.	$E_{\rm pc}(1)$	$E_{\rm pa}(1)$	$E_{1/2}(1)$	$E_{\rm pc}(2)$	$E_{\rm pa}(2)$	$E_{1/2}(2)$
1	0.52	0.60	0.57	0.76	0.84	0.80
2	0.51	0.60	0.56	0.76	0.85	0.80
2a	0.51	0.58	0.54	0.76	0.82	0.79
2b	0.50	0.57	0.54	0.75	0.82	0.79
a E in V			D. NDE	D4	141-	





Fig. 5 Cyclic voltammogram curves of 2, 2a, and 2b.

Electrochemical properties

The electrochemical properties of compounds 1, 2, 2a, and 2b were investigated by cyclic voltammetry and carried out at the room temperature under argon in THF with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte, Ag/AgCl as the reference electrode, and platinum as working and counter electrodes. The corresponding results are listed in Table 3. As shown in Fig. 5, two reversible single-electron oxidation waves are observed, corresponding to $E_{1/2}(1)$ and $E_{1/2}(2)$ of the TTF derivatives system. Upon coordination, the observed shifts always move toward more cathodic potentials and only $E_{1/2}(1)$ values are affected significantly, whereas $E_{1/2}(2)$ values remain almost unchanged. The downshift of the potentials can be explained by the formation of the negative enolate ion, which coordinates to the M(II) ions.

Magnetic investigations

Fig. 6 shows the magnetic behaviour of $[Co(TTF-ph-tfac)_2-(CH_3OH)_2]$ (**2b**) under an applied field of 1000 Oe in the form of $1/\chi_M vs. T$ and $\chi_M T vs. T$. The $\chi_M T$ value of **2b** at 300 K is 2.3 cm³ K mol⁻¹, which is higher than the spin-only value (1.875 cm³ K mol⁻¹) expected for a magnetically isolated highspin Co^{II} ion with g = 2.0 owing to the significant orbital contribution characteristic for the HS Co^{II} ion (for HS Co^{II}, the $\chi_M T$ value normally ranges from 2.3 to 3.4 cm³ mol⁻¹ K).²³ As the sample is cooled from room temperature, the $\chi_M T$ value only slightly decreases from 2.3 cm³ mol⁻¹ K to 2.2 cm³ mol⁻¹ K at 100 K and then decreases rapidly at low temperatures, reaching a value of 1.6 cm³ mol⁻¹ K at 2 K. For this complex, the decrease of the $\chi_M T$ product at low



Fig. 6 Plots of $\chi_M T vs. T$ and $\chi_M^{-1} vs. T$ for **2b**. The solid line shows the best fits to the model (see the text).

temperature may be ascribed to the presence of spin-orbit coupling and the intermolecular antiferromagnetic interaction. The high-temperature data (above 100 K) can be fitted to the Curie-Weiss law with $C = 2.30 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -0.29 \text{ K}$. This indicates a nearly perfect paramagnetic system with very weak antiferromagnetic interactions between the spin centres. As complexes **2a** and **2b** are isostructural, the nearest Co···Co separation should be *ca*. 5.218(3) Å for **2b** and TTF-ph-tfac ligands in **2b** interact with methanol molecules through H-bonds O-H···O (*ca*. 1.910(3) Å) to form columns along the *a*-axis (the same like those in **2a**). The hydrogen bonds should be the magnetic interaction pathway responsible for the weak antiferromagnetic interaction.

Conclusions

In this article, we described the synthesis and full characterization of a new TTF-ph-tfacH and its new coordination complexes 2a and 2b. The structural analysis from PXRD experiments shows that 2b has the identical crystal structure as that of 2a. In complex 2b, the TTF is neutral and therefore the magnetic properties reveal a paramagnetic behavior corresponding to isolated S = 3/2 spins of the Co^{II} centers with a weak antiferromagnetic coupling. Upon coordination, the observed shifts are found to move toward more cathodic potentials and only $E_{1/2}(1)$ values are affected, whereas $E_{1/2}(2)$ values remain almost unchanged. The downshift of the potentials can be explained by the formation of the negative enolate ion, which coordinates to the M(II) ions. Further researches on this novel attractive system will focus on the change of axial ligands by bridging ligands, to obtain quite sophisticated architectures and new functionalities and properties. Moreover, chemical and electrochemical oxidation of this complex to prepare radical-cation salts is currently under investigation in our group.

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