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Tetrathiafulvalene–Imine–Pyridine Assemblies for Pb^{2+} Recognition

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A series of donor–π–acceptor systems incorporating a tetrathiafulvalene moiety as the donating unit have been designed and synthesized. The efficiency of the imine (–C=N–) bond as a conjugated π-linker in promoting intramolecular charge transfer is demonstrated and supported by calculations at the B3LYP/6-31G(d,p) level of theory. This property has been explored in the case of pyridyl-substituted systems which exhibit in particular a high binding affinity and selectivity for Pb^{2+} ($\log K = 3.5$ in CH_2Cl_2/CH_3CN), as shown by UV/Vis and ^1H NMR titrations as well as by remarkable colorimetric and electrochemical signaling.

Introduction

Tetrathiafulvalene (TTF) and its derivatives are well-established organic π donors (D) which have been extensively studied for various applications, in particular, in the field of conducting organic materials involving intermolecular charge-transfer interactions with various π-accepting molecules (A).[1] In the last decade, a strong interest has also emerged in D–A systems that are covalently grafted through a π- or σ-bonded molecular bridge, in particular because of their potential application in fields such as molecular electronics, nonlinear optics, and photovoltaics. Such systems potentially present low HOMO–LUMO gaps which is of prime importance for the good performance of organic electronic devices.[2] The tuning of the HOMO–LUMO gap by applying external stimuli remains a challenge and therefore the development of responsive D–A systems is very appealing. In this context, TTF derivatives have been widely used as the donor D counterpart.[1e,3] Such responsive systems with valuable optical and electronic properties are also highly desirable in redox sensor materials. On the other hand, the introduction of a pyridine unit as the electron-acceptor part in a D–A system appears promising as its well-known coordination properties with metal cations should modify the electron effect promoted by the A unit. A number of TTF–pyridine systems have already been described[4] for different purposes; in particular the coordination properties of the pyridyl unit in the solid state have been explored. However, very few of these systems have been investigated as potential responsive ligands in solution.[4a,4d,4e] We have been involved for some years in the construction of TTF-based redox-responsive ligands whose redox properties are altered upon cation or anion binding.[5] The working mode of such systems is based on through-space electrostatic interactions between the redox-active TTF core and the bound charged guest. Alternatively, perturbation of the electronic properties of such systems may also be observed if the redox-active and the binding subunits are connected though a conjugated π system through a so-called through-bond interaction.[6] Of course, in this case the nature of the conjugated junction is of critical importance. Comparison between double bond and triple bond linkers has already been made on various occasions. In the case of TTF derivatives, we have compared the behavior of acetylenic-conjugated derivatives with that of their ethylenic analogues.[7] Recent reports in the literature by Wu and Tung and their co-workers describe and compare the efficiency of intramolecular charge transfer in TTF–CH=CH–pyridine (**A**)[4d,4r] and TTF–C≡C–pyridine (**B**) ligands.[4a] These reports prompted us to describe our findings concerning the use of the imine junction which can be introduced as an alternative π-linker. Imine derivatives are generally very easy to prepare compared with other multiple-bond linkers such as azine, ethylenic, or acetylenic derivatives. They have already been investigated and advantageously used as conjugated linkers in different delocalized systems involving, for example, metallocenes,[8] conjugated polymers,[9] or porphyrinic systems.[10] Therefore we propose here to complete the study on TTF–π–pyridine systems that have been reported in the literature[4a,4d] by studying the efficiency of the imine junction as a conjugated linker in intramolecular charge transfer.

The synthesis of TTF–imine derivatives by the aza-Wittig methodology is described herein for the first time. The geometry optimization and orbital energies of the prototype system, imine **3a**, have been calculated by DFT. The role

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of the imine bond as a conjugated linker is illustrated by absorption spectroscopy studies. In particular, the strength of the electron-acceptor subunit can be tuned either by changing substituents or by the binding of a metal cation to the pyridyl unit. The colorimetric response in the case of lead(II) proved remarkable. The binding event is also demonstrated by ^{1}H NMR titration studies and the redox-responsive behavior by cyclic voltammetry experiments. In short, such electroactive systems allow the extent of π conjugation as a function of the binding state to be probed.

Results and Discussion

Frontier Orbitals

In order to check the effect of an imine connecting bond on the geometry and the delocalization state of the conjugated system, we calculated the optimized geometry and the orbital energies of compound **3a**, that is, the simplest system containing the basic elements of a TTF–π–pyridine structure. The analysis was performed by ab initio density functional calculations using the Gaussian03 software package.[11] Becke's three-parameter gradient-corrected functional (B3LYP) with a polarized 6-31G(d,p) basis set was used for full geometry optimization. Frontier orbitals are given in Figure 1 and demonstrate that most of the electron density of the HOMO is located on the TTF fragment, while the LUMO is essentially distributed over the pyridine–imine–dithiole ensemble. This qualitative result is very similar to observations made with the ethylenic or acetylenic analogues **A** and **B**. The dihedral angle between the pyridine unit and the 1,3-dithiole moiety appears[12] slightly higher in **3a** than in the ethylenic analogue **A** (39 vs. 33°, respectively), accounting for a more important distortion around the imine junction. This tendency has already been observed, for example, with (*E*)-benzalanilines and (*E*)-stilbenes.[13] This difference does not seem to alter significantly the HOMO and LUMO energies of **3a**, which appear only slightly lower than those of **A** (**A**: E_{HOMO} = –4.708 eV; E_{LUMO} = –2.014 eV), as expected from the contribution of the electron-accepting imine nitrogen atom. Note, the difference in the HOMO–LUMO energies is exactly the same (= 2.694 eV) whether the junction is imine or ethenyl, which illustrates a similar efficiency in the conjugation of the delocalized system.

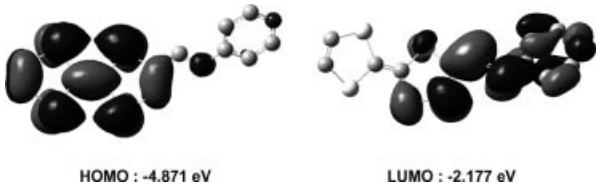
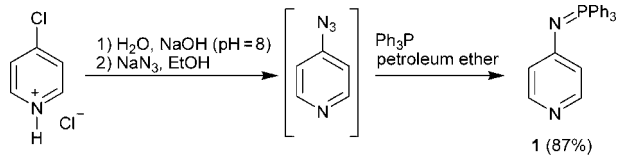


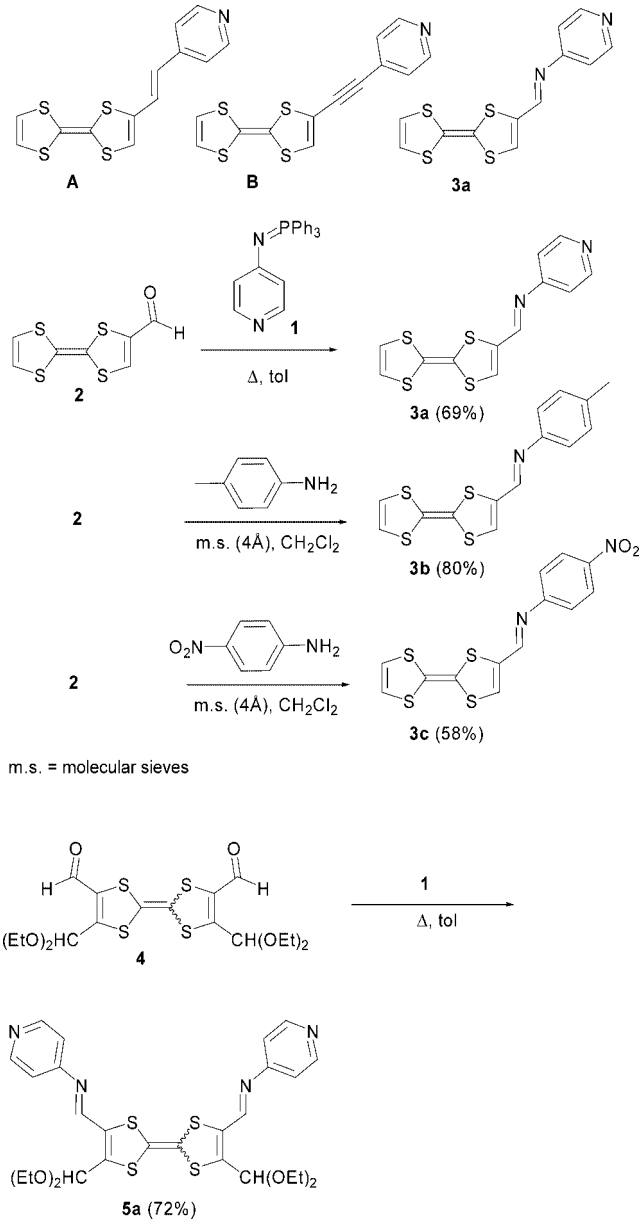
Figure 1. Frontier orbitals of **3a** calculated by DFT at the B3LYP/6-31G(d,p) level of theory.

Synthesis

Imine–TTF derivatives **3b**,**c** were prepared by treatment of the corresponding TTF aldehyde **2** with an aromatic amine in the presence of molecular sieves (4 Å) (see Scheme 2). Unlike observations made recently upon the synthesis of the 2-pyridyl isomer of **3a**[4b] or with a calixarene–imine–TTF derivative,[14] yields appeared to be low. Also the reactions proved to be time-consuming when synthesizing the pyridine derivatives **3a** and **5a** under these experimental conditions. We therefore developed an alternative strategy using the aza-Wittig reaction. The scope and



Scheme 1. Synthesis of the iminophosphorane **1**.



Scheme 2. Synthesis of the conjugated TTF–imine systems.

efficiency of this reaction have been reviewed recently.[15] Iminophosphorane **1** was synthesized from 4-aminopyridine and dibromotriphenylphosphorane (Ph_3PBr_2) according to a literature procedure.[16] The yield of **1** obtained by this route was moderate and nonreproducible in our hands (35–50%) and we therefore developed an alternative method starting from *p*-chloropyridine hydrochloride (Scheme 1). The 4-azidopyridine[17] intermediate was not isolated and was directly engaged in a Staudinger reaction with triphenylphosphane to afford iminophosphorane **1** in high yield. This methodology provides a new and expedient access to **1**, which is a very useful synthetic intermediate.

The aza-Wittig reaction was then carried out on formyl-TTF **2**[18] or diformyl-TTF **4**,[19] producing the target TTF–imine–pyridine derivatives **3a** and **5a** (*Z* + *E* isomers) in good yields (Scheme 2).

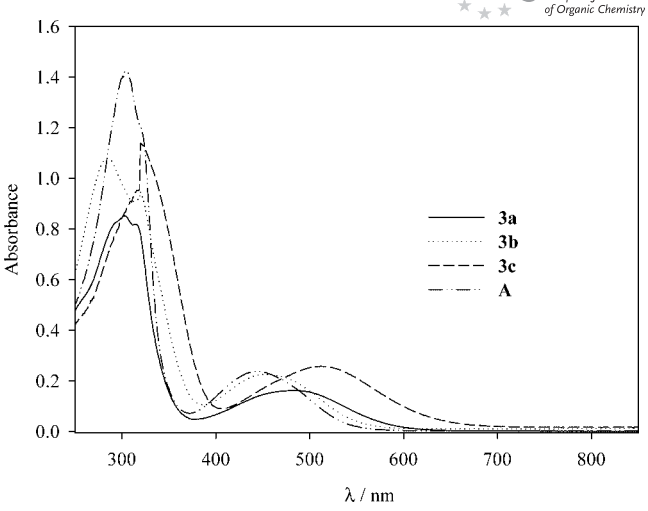


Figure 2. Absorption spectra of TTF derivatives **3a**–**c** in CH_2Cl_2/CH_3CN ($c = 5\times10^{-5}$ mol L^{-1}).

Absorption Spectroscopy

The TTF derivatives **3** and **5** exhibit absorption spectra with similar shapes, that is, a strong absorption band (extinction coefficients $\varepsilon \approx 2\times10^4$ dm^3 mol^{-1} cm^{-1}) at a high energy ($\lambda < 350$ nm) and a moderate absorption band in the region 380–650 nm (Table 1 and Figure 2). Note, the latter is not present in the parent unsubstituted TTF system studied under the same conditions and is also absent in a solution containing a mixture of TTF and pyridine which underlines the intramolecular connecting role of the conjugated linker. The higher energy band was therefore assigned to a local transition within the TTF moiety whereas the lower energy absorption corresponds to intramolecular charge transfer (ICT) from the HOMO in TTF to the LUMO in the electron-accepting unit.

Table 1. Maximum absorption wavelength[a] (λ_{max}) and oxidation potentials[b] (E^i_{ox}) of compounds **3** and **5**.

	3a	**3b**	**3c**	**5a**	**A**
λ_{max} [nm]	484	453	512	510	444
E^1_{ox} [V] vs. Ag/AgCl	0.47	0.43	0.47	0.58	0.37
E^2_{ox} [V] vs. Ag/AgCl	0.86	0.86	0.88	0.98	0.78

[a] $c = 5\times10^{-5}$ M in CH_2Cl_2/CH_3CN (1:1, v/v). [b] $c = 1\times10^{-3}$ mol L^{-1} in CH_2Cl_2/CH_3CN (1:1, v/v), 100 mV s^{-1}, NBu_4BF_4 ($c = 10^{-1}$ mol L^{-1}).

As expected from the electron effect induced by the substituents, a significant variation in λ_{max} is observed between the tolyl derivative **3b** (453 nm) and the electron-accepting nitrophenyl derivative **3c** (512 nm). In agreement with the moderate electron-accepting character of the N-heteroaromatic ring, the pyridyl-substituted derivatives **3a** and **5a** exhibit intermediate values. Note, the λ_{max} values of the imine derivatives **3a**,**c** are significantly higher (a systematic redshift of around 50 nm) than those of the corresponding ethylenic or acetylenic analogues, that is, λ_{max} = 512 nm for **3c** compared with 465 nm for its acetylenic analogue (recorded in acetonitrile)[4a] and λ_{max} = 484 nm for the pyridyl derivative **3a** compared with 444 nm for **A** or 432 nm for **B** (recorded in acetonitrile).[4a] In short, these observations account for 1) an efficient electronic communication allowed by the imine junction between the TTF electron-donating part and the electron-accepting counter unit, similar to that of ethylenic or acetylenic linkages, and 2) the electron-accepting contribution of the nitrogen atom of the imine junction.

The absorption spectra of **3c**, taken as an illustrative example, were also recorded in solvents of various polarities (see Table S1 in the electronic supporting information). This study shows a negative solvatochromism (λ_{max} = 499 and 522 nm in acetonitrile and toluene, respectively), that is, a blueshift when the polarity is increased, in accordance with intramolecular charge transfer.

Cyclic Voltammetry

Compounds **3a**–**c** and **5a** exhibit the usual two-step reversible one-electron oxidations of TTF derivatives, corresponding to the successive formation of a cation radical and a dication (Table 1). Small differences are observed in the oxidation potentials (E^i_{ox}) of **3a**–**c**, in good agreement with the electron effect of the substituent on the aromatic part. The tolyl-substituted system **3b** appears easier to oxidize than the electron-accepting nitrophenyl and pyridyl derivatives **3c** and **3a**, confirming a conjugation through the imine junction. In addition, as already shown by the calculations of E_{HOMO} in the gas phase, the solution electrochemistry demonstrates 1) that compound **3a** is a very good π donor (low E^1_{ox} potential) and 2) that this π-donating ability is slightly less than that of the ethenyl analogue **A**, as expected from the electron-accepting character of the imine nitrogen atom in **3a**.

Binding Properties: UV/Vis Titrations

The pyridyl moiety is well known for its coordination to various metal cations through the donating nitrogen atom. Binding studies carried out on TTF–imine–pyridine com-

pounds therefore could help to probe the efficiency of the imine junction as a conjugated linker. In particular, coordination of a cation by the pyridyl part should, if ICT between TTF and the acceptor moiety occurs, be accompanied by exploitable optical or electrochemical outputs. We therefore investigated the metal binding of a wide range of cationic solutions (Na^+, Cs^+, Ba^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Zn^{2+}, and Pb^{2+}) to TTF derivatives **3a**. Remarkably, we observed a spectacular color change in the solution of **3a**, from orange to deep blue, when a Pb^{2+} solution was introduced, whereas the introduction of alkali or alkaline-earth cations did not provoke any color change (see Figure S1 in the electronic supporting information). In addition, only a moderate color change was observed with other transition metals. The affinity of pyridyl coordinating groups towards lead(II) is well established. An immediate consequence of such a binding affinity lies in the possibility of using **3a** for the colorimetric detection of Pb^{2+}.

Absorption spectroscopy titration experiments were carried out by the progressive introduction of a lead perchlorate solution into a solution of the 4-pyridyl derivative **3a** in CH_2Cl_2/CH_3CN (Figure 3). The resulting electronic spectra

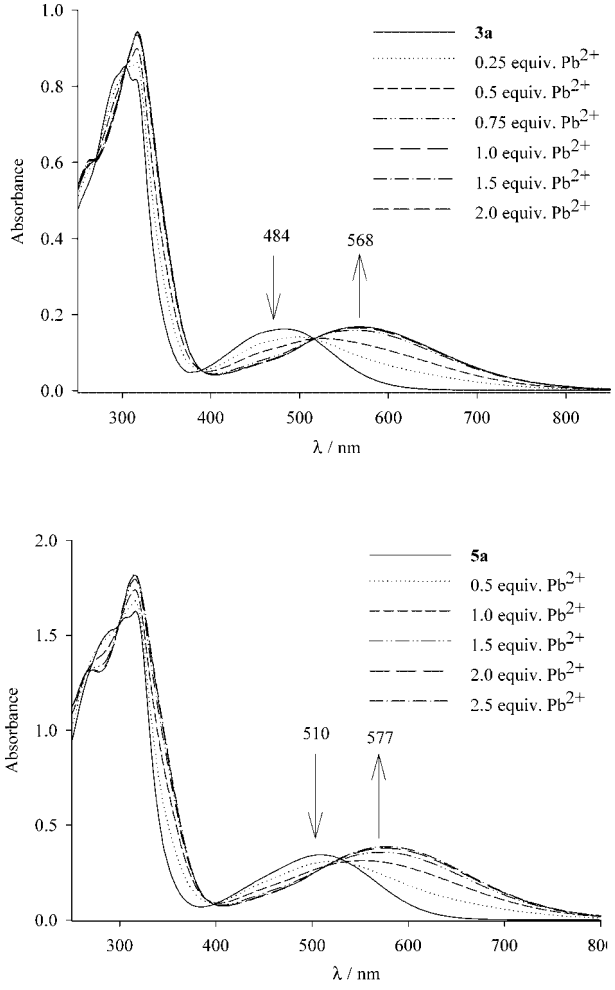


Figure 3. UV/Vis titration study of **3a** (top) and **5a** (bottom) [$c = 5 \times 10^{-5}$ mol L^{-1} in CH_2Cl_2/CH_3CN (1:1, v/v)] in the presence of $Pb(ClO_4)_2$.

clearly show the appearance of a new low-energy band centered on 568 nm, detrimental to the initial ICT band at 484 nm, and the color of the solution was observed to change from orange to blue. This progressive change in the spectra revealed isosbestic points at 305, 389, and 516 nm, correlated to the presence of only two species in equilibrium in solution, namely the free ligand **3a** and the **3a**·Pb^{2+} complex. Note, no more absorption changes were observed on addition of in excess of 1 equiv. of $Pb(ClO_4)_2$ suggesting a 1:1 stoichiometry of the complex. Control experiments were carried out by adding aliquots of lead(II) solutions to **3c**. No change in the absorption spectrum was observed (Figure S2) indicating that coordination takes place exclusively at the pyridyl nitrogen atom in **3a** and that no metal binding contribution exists from the imine nitrogen atom.[20] The binding constant was evaluated using the Benesi–Hildebrand method[21] (Figure S3) and gave a $\log K$ value of 3.5 in a CH_2Cl_2/CH_3CN mixture. Binding of the lead cation by the pyridyl unit is therefore accompanied by a spectacular redshift of the ICT band of 84 nm, illustrating the fact that the electron-accepting ability of the pyridyl moiety is increased once coordinated to a cation leading to a lowering of the energy of the ICT band. Very similar behavior was observed with the dipyridyl derivative **5a** for which a new band developed at +67 nm. The same $\log K$ value (= 3.5) as for **3a** was observed with, in this case, a 2:1 stoichiometry between the metal cation and the ligand (Figure 3 and Figure S4). Such experimental findings confirm the favorable conjugation promoted by the imine group across the whole molecule.

Binding Properties: ^{1}H NMR Titrations

^{1}H NMR titration experiments were carried out by introducing aliquots of $Pb(ClO_4)_2$ into deuteriated (CD_3CN/CD_2Cl_2) solutions of **3a**. The evolution of the NMR spectra is presented in Figure 4. Significant changes are observed upon the introduction of the lead(II) solution, in particular for pyridyl signals H_b, which are shifted downfield, and TTF protons ($H_{1,2,3}$), which gradually disappear. At this stage, the location of the metal binding on ligand **3a** needs to be confirmed since in principle two nitrogen binding sites coexist and because, considering the molecular geometry of the ligand, the two =N– atoms cannot both contribute to the binding in a cooperative way.[22] As for the UV/Vis studies described above, it appears that the ^{1}H NMR spectrum does not vary when more than 1 equiv. of cation is added during the titration, confirming a 1:1 stoichiometry of the complex between **3a** and Pb^{2+}. This point, together with the fact that the ^{1}H NMR shifts observed upon the binding of Pb^{2+} by **3a** are very similar to those observed under the same conditions with compound **A** (Figure S5), devoid of an imine nitrogen atom, confirm that the binding process takes place on the pyridyl nitrogen atom. This finding therefore is markedly different to a very recent observation made with the 2-pyridyl isomer of **3a**, for which a cooperative Cu^{II} binding mode involving both nitrogen atoms was reported by the authors.[4b,22] Again, very similar behavior

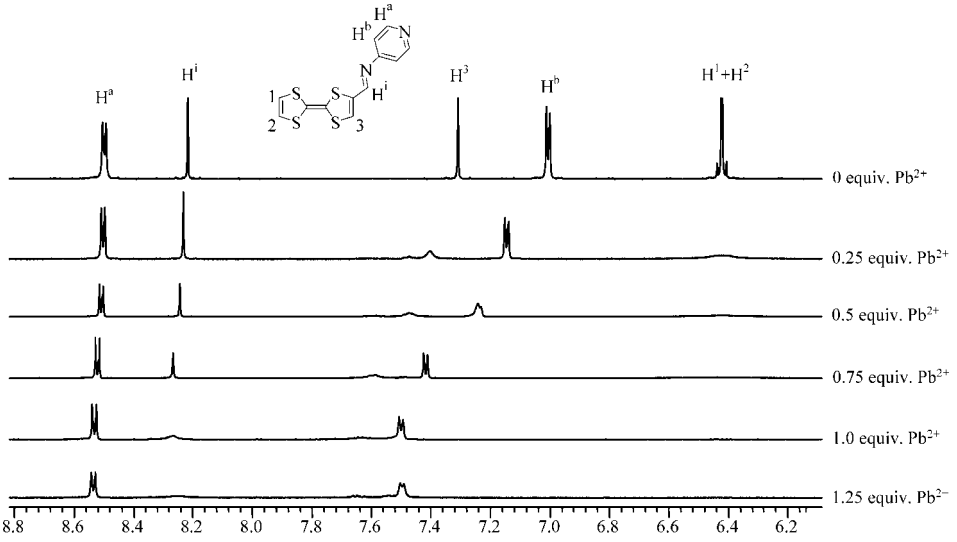


Figure 4. ^1H NMR spectra of **3a** ($c = 9.5 \times 10^{-3}$ mol L^{-1}) in CD_3CN/CD_2Cl_2 (1:1, v/v) in the presence of increasing amounts of $Pb(ClO_4)_2$.

was observed for the dipyridyl analogue **5a** (Figure S6) with no additional variation in the chemical shifts on addition of more than 2 equiv. of lead(II) cations.

Binding Properties: Cyclic Voltammetry

Treatment of an electrolytic solution of **3a** with lead perchlorate in a CH_2Cl_2/CH_3CN mixture causes significant changes in the TTF oxidation potentials (Figure 5) which are significantly shifted to higher potentials with an excess of lead(II) (**3a**: $\Delta E^1_{ox} = +48$ mV; $\Delta E^2_{ox} = +28$ mV). These values do not evolve further on addition of more than 1 equiv. of metal cation. Similar qualitative behavior was observed with compound **5a** (Figure S7). Therefore the redox-active TTF moiety appears more difficult to oxidize once Pb^{2+} is bound to the pyridyl unit. Such variation can be explained by the increase in the electron-accepting character of the pyridyl unit once it is bonded to a metal cation which therefore alters the donating ability of the TTF unit. It has to be noted that this redox behavior is different to that observed with TTF-based redox-switchable ligands, which classically correspond to a spatially close association of a TTF moiety and a binding unit [e.g., poly(ethylene glycol)]. In these cases the second redox potential, corresponding to TTF^{2+} formation (E^2_{ox}), remains constant, which corresponds to the expulsion of the initially bound metal cation outside of the binding site because of through-space electrostatic interactions between TTF^{2+} and the metal cation.[5g] The situation is of course different with **3a** for which there is no possible electrostatic through-space interaction between the bound cation and the oxidized TTF framework and therefore the electrochemical potential changes are in this case assigned to a through-bond interaction.[6] As expected, compounds **3c**,**d**, devoid of pyridyl-coordinating units, did not undergo any change to their CV upon addition of lead perchlorate (Figure S8).

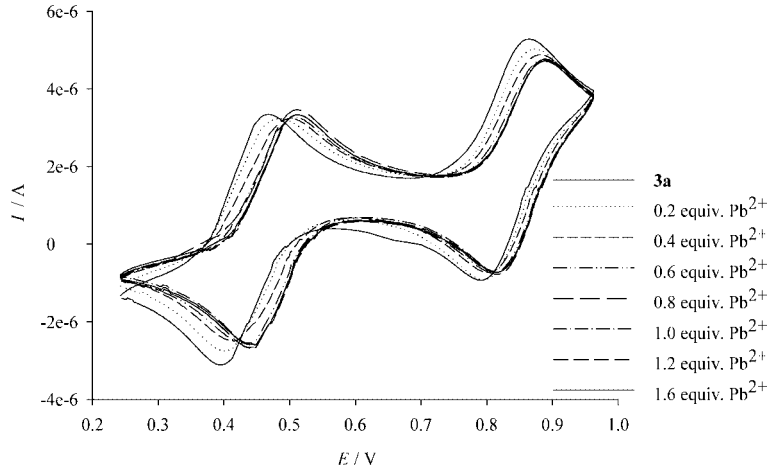


Figure 5. CV titration of compound **3a** ($c = 7.5 \times 10^{-4}$ mol L^{-1}) in CH_2Cl_2/CH_3CN (1:1, v/v) in the presence of increasing amounts of lead perchlorate [70 mV s^{-1}, NBu_4BF_4 ($c = 10^{-1}$ mol L^{-1}), vs. Ag/AgCl].

Conclusion

A family of TTF–C=N–A derivatives (A = acceptor unit) have been synthesized by a straightforward aza-Wittig coupling reaction. Spectroscopic and electrochemical measurements demonstrate the efficiency of the conjugated imine bond in intramolecular charge transfer between TTF and the acceptor unit. This behavior is similar to that observed with related compounds bearing an ethylenic or acetylenic linker. This ICT ability was further explored in the case of pyridyl-substituted systems for which it is possible to tune the ICT upon lead(II) coordination and which is accompanied by remarkable color changes (orange to deep blue) as well as by positive shifts of the two redox potentials of the TTF unit as a result of a through-bond interaction.

Experimental Section

Materials and Reagents: Where necessary, solvents were purified prior to use and stored under nitrogen. Unless stated otherwise, commercial grade chemicals were used without further purification. NMR spectra were recorded with a Bruker Avance DRX 500 instrument. The mass spectra were recorded with a Bruker Biflex-IIITM (MALDI-TOF), a JEOL JMS 700 (HRMS-EI), or a Thermoelectron Trace DSQ spectrometer (EI). IR spectra were recorded with a FTIR BIORAD FTS 155 spectrometer. The cyclic voltammetry (CV) studies were carried out by using an EGG PAR 273 or 273A potentiostat.

Iminophosphorane 1: Compound **1** was initially prepared from 4-aminopyridine and dibromotriphenylphosphorane (Ph_3PBr_2) according to a literature procedure.[16] However, the yield of **1** was moderate and nonreproducible in our hands (35–50%) and we therefore developed an alternative method to reach **1** starting from *p*-chloropyridinium chloride.

4-Chloropyridinium hydrochloride (34.8 g, 231.98 mmol) was dissolved in water (115 mL) and a solution of sodium hydroxide (6 M) was added until neutral pH. Ethanol (115 mL) was then added as well as NaN_3 (30 g, 461 mmol). The solution was heated at reflux for one night and then successively concentrated in vacuo and extracted with diethyl ether (3 × 350 mL). The organic phase are dried with $MgSO_4$ and the solvent evaporated to afford an orange volatile liquid corresponding to 4-azidopyridine. This liquid was dissolved without purification in petroleum ether (100 mL) and added dropwise to a solution of triphenylphosphane (61 g, 232.57 mmol) in petroleum ether (800 mL). The formation of the iminophosphorane **1** was manifested by evolution of nitrogen gas and precipitation of a white solid. The reaction mixture was stirred for an additional 4 h and filtered through a glass frit. The solid was washed with warm petroleum ether (500 mL) and dried in a desiccator. Compound **1** was obtained as a white solid (71.55 g, 202.12 mmol, 87% yield). M.p. 154–155 °C. ^{1}H NMR ($CDCl_3$): δ = 8.04 (d, J = 5.16 Hz, 2 H, H_{pyr}), 7.74–7.69 (m, 6 H, H_{arom}), 7.58–7.54 (m, 3 H, H_{arom}), 7.49–7.45 (m, 6 H, H_{arom}), 6.57 (d, J = 5.16 Hz, 2 H, H_{pyr}) ppm. ^{31}P NMR ($CDCl_3$): δ = 7.55 ppm. IR (KBr): $\tilde{\nu}$ = 1588, 1494, 1361, 1110, 719, 692 cm^{-1}. MS (MALDI TOF): calcd. for $C_{23}H_{19}N_2P$ $[M]^{+\cdot}$ 354.1; found $[MH]^+$ 355.2.

TTF–Imine–4-Pyridyl (3a): Monoformyltetrathiafulvalene (**2**) (67 mg, 0.29 mmol) was dissolved in distilled toluene (30 mL). Iminophosphorane **1** (141.6 mg, 0.40 mmol) was added in one portion and the reaction mixture was heated at reflux for 24 h. Evaporation of the solvent in vacuo produced a brown oil which was purified by chromatography through a silica gel column [AcOEt + triethylamine (1%, v/v)]. Evaporation of the solvent afforded a red solid (63 mg, 0.20 mmol, 69% yield). M.p. 155–156 °C. ^{1}H NMR ([D$_6$]-acetone): δ = 8.51 (dd, J = 1.59, J = 4.37 Hz, 2 H, H_{pyr}), 8.43 (s, 1 H, H_{imine}), 7.63 (s, 1 H, S-CH-C), 7.07 (dd, J = 1.59, J = 4.76 Hz, 2 H, H_{pyr}), 6.63 (dd, J = 6.34, J = 10.33 Hz, 2 H, S-CH=CH-S) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 158.14 (C_{imine}), 155.06, 151.71 (C_{pyr}), 138.78, 134.63, 120.58, 120.25 ($C_{lateral}$, TTF), 116.51 (C_{pyr}), 114.60, 107.21 ($C_{central}$, TTF) ppm. IR (KBr): $\tilde{\nu}\tilde{\nu}$ = 1605, 1584, 1536, 1479 cm^{-1}. HRMS: calcd. for $C_{12}H_8N_2S_4$ $[M]^{+\cdot}$ 307.95704; found 307.9564.

TTF–Imine–4-Tolyl (3b): Monoformyltetrathiafulvalene (**2**) (110.3 mg, 0.47 mmol) was dissolved in CH_2Cl_2 (100 mL) and *p*-toluidine (185.1 mg, 1.72 mmol) was added. The reaction mixture was stirred for 7 h in the presence of molecular sieves (4 Å, 3 g). The latter was separated by filtration and rinsed with CH_2Cl_2 (50 mL). The filtrate was then concentrated in vacuo and the residue obtained was purified by chromatography through a silica gel column [petroleum ether/CH_2Cl_2 (1:1, v/v) + triethylamine (1%, v/v)]. A violet solid was obtained after evaporation (110 mg, 0.34 mmol, 80%). M.p. 134 °C. ^{1}H NMR (CD_2Cl_2/CD_3CN, 1:1, v/v): δ = 8.27 (s, 1 H, H_{imine}), 7.17 (d, J = 7.94 Hz, 2 H, H_{pyr}), 7.13 (s, 1 H, S-CH-C), 7.06 (d, J = 7.94 Hz, 2 H, H_{pyr}), 6.43 (d, J = 2.38 Hz, 2 H, S-CH=CH-S), 2.32 (s, 3 H, CH_3) ppm. MS (DSQ): calcd. for $C_{14}H_{11}NS_4$ $[M]^{+\cdot}$ 320.9; found 320.8.

TTF–Imine–4-Nitrophenyl (3c): Monoformyltetrathiafulvalene (**2**) (98 mg, 0.42 mmol) was dissolved in CH_2Cl_2 (100 mL) and 4-nitroaniline (138.1 mg, 0.84 mmol) was added. The reaction mixture was stirred for 6 h in the presence of molecular sieves (4 Å, 3 g). The latter was separated by filtration and rinsed with CH_2Cl_2 (60 mL). The filtrate was then concentrated in vacuo and the residue obtained was purified by chromatography through a silica gel column [petroleum ether/CH_2Cl_2 (8:2, v/v) + triethylamine (4%, v/v)]. A blue-violet solid was obtained after evaporation (86 mg, 0.24 mmol, 58%). M.p. 189 °C. ^{1}H NMR ([D$_6$]acetone): δ = 8.52 (s, 1 H, H_{imine}), 8.27 (d, J = 9.14 Hz, 2 H, H_{pyr}), 7.70 (s, 1 H, S-CH-C), 7.40 (d, J = 9.14 Hz, 2 H, H_{pyr}), 6.67 (d, J = 4.37 Hz, 2 H, S-CH=CH-S) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1595, 1564, 1530, 1510, 1330 cm^{-1}. MS (DSQ): calcd. for $C_{13}H_8N_2O_2S_4$ $[M]^{+\cdot}$ 351.9; found 351.8 $[M]^{+\cdot}$, 305.8 $[M - NO_2]^{+\cdot}$.

TTF–Diimine–4,4′-Dipyridyl (5): Diformyltetrathiafulvalene diacetal (**4**) (*Z*/*E* mixture) (133 mg, 0.29 mmol) was dissolved in distilled toluene (45 mL). Iminophosphorane **1** (203 mg, 0.57 mmol) was added in one portion and the reaction mixture was heated at reflux for 48 h. Evaporation of the solvent in vacuo produced a solid material which was purified by chromatography through a silica gel column [AcOEt + triethylamine (1%, v/v)]. Evaporation of the solvent afforded **5a** as a mixture of *Z*/*E* geometric isomers as a violet solid (130 mg, 0.21 mmol, 72% yield). ^{1}H NMR ([D$_6$]acetone): δ = 8.68 (s, 2 H, H_{imine}), 8.55 (m, 4 H, H_{pyr}), 7.09 (m, 4 H, H_{pyr}), 5.99, 5.98 [s, 2 H, $H_{acetal\ (E/Z)}$], 3.72 (m, 8 H, OCH_2), 1.22 (t, J = 6.75 Hz, 6 H, CH_3) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 157.12 (C_{imine}), 152.68, 152.64 (C_{pyr}-N_{imine}), 151.03, 150.09 (C_{pyr}-N_{pyr}), 148.27, 148.09 (=**C**-C_{imine}), 132.91, 132.74 (=**C**-C_{acetal}), 115.64 (C_{pyr}), 108.42 (C=$C_{central}$), 96.73, 96.71 (C_{acetal}), 61.77, 61.73 (CH_2), 14.47 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1633, 1586, 1526, 1496, 1483, 1437, 1350 cm^{-1}. HRMS: calcd. for $C_{28}H_{32}N_4O_4S_4$ $[M]^{+\cdot}$ 616.13064; found 616.1316.

Supporting Information (see also the footnote on the first page of this article): UV/Vis and ^{1}H NMR spectra and CV titration curves.

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