

Ming Xu, Yong Ji, Jing-Lin Zuo,* Yi-Zhi Li and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University,
Nanjing 210093, China.

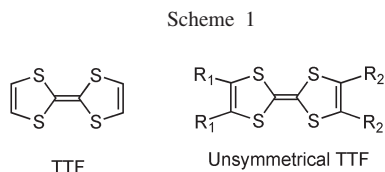
Received December 16, 2004

Two new unsymmetrical tetrathiafulvalene (TTF) derivatives, 2,3-bis(cyanoethylthio)-6,7-(methylethylenedithio)tetrathiafulvalene (**6a**) and 2,3-bis(cyanoethylthio)-6,7-(cyclopentodithio)tetrathiafulvalene (**6b**), have been prepared and characterized by NMR, MS, IR and Elemental analyses. The molecular structures have been determined by X-ray crystallography. Their redox properties have been investigated by cyclic voltammetry in dichloromethane solution and each compound shows two reversible single-electron redox couples.

J. Heterocyclic Chem., **42**, 847 (2005).

Introduction

Over the past 20 years, there has been extensive research in the synthesis of new tetrathiafulvalene (TTF) and related derivatives with the aim of preparing organic conductors and superconductors [1]. Recently, more interest in functional molecular materials based on TTF (Scheme 1) molecules has attracted much attention from chemists, physicists and materials scientists. TTF moiety possesses a fully extended electronically delocalized core and the delocalization can be further extended by choice of appropriate R groups [2-5]. The number and position of the sulfur atoms in those substituents show significant effect on the packing of the donor molecules in the crystalline structure. As a consequence, it is possible by modifying the substituents on the TTF core to obtain a wide range of structures and physical properties. They may have some potential applications, such as in Langmuir-Blodgett film, chemosensors [6-8], magnetic [9-11], non-linear optics [12-14], switches and others [15]. In addition, the TTF moiety is also a prime candidate in the synthesis of macrocyclic hosts for electron-deficient compounds [16-17]. Most reported TTF donors are symmetrical because of their ease of synthesis. During the past two decades, there has been much synthetic effort on unsymmetrical tetrathiafulvalenes and their derivatives. Some satisfactory results have been attained with approach to the successful preparation of varieties of functionalized unsymmetrical TTF [18]. But they are less studied compared to the symmetric analogues. The reason is that the separation and purification of unsymmetrical TTF are more difficult and troublesome experimentally.



Most of unsymmetrical TTF derivatives can successfully be available by refluxing their corresponding

thiones/ones in the presence of phosphine [19] or phosphite in one pot. In this paper, we adopt the similar method to synthesize two new unsymmetrical TTF compounds, 2,3-bis(cyanoethylthio)-6,7-(methylethylenedithio)tetrathiafulvalene (**6a**) and 2,3-bis(cyanoethylthio)-6,7-(cyclopentodithio)tetrathiafulvalene (**6b**).

Results and Discussion.

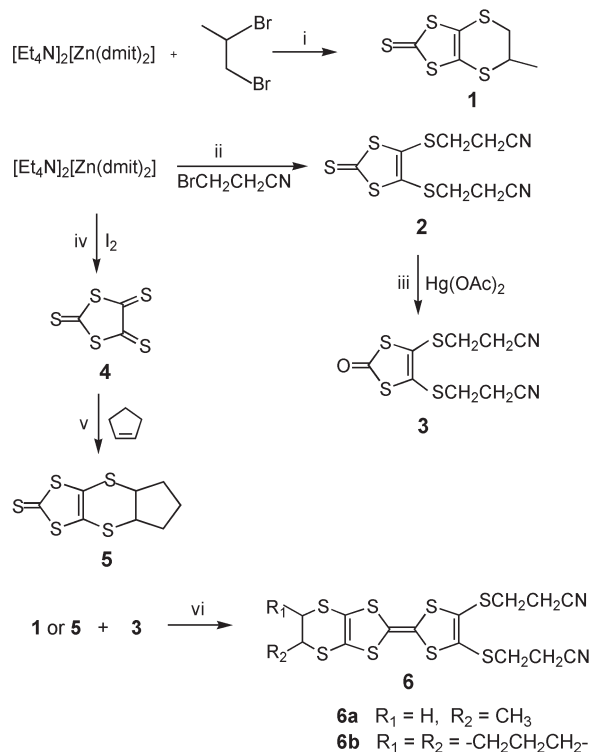
Syntheses of Unsymmetrical TTF Derivatives.

The syntheses of the target molecules **6a** and **6b** started from $(Et_4N)_2[Zn(dmit)_2]$ ($dmit = 2$ -thioxo-1,3-dithiole-4,5-bis(thiolato)) is shown in Scheme 2. Alkylation of $(Et_4N)_2[Zn(dmit)_2]$ is usually carried out in acetonitrile, acetone or tetrahydrofuran. Oligo(4,5-dihydro-1,3-dithiole-2,4,5-trithione) (**4**) which can act as an effective 4π component, reacted with cyclopentene by heating to form Diels-Alder adduct compound **5** in yield of 30%. Compound **2** was converted to compound **3** by a conventional method in high yield. Papavassiliou *et al.* prepared a series of unsymmetrical TTF derivatives using two distinct 1,3-dithiole heterocycles [20]. The method is the quickest, most general route to unsymmetrical TTF and it gives the best yields. In consideration of less reactive thione, we optimized this reaction to achieve TTF framework by coupling the 1,3-dithiole-2-thione and 1,3-dithiole-2-one. The homo-coupling products have been observed and can be removed through column chromatography. Apparently, due to the polarity of the cyanoethyl group compared to the normal alkylthio group, the symmetrical byproducts tetrakis(2'-cyanoethylthio)tetrathiafulvalene and tetrakis(alkylthio)tetrathiafulvalene have R_f values close to 0 and 1, respectively. Therefore chromatography and separation of the middle fraction gives the pure mixed coupling product.

Electrochemical Cyclic Voltammetry Studies.

The redox potentials of new electron donors **6a** and **6b** were measured in dichloromethane by cyclic voltammetry (0.1 M TBAClO₄ as supporting electrolyte, carbon fiber electrode as working electrode, scan rate 100 mV S⁻¹). Two reversible single-electron redox couples are observed.

Scheme 2



i) acetone, 40 °C, 2 d, 57%; ii) CH₃CN, reflux 1.5 h, 87%; iii) CH₃COOH/CHCl₃ (v/v 3:1), quantitative; iv) I₂, EtOH, acetone, -50 °C, 2 h, 95%; v) 1, 4-dioxane, 75 °C, 2 h, 33%; vi) P(OEt)₃, 110 °C, 2 h

Preparation of unsymmetrical TTF derivatives

For **6a**, the first one-electron oxidation peak ($E_{1/2} = 0.635$ V) is assigned to **6a**/**6a**⁺; the second reversible peak ($E_{1/2} = 0.915$ V) is assigned to **6a**⁺/**6a**²⁺. Compound **6b** shows these peaks at $E_{1/2} = 0.628$ V and 0.916 V. The redox potentials for both compounds are close, indicating that the two substitution groups here show similar electron effect on the TTF core.

Description of Crystal Structure of **6a** and **6b**.

For crystal structure analysis, the crystal data, data collection conditions and refinement data are given in Table 1.

A perspective view of the asymmetric unit with the atom-numbering scheme and the projection of the molecular entity in the lattices are shown in Figure 1. For compound **6a**, S(1), S(4), S(5), S(6), C(1) and C(6) atoms are nearly coplanar, the other sulfur atoms deviate to the same side of the core plane by 0.70–0.92 Å. The planes formed by atoms S(1), S(4), C(2), C(5) and S(5), S(6), C(7), C(8) make angles of 20.4 and 21.0°, respectively, with the central tetrathiafulvalene plane. The two cyanoethyl groups in compound **6a** are greatly deviated from this plane and bent toward the same direction. The shortest intermolecular

Table 1

Crystal Data, Data Collection and Structure Refinement for **6a** and **6b**

	6a	6b
Empirical formula	C ₁₅ H ₁₄ N ₂ S ₈	C ₁₇ H ₁₆ N ₂ S ₈
Formula weight	478.76	504.80
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2 ₁ /c
a (Å)	7.8142(17)	20.159(3)
b (Å)	11.479(3)	8.3200(11)
c (Å)	12.683(3)	12.9181(17)
α (°)	64.206(4)	90
β (°)	82.428(4)	99.359(3)
γ (°)	79.266(4)	90
Volume (Å ³)	1004.7(4)	2137.8(5)
Z	2	4
D _{calc} (g/cm ³)	1.583	1.568
μ (mm ⁻¹)	0.891	0.842
F(000)	492	1040
Crystal size	0.23 × 0.20 × 0.15	0.30 × 0.20 × 0.20
θ range for data collection (°)	1.99–25.25	2.05–25.25
Index ranges	–9 ≤ h ≤ 8 –13 ≤ k ≤ 13 –15 ≤ l ≤ 7	–24 ≤ h ≤ 23 –9 ≤ k ≤ 9 –15 ≤ l ≤ 10
No. reflections collected	5087	10465
No. independent reflections	3559	3869
R(int)	0.0322	0.0235
Data/restraints/parameters	3559/0/227	3869/0/244
Goodness-of-fit on F ²	1.031	0.916
Final R indices [I > 2σ(I)]	R ₁ = 0.0645, wR ₂ = 0.1333	R ₁ = 0.0512, wR ₂ = 0.1374
Largest difference peak and hole (e ⁻ Å ⁻³)	0.350 / –0.408	0.589 / –0.510

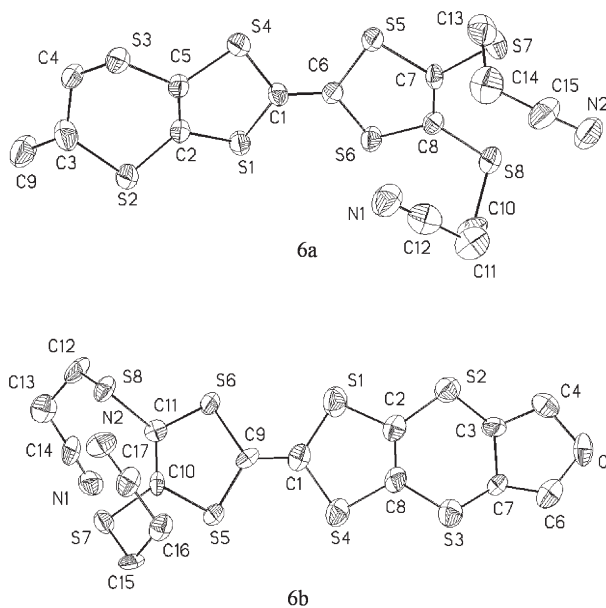


Figure 1. ORTEP view of **6a** and **6b** with atom numbering scheme: Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

S...S contacts between S(2) ...S(4') and S(2)...S(5') (Figure 2) are 3.629(2) Å and 3.680(2) Å (related by the symmetry operators of $(1+x, y, z)$), respectively, which are less than the sum of the van der Waals radii (3.70 Å). From the packing diagram of compound **6a**, the crystal consists of columns of molecules along *a* direction. The shorter intermolecular C(1)-H... S(8') contact is 3.599(7) Å (symmetry code : $1+x, -1+y, 1+z$).

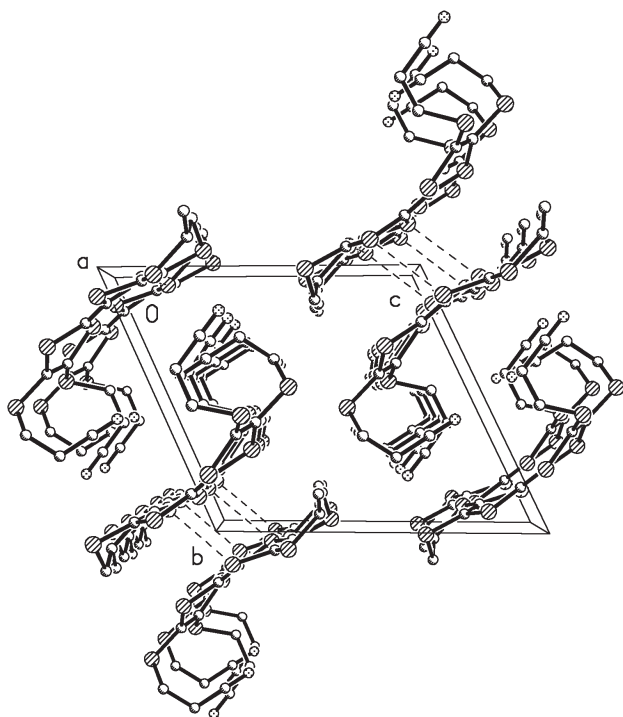


Figure 2. The packing diagram of compound **6a** view along the *a* axis (the dotted line representing S...S non-bonded contacts less than 3.7 Å).

Compound **6b** has nearly the same flat tub conformation and the most obvious difference is that the two cyanoethyl groups bent such that they point in opposite directions relative to each other (Figure 3). No short intermolecular S...S contact is observed, which may arise from the different packing modes of the external units for these two compounds. The shorter intermolecular interactions occur at C(12)-H(12A)...N(2') (3.360(5) Å, symmetry code: $x, 1/2-y, -1/2+z$); C(12)- H(12B)...N(2') (3.413(6) Å, symmetry code: $x, -1+y, z$) and C(15)-H(15B)...N(2') (3.361(5) Å, symmetry code: $x, 3/2-y, 1/2+z$).

EXPERIMENTAL

All the commercial reagents used were analytically pure and without further purification. Schlenk techniques were used in carrying out manipulation under nitrogen atmosphere. Elemental analyses for C, H, and N were performed on a Perkin-Elmer

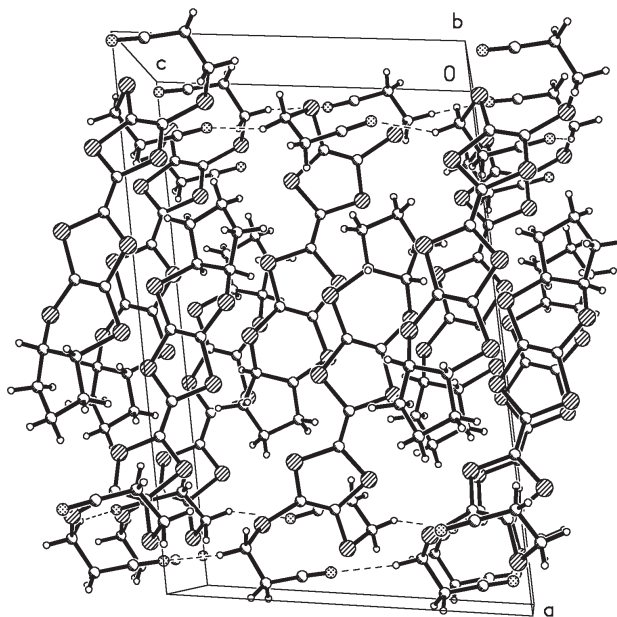


Figure 3. The packing diagram of compound **6b** view along the *b* axis (the dotted line representing shorter C-H...N interactions).

240C analyzer. The ir spectra were taken on a Vector22 Bruker Spectrophotometer ($400\text{--}4000\text{cm}^{-1}$) with KBr pellets. NMR spectra were measured on a Bruker AM 500 spectrometer. Chemical shifts were measured as δ units (ppm) relative to tetramethylsilane. EI-MS spectra were recorded on a Varian MAT 311A instrument. Melting points were determined with a X-4 digital micro melting point apparatus and uncorrected. The cyclic voltammetry was performed by a CHI660a-Analyser with the electrochemical cell using a carbon fiber as the working electrode, a platinum plate as auxiliary electrode and Ag/AgCl as reference electrode. Measurements were made in CH_2Cl_2 solution and using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. $(\text{Et}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ and oligo (1,3-dithiole-2,4,5-trithione) were prepared by literature method [21].

X-ray Structure Determination.

The single crystal of compound **6a** suitable for the X-ray structure analysis was grown from dichloromethane/diethyl ether. Single crystals of **6b** were obtained upon recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. Intensity data were measured on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation using $\omega/2\theta$ scan mode at 20 °C. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97. Non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. All hydrogen atoms were positioned geometrically and refined as riding, with C-H distances of 0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Crystallographic parameters and agreement factors are contained in Table 1. CCDC-257504 and 257505 contain the supplementary crystallographic data for this paper. These data can be obtained

free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

General Procedure.

2, 3-Bis(cyanoethylthio)-6,7-(methylethylenedithio)tetrathiafulvalene (**6a**).

In a typical procedure, **1** (6 mmol, 1.34 g) and compound **3** (4 mmol, 1.15 g) in 35 ml of P(OEt)₃ were placed in a 50 ml round bottom 3-neck flask fitted a reflux condenser. The mixture was then heated to 110 °C. After reacting for 1 h, the red solution was cooled to room temperature and 50 ml of methanol was added. The mixture was further cooled in a refrigerator. A crude precipitate was obtained at -20 °C and it was dissolved into dichloromethane. **6a** was isolated by silica gel column chromatography. The solution was concentrated, ethanol added and cooled to -20 °C. Orange yellow needle crystals were obtained. Yield: 35% (based on **3**), mp 128–130 °C; ir (KBr) ($\nu_{\max}$, cm⁻¹): 1410 (C-S), 1634 (C=C), 2248 (C≡N); MS (EI): m/z (%) = 478 (M⁺, 22); ¹H nmr (500 MHz, CDCl₃): δ 1.50 (d, 3H, J = 6.90 Hz, CH₃), 2.74 (t, 4H, J = 6.90 Hz, SCH₂CH₂CN), 3.05 (dd, 1H, J = 12.9 Hz, J = 7.60 Hz, SCHHCH), 3.09 (t, 4H, J = 6.90 Hz, SCH₂CH₂CN), 3.22 (dd, 1H, J = 12.9 Hz, J = 2.60 Hz, SCHHCHCH₃), 3.69 (m, 1H, J = 2.60 Hz, SCHCH₃); ¹³C nmr (500 MHz, CDCl₃): δ 128.45, 117.80, 39.43, 37.39, 31.76, 21.28, 19.29.

Anal. Calcd for C₁₅H₁₄N₂S₈: C, 37.65; H, 2.92; N, 5.58. Found: C, 37.74; H, 2.98; N, 5.74.

2, 3-Bis(cyanoethylthio)-6,7-(cyclopentodithio)tetrathiafulvalene (**6b**).

Compound **6b** was obtained in a similar method as an orange yellow needle crystal in 38% yield. mp 133–134 °C; ir (KBr) ($\nu_{\max}$, cm⁻¹): 1404 (C-S), 1627 (C=C), 2249 (C≡N); MS (EI): m/z (%) = 504 (M⁺, 18); ¹H nmr (500 MHz, CDCl₃): δ 1.82 (dd, 2H, J = 14.0 Hz, J = 6.0 Hz, CH₂CH₂CH₂), 1.98 (q, 2H, J = 4 Hz, SCHCHHCH₂), 2.21 (q, 2H, J = 5.5 Hz, SCHCHHCH₂), 2.75 (t, 4H, J = 6 Hz, SCH₂CH₂CN), 3.10 (t, 4H, J = 6 Hz, SCH₂CH₂CN), 3.81 (dd, 2H, J = 5.5 Hz, J = 6 Hz, SCHCH₂); ¹³C nmr (500 MHz, CDCl₃): δ 128.44, 125.75, 117.88, 54.36, 33.33, 31.85, 25.29, 19.38.

Anal. Calcd for C₁₇H₁₆N₂S₈: C, 40.47; H, 3.17; N, 5.55. Found: C, 40.42; H, 3.22; N, 5.59.

Acknowledgements.

This work was supported by The Major State Basic Research Development Program (G2000077500), the National Natural

Science Foundation of China (NSF20201006 and 90101028).

REFERENCES AND NOTES

- [1a] J. Roncali, *J. Mater. Chem.*, **7**, 2307 (1997); [b] M. R. Bryce, *Chem. Soc. Rev.*, **20**, 355 (1991); [c] P. Day and M. Kurmoo, *J. Mater. Chem.*, **7**, 1921 (1997).
- [2] N. Robertson, L. Cronin, *Coord. Chem. Rev.*, **227**, 93, (2002).
- [3] R. -M. Olk, B. Olk, W. Dietzsch, R. Kirmse, E. Hoyer, *Coord. Chem. Rev.*, **117**, 99 (1992).
- [4] A. E. Pullen, R. -M. Olk, *Coord. Chem. Rev.*, **188**, 211 (1999).
- [5] U. T. Mueller-Westerhoff, B. Vance and D. I. Yoon, *Tetrahedron*, **47**, 909 (1991).
- [6] J. R. Bates, P. Kathirgamanathan and R. W. Miles, *Electron. Lett.*, **31**, 1225 (1995).
- [7] J. R. Bates, P. Kathirgamanathan and R. W. Miles, *Thin Solid Films*, **299**, 18 (1997).
- [8] J. R. Bates, R. W. Miles and P. Kathirgamanathan, *Synth. Met.*, **76**, 313 (1996).
- [9] H. Oshio, *Mol. Cryst. Liq. Cryst. A.*, **233**, 283 (1993).
- [10] H. Imai, T. Inabe, T. Otsuka, T. Okuno and K. Awaga, *Phys. Rev. B.*, **54**, R6838 (1996).
- [11] H. Tajima, M. Inokuchi, A. Kobayashi, A. Sato, T. Naito, H. Kobayashi and H. Kuroda, *Synth. Met.*, **85**, 1585 (1997).
- [12] H. Li, D. Zhou, C. Huang, J. Xu, T. Li and X. Xia, *J. Chem. Soc., Faraday Trans.*, **92**, 2585 (1996).
- [13] J. L. Zuo, T. M. Yao, F. You, X. Z. You, H. K. Fun and B. C. Yip, *J. Mater. Chem.*, **6**, 1633 (1996).
- [14] T. Geisler, K. Pedersen, A. E. Underhill, A. S. Dhindsa, D. R. Greve, T. Bjornholm and J. C. Petersen, *J. Phys. Chem. B.*, **101**, 10625 (1997).
- [15a] P. R. Ashton, R. A. Bissell, N. Spencer, J. F. Stoddart and M. S. Tolley, *Syn. Lett.*, 923 (1992); [b] M. B. Nielsen, S. B. Nielsen and J. Becher, *Chem. Commun.*, 475 (1998); [c] M. R. Bryce, *Adv. Mater.*, **11**, 11 (1999).
- [16] T. K. Hansen, T. Jorgensen, P. C. Stern and J. Becher, *J. Org. Chem.*, **57**, 6403 (1992).
- [17] S. Flink, B. A. Boukamp, A. van den Berg, D. N. Reinhoudt and F. C. J. M. van Veggel, *J. Am. Chem. Soc.*, **120**, 4652 (1998).
- [18a] Y. Misaki, H. Fujiwara and T. Yamabe, *J. Org. Chem.*, **61**, 3650 (1996); [b] L. Kaboub, J. -P. Legros, B. Donnadieu, A. -K. Gouasmia, L. Boudiba and J. -M. Fabre, *J. Mater. Chem.*, **14**, 351 (2004); [c] N. Gautier, R. Samuel, Y. Sahin, E. Levillain, L. -L. Stephanie and P. Hudhomme, *Org. Lett.*, **6**, 1569 (2004); [d] M. Hasegawa, J. -I. Takano, H. Enozawa, Y. Kuwatani and M. Iyoda, *Tetrahedron Lett.*, **45**, 4109 (2004); [e] K. A. Nielsen, W. -S. Cho, J. O. Jeppesen, V. M. Lynch, J. Becher and J. L. Sessler, *J. Am. Chem. Soc.*, **126**, 16296 (2004); [f] N. Avarvari and M. Fourmigue, *Chem. Commun.*, 2794 (2004).
- [19] M. F. Hurley and J. Q. Chambers, *J. Org. Chem.*, **46**, 775 (1981).
- [20] G. C. Papavassiliou, G. A. Mousdis, S. Y. Yiannopoulos, V. C. Kakoussis and J. S. Zambounis, *Synth. Met.*, **27**, B373 (1988).
- [21] N. Svenstrup and J. Becher, *Synthesis*, 215 (1995).