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Tetrahedron 64 (2008) 1345–1350

Tetrahedron

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Synthesis of new ethynylbipyridine-linked mono- and bis-tetrathiafulvalenes: electrochemical, spectroscopic, and Ru(II)-binding studies

Christine Goze [a], Shi-Xia Liu [a,*], Claudia Leiggener [b], Lionel Sanguinet [c], Eric Levillain [c], Andreas Hauser [b], Silvio Decurtins [a]

[a] *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland*
[b] *Département de chimie physique, Université de Genève, 30 quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland*
[c] *Chimie, Ingénierie Moléculaire et Matériaux d'Angers (CIMMA) CNRS, UMR 6200,*
Université d'Angers, 2 bd Lavoisier, 49045 Angers Cedex, France

Received 11 October 2007; received in revised form 2 November 2007; accepted 16 November 2007
Available online 22 November 2007

Abstract

Two new ethynylbipyridine-linked mono- and bis-tetrathiafulvalene (TTF) derivatives, together with a Ru(II) complex, were synthesized using Sonogashira coupling reactions and characterized by UV/vis spectroscopy and cyclic voltammetry. They display a clear electrochemically amphoteric behavior consisting of two reversible single-electron oxidation waves (typical for TTF derivatives) and one reversible single-electron reduction wave (bpy) and act as donor–acceptor (D–A) systems. Furthermore, for the Ru(II) complex, a quite intense fluorescence originating from the ^{3}MLCT state is observed.

Keywords: Tetrathiafulvalene; Ruthenium(II) complex; Photophysical properties; Cyclic voltammetry; Donor–acceptor systems

1. Introduction

Tetrathiafulvalene (TTF) and its derivatives are well-known as π electron-donor materials in the field of organic conductors.[1] As a result of progress in synthetic TTF chemistry, TTFs have been incorporated into a number of macrocyclic, molecular, and supramolecular systems in order to create multifunctional materials with desired structures, stability, and physical properties.[1–3] Therefore, considerable efforts are currently devoted to the modification of the TTF core with substituents such as pyridine-type heterocycles,[4] acetylacetonates,[5] and phosphines,[6] all of which are well tailored for a chelating coordination function toward various transition metal ions. On the other hand, TTFs are frequently used as donor units in donor–acceptor (D–A) ensembles, which are of considerable research interest due to their potential applications in sensors, optoelectronics, and molecular devices.[3,7] D–π–A systems have gained increasing attention as the π-conjugated spacer may optimize the communication between the D and A units.[3,8] Furthermore, an acetylenic spacer can offer an excellent control of the distance between the D and A centers because of its linearity and rigidity, and concomitantly provide a synthetic handle for further elaboration of sophisticated molecular structures.[9] To gain insight into such intramolecular electronic interactions, such D–A systems containing TTFs and triple bond linkages have been studied recently.[10] For example, Martín et al. have demonstrated that through a specific exchange of C=C for C≡C the long-range photo-induced electron transfer in D–A conjugates can be considerably altered.[10a] Moreover, the π-conjugation is disrupted by a neutral TTF unit in TTF–OXD (OXD=2,5-diphenyl-1,3,4-oxadiazole) hybrids.[10b]

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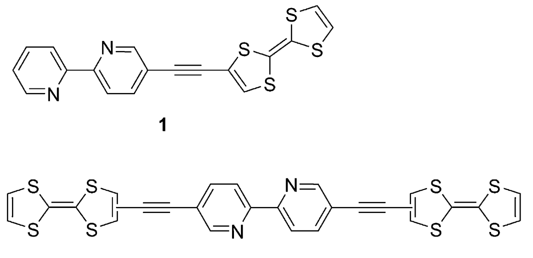
[*] Corresponding author. Tel.: +41 31 6314296; fax: +41 31 6313995.
E-mail address: liu@iac.unibe.ch (S.-X. Liu).

0040-4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.11.056



Scheme 1. Molecular structures of compounds **1** and **2**.

The combination of TTFs and ruthenium(II) chromophores is stimulated by the development of new antenna and charge separation systems,[11] as well as new photoredox switches.[3b,12] Only a few papers on such systems appeared until now. In most cases, the presence of the TTF induces a quenching of the luminescence of the ruthenium(II) complex. Interestingly, we recently reported three Ru(II) complexes bearing the TTF-fused dipyrido[3,2-*a*:2′,3′-*c*]phenazine (TTF–dppz) ligand, demonstrating that the complex with one TTF–dppz exhibits luminescence from the Ru(II)→dppz metal-to-ligand charge transfer (^{3}MLCT) state, whereas for the other two complexes, a radiationless pathway via electron transfer from a second TTF–dppz ligand quenches the ^{3}MLCT luminescence. Remarkably, the TTF fragments as electron donors thus induce a long-lived ligand-to-ligand charge separated (LLCS) state.[11a]

Mono- and bis(tetrathiafulvaleno)bipyridines **1** and **2** (Scheme 1) can be regarded as π-amphoteric molecules with TTF donor and bipyridine acceptor parts linked through ethynyl spacers. Herein, we report the synthesis of **1** and **2**, the formation of the Ru(II) complex with **1**, as well as their electrochemical and photophysical properties in order to elucidate intramolecular D–A interactions.

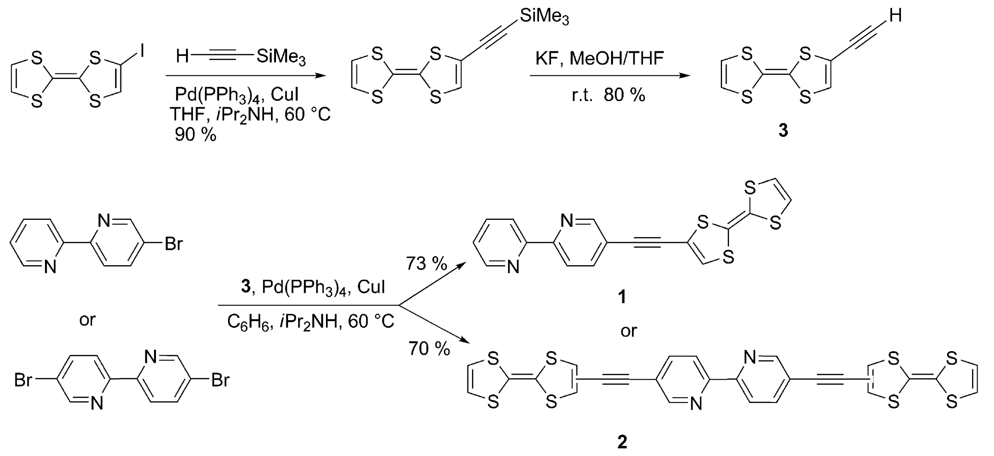
2. Results and discussion

The target compounds **1** and **2** were synthesized under typical Sonogashira coupling conditions[13] as shown in Scheme 2. The key precursor, 2-ethynyl-TTF **3**, was prepared according to the modified reported procedure.[14] The starting material, 2-iodotetrathiafulvalene, prepared by treatment of tetrathiafulvalenyllithium with perfluorohexyl iodide (PFHI),[15] reacted with trimethylsilylacetylene in triethylamine for 16 h, catalyzed by CuI and $Pd(PPh_3)_4$ at 60 °C to afford 2-trimethylsilylethynyl TTF in 90% yield. The subsequent conversion to the corresponding ethynylated compound **3** is straightforward and does not require special conditions (Scheme 2). Deprotection in the presence of 5 equiv of KOH for 16 h led to **3** in 80% yield. In this case, the overall yield of **3** is remarkably improved.

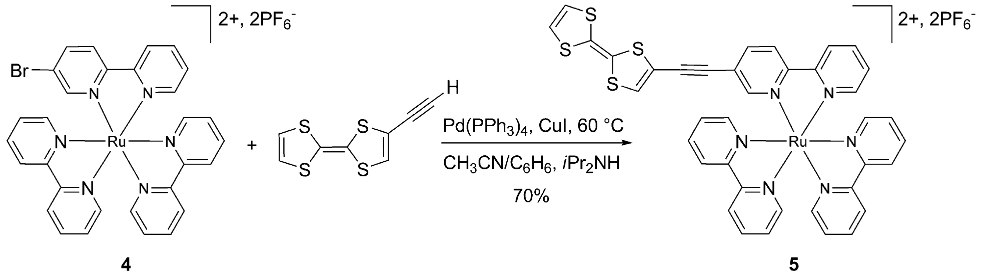
The Sonogashira coupling of **3** with 5-bromo and 5,5′-dibromobipyridine in argon-degassed benzene/*i*-Pr_2NH and catalyzed by CuI and $Pd(PPh_3)_4$ at 60 °C led to the corresponding coupling products **1** and **2** in 73 and 70% yields, respectively. However, Ru(II) complexes could not be obtained by the direct coordination of $[Ru(bpy)_2Cl_2]$ with acetylenic TTF ligands **1** and **2**. This problem can be circumvented by using pivotal starting materials bearing unsubstituted bpy ligands and 5-bromo-substituted or 5,5′-dibromo-substituted bpy ligands for performing Sonogashira cross-coupling reactions with the ethynyl fragments to provide the desired complexes in very good yields.[16] Scheme 3 outlines the synthetic route used for the generation of the Ru(II) complex **5**. Unfortunately, all attempts to obtain the Ru(II) complex of **2** were unsuccessful so far.

^{1}H NMR, ^{13}C NMR spectroscopy (except for compound **2**, which is not soluble enough), mass spectrometry, and satisfactory elemental analyses confirmed the identities of all new compounds.

The redox properties of compounds **1** and **5** were investigated by cyclic voltammetry (CV) measurements. Unfortunately, CV measurements of ligand **2** were not possible due to its poor solubility. The electrochemical data of **1** and **5** are collected in Table 1 together with those of TTF and analogous $[Ru(bpy)_3]^{2+}$, Ru(bpyDBT′) bearing 2-ethynyl-3,4-dibutylthiophene[17] instead of 2-ethynyl-TTF, for comparison. All of them show a clear electrochemically amphoteric behavior consisting of two reversible single-electron oxidation



Scheme 2. Synthesis of compounds **1** and **2**.



Scheme 3. Synthesis of Ru(II) complex **5**.

Table 1
Redox potentials[a] (*V* vs SCE) of compounds **1**, **5**, and references

Compound	E_1^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}
TTF[b]		0.30	0.74	
1[c]	−1.15	0.32	0.67	
5	−1.04	0.53	0.89	1.30
Ru(bpyDBT′)[b]	−1.18			1.26
$[Ru(bpy)_3]^{2+}$[b]	−1.34			1.27

[a] One-electron half-wave potential for redox processes, in CH_3CN/CH_2Cl_2 (v/v=80:20), with n-Bu_4PF_6 (0.1 M), at 100 mV/s.

[b] In CH_3CN, see Ref. 17.

[c] Scan rate: 1 mV/s.

waves as is typical for TTF derivatives and one reversible single-electron reduction wave for bpy. Moreover, complex **5** possesses one more reversible oxidation wave at 1.30 V, which is due to the Ru(II/III) couple. The Ru(II/III) potential is quite comparable with those of the reference compounds. The presence of the ethynylbipyridine as such does not have a substantial effect on the electron-donating ability of **1**. However, upon coordination, all three redox waves are positively shifted, indicating that the presence of Ru(II) strongly decreases the electron density on the TTF and bpy units, thus making oxidation of TTF less favorable while reduction of bpy becomes easier. Furthermore, the first reduction step is shifted to a much more positive potential than that for $[Ru(bpy)_3]^{2+}$, but similar to that for Ru(bpyDBT′). This feature clearly indicates that the first reduction is localized on the ethynyl-substituted bipyridine ligand.

The UV–vis absorption spectra of ligands **1** and **2** in $CHCl_3$ as well as of the Ru(II) complex **5** in CH_3CN together with those of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(5\text{-bromo-}2,2'\text{-bpy})]^{2+}$ (**4**), are presented in Figures 1 and 2, respectively. For the ligands **1** and **2**, comparatively strong absorption bands in the blue with long tails stretching down to 15,000 cm^{-1} are observed. They are essentially attributed to several overlapping $\pi\pi^*$ transitions located on the TTF, but some charge transfer (CT) character involving the TTF unit(s) as donor(s) and bpy as an acceptor through the triple bond may also be present. The latter is consistent with both the shift from 35,000 cm^{-1} to 30,000 cm^{-1} for the peak maximum and the increase in absorption intensity on going from **1** to **2**. The strong rise above 40,000 cm^{-1} is attributed to the $^1\pi\pi^*$ transition located on the bpy.

The absorption spectrum of complex **5** shown in Figure 2 consists of a very broad low-energy absorption band with a maximum at 22,000 cm^{-1} (460 nm) and a very intense band at 35,000 cm^{-1}. The latter corresponds to the $^1\pi\pi^*$ transition of bpy in the complex. With reference to the absorption spectra of the reference Ru(II) complexes included in Figure 2, the band at 22,000 cm^{-1} can be attributed to a ^{1}MLCT transition. The somewhat larger absorption intensity and tail toward the red for **5** are possibly due to a contribution of the underlying intraligand CT transition.

Upon excitation at 22,000 cm^{-1}, complex **5** exhibits a quite intense ^{3}MLCT luminescence band centered at 15,500 cm^{-1}

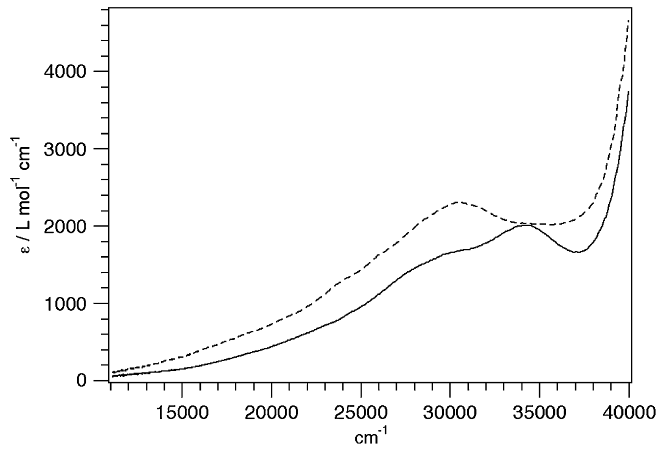


Figure 1. UV–vis absorption spectra of **1** (solid line) and **2** (dash line) in $CHCl_3$.

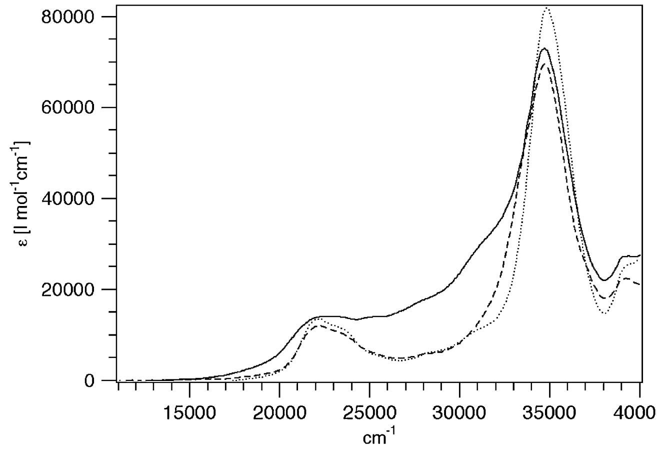


Figure 2. UV–vis absorption spectra of **5** (solid line), $[Ru(bpy)_3]^{2+}$ (dotted line), and **4** (broken line) in CH_3CN.

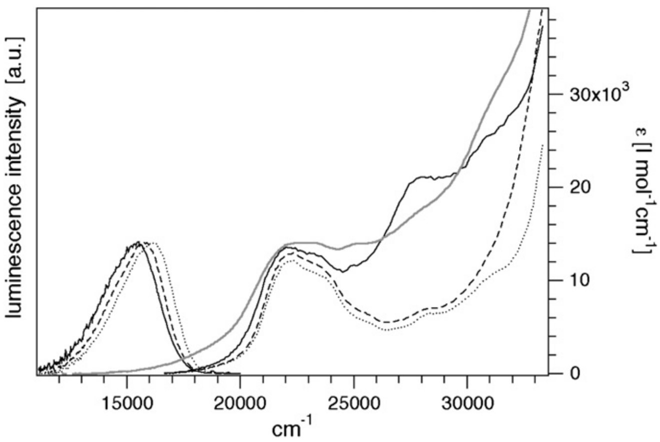


Figure 3. Luminescence (left) and excitation spectra (right) of **5** (solid line), $[Ru(bpy)_3]^{2+}$ (dotted line), and **4** (broken line) in CH_3CN. The absorption spectrum of **5** is included (light gray line).

(646 nm). Figure 3 shows the luminescence spectrum and the excitation spectrum of **5** as well as the corresponding spectra of the two reference complexes. The emissions from **4** and **5** are red-shifted relative to that of $[Ru(bpy)_3]^{2+}$. This red shift is consistent with the fact that the substituted bpy ligands are more easily reduced compared to unsubstituted bpy, in agreement with CV results. Therefore, the enhanced electron-accepting ability and conjugation of the bpy acceptor arising from the linkage of ethynyl-TTF appears to play a role in the electronic nature of the emitting ^{3}MLCT state.

Luminescence lifetimes and quantum efficiencies were determined for all three complexes and are summarized in Table 2. For **5**, the lifetime and quantum efficiency of the luminescence are 1048 ns and 0.014, respectively. Compared to **4** (the reference complex without ethynyl-TTF), the luminescence lifetime of complex **5** is the same within experimental accuracy, whereas the quantum efficiency is substantially lower. This results in seemingly very different radiative but almost equal non-radiative relaxation rate constants for the two complexes. At first sight, this does not make sense. In fact the key question to ask is, why isn't the ^{3}MLCT luminescence quenched altogether by electron transfer quenching from the TTF donor. Well, **5** actually possesses two almost equally energetic ^{3}MLCT states, one corresponding to a transfer of the electron to one of the non-substituted bpy ligands, the other one to a transfer to the ligand with the ethynyl-TTF substituent, the latter being just slightly lower in energy. If the unpaired electron of the ^{3}MLCT state is sitting on this ligand, the resulting Coulomb barrier may slow down the electron transfer from the TTF unit to the formally Ru^{3+} central ion. If on the other hand the unpaired electron sits on one of the non-substituted bpy ligands, rapid electron transfer quenching from the TTF is possible in competition with electron hopping of the unpaired electron to the substituted ligand. In the absorption process, the excitation to the ^{1}MLCT states on either ligand and fast intersystem crossing to the corresponding ^{3}MLCT states occurs non-selectively. Therefore, some complexes find themselves in the ^{3}MLCT state with the electron residing on the substituted ligand, some in the ^{3}MLCT state with the electron on a naked bpy. The former will show the classic emission with a lifetime and intrinsic quantum efficiency in line with the reference compound **4**, the latter will be almost totally quenched, resulting in a lower overall quantum efficiency.

Table 2
Luminescence maxima (λ_{max}), relative intensity (I_{em}), quantum yield (Φ_{em}), and lifetime (τ) in acetonitrile

	λ [nm]	I_{em} [%]	Φ_{em}	τ [ns]
$[Ru(bpy)_3]^{2+}$	620	100	0.062	854
4	636	117	0.072	1019
5	646	22	0.014	1048

3. Conclusion

In summary, two new ethynylbipyridine-linked mono- and bis-tetrathiafulvalene derivatives **1** and **2**, together with Ru(II) complex **5**, were synthesized using Sonogashira coupling reactions. They display a clear electrochemically amphoteric behavior. Interestingly, for Ru(II) complex **5**, the luminescence originating from the ^{3}MLCT state is not quenched by electron transfer from the TTF unit to the formally Ru^{3+} central ion. Furthermore, the novel feature of these promising new donors is that they contain a chelating coordination function, which provides unprecedented opportunities for the attachment of a wide range of paramagnetic transition metal ions to the donor system, leading to the formation of bifunctional materials.[4] This work is now under investigation and will be published in due course.

4. Experimental

4.1. Equipment

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300.18 and 75.5 MHz, respectively: chemical shifts are reported in parts per million relative to TMS. The following abbreviations were used: s (singlet), d (doublet), t (triplet), and m (multiplet). Elemental analyses were performed on a Carlo Erba EA 1110 CHN apparatus. EI mass spectra were recorded using an Auto SpecQ spectrometer. ESI-MS was carried out with a FTMS 4.7 TBioAPEX II TOF apparatus. Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a platinum millielectrode, a platinum wire counter-electrode, and a silver wire used as quasi-reference electrode. The electrochemical experiments were carried out under dry and oxygen-free atmosphere ($H_2O<1$ ppm, $O_2<1$ ppm) in CH_3CN/CH_2Cl_2 (80:20) (0.8 mM) with Bu_4NPF_6 (TBAP) (0.1 M) as supporting electrolyte. The voltammograms were recorded on an EGG PAR 273A potentiostat with positive feedback compensation. Based on repetitive measurements, absolute errors on potentials were estimated around ±5 mV. Photophysical measurements were performed on solutions of the ligands in $CHCl_3$ ($c=1\times10^{-5}$ M) and the Ru(II) complexes in CH_3CN ($c=1\times10^{-5}$ M) at room temperature. For luminescence measurements the solutions were degassed by bubbling N_2 (gas) through them for 30 min. Absorption spectra were recorded on a Variant Cary 5000 UV/vis/NIR spectrophotometer. Emission and excitation spectra were measured on a Horiba Fluorolog 3 instrument. Luminescence lifetimes were measured by exciting the samples with the second harmonic (532 nm) of a pulsed Quantel Brilliant Nd:YAG laser. The system used for detection consisted of a Spex 270M monochromator, a Hamamatsu R928 photomultiplier, and a Tektronix TDS 540B oscilloscope. The signals were detected at 620 nm.

4.2. Materials

Air- and/or water-sensitive reactions were conducted under argon using dry, freshly distilled solvents. Unless otherwise stated, all reagents were purchased from commercial sources and used without additional purification. 5-Bromobipyridine,[18] 5,5′-dibromobipyridine,[19] 2-iodotetrathiafulvalene,[15] [Ru(2,2-bipyridine)$_2$Cl$_2$](PF$_6$)$_2$,[20] and [Ru(2,2-bipyridine)$_2$(5-bromo-2,2′-bipyridine)](PF$_6$)$_2$[16a] were prepared according to literature procedures. 2-Ethynyltetrathiafulvalene was prepared according to a modified literature procedure as described in the text.

4.2.1. 2-Trimethylsilylethynyltetrathiafulvalene

A Schlenk flask was charged with 2-iodotetrathiafulvalene (200 mg, 0.6 mmol), trimethylsilylacetylene (128 μL, 0.91 mmol), Pd(PPh$_3$)$_4$ (41 mg, 6 mol %) in THF, and *i*-Pr$_2$NH, and Ar-purged. CuI (12 mg, 10 mol %) was added and the solution was heated under argon at 60 °C for 16 h. After complete consumption of the starting material, the solvent was removed under vacuum. The crude product was purified by column chromatography on a column packed with silica gel, eluting with cyclohexane. The analytically pure product was obtained after recrystallization in a mixture of CH$_2$Cl$_2$/hexane (162 mg, 90%).

4.2.2. 2-Ethynyltetrathiafulvalene

Solid KF (96 mg, 1.65 mmol) was added to a stirred solution of 2-trimethylsilyltetrathiafulvalene (100 mg, 0.33 mmol) in tetrahydrofuran/methanol (50 ml, 1:1 v/v). After complete consumption of the starting material (16 h), the solution was concentrated by rotary evaporation to give a crude product, which was purified by column chromatography on a column packed with alumina, eluting with a mixture of hexane/dichloromethane 99:1 to yield 2-ethynyltetrathiafulvalene (60 mg, 80%).

4.2.3. Compound *1*

A Schlenk flask equipped with a septum, a Teflon-coated magnetic stirring-bar, and an argon inlet was charged with 5-bromo-2,2′-bipyridine (77 mg, 0.24 mmol) and 2-ethynyltetrathiafulvalene (55 mg, 0.24 mmol) in argon-degassed benzene/*i*-Pr$_2$NH (5/5 ml), and finally Pd(PPh$_3$)$_4$ (16 mg, 6 mol %) and CuI (4.5 mg, 10 mol %) were added as a solid. The solution was heated at 60 °C, until complete consumption of the starting material occurred (determined by TLC). After cooling, the precipitate was filtered and washed with two portions of water (20 ml) and two portions of diethyl ether (10 ml). The analytically pure compound was obtained by double recrystallization in a mixture of CH$_2$Cl$_2$/hexane (59 mg, 73%).

^{1}H NMR (CDCl$_3$) δ: 8.70 (d, 2H, J=1.5 Hz), 8.37 (t, 2H, J=7.5 Hz), 7.84–7.80 (m, 2H), 7.34–7.29 (m, 1H), 6.34 (s, 1H), 6.22 (s, 2H). ^{13}C NMR (DMSO-d_6) δ: 133.7, 133.4, 132.0, 131.9, 131.5, 131.4, 128.8, 128.7. MS (EI): *m/z* 382.99 (M$^+$). Anal. Calcd for $C_{18}H_{10}N_2S_4$: C, 56.51; H, 2.63; N, 7.32. Found: C, 56.37; H, 2.85; N, 7.46.

4.2.4. Compound *2*

Prepared following experimental conditions for **1**; from 5,5′-dibromo-2,2′-bipyridine (100 mg, 0.32 mmol) and 2-ethynyltetrathiafulvalene (146 mg, 0.64 mmol), Pd(PPh$_3$)$_4$ (22 mg, 6 mol %), CuI (6.1 mg, 10 mol %), benzene (6 ml), and *i*-Pr$_2$NH (6 ml); double recrystallization in a mixture of CH$_2$Cl$_2$/hexane to give 136 mg (70%) of **2**.

^{1}H NMR (acetone-d_6) δ: 8.80 (d, 2H, J=1.5 Hz), 8.52 (t, 2H, J=7.5 Hz), 8.12–7.96 (m, 2H), 7.13 (s, 2H), 6.67 (s, 4H). MS (EI): *m/z* 608.90 (M$^+$). Anal. Calcd for $C_{26}H_{12}N_2S_8$: C, 51.29; H, 1.99; N, 4.60. Found: C, 51.43; H, 2.05; N, 4.39.

4.2.5. Ru(II) complex *5*

In a Schlenk flask, to a stirred degassed acetonitrile/benzene (5:5 ml) solution of the precursor [Ru(2,2-bipyridine)$_2$(5-bromo-2,2′-bipyridine)](PF$_6$)$_2$ (130 mg, 0.14 mmol), were added sequentially Pd(PPh$_3$)$_4$ (12 mg, 6 mol %), CuI (2.7 mg, 10 mol %), diisopropylamine (1.5 ml), and 2-ethynyltetrathiafulvalene (40 mg, 0.17 mmol). The mixture was heated under argon for 16 h until the complete consumption of the starting material occurred (determined by TLC). After cooling down to room temperature, an aqueous solution of KPF$_6$ was added and the organic solvent was then removed under vacuum. The crude precipitate was washed twice with water and once with diethyl ether, and then was purified by chromatography on alumina eluting with CH$_2$Cl$_2$/MeOH (99:1). The analytically pure compound was obtained by double recrystallization in a mixture of CH$_2$Cl$_2$/hexane (106 mg, 70%).

^{1}H NMR (CD$_3$CN) δ: 8.53–8.46 (m, 6H), 8.09–8.02 (m, 6H), 7.82 (d, 1H, J=1.9 Hz), 7.79–7.77 (m, 1H), 7.71–7.64 (m, 4H), 7.42–7.35 (m, 5H), 6.86 (s, 1H), 6.50 (s, 2H). ^{13}C NMR (CD$_3$CN) δ: 158.1, 158.0, 157.9, 157.4, 154.3, 153.1, 152.85, 152.79, 152.6, 140.7, 140.0, 138.9, 131.0, 128.8, 128.7, 128.6, 126.0, 125.55, 125.51, 125.4, 124.9, 126.3, 120.6, 120.5, 117.7, 117.4, 114.6. ESI-MS: 940.98 ([M−PF$_6$]$^+$). Anal. Calcd for $C_{38}H_{26}F_{12}N_6P_2RuS_4$: C, 42.03; H, 2.41; N, 7.74. Found: C, 42.35; H, 2.65; N, 7.94.

Acknowledgements

This work was supported by the Swiss National Science Foundation (grant No. 200020-116003 and COST Action D31).

References and notes

1. (a) Yamada, J.; Sugimoto, T. *TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene*; Springer: Berlin, 2004; (b) William, J. M.;

Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors*; Prentice Hall: Englewoods Cliffs, NJ, 1992; (c) Khodorkovsky, V.; Becker, J. Y. *Organic Conductors: Fundamentals and Applications*; Farges, J. P., Ed.; Marcel Dekker: New York, NY, 1994; Chapter 3, p 75; (d) Batail, P., Ed.; *Chem. Rev.* **2004**, *104*, 4887, special issue on molecular conductors.

2. (a) Jorgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41; (b) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153; (c) Segura, J. L.; Martin, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372; (d) Jeppesen, J. O.; Becher, J. *Eur. J. Org. Chem.* **2003**, 3245; (e) Day, P.; Kurmoo, M. *J. Mater. Chem.* **1997**, *7*, 1291; (f) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355; (g) Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481; (h) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.
3. (a) Jia, C. Y.; Liu, S.-X.; Tanner, C.; Leiggener, C.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem. Commun.* **2006**, 1878; (b) Jia, C.; Liu, S.-X.; Tanner, C.; Leiggener, C.; Neels, A.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem.—Eur. J.* **2007**, *13*, 3804; (c) Dumur, F.; Gautier, N.; Gallego-Planas, N.; Sahin, Y.; Levillain, E.; Mercier, N.; Hudhomme, P.; Masino, M.; Girlando, A.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. *J. Org. Chem.* **2004**, *69*, 2164; (d) Fuks-Janczarek, I.; Luc, J.; Sahraoui, B.; Dumur, F.; Hudhomme, P.; Berdowski, J.; Kityk, I. V. *J. Phys. Chem. B* **2005**, *109*, 10179; (e) Loosli, C.; Jia, C. Y.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988.
4. (a) Liu, S.-X.; Dolder, S.; Franz, P.; Neels, A.; Stoeckli-Evans, H.; Decurtins, S. *Inorg. Chem.* **2003**, *42*, 4801; (b) Jia, C.; Liu, S.-X.; Ambrus, C.; Neels, A.; Labat, G.; Decurtins, S. *Inorg. Chem.* **2006**, *45*, 3152; (c) Dolder, S.; Liu, S.-X.; Beurer, E.; Ouahab, L.; Decurtins, S. *Polyhedron* **2006**, *25*, 1514; (d) Liu, S.-X.; Dolder, S.; Pilkington, M.; Decurtins, S. *J. Org. Chem.* **2002**, *67*, 3160; (e) Devic, T.; Avarvari, N.; Batail, P. *Chem.—Eur. J.* **2004**, *10*, 3697; (f) Devic, T.; Rondeau, D.; Şahin, Y.; Levillain, E.; Clérac, R.; Batail, P.; Avarvari, N. *Dalton Trans.* **2006**, 1331; (g) Ota, A.; Ouahab, L.; Golhen, S.; Cador, O.; Yoshida, Y.; Saito, G. *New J. Chem.* **2005**, *29*, 1135; (h) Hervé, K.; Liu, S.-X.; Cador, O.; Golhen, S.; Le Gal, Y.; Bousseksou, A.; Stoeckli-Evans, H.; Decurtins, S.; Ouahab, L. *Eur. J. Inorg. Chem.* **2006**, 3498; (i) Gavrilenko, K. S.; Le Gal, Y.; Cador, O.; Golhen, S.; Ouahab, L. *Chem. Commun.* **2007**, 280; (j) Liu, S.-X.; Ambrus, C.; Dolder, S.; Neels, A.; Decurtins, S. *Inorg. Chem.* **2006**, *45*, 9622; (k) Dolder, S.; Liu, S.-X.; Le Derf, F.; Sallé, M.; Neels, A.; Decurtins, S. *Org. Lett.* **2007**, *9*, 3753.
5. (a) Zhu, Q.-Y.; Bian, G.-Q.; Zhang, Y.; Dai, J.; Zhang, D.-Q.; Lu, W. *Inorg. Chim. Acta* **2006**, *359*, 2303; (b) Massue, J.; Bellec, N.; Chopin, S.; Levillain, E.; Roisnel, T.; Clérac, R.; Lorcy, D. *Inorg. Chem.* **2005**, *44*, 8740; (c) Bellec, N.; Lorcy, D. *Tetrahedron Lett.* **2001**, *42*, 3189.
6. (a) Pellon, P.; Gachot, G.; Le Bris, J.; Marchin, S.; Carlier, R.; Lorcy, D. *Inorg. Chem.* **2003**, *42*, 2056; (b) Smucker, B. W.; Dunbar, K. R. *J. Chem. Soc., Dalton Trans.* **2000**, 1309; (c) Cerrada, E.; Diaz, C.; Diaz, M. C.; Hursthouse, M. B.; Laguna, M.; Light, M. E. *J. Chem. Soc., Dalton Trans.* **2002**, 1104; (d) Devic, T.; Batail, P.; Fourmigue, M.; Avarvari, N. *Inorg. Chem.* **2004**, *43*, 3136; (e) Guerro, M.; Roisnel, T.; Pellon, P.; Lorcy, D. *Inorg. Chem.* **2005**, *44*, 3347.
7. (a) Peperichka, D.; Bryce, M. R.; Pearson, C.; Petty, M. C.; McInnes, E. J. L.; Zhao, J. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4635; (b) Wu, J.-C.; Liu, S.-X.; Neels, A.; Le Derf, F.; Sallé, M.; Decurtins, S. *Tetrahedron* **2007**, *63*, 11282; (c) Diaz, M. C.; Illescas, B. M.; Martin, N.; Perepichka, I. F.; Bryce, M. R.; Levillain, E.; Viruela, R.; Orti, E. *Chem.—Eur. J.* **2006**, *12*, 2709.
8. (a) Carroll, R. L.; Gorman, C. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378; (b) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482.
9. (a) Iyoda, M.; Hasegawa, M.; Miyake, Y. *Chem. Rev.* **2004**, *104*, 5085; (b) Wang, C. S.; Batsanov, A. S.; Bryce, M. R. *Chem. Commun.* **2004**, 578; (c) Hasegawa, M.; Takano, J.; Enozawa, H.; Kuwatani, Y.; Iyoda, M. *Tetrahedron Lett.* **2004**, *45*, 4109; (d) Hara, K.; Hasegawa, M.; Kuwatani, Y.; Enozawa, H.; Iyoda, M. *Chem. Commun.* **2004**, 2042; (e) Enozawa, H.; Hasegawa, M.; Takamatsu, D.; Fukui, K.; Iyoda, M. *Org. Lett.* **2006**, *8*, 1917; (f) Andersson, A. S.; Kilsa, K.; Hassenkam, T.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M.; Nielsen, M. B.; Diederich, F. *Chem.—Eur. J.* **2006**, *12*, 8541.
10. (a) Atienza, C.; Martin, N.; Wielopolski, M.; Haworth, N.; Clark, T.; Guldi, D. M. *Chem. Commun.* **2006**, 3202; (b) Wang, C. S.; Pâlsson, L.-O.; Batsanov, A. S.; Bryce, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 3789; (c) Zhao, Y.-.P.; Wu, L. Z.; Liu, G. S.; Xue, H.; Zhang, L. P.; Tung, C. H. *J. Org. Chem.* **2007**, 3632.
11. (a) Goze, C.; Leiggener, C.; Liu, S.-X.; Sanguinet, L.; Levillain, E.; Hauser, A.; Decurtins, S. *ChemPhysChem* **2007**, *8*, 1504; (b) Campagna, S.; Serroni, S.; Punteriero, F.; Loiseau, F.; De Cola, L.; Kleverlaan, C. J.; Becher, J.; Sorensen, A. P.; Hascoat, P.; Thorup, N. *Chem.—Eur. J.* **2002**, *8*, 4461.
12. (a) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11; (b) Schaumburg, K.; Lehn, J. M.; Goulle, V.; Roth, S.; Byrne, H.; Hagen, S.; Poplawski, J.; Brunfeldt, K.; Bechghaard, K.; Bjornholm, T.; Frederiksen, P.; Jorgensen, M.; Lerstrup, K.; Sommer-Larsen, P.; Goscinski, O.; Calais, J. L.; Eriksson, L. *Nanostructures Based on Molecular Materials*; Göpel, W., Ziegler, C., Eds.; VCH: Weinheim, 1992; p 153.
13. (a) Sonogashira, K. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, p 521; (b) Sonogashira, K. *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; p 203; (c) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46.
14. Otsubo, T.; Kochi, Y.; Bitoh, A.; Ogura, F. *Chem. Lett.* **1994**, 2047.
15. (a) Green, D. C. *J. Org. Chem.* **1979**, *44*, 1476; (b) Wang, C. S.; Ellern, A.; Khodorkovsky, V.; Bernstein, J.; Becker, J. Y. *J. Chem. Soc., Chem. Comm.* **1994**, 983.
16. (a) Kozlov, D. V.; Tyson, D. S.; Goze, C.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2004**, *43*, 6083; (b) Goze, C.; Kozlov, D. V.; Tyson, D. S.; Ziessel, R.; Castellano, F. N. *New J. Chem.* **2003**, *27*, 1679; (c) Goze, C.; Kozlov, D. V.; Castellano, F. N.; Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **2003**, *44*, 8713.
17. Liu, Y.; De Nicola, A.; Reiff, O.; Ziessel, R.; Schanze, K. S. *J. Phys. Chem. A* **2003**, *107*, 3476.
18. (a) Shen, X.; Moriuchi, T.; Hirao, T. *Tetrahedron Lett.* **2003**, *44*, 7711; (b) Fargeas, V.; Favresse, F.; Mathieu, D.; Beaudet, I.; Charrue, P.; Lebret, B.; Piteau, M.; Quintard, J.-P. *Eur. J. Org. Chem.* **2003**, 1711.
19. Schwab, P. F. H.; Fleischer, F.; Michl, J. *J. Org. Chem.* **2002**, *67*, 443.
20. Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. *J. Am. Chem. Soc.* **1977**, *99*, 4947.