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Synthesis and Characterization of a New Family of Spin Bearing TTF Ligands

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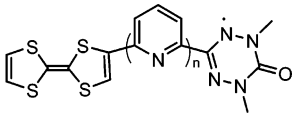
Received December 16, 2005



(**1**) n = 1; (**2**) n = 2

The syntheses and characterization of two new tetrathiafulvalene (TTF) derivatives bearing pyridine-based substituents and 1,5′-dimethyl-6-oxoverdazyl radicals are described. The TTF-pyridine and bipyridine aldehydes were prepared via a palladium-catalyzed cross-coupling reaction between mono(tributylstannyl)-tetrathiafulvalene (**3**) and the appropriate formylpyridyl halides (**4**). The radical precursors, the corresponding 1,2,4,5-tetrazanes, were prepared by condensation of the bis(1-methylhydrazide) of carbonic acid with the TTF bearing pyridyl aldehyde. Oxidation of tetrazanes **8** and **9** with 1,4-benzoquinone afforded the donor radicals **1** and **2** as 1:1 complexes with hydroquinone. Both complexes are stable in the solid state and their electronic properties have been characterized by EPR, cyclic voltammetry, and UV/vis spectroscopy. The TTF core of both compounds was oxidized both chemically and electrochemically to afford the corresponding cation diradical species. The electronic properties of both donor radicals have been probed by cyclic voltammetry, UV−vis spectroscopy, and preliminary EPR measurements.

Introduction

The synthesis and investigation of molecule-based materials involving interplay and synergy between multiple physical properties is currently an active area of research at the forefront of solid-state science.[1,2] Indeed, the construction of molecule-based materials which possess two or more properties such as electrical conductivity and magnetic interactions is currently a challenging target.[3,4] These combinations of properties lead to competition, coexistence, or cooperativity between the desired properties, the latter being the most difficult to realize.[5−7] One successful class of organic building blocks exploited for the preparation of hybrid conducting and magnetic materials are tetrathiafulvalene (TTF) derivatives.[8] The characteristic features of this class of organic conductors can be summarized as follows: (i) the constituent donor/acceptor molecules are planar so that their π-orbitals overlap with each other giving the π-electrons a small kinetic energy, hence it is these π-electrons that play a role in the electron transport process, and (ii) they have low dimensionality in their electronic nature, which results in the appearance of insulating states at low temperatures together with a range of physical phenomena such as charge-density wave (CDW) and spin density wave (SDW) states. In these systems, when the π-electronic system of the donor molecules is in the marginal region between metal and insulator phases, magnetic ordering of the paramagnetic centers should affect the transport properties of the donor layer. Hybrid organic/inorganic molecular magnets assembled from TTF-type donor molecules and paramagnetic transition metal ions are therefore good targets for the development of materials which combine magnetic interactions and electronic properties.[2,9] In this respect, several compounds have been isolated and characterized. Particular highlights include the first paramagnetic metal ET-$[CuCl_4]$,[10,11] salts $(ET)_2(Cu(NCS)_2)$ (ET = bisethylenedithioltetrathiafulvalene) and $(ET)_2(N(CN)_2)X$ (X = Cl or Br)

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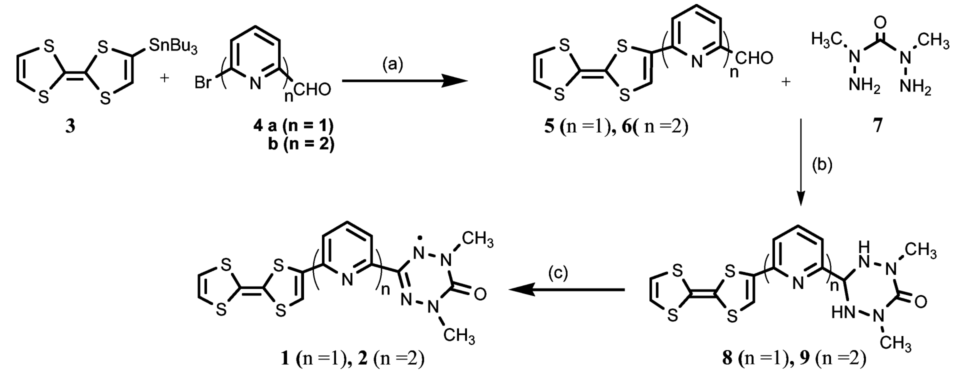
10.1021/jo0525938 CCC: $33.50

SCHEME 1. Synthetic Pathway for the TTF-Pyridyl-Verdazyl Series[a]



[a] Reagents and conditions: (a) toluene, Pd(PPh$_3$)$_4$, 115 °C, overnight; (b) MeOH, reflux, 45 min; (c) 1,4-benzoquinone, C_6H_6, 60 °C, 1 h.

which become superconducting at low temperatures,[12−14] and the paramagnetic superconducting radical salt (ET)$_4$[Fe(oxalate)$_3$]·H$_2$O·C$_6$H$_5$CN,[15] a layer structured TTF salt with a mixed Cr(III)/Mn(II) oxalate network with independent electrical and ferromagnetic properties.[16] Research in our laboratory is focused on the design and characterization of new hybrid organic/inorganic materials where the important feature is the interplay of electrical transport and magnetism. From the viewpoint of designing new stable organic donor ligands that possess a ferromagnetic exchange interaction between a localized spin on a stable radical unit and a π-spin generated on a TTF donor unit, we propose an open shell donor, where the π-donor and π-radical units are connected through cross-conjugation via heterocyclic aromatic linkers. To obtain an organic metallic ferromagnet, the donor unit is required to possess a sufficient conduction path when the donors are assembled and partially doped.[17,18] As a prototype for this purpose, we present here the synthesis and characterization of two spin diverse building blocks, namely, TTF-based donors appended with a verdazyl radical bridged by pyridyl linkers. We also describe studies of these donor radicals which are aimed at understanding their fundamental electronic properties. These compounds should make suitable ligands for chelation to transition metal ions and these data will be extremely useful in understanding the properties of subsequent transition metal complexes.

Results and Discussion

Preparation of the TTF-Pyridyl Verdazyl Ligands. The donor radicals **1** and **2** were prepared by the synthetic pathway outlined in Scheme 1. Lithiated TTF was treated with tributyltin chloride to afford the tributylstannyl derivative **3**.[19] This compound was then converted to the *o*-formyl derivatives **5** and **6** via cross coupling reactions together with 6-bromo-2-formylpyridine and 6-bromo-6′-formyl-2,2′-bipyridine, respectively. The verdazyl radicals were prepared from the *o*-formylpyridyl-TTF derivatives following the synthetic route previously reported first by Neugebauer[20] and more recently by Hicks et al.[21] Treatment of the TTF-aryl aldehydes with **7** gave the corresponding 3-substituted tetrazanes **8** and **9**, respectively. Oxidation of the tetrazanes to the corresponding verdazyl radicals was achieved by treatment of benzene solutions of the tetrazanes with *p*-benzoquinone to produce the desired radicals as 1:1 complexes with hydroquinone (hq) which were then separated by flash chromatography to afford **1** and **2**. Formation of the verdazyl radicals can be monitored by IR spectroscopy since on formation of the verdazyl:hq complex an OH str is visible at 3200 cm^{-1} and the C═O str is shifted from 1630 to 1690 cm^{-1}.[21] Furthermore, in the radicals there is an absence of NH stretches above 3400 cm^{-1} in comparison to the tetrazanes which have multiple bands in this region.[22] By analogy with previous observations for aryl verdazyl radical systems,[21] we find these compounds to be indefinitely stable; they require no special handling and can be stored for up to a month without decomposition.

Characterization of the TTF-Pyridyl Verdazyl Radicals: Electrochemical Studies. The redox potentials of the novel TTF-based compounds (**1**−**11**) have been determined by cyclic voltammetry at room temperature in acetonitrile solutions, using a glassy carbon electrode as the working electrode, Ag/AgCl as a reference, and tetrabutylammonium hexafluorophosphate (0.1M) as a supporting electrode. The redox potential values are collected in Table 1, together with the parent TTF and compounds **10** and **11** for comparison purposes.[21] Compounds **5** and **6** show reversible oxidation processes at relatively low

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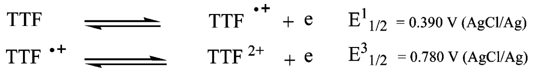
TABLE 1. Redox Potential Values (±0.01 V) for Selected Compounds (V vs AgCl/Ag)[a]

compd	$*E^1_{1/2/ox}$	$*E^2_{p/ox}$	$*E^3_{1/2/ox}$	$E^3_{1/2/ox} - E^1_{1/2/ox}$ (mV)
TTF	0.390		0.780	390
1	0.420		0.830	410
2	0.410		0.875[c]	
5	0.430		0.820	390
6	0.430		0.820	390
8	0.430	0.760	0.820	390
9	0.430	0.770	0.820	390
10		0.740		
11		0.650[b]		

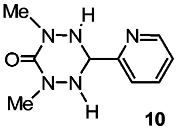
[a] Experimental conditions: CH_3CN as a solvent; GCE as a working electrode; Bu_4NPF_6 as a supporting electrolyte; 100 mV s^{-1}. [b] Quasi-reversible wave.[21] [c] Irreversible wave. $E_{1/2}$ is the average of oxidation and reduction peak potentials.

SCHEME 2. Electrochemical Oxidation of TTF



potential values. This mirrors the well-documented first and second oxidation potentials of TTF, corresponding to the formation of the radical cation and radical dication, respectively, Scheme 2.[23] These potentials are only slightly anodically shifted (30−40 mV) relative to the parent TTF measured under the same experimental conditions. Indeed, this is the case for all of the TTF derivatives (**1**−**9**) since the electron withdrawing nature of the pyridine ring makes the oxidation of the TTF moiety a little more difficult.[19,24]

Conversion of the TTF-pyridine aldehydes **5** and **6** to their corresponding tetrazones **8** and **9** does not affect the first and second oxidation potentials of their TTF moieties. For comparison, the cyclic voltammograms corresponding to the oxidation of tetrazane **8** and verdazyl radical **1** are shown in Figure 1. For compound **8**, an additional wave at around 0.760 V is just visible, 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 tetrazone can be carried out electrochemically. This value is in agreement with that observed for the reference compound **10**.[21]



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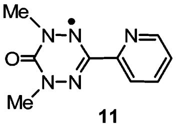

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The verdazyl radicals **1** and **2** show two reversible oxidation waves at relatively low potential values (Figure 1, bold line), corresponding to the formation of the radical cation ($TTF^{•+}$) and the dication (TTF^{2+}) species of the TTF moiety, Scheme 2. The close resemblance of the first and second oxidation potential to those of TTF indicates that the diradical cations $\mathbf{1}^{•+}$ and $\mathbf{2}^{•+}$ most probably have an open shell diradical structure in which each unpaired electron is distributed separately on the TTF and verdazyl moieties.[25] This is consistent with the electronic features of other previously reported cross-conjugated systems, i.e., the electronic structure most likely resembles that of a disjoint system in which two electron spins reside on separate moieties. Comparing the peak currents for both waves, it is evident that the second oxidation wave is a two-electron process corresponding to the oxidation of the verdazyl radical, as well as the TTF-radical cation. For compound **1** the oxidation potential of the pyridyl verdazyl radical substituents is anodically shifted when compared with **11**. This is most likely due to the fact that it is more difficult to remove an electron from a diradical cation species, since electrostatic repulsion together with the proximity of the positive charge on the TTF makes this oxidation a more unfavorable process. The difference $E^3_{1/2} - E^1_{1/2}$ is consistent for all TTF derivatives, providing evidence to support the generation of stable radical cation and dication species. Irreversible reduction waves corresponding to the pyridyl and bipyridyl groups acting as electron acceptors were also observed at more negative potentials for all compounds.

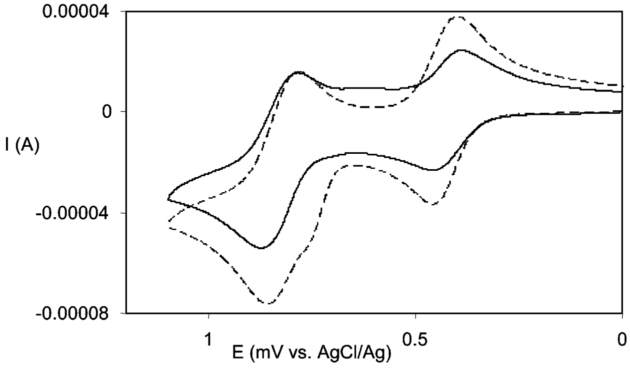

FIGURE 1. Oxidation of **8** (dashed line) and **1** (bold line) in CH_3CN at 0.1 V/s, using a glassy carbon electrode.

TABLE 2. UV−Vis Absorption Spectrum λ_{max} of Selected TTF Derivatives (10^{-4} M in CH_2Cl_2)

compd	λ_{max}/nm
TTF	300
$TTF^{•+}$	400, 650
Pyr-Verd **10**	410, 450
1	292,[a] 404[b]
$\mathbf{1}^{•+}$	404, 450, 550[b]
2	294,[a] 404
5	318,[a] 428[b]
6	316,[a] 428[b]
8	293,[a] 445[b]
$\mathbf{8}^{•+}$	410, 440, 550[b]
9	303,[a] 416[b]

[a] Shoulder. [b] Broad.

UV−Vis Studies. The UV−vis spectra of the TTF-pyridyl-verdazyl radicals **1** and **2** exhibit two characteristic absorption bands with maxima at $\lambda = 290$ and 400 nm. The band around 290 nm corresponds to absorptions from the neutral TTF moiety and is in good agreement with literature values.[22] A broad band is present in the region $\lambda_{max} = 370-550$ nm, which can be assigned as overlapping absorptions attributed to both the verdazyl radicals and the pyridyl moieties.[26] λ_{max} values for selected compounds together with the pyr-verdazyl radical **10** for comparison purposes are shown in Table 2.

Spectroelectrochemistry and EPR Studies. Spectroelectrochemistry experiments were conducted on both the tetrazone **8**

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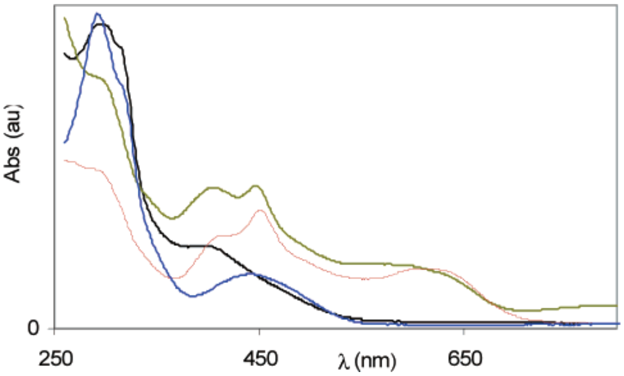


FIGURE 2. UV−visible spectra of **8** (blue line) and its radical cation **8**$^{\bullet+}$ (red line), **1** (black line), and the diradical cation **1**$^{\bullet+}$ (green line) generated by controlled potential electrolysis (0.420−0.430 V vs AgCl/Ag) in CH_3CN.

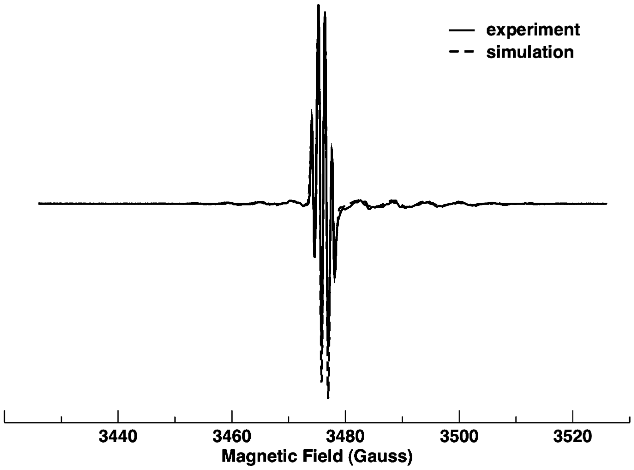


FIGURE 3. EPR spectrum of **1** in acetonitrile at 298 K. The pattern of four strong lines is due to the hyperfine coupling of the unpaired electron of the TTF radical cation to the three ring protons. The dashed line is a simulation that yields $a(H) = 1.2$ G. The pattern of broad weak lines on either side of the four central peaks is due a small amount of the verdazyl radical.

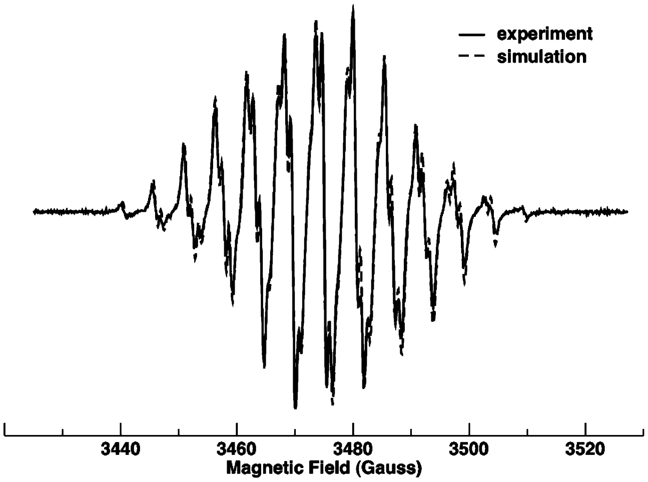


FIGURE 4. EPR spectrum of **1** in THF at 298 K. The pattern of lines is due to the hyperfine coupling of the unpaired electron of the verdazyl radical to the four nitrogen nuclei and the six methyl protons. The dashed line is a simulation that yields the following values for the hyperfine coupling constants $a(N_{2,4}) = 6.5$ G, $a(N_{1,5}) = 5.5$ G, and $a((CH_3)_{1,5}) = 5.2$ G.

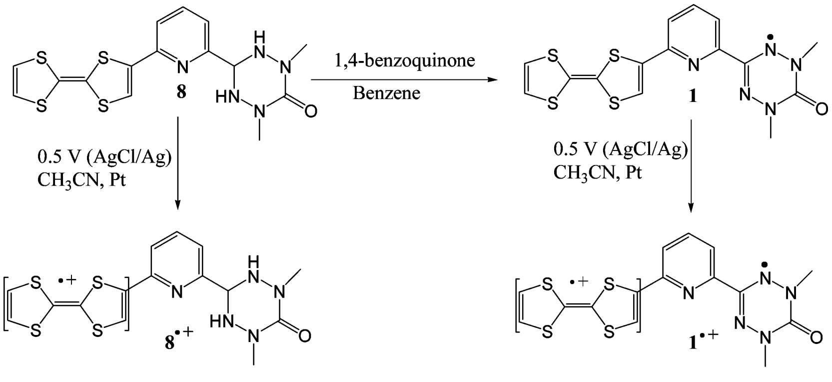
and the verdazyl radical **1** to follow the selective one-electron oxidation of the neutral TTF to the radical cation by UV−vis and EPR spectroscopy. In both cases a potential of 0.420−0.430 V (vs AgCl/Ag) was applied, which matches the first oxidation potential for the TTF. UV−visible spectra were recorded as a function of controlled potential electrolysis for the tetrazone **8** and its corresponding verdazyl radical **1**, Figure 2. In the region between 350 and 750 nm, the UV−visible spectrum of **8** displays a broad band at 445 nm that can be assigned to absorptions from the pyridine-tetrazone moiety. After consumption of one electron, the spectrum clearly changes (Figure 2, red line).

The original absorption at 445 nm is now split into two bands and a second broad band between 550 and 650 nm is observed. These two additional bands are consistent with the formation of the TTF-radical cation **8**$^{+\bullet}$. This is supported by EPR studies on this sample, which showed intense signals characteristic of a TTF radical cation, Figure 3.

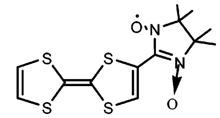
The neutral radical **1** has two absorption bands in the UV−vis spectrum, the first at 292 nm assigned to the neutral TTF moiety and the second at 404 nm assigned to absorptions from the pyridine-verdazyl radical, Figure 2, black line. The EPR spectrum of **1** at 298 K showed a set of signals consistent with other 4,6-dimethyl-6-oxoverdazyls with aryl groups in the 3-position,[21,22] Figure 4.

Spectral simulations for **1** afforded hyperfine coupling constants in agreement with data previously reported for **10** by Hicks et al.[21] Hyperfine coupling to the pyridine or bipyridine ring atoms also was not observed in these systems. Oxidation of **1** afforded the diradical cation **1**$^{\bullet+}$ resulting in two new absorptions at 450 nm and between 550 and 650 nm, Figure 2, green line. The EPR spectrum of **1**$^{\bullet+}$ at 80 K shows features

SCHEME 3. Electrochemical Oxidation of the TTF Moieties of Compounds 8 and 1



which can be tentatively assigned to the zero-field splitting components of the triplet state of the diradical (see the Supporting Information). Variable-temperature EPR studies of our diradical cations are currently underway to fully elucidate (i) the multiplicity of their ground-states and (ii) the sign of their exchange interactions. Evidence from the literature for TTF-based donor radicals **12** and **13** carrying nitronyl nitroxide groups, linked via cross conjugation, suggests that the sign of the exchange interaction is strongly influenced by the nature of the bridge linking the two radicals.[25,27]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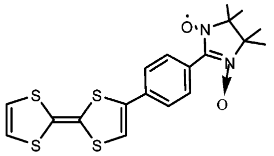
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For compound **12**, the two radicals are considered to be severely twisted due to steric repulsion leading to a breakdown of the electronic feature of a spin polarized donor. This unfavorable steric hindrance was released by inserting an aromatic spacer group, and a spin polarized donor **13** was obtained, giving rise to a triplet ground state species. Further studies are currently in progress to investigate if our compounds can be classified as "spin polarized donors" upon one-electron oxidation. Studies of the intermolecular exchange interactions in the diradical cation species will be reported in due course. Preliminary investigations are very encouraging and the versatility of our synthetic strategy will enable us (i) to prepare several new classes of TTFs appended with stable spin bearing units and (ii) to examine a range of conjugated linkers and assess their suitability for yielding ground state triplet cation diradicals. If a columnar stacking of these donors is realized and partially doped, such a self-assembled material could afford an organic ferromagnet.

Concluding Remarks

In our quest for dual property materials, the pairing between stable verdazyl radicals and TTFs has afforded a new family of spin bearing ligands. Although several organic donor radicals which carry a stable radical unit have been reported,[25−29] this is the first for which the π-donor is TTF and the π-radical is verdazyl. These compounds possess two of the common hallmarks of supramolecular chemistry, namely H-bonding and π-stacking, which may provide pathways for intermolecular magnetic communication between radicals.[30] Finally, both compounds should also be capable of coordinating to metal ions and since metal−radical exchange interactions can be very strong,[31,32] this opens up a new strategy for the rational design of new hybrid organic/inorganic systems for which there is interplay between magnetism and conductivity.

Experimental Section

Synthesis of 6-Bromo-6′-formyl-2,2′-bipyridine (4b). $Pd(PPh_3)_4$ (0.240 g, 0.21 mmol) was added to a solution of 6-bromo-2-tributylstannylpyridine (3.576 g, 8.00 mmol) and 6-bromo-2-formylpyridine (4.120 g, 22.00 mmol) in toluene (300 mL). The reaction mixture was heated to 115 °C for 17 h and the progress of the reaction was monitored by TLC. On completion, the solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 (100 mL) and washed twice with NH_4Cl (60 mL) followed by 5% EDTA (2 × 20 mL). The combined organics were then dried over $MgSO_4$ and filtered and the solvent was evaporated under reduced pressure. The resulting crude product was purified via chromatography (SiO_2, R_f 0.35, CH_2Cl_2) affording 6-bromo-6-formyl-2,2′-bipyridine as a white solid, yield 0.870 g (46%). The NMR data were consistent with that described in the literature.[33]

Synthesis of 6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)pyrid-2-ylcarboxaldehyde (5). $Pd(PPh_3)_4$ (0.200 g, 0.17 mmol) was added to a solution of stannyltetrathiafulvalene (1.600 g, 3.24 mmol) and 6-bromo-2-formylpyridine (0.446 g, 2.40 mmol) in toluene (20 mL). The reaction mixture was heated overnight to 115 °C and the reaction was monitored by TLC. On completion, the solution was poured into water (100 mL) and the product was extracted with CH_2Cl_2 (3 × 60 mL). The combined organics were then washed with water (2 × 100 mL), dried over $MgSO_4$, and filtered. After evaporation of the solvent under reduced pressure, the crude product was purified by chromatography (SiO_2, R_f 0.2, 1:1 pentane/CH_2Cl_2) to afford **5** as a red/orange solid, yield 0.420 g (57%). Mp 150 °C. ^1H NMR (DMSO-d_6, 300 MHz) δ (ppm) 9.95 (s, 1H), 8.20 (m, 2H), 7.95 (s, 1H), 7.85 (m, 1H), 6.80 (s br, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 193.2, 152.7, 151.2, 138.0, 137.3, 123.5, 120.3, 119.9, 119.7, 119.4, 112.6, 108.71. MS LSIMS m/z 309 (M^+, 100%). Anal. Calcd for $C_{12}H_7NOS_4$: C, 46.58; H, 2.28; N, 4.53. Found: C, 46.31; H, 2.25; N, 4.41.

Synthesis of 6-(6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)-pyridin-2-yl)-2,2-bipyrid-6′-yl-carboxaldehyde (6). $Pd(PPh_3)_4$ (0.200 g, 0.17 mmol) was added to a solution of tristannyltetrathiafulvalene (1.600 g, 3.24 mmol) and 6-bromo-2-formylpyridine (0.446 g, 2.40 mmol) in toluene (20 mL). The reaction mixture was heated to 115 °C overnight. The progress of the reaction was monitored by TLC and on completion the solvent was evaporated under reduced pressure. The resulting crude product was purified by chromatography (SiO_2, R_f 0.2, 1:1 pentane/CH_2Cl_2) to afford **6** as a red solid, yield 0.480 g (75%). Mp 212 °C. ^1H NMR (DMSO-d_6, 300 MHz) δ (ppm) 10.08 (s, 1H), 8.57 (d, $J = 7.7$ Hz, 1 H), 8.40 (d, $J = 7.5$ Hz, 1H), 8.28 (t, $J = 7.7$ Hz, 1H), 8.05 (m, 3H), 7.82 (s, 1H), 6.76 (s, 2H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 193.1, 154.9, 153.4, 152.0, 179.7, 139.2, 138.3, 137.1, 124.7, 122.1, 120.5, 120.2, 120.2, 119.9, 119.4, 111.4, 107.40. MS LSIMS m/z 386 (M^+, 19%). Anal. Calcd for $C_{12}H_7NOS_4$: C, 52.82; H, 2.61; N, 7.25. Found: C, 52.55; H, 2.44; N, 6.95.

Synthesis of 6-(6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)-pyrid-2-yl)-1,5-dimethyl-1,2,4,5-tetrazane 6-Oxide (8). A solution of **5** (0.455 g, 1.47 mmol) and carbonic acid bis(1-methylhydrazine) **7** (0.182, 1.54 mmol) in MeOH (50 mL) was refluxed for 45 min after which time the solution turned orange and a solid precipitated. The solvent was then evaporated under reduced pressure and the resulting solid was purified by chromatography (SiO_2, EtOAc). The product was then dissolved in dichloromethane and reprecipitated by the addition of methanol to afford **8** as an orange solid, yield 0.480 g (80%). Mp 180 °C. ^1H NMR (DMSO-d_6, 300 MHz) δ (ppm) 7.90 (t, $J = 7.8$ Hz, 1 H), 7.80 (d, $J = 7.4$ Hz, 1H), 7.75 (s, 1H), 7.49 (d, $J = 7.4$ Hz, 1H), 6.76 (s, 2H), 5.66 (d, $J = 9.8$ Hz, 2H), 5.93 (t, $J = 9.8$ Hz, 1 H), 3.00 (s, 6H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 154.6, 154.6, 149.3, 137.8, 136.9, 121.7, 120.2, 120.0, 119.2, 111.1, 107.7, 69.4, 37.5. MS LSIMS m/z 409 (M^+,

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75%). Anal. Calcd for $C_{15}H_{15}N_5OS_4$: C, 43.99; H, 3.69; N, 17.10. Found: C, 44.15; H, 3.78; N, 16.74.

Synthesis of 6-(6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)-2,2′-bipyrid-6′-yl)-1,5-dimethyl-1,2,4,5-tetrazane 6-Oxide (9). A solution of **6** (0.220 g, 0.57 mmol) and carbonic acid bis(1-methylhydrazine) (0.182, 0.59 mmol) in MeOH (50 mL) was refluxed for 45 min after which time the solution turns an orange color and a small amount of solid precipitated. The solvent was then evaporated under reduced pressure and the resulting crude product was purified by chromatography (SiO_2, EtOAc, then MeOH) to afford **9** as an orange solid, yield 0.220 g (80%). Mp 205 °C. ^1H NMR (DMSO-d_6, 300 MHz) δ (ppm) 8.62 (d, $J = 7.6$ Hz, 1H), 8.35 (d, $J = 7.7$ Hz, 1H), 8.10 (m, 3H), 7.85 (s, 1H), 7.70 (d, $J = 7.4$ Hz, 1H), 6.82 (s, 2H), 5.88 (d, $J = 10.6$ Hz, 2H), 5.05 (t, $J = 10.6$ Hz, 1H), 3.09 (s, 6H). ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm)154.6, 154.5, 154.1, 153.9, 149.1, 138.5, 138.0, 137.4, 123.6, 120.2, 120.2, 120.1, 120.0, 119.7, 111.3, 107.5, 69.3, 37.7. IR (KBr) υ (cm^{-1}) 3452, 1619, 15.62, 1433, 1385. MS LSIMS *m*/*z* 406 (M$^+$, 16%). Anal. Calcd for $C_{15}H_{15}N_5OS_4$: C, 49.36; H, 3.73; N, 17.27. Found: C, 49.02; H, 3.96; N, 17.01.

Synthesis of 6-(6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)-pyrid-2-yl)-1,5-dimethyl-6-oxoverdazyl (1). 1,4-Benzoquinone (0.044 g, 0.41 mmol) was added in one portion to a solution of **8** (0.100 g, 0.25 mmol) in benzene (10 mL). The reaction mixture was stirred for 1 h at 60 °C, after which time the solution turned brown. The solvent was then evaporated under reduced pressure and the crude product was purified via chromatography (SiO_2, EtOH, followed by MeOH) to afford the radical **1** as a yellow-orange solid, yield 0.073 g (75%). Mp 240 °C, IR (KBr) υ (cm^{-1}) 3064, 1687, 1562, 1454. MS LSIMS *m*/*z* 406 (M$^+$, 100%). HRMS for $C_{15}H_{12}N_5OS_4$ [M$^+$] calcd 405.9924, found 405. 9906.

Synthesis of 6-(6-(2-(1,3-Dithiol-2-ylidene)-1,3-dithiol-4-yl)-2,2′-bipyrid-6′-yl)-1,5-dimethyl oxoverdazyl (2). 1,4-Benzoquinone (0.042 g, 0.40 mmol) was added in one portion to a solution of **9** (0.100 g, 0.25 mmol) in benzene (10 mL). The reaction mixture was refluxed for 3 h after which time the solution turns brown. The solvent was removed by evaporation under reduced pressure and the crude product was purified by chromatography (SiO_2, EtOAc, and then MeOH) to afford radical **2** as a green solid, yield 0.110 g (85%). Mp 233 °C. IR (KBr) υ (cm^{-1}) 3326, 1688, 1562, 1510, 1440, 1238, 1213, 1096. MS LSIMS *m*/*z* 404 (M + 1, 40%). HRMS for $C_{20}H_{15}N_6OS_4$ [M$^+$] calcd 483.0190, found 483.0199.

Acknowledgment. We thank NSERC, CRC and CFI of Canada, as well as the OTI and Brock University, for financial support for this research.

Supporting Information Available: General experimental procedures and the EPR spectrum of the TTF-pyridine−verdazyl diradical cation $\mathbf{1}^{\bullet+}$ at 80 K. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0525938