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An Original Redox-Responsive Ligand Based on a π-Extended TTF Framework

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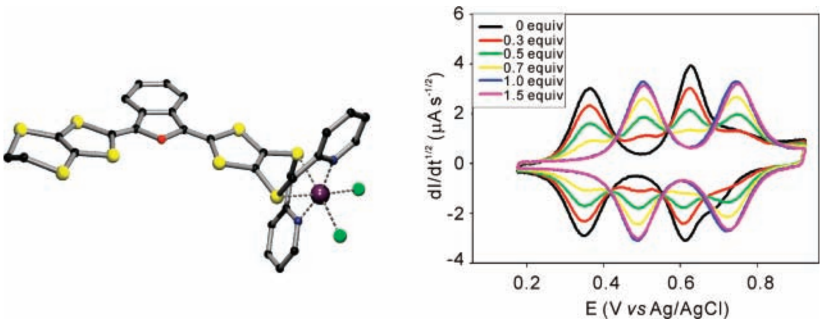
ABSTRACT



The synthesis of the first π-extended tetrathiafulvalene (TTF) ligand featuring a furanoquinonoid spacer and pyridyl functional groups is described. This compound shows an unprecedented electrochemical sensing behavior and excellent coordinating properties toward selected divalent metal ions. Solid-state structures of the free ligand and its Ni(II)Cl_2 complex are described.

The search for molecular organic metals based on tetrathiafulvalene (TTF) derivatives has triggered the development of π-extended analogues.[1,2] It has been demonstrated that the extension of the TTF core not only leads to stabilized oxidized states and easy access to polycation states due to a diminution of Coulombic repulsion and mesomeric effects but also gives rise to an energetically narrower HOMO−LUMO gap.[1] Moreover, it can enhance the dimensionality in materials by increasing the number of $\pi-\pi$ and/or chalcogen⋯chalcogen interactions.[2] As a consequence, a variety of π-extended TTF derivatives have been prepared. However, to the best of our knowledge, no π-extended TTF systems which incorporate binding sites for the complexation of transition-metal ions have been reported yet. On the other hand, plenty of TTF derivatives, which act as ligands toward metal ions, have been studied in the fields of redox-active sensors, multifunctional materials, artificial antenna systems, and single-component molecular metals.[3] Almost all reported systems are based on TTF derivatives with an unaltered central TTF core. In the context of recognition of metal ions in redox-active sensors, a large amount of work has mainly focused on TTF crown ether derivatives,[4] while other systems

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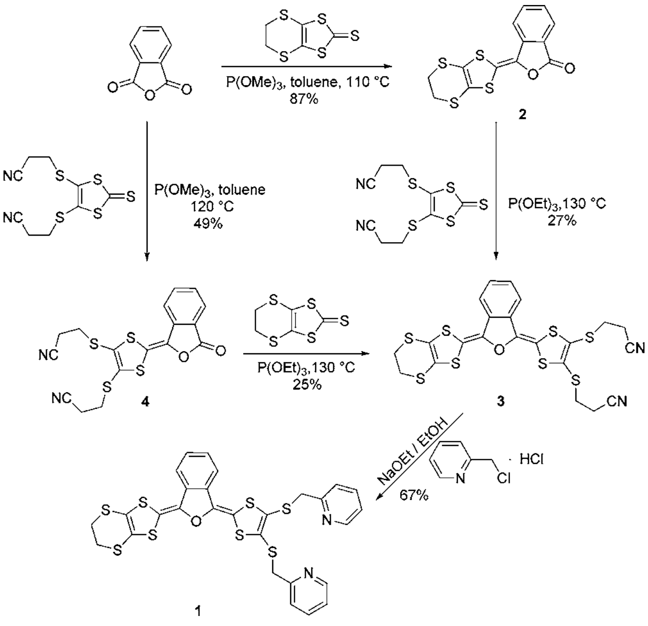
associate the TTF moiety to noncyclic binding units such as polyether chains or pyridyl units.[5] Following these considerations, an extended TTF based ligand **1**, featuring a furanoquinonoid spacer and pyridyl functional groups, has been prepared. It should be pointed out that this compound is designed to permit the detection of metal cations by binding-induced changes in the redox properties and also to improve the π−d interactions between the conducting π electrons and localized d spins upon oxidation of its corresponding paramagnetic transition metal complexes.[6] Herein, we report the synthesis of the π-extended TTF ligand **1** incorporating pyridyl moieties and demonstrate that **1** acts as a highly effective redox sensor for the detection of Ni^{2+}, Pd^{2+}, and Pb^{2+} ions.

Following the similar synthetic procedure reported for the preparation of furanoquinonoid extended TTF systems[7] and taking advantage of the well-established cyanoethyl deprotection method,[3,8] the extended TTF ligand **1** was obtained (Scheme 1). The key precursor **3** was synthesized via a triethyl phosphite mediated cross-coupling reaction starting from two different chalcogenone precursors **2**[7c] and **4**. The latter were prepared in good yields by the cross-coupling reaction of phthalic anhydride with the corresponding thiones in the presence of an excess of trimethylphosphite in refluxing toluene. Finally, **3** undergoes a deprotection reaction under basic conditions and a subsequent nucleophilic displacement reaction with 2-picolylchloride to afford **1** in 67% yield. The molecular structures of all compounds were confirmed by spectroscopic data (NMR, MS, IR) as well as by X-ray structure analysis in the case of **1** and its Ni(II) complex.

Scheme 1. Synthesis of the Extended TTF Ligand **1**



Ligand **1** crystallizes as yellow blocks in the triclinic space group $P\bar{1}$. Its molecular structure is shown in Figure 1. Both dithiafulvenyl rings are slightly tilted to opposite sides of the benzofurano mean plane by 8.3° (C1−C2−C5 ring) and 2.3° (C14−C15−C16 ring), respectively. This deviation from planarity may be attributed to steric hindrance between periplanar H atoms of the central benzenic ring and S atoms of dithiafulvenyl heterocycles, with S1−H8A (2.692 Å) and S6−H11A (2.647 Å) distances.

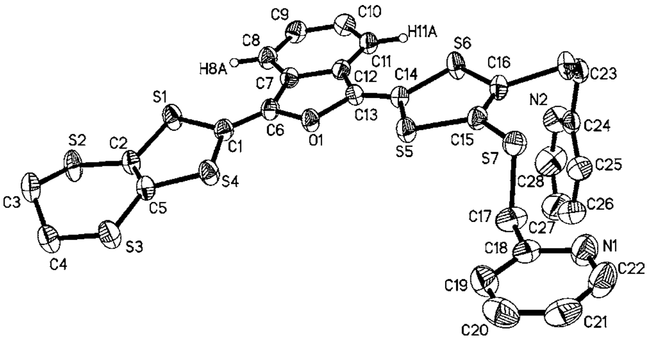


Figure 1. ORTEP (50% probability ellipsoids) structure of **1**. Hydrogen atoms are partially omitted.

The ligand **1** is capable of binding to metal ions in a chelating, tetradentate manner. For example, orange needle-like single crystals grew from a methanol/dichloromethane solution of NiCl$_2$ and ligand **1**, resulting in [Ni(**1**)Cl$_2$]·CH$_3$OH·(CH$_2$Cl$_2$)$_{0.5}$ (space group $\bar{P}1$). Figure 2 depicts the molecular structure. The Ni(II) atom is cis-coordinated to two chloride atoms (Ni−Cl 2.345(2), 2.368(2) Å), trans-coordinated to two pyridyl nitrogen atoms (Ni−N 2.094(6), 2.097(5) Å), and chelated by the two sulfanyl sulfur atoms (Ni−S 2.403(2), 2.418(2) Å), which is, from this point of view, in analogy to the Ni(II) complex with the corresponding non-extended TTF ligands.[6a] The largest distortion from idealized octahedral geometry around the nickel ion is observed for the pyridyl nitrogen atoms (N1−Ni1−N2 165.7(2)°).

In the crystal structure the complexes are stacked in a head-to-tail manner along the *a*-axis (Supporting Information). These stacks are linked by some unconventional C−H···Cl

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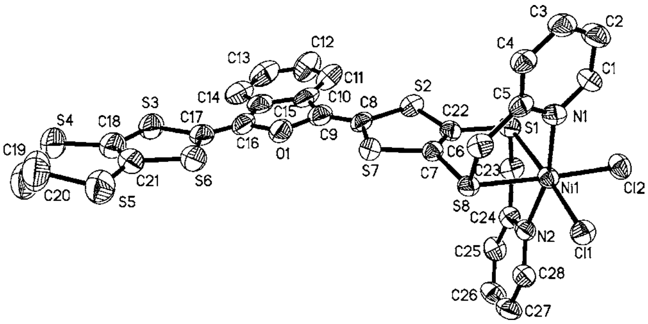


Figure 2. ORTEP (50% probability ellipsoids) structure of [Ni-(**1**)Cl_2]. Hydrogen atoms and solvent molecules are omitted.

contacts but no short inter- or intrastack S···S contacts are observed due to the bulky coordination sphere. Interestingly, the stacking forms alternating organic and inorganic layers, similar to the crystal packing usually observed in conducting CT salts.

The extended TTF ligand **1** undergoes two well-separated reversible one-electron oxidation processes to the radical cation and the dication, respectively. In general, recognition of a given metal cation by TTF-based redox-responsive ligands is manifested by a positive shift of the first oxidation potential E^1_{ox}. This corresponds to a decrease in its π-donating ability as a result of the binding of a positively charged guest ion in close proximity to the TTF core.[4] However, usually the second oxidation potential E^2_{ox} remains almost constant, independent of the amount of the added metal cation, which is attributed to the expulsion of the cation because of electrostatic forces between the cation and the doubly oxidized TTF^{2+} unit. It is noteworthy that a slightly positive shift of E^2_{ox} was recently observed upon addition of Pb^{2+} ions to the vinyl- or acetylene-linked pyridine−TTF systems.[5]

The electrochemical recognition ability of ligand **1** was investigated by cyclic voltammetry (CV). A variety of metal cations were tested: Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ni^{2+}, Pd^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, but only Ni^{2+}, Pd^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} gave significant responses (Table 1). Figure 3 presents the deconvoluted cyclic voltammogram of **1** as a function of added Pd^{2+} concentration.

Table 1. Oxidation Potentials of **1** and Shifts of Potentials in the Presence of Selected Transition Metal Ions[a]

	1	**1** + Zn^{2+}	**1** + Cd^{2+}	**1** + Pb^{2+}	**1** + Pd^{2+}	**1** + Ni^{2+}
E^1_{ox}	390	470	460	480	540	540
$\Delta E^{1\,b}$		+80	+70	+90	+150	+150
E^2_{ox}	650	650	650	680	780	790
$\Delta E^{2\,b}$		0	0	+30	+130	+140

[a] The data are given in mV vs AgCl/Ag in CH_2Cl_2/CH_3CN (1/1) and $^nBu_4NPF_6$ (0.1 mol dm^{-3}) as the supporting electrolyte, [**1**] = 1 mmol dm^{-3}. [b] In the presence of 1.5 equiv of M^{2+}.

In the case of Zn^{2+} and Cd^{2+}, positive shifts of E^1_{ox} are observed, whereas E^2_{ox} remains unchanged, indicating that expulsion of the cations from the ligand coordination sphere must take place at the second potential. This can be described with the equilibrium processes shown in Scheme 2 in black.

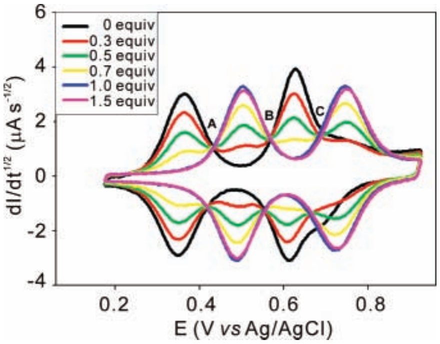
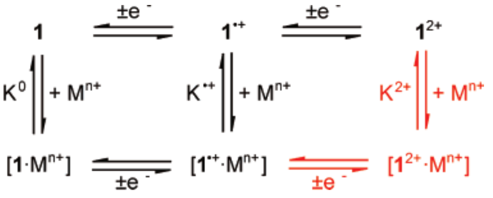


Figure 3. Deconvoluted cyclic voltammogram of compound **1** (10^{-3} M) in the presence of increasing amounts of $Pd(ClO_4)_2$: CH_2Cl_2/CH_3CN (1/1); Bu_4NPF_6 (0.1 M); 100 mV/s; Pt working electrode, diameter 1 mm.

Scheme 2. Equilibrium Reactions during the Electrochemical Titration of **1** with M^{n+} [a]



[a] Black: M^{n+} = Ni^{2+}, Pd^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. Red: M^{n+} = Ni^{2+}, Pd^{2+}, and Pb^{2+}.

In contrast to these metal cations, the addition of Pb^{2+} results not only in a large positive shift of E^1_{ox} but also in a small shift of E^2_{ox}. From the change in the second potential it may therefore be deduced that Pb^{2+} must still be coordinated to the dication $\mathbf{1}^{2+}$. An expansion of the square scheme can therefore be proposed, as shown in red in Scheme 2. Remarkably, this behavior is even more pronounced in the cases of Ni^{2+} and Pd^{2+}, giving rise to an unprecedented four-wave behavior (Figure 3). At particular potentials (A−C), constant currents upon addition of metal cations are observed, as is the case for isosbestic points in spectroscopy, indicative of a concomitant appearance of the corresponding complex at the expense of the free ligand **1**. It is the first time that the large shifts (ca. 150 mV) of the two oxidation potentials of TTF-based sensors have been reported. This observation accounts for the high stability of the metal complexes even though the redox unit is oxidized to the dication. This remarkably illustrates the effect of the π-extension of the TTF backbone, with a lowering of Coulombic repulsion between the oxidized redox unit and the metal cation.

A comparison of the ^1H NMR spectra ($CD_3CN/CDCl_3$ (1:1), 298 K) of ligand **1** in the absence and presence of Pb-

$(ClO_4)_2$ reveals significant chemical shift differences particularly for the resonances associated with the pyridine protons. As a result, ^{1}H NMR titration experiments were carried out to determine the binding constant (K). Addition of an excess of Pb^{2+} ($>$1.0 equiv) does not cause any further changes in the ^{1}H NMR spectrum of **1**, suggesting the formation of the stoichiometric **1**·Pb^{2+} complex. The binding constant was obtained using the curve fitting program[9] EQNMR, giving an average log K value of 5.0 for the **1**·Pb^{2+} complex (Supporting Information).

Ligand **1** is the first example of an extended TTF derivative functionalized with binding site groups for transition metal ions. Its binding properties toward a variety of metal ions were investigated by single-crystal X-ray analysis, CV as well as ^{1}H NMR in the case of Pb^{2+}. CV titration experiments reveal strong positive shifts of the two oxidation potentials of **1** in the presence of Ni^{2+}, Pd^{2+}, and Pb^{2+}. Particularly, the observation of a four-wave behavior in the case of Ni^{2+} and Pd^{2+} accounts for the high stability of the complex, even when the ligand **1** is oxidized to the dication. In summary, the construction of the first redox-responsive system based on an extended TTF framework leads to an unprecedented electrochemical behavior in the series of TTF-based ligands.

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Supporting Information Available: Experimental procedure and characterization data for compounds **1**−**4**; NMR spectra of compounds **1**, **3**, and **4**; NMR titration measurements of ligand **1** with Pb^{2+}; CIF files for **1** and its Ni^{2+} complex as well as crystal packing of Ni^{2+} complex with **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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