

Tetrathiafulvalene-*s*-tetrazine: versatile platform for donor–acceptor systems and multifunctional ligands†‡

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The structurally characterized tetrathiafulvalene-1,2,4,5-tetrazine donor–acceptor system shows redox tuneable intramolecular charge transfer, solvatochromic and electrochromic behaviour. Attachment of a dipicolyl-amine chelating unit affords a multifunctional ligand, which allows the preparation of the ZnCl₂ complex in which an anion- π interaction is seen.

s-Tetrazines or 1,2,4,5-tetrazines (TTZ), are well-known electron-deficient nitrogen based heterocycles¹ and have been extensively used in the past particularly as electron poor dienes in inverse demand cycloaddition reactions,² high-nitrogen energetic compounds,³ or in coordination chemistry as 3,6-dipyridyl derivatives.⁴ More recently, their optical and electrochemical properties triggered their use in the field of π -conjugated systems for solar cells.⁵ Indeed, most of the tetrazine derivatives go by a reversible and facile one-electron reduction process towards the formation of stable radical anions,⁶ due to the presence of a low lying π^* LUMO. On the other hand, their intense orange-red colour is due to a comparatively weak low-energy, symmetry forbidden, $n-\pi^*$ transition, also responsible for the fluorescent properties of many TTZ derivatives.⁷ Very often, the HOMO of tetrazines consists of a linear combination of the nitrogen lone pairs, however a π type orbital is generally very close in energy and, upon the presence of electron donor substituents, it eventually becomes the HOMO.

Moreover, it was shown that in the presence of electron rich compounds such as triphenylamine, the fluorescence can be quenched.^{7a} Nevertheless, in a very recent series of covalently linked tetrazine-triphenylamine derivatives, the fluorescence of the tetrazine unit could be switched on upon oxidation of the amine.⁸ Note however, that although these compounds can be regarded in principle as donor–acceptor (D–A) systems, no intramolecular charge transfer (ICT) bands were detected in the UV-vis spectra. A well-known electron donor unit, extensively investigated in diverse fields,⁹ is tetrathiafulvalene (TTF), which can be chemically or electrochemically oxidized reversibly to the radical cation TTF^{•+} and the dication TTF²⁺. Accordingly, TTF derivatives have been incorporated in covalent D–A systems that show promise for applications in molecular electronics, nonlinear optics, and photovoltaics.¹⁰ Although a large variety of acceptors have been associated with TTF in different ways,^{10,11} only a few examples of direct non-fused covalent connections between TTF and acceptors such as 1,3,5-triazine,¹² pyridinium,¹³ or oxophenalenoxyl,¹⁴ have been described so far. On the other hand, TTF was also incorporated in the structure of various ligands with the aim of accessing electroactive metal complexes and multifunctional materials.¹⁵ However, TTF and TTZ units have never been covalently combined in a linked D–A system, in which an ICT band from TTF towards the accepting TTZ ring is expected to occur, with the aim of using such an assembly as the backbone for multifunctional ligands. We report herein the synthesis, solid-state structure and photophysical study of an unprecedented TTF-TTZ-Cl system, supported by theoretical calculations, together with the dipicolyl-amino ligand derived thereof and its ZnCl₂ complex.

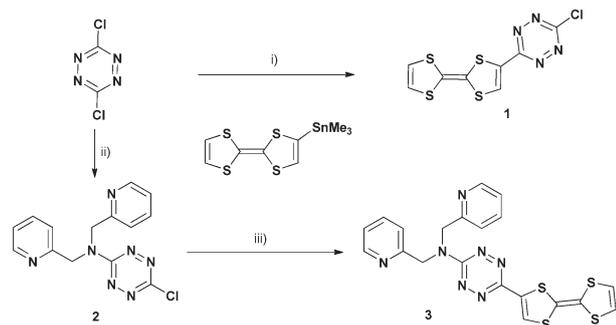
The palladium catalyzed Stille type cross-coupling reaction between the 3,6-dichloro-1,2,4,5-tetrazine¹⁶ (3,6-Cl₂-TTZ) and TTF-SnMe₃¹⁷ provided the TTF-TTZ-Cl compound **1** as a black polycrystalline solid after chromatographic work-up (Scheme 1, and ESI†). Dark blue crystalline needles of **1**, suitable for X-ray analysis, were grown upon slow diffusion of pentane onto a solution of dichloromethane (DCM)–cyclohexane (1 : 1). The compound crystallizes in the monoclinic system, space group *P*₂₁/*c*, with one independent molecule in the unit cell (see ESI†, ‡). The donor and acceptor parts are coplanar (Fig. S1 in the ESI†), as attested by

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† Electronic supplementary information (ESI) available: Experimental and X-ray details, CV measurements, photophysics, DFT calculations. CCDC reference numbers 888570 (**1**) and CCDC 888571 ((**3**)-ZnCl₂). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra21702g

‡ Crystal data for **1**: C₈H₃ClN₄S₄, M = 318.87, monoclinic, space group *P*₂₁/*c*, *a* = 7.4751(11), *b* = 22.522(2), *c* = 7.5169(9), α = 90.000 (11), β = 109.736(9), γ = 90.000 (12), *V* = 1191.2(3) Å³, *Z* = 4, *T* = 293(2)K, μ = 1.000 mm⁻¹, *D*_c = 1.778 g cm⁻³, 14 171 refl. measured, 3099 refl. with *I* > 2 σ (*I*), *R*₁ = 0.0516, *wR*₂ = 0.0852. For (**3**)ZnCl₂: C₂₀H₁₅C₁₂N₇S₄Zn, M = 617.90, triclinic, space group *P* $\bar{1}$, *a* = 8.7852(17), *b* = 9.2555(14), *c* = 16.386(4), α = 74.976(17), β = 88.387(14), γ = 72.238(14), *V* = 1223.6(4) Å³, *Z* = 2, *T* = 293(2)K, μ = 1.589 mm⁻¹, *D*_c = 1.677 g cm⁻³, 16 903 refl. measured, 4739 refl. with *I* > 2 σ (*I*), *R*₁ = 0.0430, *wR*₂ = 0.0817.



Scheme 1 Synthesis of TTF-TTZ **1** and **3**. Reaction conditions: (i) TTF-SnMe₃, Pd(PPh₃)₄, toluene, 60 °C; (ii) di(2-picoly)l-amine, MTBE, r.t.; (iii) TTF-SnMe₃, Pd(PPh₃)₄, toluene, reflux.

the dihedral angle of 2.1° between their mean planes, very likely as a result of a certain degree of conjugation. Bond lengths and angles are in the typical range for neutral TTFs. The molecules stack in a head-to-tail fashion in columns along the *a* direction, with short D⋯A distances of 3.47 Å. Furthermore, short S⋯S intermolecular contacts (3.63 Å) and CH⋯N hydrogen bonds (2.40 and 2.68 Å) are established in the *bc* plane between molecules belonging to parallel columns (Fig. S2 and Fig. S3 in the ESI†).

Cyclic voltammetry measurements show the classical pair of reversible oxidation waves, from TTF to TTF^{•+} and TTF²⁺ at +0.50 V and +0.92 V vs. SCE, respectively, while the reversible reduction of the tetrazine ring occurs at -0.45 V vs. SCE (Fig. S6 in the ESI†). The intense blue-violet colour of **1** in DCM is due to the fairly intense ¹ICT band (see below) centred at 19 000 cm⁻¹, with an extinction coefficient of around 5000 M⁻¹ cm⁻¹ (Fig. 1 and ESI†). However, based on the electrochemical data, that is the difference between the first oxidation and first reduction potential being only 0.95 V, the lowest energy charge transfer transition is expected at substantially lower energies and also at lower energy compared to

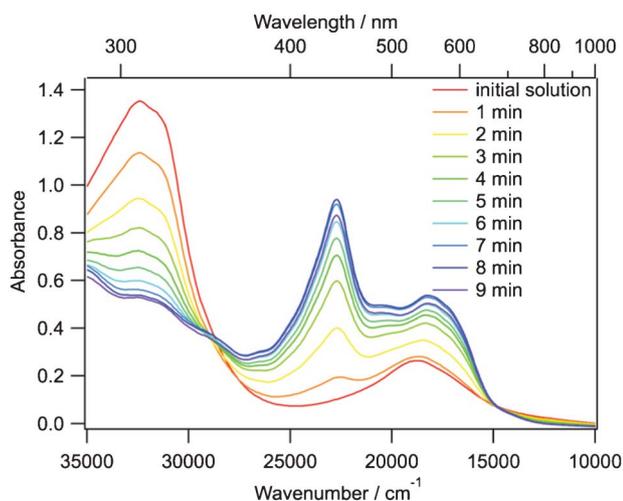


Fig. 1 UV-vis absorption of **1** (9.0×10^{-4} M) during electrochemical oxidation at 0.60 V vs. the Ag wire pseudo reference (corresponds to 0.70 V vs. SCE) in DCM at room temperature, (*n*-Bu₄N)PF₆, 0.1 M, cell length: 0.7 mm.

say the TTF-triazine systems.¹² Careful inspection of the spectrum on the low-energy side reveals a long tail into the near infrared (NIR) region. This could indicate a weak transition centred at around 12 000 cm⁻¹ within the tail. Obviously, the typical TTZ *n*-π* band, occurring at λ_{max} = 515 nm (19 420 cm⁻¹) in the 3,6-Cl₂-TTZ precursor with a relatively weak ε of around 500 M⁻¹ cm⁻¹,⁷ is masked by the much more intense and broad ¹ICT band. In the higher energy region intense absorption bands can be observed between 25 000 cm⁻¹ and 35 000 cm⁻¹, ascribed to the superposition of the π-π* transition of the TTF and TTZ subunits. Note that the UV-vis spectrum of a DCM solution containing a mixture of TTF and 3,6-Cl₂-TTZ is the sum of the individual spectra of the two components, thus demonstrating that no intermolecular ICT occurs (Fig. S7 in the ESI†). Interestingly, the large solubility of **1** in a variety of organic solvents allows a detailed study of its solvatochromic behaviour (Fig. S12 in the ESI†). Accordingly, when changing from non-polar solvents (toluene, ν_{max} = 18 904 cm⁻¹) to intermediate polar solvents (DCM, ν_{max} = 18 797 cm⁻¹; CHCl₃, ν_{max} = 18 762 cm⁻¹), the absorption band of the ¹ICT transition is slightly red-shifted. However, as the solvent polarity increases from DCM to CH₃CN (ν_{max} = 19 342 cm⁻¹), the CT absorption band is slightly blue-shifted, while a large blue shift is observed in methanol (ν_{max} = 21 413 cm⁻¹), without any intermolecular aggregation being evident. This observation is consistent with the cooperative effect of a polar ground state and hydrogen bonding.

In order to properly assign the electronic transitions observed for **1**, theoretical calculations have been performed at the DFT/PBE level for the geometry optimization, and TDDFT/PBE0 level for the electronic excitation. The *C_i* ground-state geometry of **1**, optimized from the experimental X-ray starting structure, is in agreement with the latter (Fig. S15 in the ESI†). In particular, the calculated dihedral angle S-C-C-N of 0.9° confirms the planar arrangement of the subunits. The analysis of the frontier orbitals is particularly interesting. Thus, the HOMO is the classical TTF π type orbital, while the LUMO, particularly low in energy (-3.363 eV), is a π* TTZ orbital. Moreover, the *n*_{TTZ} orbital, involved in the *n*-π* transition of tetrazines, is only the HOMO - 2, although it is rather close in energy (-7.516 eV) to HOMO - 1 (-7.170 eV), also a TTF π orbital, but with some π contribution from the TTZ unit. Note that the LUMO + 1, involved in several low energy transitions (*vide infra*), is a π type orbital implying the presence of a Cl-TTZ unit and also an adjacent dithiol ring (Fig. 2 and Fig. S16 in the ESI†).

The calculated electronic excitations show that the lowest energy singlet transition at 10 388 cm⁻¹ ascribed to the formally forbidden S₀ → S₁ excitation, corresponds to an ICT and very well explains the tail centred at 12 000 cm⁻¹ in the UV-vis spectrum (*vide supra*). Moreover, the strong absorption band at 19 000 cm⁻¹ (calculated at 15 878 cm⁻¹) still essentially represents an ICT transition now attributed to the S₀ → S₂ (HOMO → LUMO + 1) excitation, while the weak TTZ based HOMO - 2 → LUMO + 1 transition (18 795 cm⁻¹) corresponds to an *n*-π* excitation. At higher energy the structured rich absorptions illustrate that the π-π* transitions in the range of S₀ → S₈ to S₀ → S₁₃ have a dominant contribution from the TTF subunit, however, the S₀ →

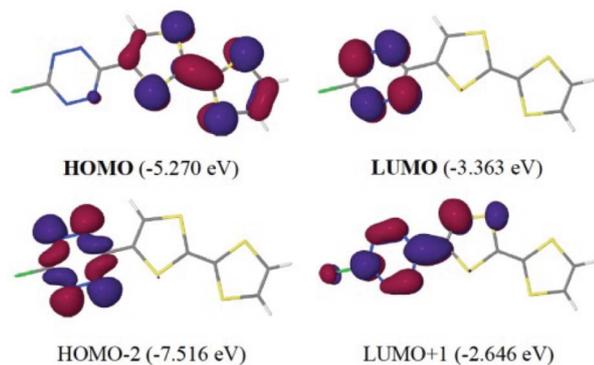


Fig. 2 HOMO (top left), HOMO – 2 (bottom left), LUMO (top right) and LUMO + 1 (bottom right) of **1**.

S8 and S0 → S9 transitions have strong contributions attributed to an ICT process from the HOMO – 1 to the LUMO + 1 (Table S5 in the ESI†). Not unexpectedly, the fluorescence of the tetrazine unit in **1** is reductively quenched because of the presence of the donor,^{1b} but there is no Stokes shifted luminescence from the lowest energy ICT band instead (Fig. S11 in the ESI†). This result can be rationalized by the TDDFT calculations, since although the very weak oscillator strength (0.019) of the S0 → S1 transition would result in a potential luminescence in the NIR, as the associated long radiative lifetime of the corresponding emission is easily quenched by the surrounding environment. Note that there is no discernible photodecomposition with prolonged irradiation at 18 000 cm⁻¹ (530 nm), thus, compound **1** can be considered as photostable (Fig. S11 in the ESI†). Spectroelectrochemical (or chemical) (see ESI†) oxidation of **1** was performed in DCM solution at room temperature (Fig. 1). Stable oxidized radical cation TTF^{•+} species are formed, as can be inferred from the decrease in intensity of the π–π* and ¹ICT bands between 30 000 and 35 000 cm⁻¹ attributed to the TTF unit of the neutral species, and the occurrence of new bands in the range of 13 000 to 25 000 cm⁻¹, typical for TTF^{•+}.¹⁸ The compound **1** thus constitutes a valuable functional precursor for the preparation of conducting charge transfer complexes.

In order to evaluate the possibility for the further use of the TTF-TTZ moiety as the backbone for functional ligands, the attachment of the dipicolyl-amine (dipic) chelating unit, which provided various transition metal complexes,¹⁹ has been attempted by direct substitution with **1**. However, this reaction gave a low yield, and therefore compound **2** had to be synthesized first, and subsequently the TTF unit was attached by cross-coupling to give the D–A ligand **3** as a black solid (Scheme 1 and ESI†). Both oxidation potentials of the TTF unit are comparable to those of **1**, while the reduction of the TTZ ring occurs at much lower potential (–0.93 V vs. SCE), a likely consequence of the less electronegative substituent dipicolyl-amine (Fig. S6 in the ESI†). This feature is also confirmed by the blue shift of the ICT band which is now centred at 427 nm.† Then, the ligand **3** was reacted with zinc chloride in a preliminary test of coordination, and the corresponding complex (**3**)–ZnCl₂ was thus isolated as dark brown single crystals. The complex crystallizes in the triclinic system,

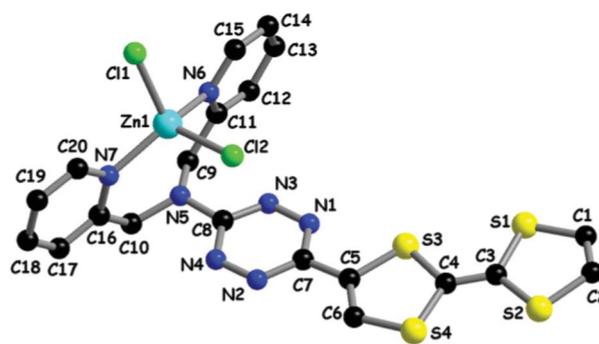


Fig. 3 Molecular structure of (**3**)–ZnCl₂ with the numbering scheme.

space group $P\bar{1}$, with one independent molecule in the unit cell.† As in the case of **1**, the TTF and TTZ units are practically coplanar (Fig. 3), as shown by the dihedral angle of 7° between them, and the TTF bond lengths and angles are typical for the neutral species (Table S3 in the ESI†).

The Zn(II) ion lies in a distorted tetrahedral coordination geometry formed by two chloride ions, with Zn–Cl distances of 2.264(1) Å (Cl2) and 2.286(1) Å (Cl1), and two pyridine nitrogen atoms with Zn–N bond lengths of 2.056(3) Å (N6) and 2.051(3) Å (N7), although in general the tertiary amine nitrogen atom of dipic ligands is involved in an albeit longer coordinative bond, with the Zn(II) centre in ZnCl₂ complexes.^{19,20} In the present case the Zn1...N5 distance of 2.70 Å is obviously too large to consider it as such. This is possibly due to a Cl...TTZ anion–π interaction, as demonstrated by the short separation of 3.24 Å between Cl2 and the centroid of the TTZ ring. Anion...TTZ interactions are energetically favourable and play an important role in directing the supramolecular organization of coordination complexes.²¹ This feature very likely influences the crystal packing and properties of complexes based on the ligands **2** and **3**.

In summary, the unprecedented covalently linked donor–acceptor system TTF-TTZ-Cl, having an almost planar structure in the solid state, shows low energy π_{TTF} → π*_{TTZ} ICT transitions. Short D...A contacts are established in the solid state. Solvatochromic behaviour and the formation of stable radical cation species are seen. Besides the redox tuneable ICT and electrochromic behaviour, TTF-TTZ is shown to be a promising platform for the synthesis of multifunctional ligands such as TTF-TTZ-dipic. In the corresponding ZnCl₂ complex, clear structural evidence for anion–π interaction is provided.

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