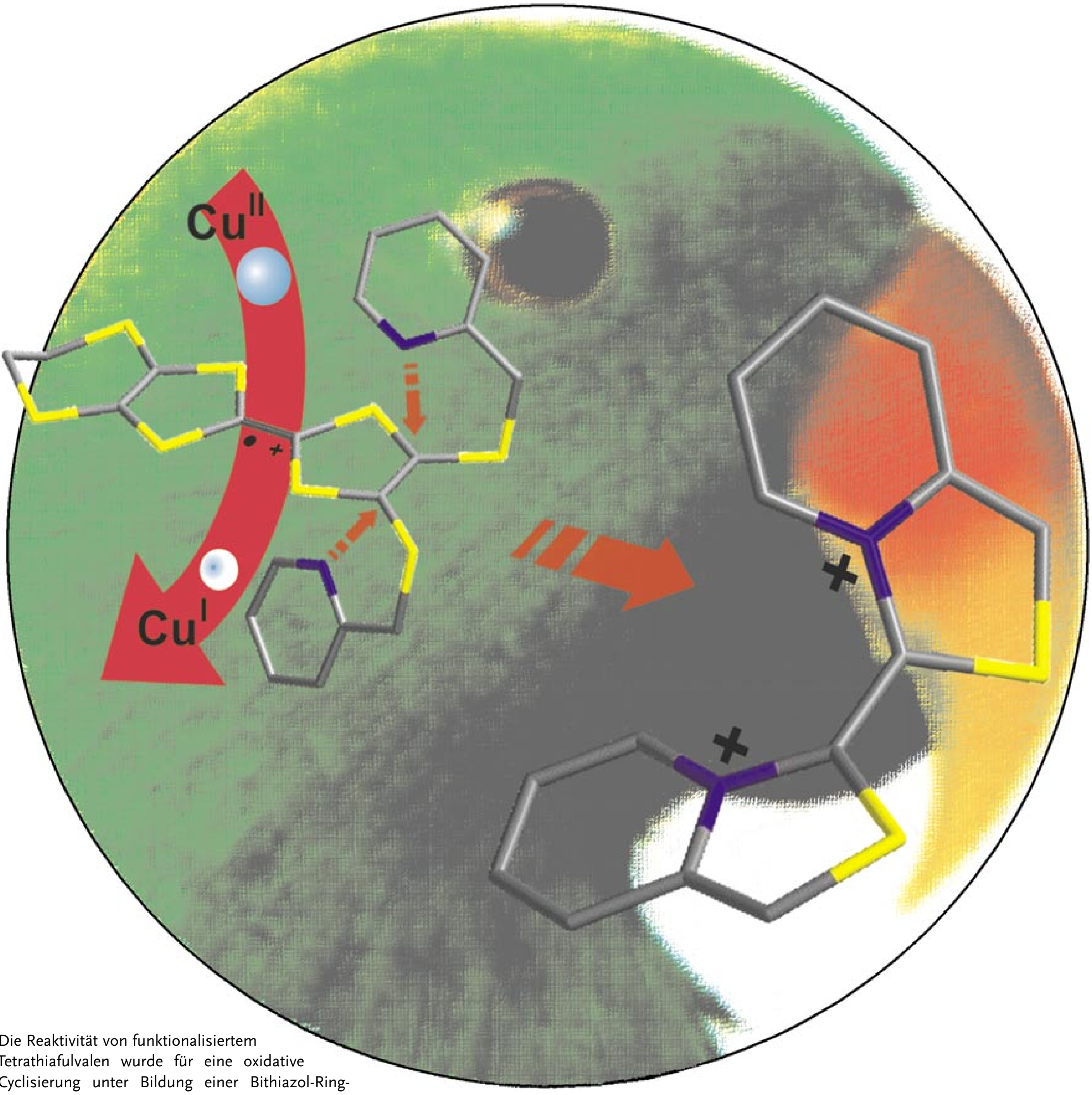
Zuschriften



Die Reaktivität von funktionalisiertem Tetrathiafulvalen wurde für eine oxidative Cyclisierung unter Bildung einer Bithiazol-Ringanordnung genutzt. Die elektronischen Eigenschaften dieses neuen Chromophors und der Dichroismus der Einkristalle sind erklärbar durch einen fast reinen HOMO→LUMO-ππ*-Übergang, der rechtwinklig zu den molekularen und kristallographischen C_2-Achsen polarisiert ist. Mehr dazu erfahren Sie in der Zuschrift von S. Decurtins et al. auf den folgenden Seiten.

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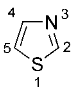
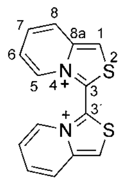
Heterocycle Synthesis

Tetrathiafulvalenes Acting as Leaving Groups: A Route to Bithiazoles[**]

Shi-Xia Liu, Christian Tanner, Antonia Neels,
Stefan Dolder, Samuel Leutwyler, Philippe Renaud,
*Peter Bigler, and Silvio Decurtins**

The five-membered heterocyclic 1,3-thiazole ring system is found in many natural products,[1–3] and alkylbithiazole oligomers have also been tested for organic electronic applications.[4] Here, we consider the extension of monocyclic heterocycles to bicyclic systems. The annulation of a benzene ring to a heterocycle generally results in change of properties, depending on the annulation topology. Specifically, in the case of thiazoles, the annulation of a benzene ring by means of the established cyclocondensation of *ortho*-aminothiophenols with carboxylic acids or aldehydes yields benzo[*d*]thiazoles. Two notable examples of thiazoles fused at face *d* (at the 4,5 bond) are thiazole orange, a powerful intercalator dye with base-stacking ability,[5] and luciferin, which causes bioluminescence in insects.[6] In contrast, however, there are few reports on thiazoles fused at face *c* (at the 3,4 bond),[7] and there are, to our knowledge, no structural reports of the thiazolo[3,4-*a*]pyridinium ring system. Here, the facile conversion of a tetrathiafulvalene (TTF) derivative into 3,3′-bithiazolo[3,4-*a*]pyridinium (**1**), a stable heterocyclic 10+10 π electron system, is particularly noteworthy because it extends the synthetic utilities of TTFs and it provides a new and straightforward entry to a particular class of fused-ring systems.





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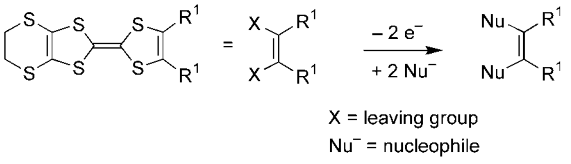
The well-known TTFs π-donor form stable radical cation species which in combination with acceptor molecules give rise to conducting and superconducting materials.[8] Current activities in this research field comprise the functionalization of the TTF backbone. As an example, functionalization with ligating groups such as pyridine aims at binding metal ions to the organic donor unit which, consequently, leads to organic/inorganic hybrid materials.[9] During this work we discovered that the pyridine-functionalized redox-active TTF ligand 4,5-bis(2-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene (ET-2Py)[9a] underwent ring transformation to give a 3,3′-bithiazolo[3,4-*a*]pyridinium. It must be noted that the synthesis of a parent, nonfused dithiadiazafulvalene (DTDAF) has been reported.[10] In contrast to the pyridine-fused bithiazole compound (**1**), DTDAFs are air-sensitive but can be trapped, for example, as a charge-transfer salt, due to their good electron-donor properties.

Herein we describe the synthesis, the single-crystal X-ray structure, the photophysical properties, and a theoretical investigation of the electronic structure of the dicationic, bis(bicyclic) ring assembly **1**. Thus the reaction of ET-2Py, or alternatively its Ni^{II} complex $[NiCl_2(ET\text{-}2Py)]$,[9c] with $Cu(ClO_4)_2$ gave yellow needlelike single crystals of $\mathbf{1}(ClO_4)_2$.[11] The Cu^{II}-mediated oxidative cyclization may proceed through the mechanistic pathway outlined in Scheme 1. One-electron oxidation of the TTF moiety affords an electrophilic radical cation **2** that reacts intramolecularly by means of a 5-*exo*-trig cyclization with the nucleophilic pyridyl residue.[12] After fragmentation of the intermediate spirocyclic compound **3**, a dihydrothiazolopyridinium derivative **4** is formed. Oxidation of the 1,3-dithiol-2-yl radical gives the cation **5**, which undergoes a second nucleophilic 5-*exo*-trig cyclization. β Fragmentation of the dithioate residue in **6** furnishes 1*H*,1′*H*-3,3′-thiazolo[3,4-*a*]pyridin-4-ium (**7**). Finally, aromatization of the thiazole moiety under oxidative conditions affords the observed final product **1**.

Interestingly, in this reaction, the TTF moiety acts as a pair of bis-vicinal leaving groups bonded to an ethylene residue that can be triggered by two one-electron oxidation processes. To the best of our knowledge, this reactivity of TTF has not been exploited and could be general for the transformation depicted in Equation (1).[13] A detailed examination of the rearrangement by replacing the pyridinyl groups on the the TTF ligands with functional groups such as pyrazinyl and quinolinyl is now under investigation.

The single-crystal structure of $\mathbf{1}(ClO_4)_2$ comprises dicationic ring assemblies and perchlorate anions in a 1:2 ratio. The compound crystallizes in the tetragonal crystal system, polar space group *I*$\bar{4}$*cd*. The yellow crystals have a needle-shaped morphology, in which the *c* axis lies parallel to the needle axis. In the structure of the ring assembly (Figure 1) the asymmetric unit is one half of the molecule, and the other half is generated by rotation about a crystallographic twofold axis that bisects the C3−C3′ bond. Each fused bicyclic heterocycle is virtually planar (rms deviation from a least-squares plane through all atoms amounts to only 0.023 Å;



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[*] Dr. S.-X. Liu, C. Tanner, S. Dolder, Prof. S. Leutwyler, Prof. P. Renaud, Prof. P. Bigler, Prof. S. Decurtins
Departement für Chemie und Biochemie
Universität Bern
Freiestrasse 3, 3012 Bern (Switzerland)
Fax: (+41) 31-631-3995
E-mail: decurtins@iac.unibe.ch

Dr. A. Neels
Institut de Chimie
Université Neuchâtel
Av. de Bellevaux 51
2007 Neuchâtel (Switzerland)

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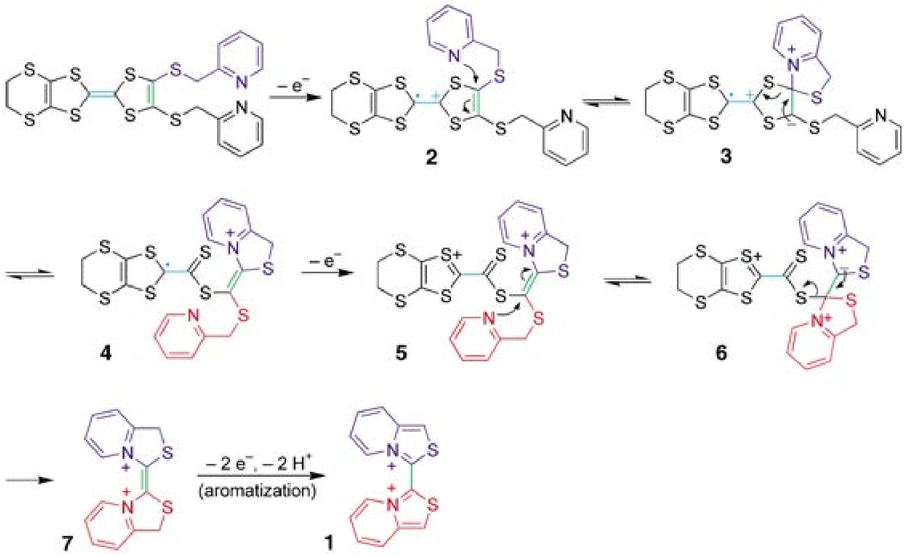


Scheme 1. Proposed mechanistic pathway for **1**.

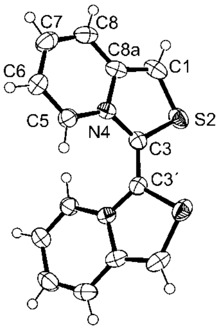


Figure 1. X-ray crystal structure of **1** in **1**$(ClO_4)_2$ (ORTEP, thermal ellipsoids set at the 50% probability level). For bond lengths see Table 1; selected bond angles [°]: C1-S2-C3 92.47(11), S2-C3-N4 111.56(15), C3-N4-C8a 113.24(18), N4-C8a-C1 111.2(2), C8a-C1-S2 111.48(18), N4-C3-C3′ 126.08(16), S2-C3-C3′ 122.28(11).

maximum deviation for C1: 0.037 Å); the molecule has a *cis* arrangement about the central C3–C3′ bond with a dihedral angle of 54.4°. The compound exists in its most stable conformation as a chiral molecule; however, both enantiomeric forms are present in the solid state in equal amounts.[14]

With regard to the electronic structure of **1**, the individual bond lengths are of interest. For the annulated six-membered heterocycle, distinct C–C bond-length alternations are observed (Table 1), indicating some dienic character. The ratio of the C5–C6 (1.345 Å) and C6–C7 (1.426 Å) bond lengths, 0.94, clearly diverges from unity. In pyridine, which may serve as a reference for aromaticity, the ratio of the C2–C3 (1.395 Å) and C3–C4 (1.394 Å) bond lengths is practically unity. Moreover, the C–N bond in pyridine is considerably shorter (1.340 Å) than those within the fused bicyclic systems (Table 1), which agrees with the expectation that annulation affects the bond lengths with an appreciable increase in the length of the C–N bond. The C–S bonds (Table 1) are slightly shorter than cited values of a thiazole derivative (av 1.705 Å)[15] and therefore, they may be involved in resonance. For the central C3–C3′ bond linking the two bicyclic residues, a length of 1.430 Å is found, indicating its predominantly σ character. The bond angles of the six-membered ring are found to be 120° to within 1.2°; the C1-S2-C3 angle (92.47°) lies within the expected range.[15]

Table 1: Bond lengths [Å] and twist angles [°] of **1** observed and calculated by the MP2/6-31G(d,p) method for a fully relaxed structure.

Bonds and angle	Obsd.	Calcd.	Δ (obsd.–calcd.)
N4–C5	1.384(3)	1.379	+0.005
C5–C6	1.345(3)	1.369	–0.024
C6–C7	1.426(4)	1.416	+0.010
C7–C8	1.345(4)	1.376	–0.031
C8–C8a	1.410(3)	1.411	–0.001
C8a–N4	1.398(3)	1.401	–0.003
C8a–C1	1.381(3)	1.398	–0.017
C1–S2	1.684(3)	1.680	+0.004
S2–C3	1.683(2)	1.706	–0.023
C3–N4	1.353(3)	1.387	–0.034
C3–C3′	1.430(4)	1.435	–0.005
N4-C3-C3′-N4′	54.4	76.4	–22.0

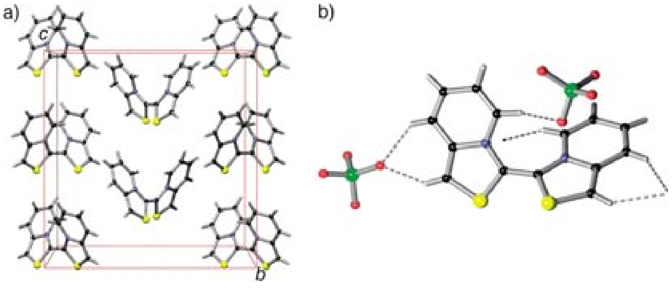
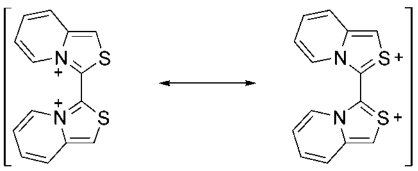


Figure 2. a) [100] Projection of **1**$(ClO_4)_2$, accentuating the alignment of the bis(bicycle)s. ClO_4^- ions are omitted. b) Hydrogen-bonding pattern of **1**$(ClO_4)_2$.

Figure 2a highlights the mutual arrangement of the bis(bicyclic) dications. A noticeable feature is the parallel orientation of the ring assemblies along the *c* axis which, of course, is related to their C_2 symmetry and is also expressed through the polar space group of the crystal structure. There are several C–H···O contacts in the crystal packing with the following donor···acceptor distances: C1···O1 3.153(4), C8···O1 3.351(4), C5···O3 3.277(4) Å. Figure 2b displays the hydrogen-bonding pattern of the crystal structure of **1**$(ClO_4)_2$.

Ab initio calculations of **1** in the electronic ground state were performed at the correlated level using the Gaussian 98 package.[16] The calculated bond lengths are in very good agreement with the experimental values and are typically 0.0–0.02 Å longer than those observed (Table 1). A calculation for a constrained structure (twist angle 54.4°) gave no significant changes in bond lengths. However, the calculated twist angle θ around the central C3–C3′ bond (the N4-C3-C3′-N4′ dihedral angle) is 76.4°, which is 22° larger than that measured in the crystal structure. That can be ascribed to crystal packing and hydrogen-bonding effects. Further details of the energy dependence on θ are discussed below.

The atomic charges were obtained by fitting the electrostatic potential (ESP) to atom-centered monopoles using the Merz–Singh–Kollmann (MSK)[17,18] and CHelpG[19] schemes. The ESP charges predict that the positive charge is equally distributed between N and S atoms. The CHelpG method produces qualitatively the same results as the MSK fit but with the positive charge less evenly distributed between N and S. In terms of valence-bond structures, the formal positive charges are either on the nitrogen or on the sulfur atoms (Scheme 2). Comparison with the calculated atomic charges leads us to conclude that both resonance structures in Scheme 2 contribute to the electronic structure of **1**.



Scheme 2. Resonance structures of **1**.

The chromophore **1** strongly absorbs at the violet end of the visible region as evidenced by its yellow color. The solution (MeCN) spectrum displays an intensive, broad absorption band around 377 nm with a ε value of $8\times 10^3\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ (Figure 3). The chromophore also shows a strongly Stokes-shifted fluorescence emission in acetonitrile solution. The chromophore shows an emission maximum of 508 nm when it is excited at 420 nm (Figure 3). Furthermore, the excitation spectrum between 470 and 300 nm (emission at 510 nm) compares well with the corresponding absorption profile. The fluorescence lifetime in MeCN was determined as $\tau = 2.8\pm 0.1$ ns.

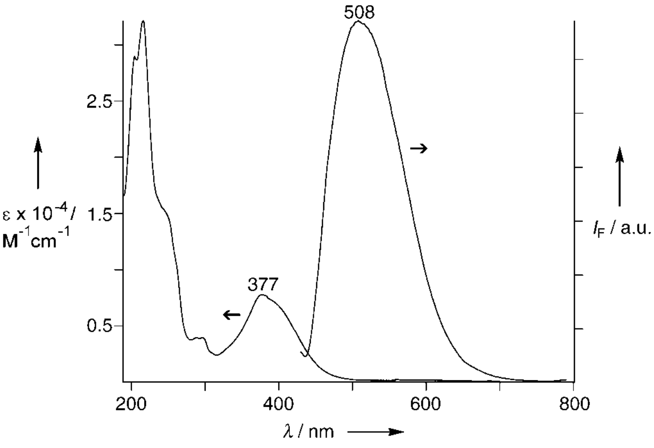


Figure 3. Electronic absorption and emission fluorescence spectra of $\mathbf{1}(\mathrm{ClO_4})_2$ in acetonitrile solution at 298 K ($\lambda_{\mathrm{exc}} = 420$ nm).

To rationalize the electronic properties of the first excited state of **1**, CIS/6-31G(d,p) calculations were performed for the MP2/6-31G(d,p) ground-state geometry constrained to the experimental twist angle ($\theta = 54.4°$). The predicted $S_1 \leftarrow S_0$ absorption energy is 3.483 eV (356 nm), with a high oscillator strength $f = 0.608$ ($f_{\mathrm{obs}} = 0.22$). The transition corresponds to a nearly pure HOMO→LUMO transition (89 %) of the $\pi\pi^*$ type. The $S_1 \leftarrow S_0$ transition dipole moment transforms as B in the point group C_2. Thus, the polarization of the absorption is perpendicular to the molecular and crystallographic C_2 axes (Figure 4), which is in perfect agreement with the dichroitic behavior of single crystals of $\mathbf{1}(\mathrm{ClO_4})_2$. The needlelike crystals appear yellow when examined with light polarized perpendicular to the needle axis (c axis) and colorless with polarization along the needle axis.

Figure 4. Orientation of the $S_1 \leftarrow S_0$ transition dipole moment.

Comparison of the HOMO and LUMO shows that $S_1 \leftarrow S_0$ electronic excitation induces a considerable charge flow from the six-membered ring to the S and N atoms, and increases the double-bond character of the central C3–C3′ bond. Despite the large twist angle θ between the two halves of the molecule there is a noticeable π-electronic overlap of helicoidal shape in both HOMO and LUMO. As θ goes to 90° this overlap drops to zero.

The calculated barrier for torsion around the angle θ is $30.1\,\mathrm{kJ\,mol^{-1}}$ at the SCF level and decreases to $25.5\,\mathrm{kJ\,mol^{-1}}$ at the MP2 correlated level. This barrier is not high enough to separate the two enantiomeric forms at room temperature, although interconversion of the two rotamers is not fast due to the large masses involved in the movement.

In summary, **1** is the first isolated and structurally characterized thiazolo[3,4-*a*]pyridinium ring assembly. In particular, the reactivity of functionalized tetrathiafulvalene has been exploited which, in turn, opens a straightforward synthetic entry to a particular class of fused-ring systems. A full photophysical analysis of the chromophoric ring assembly will be reported elsewhere.[20] A detailed examination of the synthetic pathway linking TTF and thiazole chemistry is now in progress.

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Keywords:
structure elucidation · cyclization · fluorescence · heterocycles · tetrathiafulvalene

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[11] **1**$(ClO_4)_2$: (*Caution!* Perchlorate salts can be explosive and must be handled with care). A layer diffusion between $NiCl_2$(ET-2Py)[9c] or ET-2Py[9a] (1.2×10^{-3} M) in CH_2Cl_2 and $Cu(ClO_4)_2\cdot6H_2O$ (1.2×10^{-2} M) in MeOH afforded within three weeks yellow single crystals suitable for X-ray analysis. Yield: 17%. m.p. > 300°C (decomp.); IR (KBr): $\tilde{\nu} = 1638$, 1518, 1457, 1333, 1265, 1101 cm^{-1} (ClO_4^-); ^1H NMR (D_2O): $\delta = 7.76$ (m, 1H), 7.94 (m, 1H), 8.42 (m, 2H), 9.46 ppm (s, 1H); ^{13}C NMR (D_2O): $\delta = 143.2$, 144.8, 146.9, 147.2, 150.4, 151.7, 164.7 ppm; ESI-MS (*m*/*z*): 135.02 $[C_{14}H_{10}N_2S_2]^{2+}$ (in CH_3CN), 136.01 $[C_{14}H_8D_2N_2S_2]^{2+}$ (in D_2O).

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[14] Supplementary crystallographic data for this paper are available from the IUCr electronic archives. CCDC-230147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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