Synthesis and characterization of a TTF-π-verdazyl radical—a new building block for conducting and/or magnetic systems

M'hamed Chahma,[a] Keely Macnamara,[a] Art van der Est,[a] Antonio Alberola,[b] Victor Polo[b] and Melanie Pilkington*[a]

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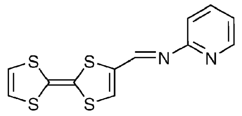
The synthetic strategy for the preparation of a TTF donor, π-appended with a spin bearing verdazyl radical has been developed. UV-Vis, electrochemical and EPR studies reveal that this is an attractive magnetic building block for subsequent oxidation that could afford new conducting and/or magnetic systems.

Introduction

By virtue of their redox properties, tetrathiafulvalene (TTF) and its derivatives have enjoyed widespread use as electron donor molecules for the formation of solid-state charge-transfer complexes.[1] TTFs are also violene-type systems which possess highly reversible electrochemical oxidations and unusual thermodynamic stability of their cation-radicals and dications.[2] Verdazyl radicals have recently attracted a great deal of attention for their applications as stable magnetic ligands that can bind transition metal ions.[3] The search for multifunctionality in molecule-based materials, in particular the combination of magnetic and electrical properties is one of the most active areas in molecular science to date.[4] In this respect, the most common strategy employed to prepare these compounds is to combine an organic donor together with a magnetic anion.[4] This approach has met with good success and afforded several classes of interesting conducting and magnetic materials that include paramagnetic superconductors,[5] as well as organic/inorganic hybrid compounds that display independent conducting and ferromagnetic behaviour.[6] In recent years, we have adopted an alternative strategy for the preparation of magnetic and/or conducting materials, namely to introduce a metal ion binding group directly onto the organic donor.[7] In this respect, we have recently reported the first imine bridged TTF-pyridine ligand **1** for which the imine nitrogen participates in chelation to a paramagnetic Cu(II) center.[8] Strategies for the covalent attachment of metal binding sites to organic donors such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and TTF are currently attracting the attention of the molecular materials community. For example, Ouahab and co-workers have recently reported radical cation salts and a trinuclear complex of **2**, a TTF conjugated to a pyridine through an alkene,[9] Xu *et al.* have reported BEDT-TTF derivatives bearing pyridine groups such as **3**[10] and more recently, Wallis and co-workers have made advances in this field by developing synthetic strategies for the preparation of novel BEDT-TTF derivatives functionalized with metal ion binding groups such as **4**.[11] As part of our research program, we are investigating synthetic strategies for the preparation of TTF donors appended with verdazyl radicals that can also function as chelating ligands for metal ions.[12] When such a donor is converted into a charge-transfer complex or a conductive diradical cation salt, a Kondo system or a conducting magnetic material might be realized depending on the degree and sign of exchange interactions in these complexes.



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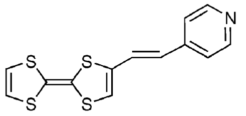

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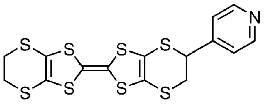

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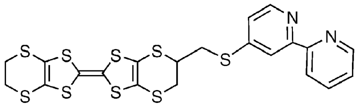

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Results and discussion

We report herein the preparative route to a new material for which a spin bearing verdazyl radical is linked to an organic building block that has conductive properties (TTF) *via* a π-ethenyl bridge. The synthetic route for the preparation of the TTF-π-verdazyl radical **8** is shown in Scheme 1.

Wittig reaction of formyl-TTF[13] together with the appropriate phosphorane afforded the formyl-TTF vinylogue **6**[14] in good yield. Condensation of **6** with carbonic acid bis(1-methylhydrazide) afforded the tetrazane **7**.[15] Oxidation of the tetrazane by treatment with 1,4-benzoquinone gave the verdazyl radical **8** and a trace of the diradical cation $\mathbf{8}^{\bullet+}$. The crude product was purified by chromatographic separation on silica gel to afford **8** as an orange/brown solid in 57% yield. CV data for compounds **6–8** in which an electron deficient group is connected to the TTF system showed small anodic shifts compared to unsubstituted TTF, consistent with the electron withdrawing nature of the appended moieties. The

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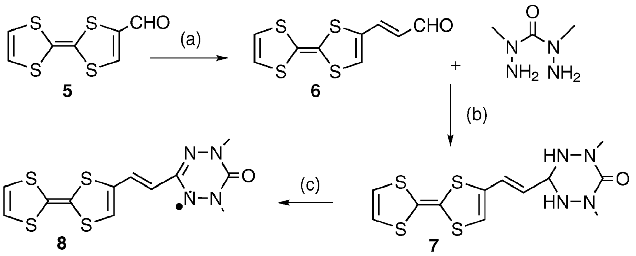
[a] *Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario, Canada L2S 3A1. E-mail: mpilkington@brocku.ca; Fax: +1 905 682 9020; Tel: +1 905 688 5550; Ext. 3403*
[b] *Dpto. de Quimica Fisica y Analitica, Universitat Jaume I, Avda. Sos Baynat s/n, 12701 Castellón, Spain*



Scheme 1 *Reagents and conditions*: (a) Ph$_3$P=CH–CHO (2 equiv.), benzene, reflux;[14] (b) MeOH, reflux, 45 min, 76% yield; (c) 1,4-benzoquinone, C$_6$H$_6$, 60 °C, 1 h, 57% yield.

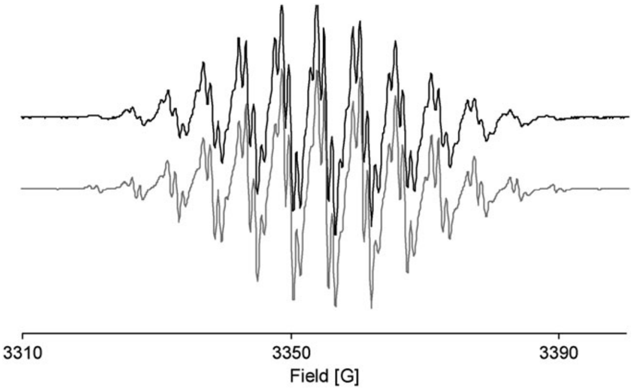
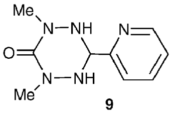


Fig. 2 EPR spectrum of **8** in THF at 298 K (black line). The pattern of lines is due to the hyperfine coupling of the unpaired electron of the verdazyl radical to the four nitrogen nuclei and the six methyl protons. The grey line corresponds to the simulated spectrum that yields the following values for the hyperfine coupling constants *a*(N2,4) = 5.45 G, *a*(N1,5) = 5.18 G and *a*((CH$_3$)1,5) = 6.36 G.

cyclic voltammogram of the tetrazane **7** (Fig. 1, bold line) exhibits two reversible oxidation waves corresponding to the formation of the TTF radical cation and radical dication, respectively. An additional irreversible wave is just visible at 0.75 V, partially overlapping with the second oxidation potential of the TTF moiety. This wave corresponds to the formation of the verdazyl radical, affirming that oxidation of the tetrazane can be carried out electrochemically. Interestingly the redox potential of the tetrazane is in very close agreement with values previously reported for compounds **9**[3] and **11**[12] indicating that substitution at the nodal position of the tetrazane has minimal effect on the electronics of the system, not surprising as the HOMO for these compounds resides on the four nitrogen atoms of the heterocyclic ring.[15] The cyclic voltammogram of the verdazyl radical **8** shows two reversible oxidation waves (Fig. 1, dashed line) confirming the presence of the radical cation TTF$^{\bullet+}$ and the dication TTF^{2+} species, respectively. Comparing the peak currents for both waves, it is evident that the second oxidation wave is a two-electron process that corresponds to the oxidation of the verdazyl radical, as well as the TTF-radical cation.

It is noticeable that the oxidation potential of the verdazyl radical substituent in **8** is quite substantially anodically shifted to a value >0.8 V when compared with the value of 0.650 V reported for Hicks's pyridine verdazyl radical **10**.[15] This is most likely due to the fact that it is more difficult to remove an electron from what is already a diradical cation species, since the electrostatic repulsion together with the proximity of the positive charge on the TTF makes the oxidation a more unfavourable process. This is in complete agreement with previous observations for compound **12**.[12] Compound **8** was characterised by EPR spectroscopy, Fig. 2. A series of 11 lines were visible at 298 K that are consistent with the presence of the 4,6-dimethyl-6-oxoverdazyl radical.[12] Spectral simulations for **8** afforded hyperfine coupling constants in agreement with data previously reported for compounds **10**[15] and **12**[12] (Table 1).



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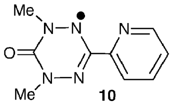

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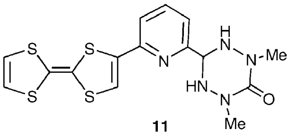

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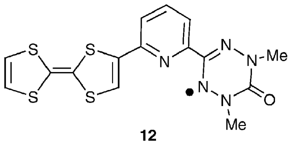

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The electrochromism of compounds **7** and **8** was studied by spectroelectrochemistry. The data for the corresponding neutral and oxidized species are given in Table 2. In both cases, a potential of 0.420–0.430 V (*vs.* AgCl/Ag) was applied which matches the first oxidation potential of the TTF, Scheme 2. Formation of the radical cation $7^{\bullet+}$ was monitered by EPR

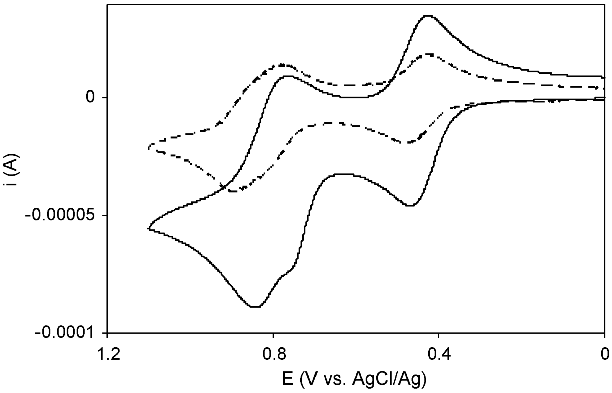


Fig. 1 Cyclic voltammetry of TTF-tetrazane **7** (bold line) and TTF-verdazyl radical **8** (dashed line) in CH$_3$CN at a scan rate of 100 mV s^{-1}.

Table 1 Electrochemical properties of selected TTF derivatives in CH$_3$CN. Scan rate 0.1 V s^{-1}. Glassy carbon

Compound	$E^1_{1/2}$[a]/V	$E^2_{1/2}$[a]/V	$E^3_{1/2}$[a]/V
TTF	0.380	—	0.770
6	0.500	—	0.860
7	0.440	0.750[b]	0.810
8	0.450	>0.800	0.860
9	—	0.740	—
10	—	0.650	—
11	0.430	0.760[b]	0.820
12	0.420	>0.800	0.830

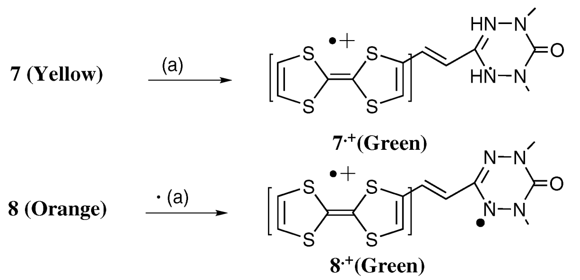
[a] Potentials are recorded *vs.* AgCl/Cl reference. [b] Irreversible wave. $E^1_{1/2}$ and $E^3_{1/2}$ are the oxidation potentials of TTF to radical cation and dication, respectively. $E^2_{1/2}$ corresponds to the oxidation of the tetrazane and verdazyl heterocycles.

Table 2 Visible absorption λ_{max} (nm) of compounds **6**, **7** and **8** in CH_3CN at 20 °C

Compound	λ_{max}/nm	Colour
6	300, 465	Red
7	300, 440	Yellow
$\mathbf{7}^{\bullet +}$	310, 410, 440, 600	Green
8	319, 419	Orange
$\mathbf{8}^{\bullet +}$	310, 405, 440, 600	Green

spectroscopy which showed a pattern of four strong lines characteristic of the TTF radical cation, Fig. 3. A pattern of broad lines on either side of the four cental peaks were also just visible showing that a small trace of the verdazyl radical was also present (Fig. 4).

The electronic spectra of compounds **6**, **7** and **8** show two bands, the first with a maxima at 300 nm consistent with absorptions from the neutral TTF moiety and a second broader band at longer wavelengths. In comparison with related systems,[16] this low-energy band in the UV-Vis region is assigned to the presence of an intramolecular charge transfer (ICT) from the TTF moiety to the acceptor group. In general, the strongest acceptor gives rise to the lowest energy ICT band which would indicate that in our case the tetrazane is a slightly better electron withdrawer than the verdazyl radical. The DFT optimized structure of the TTF-verdayl radical **8** yields a planar structure. The bond lengths between the carbon atoms forming the C–C═C–C ethenyl bridge are calculated to be 1.455 (C–C), 1.348 (C═C) and 1.463 Å (C–C) and indicate a small degree of π-conjugation. The HOMO and LUMO (see Fig. 5) are located, respectively on the TTF donor and over the four nitrogen atoms of the verdazyl acceptor. In this respect, there is negligible spatial HOMO–LUMO overlap. As a consequence, we propose that for compound **8**, the π-spacer is unlikely to mediate a strong coupling between the donor and acceptor moieties and that in this case, the intramolecular charge transfer most likely takes place *via* a superexchange pathway.[17] It is an important question that is frequently debated as to whether electron transfer (ET) in donor–bridge–acceptor compounds proceeds by hopping and/or a superexchange mechanism. In the superexchange mechanism, the bridge solely serves to mediate donor and acceptor wavefunctions, but in the hopping mechanism the electron is located at the bridge for a short time during its journey from one redox centre to the other.[18] Low energy ICT bands have been reported for a range of TTF-π-acceptor systems,[14,16,19] but the precise role that the bridge plays in the ET process of these systems has not been fully elucidated to date. Studies on donor-bridged-acceptor bis(triarylamine) triades by Lambert *et al.* have revealed that (i) the bridge-state energy is expected to have a marked influence on the ET mechanism and (ii) hopping and superexchange mechanisms do not necessarily exclude each other, but may both be present within one system.[18] Recently many pπ–dπ conjugated systems with superexchange interactions have been synthesized, exhibiting antiferro-, ferri- and/or ferromagnetic behaviour.[20] In these compounds, the direct exchange interaction between the terminal metal radical and π-radical is rather weak, but exchange interactions *via* ligands are strong in the CT configurations.[17]



Scheme 2 Electrochemical synthesis of the TTF radical cation, $\mathbf{7}^{\bullet +}$ and the diradical cation $\mathbf{8}^{\bullet +}$.

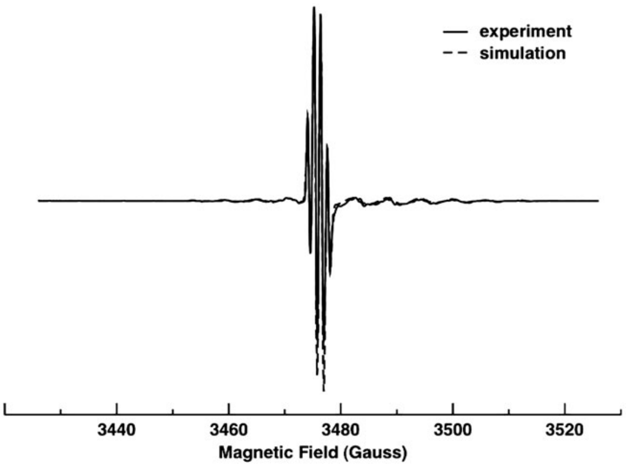


Fig. 3 EPR spectrum of $\mathbf{7}^{\bullet +}$ in acetonitrile at 298 K, *a*(H) = 1.2 G.

Selective electrochemical oxidation of **7** was achieved during which time the solution turns from bright yellow to a green colour. After consumption of one electron the UV-Vis spectrum clearly changed, the original absorption at 440 nm split into two bands at 410 and 440 nm and a second band at 620 nm was observed. These observations are further supported by EPR studies on this sample which showed intense signals characteristic of the TTF radical cation, Fig. 3. Selective electrochemical oxidation of compound **8** afforded the diradical cation $\mathbf{8}^{\bullet +}$ as a dark green compound. Once again four absorption bands were visible in the UV-Vis spectrum,

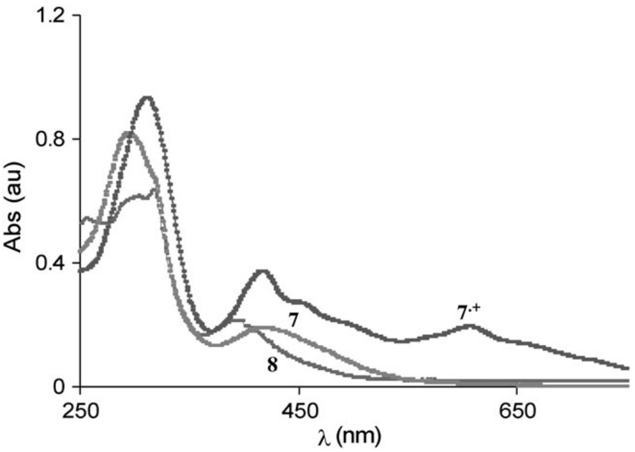


Fig. 4 UV-Vis spectra of selected TTF radical cations **7**, **8** and $\mathbf{7}^{\bullet +}$ prepared *via* electrochemical oxidation.

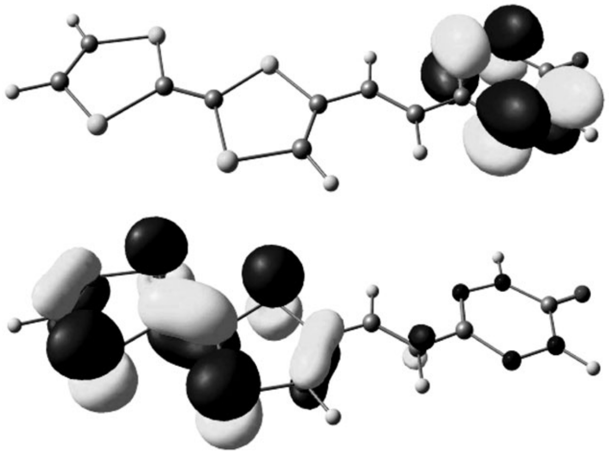


Fig. 5 Isocontour plots of LUMO (top) and HOMO (bottom) for the TTF-π-verdazyl radical **8** calculated at DFT level.

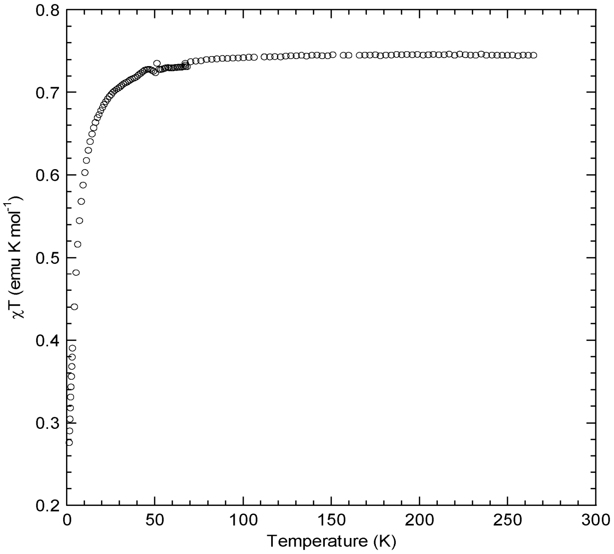


Fig. 6 χT *vs.* T plot with theoretical fitting (solid line) for a microcrystalline sample of the TTF-π-verdazyl diradical cation salt $\mathbf{8}^{\bullet+}$.

consistent with the formation of the TTF-π-verdazyl diradical cation. These additional bands are consistent with the formation of the TTF radical cation $\mathbf{7}^{\bullet+}$.[21] These observations are in complete agreement with the values recently reported for compound $\mathbf{12}^{\bullet+}$ however, due to the poor stability and solubility of $\mathbf{8}^{\bullet+}$ we have been unable to obtain reasonable EPR data to characterize this diradical cation to date. In order to investigate the magnetic properties of $\mathbf{8}^{\bullet+}$ and probe the nature of the interactions between the two radical species a PF_6 diradical cation salt was prepared. Electrocrystallisation of **8** together with NH_4PF_6 afforded a stable microcrystalline solid that was characterised as a 1 : 1 PF_6 salt by C, H, N elemental analysis. The magnetic susceptibility of this compound was measured on a SQUID magnetometer in the temperature range 2–270 K in an applied field of 1000 G. The χT *vs.* T plot is shown in Fig. 6. At 270 K a χT value of 0.76 emu K mol^{-1} is obtained that is in agreement with the theoretical value for two $S = 1/2$ radicals. The value of χT remains constant in the temperature range 270–75 K after which it begins to decrease slowly at first and then more abruptly at lower temperatures. This indicates the presence of antiferromagnetic interactions in the solid state. The magnetic behaviour of the diradical cation salt follows typical Curie–Weiss behaviour. A fitting of $1/\theta$ to the Curie–Weiss law yields values of $C = 0.76$ emu K mol^{-1} and $\theta = -1.71$ K that are consistent with the presence of two isolated $S = 1/2$ units and weak short-range antiferromagnetic interactions.

This behaviour is extremely similar to the magnetic properties recently reported for an *o*-carboranyl nitronyl nitroxide biradical for which the *o*-carborane framework and the nitronyl nitroxide radical are antiferromagnetically coupled giving rise to a singlet ground state.[22] The lack of crystallographic data for compound $\mathbf{8}^{\bullet+}$ makes it impossible to say with any certainty whether the antiferromagnetic interactions are intra- or intermolecular in nature. In order to address this, efforts to electrocrystallize a diverse range of radical cation salts of this compound are currently in progress.

Conclusion

To summarise, we report here a synthetic strategy for the preparation of the first TTF-π-verdazyl building block that links an organic donor molecule to a stable organic radical *via* an π-ethenyl spacer. DFT calculations reveal that the HOMO resides on the TTF donor and the LUMO is localized over the four nitrogen atoms of the verdazyl radical. Despite the negligible HOMO–LUMO spatial overlap, an intramolecular charge transfer band is observed in the UV-Vis spectrum that is most probably a consequence of well matched donor/acceptor redox potentials, as well as a short spacer unit. Oxidation of this compound afforded a diradical cation for which magnetic studies are consistent with a disjoint system in which the two radicals behave independently. As the temperature is lowered, antiferromagnetic interactions are observed which may either be intra- or intermolecular in nature. This work highlights a new strategy for the preparation of magnetic and conducting materials. Future studies on the electron-transfer mechanism in this and related compounds could have important implications for the design of new molecular and polymeric electron-transfer materials. Developing this work further by exploiting the coordination chemistry of the TTF-π-verdazyl radical together with appropriate paramagnetic metal ions and subsequent oxidation may afford novel materials with multifunctionality.

Experimental

General procedures and materials

Unless otherwise stated, all experiments were performed under an argon atmosphere using standard Schlenk line techniques. Solvents were dried and distilled under argon prior to use (methanol (MeOH) and acetonitrile (CH_3CN) from CaH_2; benzene, from sodium/benzophenone). All reagents were purchased from commercial sources and used as received. TTF, the formyl-TTF vinyl analogue **6** and carbonic acid bis-(1-methylhydrazone) were prepared according to literature procedures.[13–15] ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz on a Bruker DPX 300 spectometer. All UV-Vis studies were performed in freshly distilled CH_3CN on a UNICAM UV-Vis spectrometer. Infrared spectra were recorded on a Mattson FT-IR spectrometer as KBr pressed pellets. EPR spectra were recorded on a Bruker ELEXYS instrument and the spectra so obtained were simulated using the Winsim program.[23] Voltammetric measurements were performed at room temperature (22 ± 2 °C) in acetonitrile containing 0.1 M of n-Bu_4NPF_6. Glassy carbon (diameter 3 mm) was used as the working electrode. Platinum wire and AgCl/Ag were used as counter and reference electrodes, respectively. The working electrode was polished on alumina before use. *iR* compensations were applied for all experiments for potential measurements. The electrolyses of **7** and **8** were performed in a cell with two compartments at the first oxidation potential of the TTF moiety (0.42–0.43 V *vs.* Ag/AgCl) using a carbon rod as the cathode and a platinum plate as the anode.

Synthesis of TTF-π-tetrazane 7. To a solution of **6** (0.270 g, 1.04 mmol) in 100 mL of methanol was added carbonic acid bis(1-methylhydrazone) (0.158 g, 1.3 mmol). The dark brown mixture was refluxed overnight to afford a small amount yellow/orange precipitate and an orange solution. After evaporation of the solvent, the mixture was purified by flash chromatography on silica gel, eluting first with ethyl acetate and then with methanol. The product was isolated as an yellow/orange solid (0.280 g, 0.78 mmol) in 76% yield; mp 179 °C, ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 6.98 (s, 1H, TTF-H), 6.74 (s, 2H, TTF-H), 6.66 (d, J = 15.8 Hz, 1H, CH═C, bridge), 5.51 (d, J = 8.0 Hz, 2H, NH-tetrazane), 5.30 (dd, J = 15.8 Hz, J = 4.0 Hz, 1H, C═CH, bridge), 4.46 (m, 1H, CH-tetrazane), 2.90 (s, 6H, CH_3-tetrazane); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm): 155.1 (C═O, tetrazane), 133.9 (C, TTF), 128.1 (C═C, bridge), 125.8 (C═C, bridge), 122.1 (CH, TTF), 120.5 (CH, TTF), 120.4 (CH, TTF), 113.2 (C═C, TTF), 106.8 (C═C, TTF) 67.3 (C, tetrazane), 38.3 (CH_3, tetrazane). IR (KBr): ν(cm^{-1}): 3235, 3208, 1596, 1493, 1431, 1390; MS LSIMS: m/z = 358 (M^+, 40%). HRMS for $C_{12}H_{14}N_4OS_4$ [M^+] calc., 358.0050; found, 358.0049.

Synthesis of TTF-π-verdazyl radical 8. 1,4-Benzoquinone (0.070 g, 0.65 mmol) was added in one portion to a solution of **7** (0.150 g, 0.42 mmol) in benzene (50 mL). The yellow reaction mixture was refluxed for 1 h, after which time the solution turned brown. The reaction was monitored by TLC. The solvent was then evaporated under reduced pressure and the crude product was then purified *via* chromatography (SiO_2, EtOAc followed by MeOH) to afford the radical **4** as a dark orange solid, yield (0.110 g, 0.24 mmol) in 57% yield; mp 200 °C, IR (KBr): ν(cm^{-1}): 3061, 3032, 1685, 1619, 1531, 1397; MS LSIMS: m/z = 355 (M^+, 65%). HRMS for $C_{12}H_{11}N_4OS_4$ calc., [M^+] 354.9815; found, 354.9812.

Preparation of the diradical cation salt $[\text{TTF-}\pi\text{-verdazyl}]^{\bullet+}PF_6^-$ $\mathbf{8}^{\bullet+}$

7 mg of **8** were placed in the anode compartment of an H-cell containing 25 mL of 1×10^{-2} M tetrabutylammonium hexafluorophosphate in CH_2Cl_2. A constant current of 1.5 μA cm^{-2} was maintained at room temperature. A black polycrystalline material was obtained upon harvesting after 10 days. Anal. Found (calc.) for $C_{12}H_{11}OS_4N_4PF_6$ (%): C 28.5 (28.8); H 2.1 (2.2); N 11.7 (11.2).

Computational methodology for 8

All species studied were optimized using DFT calculations, in particular the B3LYP hybrid method[24] in combination of the 6-31G* basis set,[25] implemented in the GAUSSIAN03 package.[26] The nature of stationary points was confirmed by calculation of harmonic vibrational frequencies. An unrestricted methodology was employed and the calculated $\langle S^2 \rangle$ values were in excellent agreement with the theoretically expected ones.

Acknowledgements

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