[3] a) A. K. Hughes, A. Meetsma, J. H. Teuben, *Organometallics* **1993**, *12*, 1936; b) W. A. Herrmann, M. J. A. Morawietz, *J. Organomet. Chem.* **1994**, *482*, 169; c) J. Okuda, F. J. Schattenmann, S. Wocadlo, W. Massa, *Organometallics* **1995**, *14*, 789; d) D. W. Carpenetti, L. Kloppenburg, J. T. Kupec, J. L. Petersen, *Organometallics* **1996**, *15*, 1572; e) S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, *Organometallics* **1996**, *15*, 5577; f) R. Gómez, P. Gómez-Sal, A. Martín, A. Núñez, P. A. del Real, P. Royo, *J. Organomet. Chem.* **1998**, *564*, 93; g) B. Royo, P. Royo, L. M. Cadenas, *J. Organomet. Chem.* **1998**, *551*, 293; h) T. Eberle, T. P. Spaniol, J. Okuda, *Eur. J. Inorg. Chem.* **1998**, 237; i) L. Duda, G. Erker, R. Fröhlich, F. Zippel, *Eur. J. Inorg. Chem.* **1998**, 1153; j) D. Kunz, G. Erker, R. Fröhlich, G. Kehr, *Eur. J. Inorg. Chem.* **2000**, 409.

[4] a) M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255; b) Y.-X. Chen, P.-F. Fu, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 5958; c) B. E. Bosch, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1997**, *16*, 5449; d) Y.-X. Chen, T. J. Marks, *Organometallics* **1997**, *16*, 3649; e) A. Bertuleit, C. Fritze, G. Erker, R. Fröhlich, *Organometallics* **1997**, *16*, 2891; f) G. Lanza, I. L. Fragalà, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 8257; g) F. Amor, A. Butt, K. E. Du Plooy, T. B. Spaniol, J. Okuda, *Organometallics* **1998**, *17*, 5836; h) R. Gómez, P. Gómez-Sal, P. A. del Real, P. Royo, *J. Organomet. Chem.* **1999**, *588*, 22.

[5] a) J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S. Lai (Dow), EP 416815, **1991** [*Chem. Abstr.* **1991**, *115*, 93163]; b) J. M. Canich (Exxon), EP 420436, **1991** [*Chem. Abstr.* **1991**, *115*, 184145].

[6] a) P. Jutzi, U. Siemeling, *J. Organomet. Chem.* **1995**, *500*, 175; b) P. Jutzi, T. Redeker, *Eur. J. Inorg. Chem.* **1998**, 663; c) T. Cuenca, P. Royo, *Coord. Chem. Rev.* **1999**, *193–195*, 447; d) R. Kempe, *Angew. Chem.* **2000**, *112*, 478; *Angew. Chem. Int. Ed.* **2000**, *39*, 468; e) L. H. Gade, *Chem. Commun.* **2000**, 173.

[7] a) M. D. Fryzuk, S. S. S. H. Mao, P. B. Duval, S. J. Rettig, *Polyhedron* **1995**, *14*, 11; b) M. D. Fryzuk, L. Jafarpour, *Organometallics* **1999**, *18*, 4050; c) M. D. Fryzuk, P. B. Duval, S. S. S. H. Mao, M. J. Zaworotko, L. R. MacGillivray, *J. Am. Chem. Soc.* **1999**, *121*, 2478; d) I. L. Feduskin, S. Dachert, H. Schuman, *Organometallics* **2000**, *19*, 4066; e) P. Doufou, K. A. Abboud, J. M. Boncella, *J. Organomet. Chem.* **2000**, *603*, 213.

[8] J. M. Rozell, P. R. Jones, *Organometallics* **1985**, *4*, 2206.

[9] a) W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* **1980**, *31*, 123; b) D. E. Wigley, *Prog. Inorg. Chem.* **1994**, *42*, 239; c) M. J. Humphries, M. L. H. Green, M. A. Leech, V. C. Gibson, M. Jolly, D. N. Williams, M. R. J. Elsegood, W. Clegg, *J. Chem. Soc. Dalton Trans.* **2000**, 4044.

[10] A. D. Horton, J. de With, *Chem. Commun.* **1996**, 1375.

[11] No phenyl coordination of the phenyl ring to the metal was observed in solution: C. Pellecchia, A. Grassi, A. Immirzi, *J. Am. Chem. Soc.* **1993**, *115*, 1160.

[12] a) M. G. Thorn, Z. C. Etheridge, P. E. Fanwick, I. P. Rothwell, *Organometallics* **1998**, *17*, 3636; b) G. Jiménez Pindado, M. Thornton-Pett, M. B. Hursthouse, S. J. Coles, M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1999**, 1663; c) J. Sassmannshausen, A. K. Powell, C. E. Anson, S. Wocadlo, M. Bochmann, *J. Organomet. Chem.* **1999**, *592*, 84; d) P. J. W. Deckers, A. J. van der Linden, A. Meetsma, B. Hessen, *Eur. J. Inorg. Chem.* **2000**, 929.

[13] C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, *Organometallics* **1993**, *12*, 4473.

[14] a) J. Scholz, M. Schlegel, K.-H. Thiele, *Chem. Ber.* **1987**, *120*, 1369; b) A. D. Horton, J. H. G. Frijns, *Angew. Chem.* **1991**, *103*, 1181; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1152.

[15] a) K. Shelly, D. C. Finster, Y. J. Lee, W. R. Scheidt, C. A. Reed, *J. Am. Chem. Soc.* **1985**, *107*, 5955; b) M. Laguna, M. D. Villacampa, M. Contel, J. Garrido, *Inorg. Chem.* **1998**, *37*, 133; c) A. S. Batsanov, S. P. Crabtree, J. A. K. Howard, C. W. Lehmann, M. Kilner, *J. Organomet. Chem.* **1998**, *550*, 59.

[16] P. Royo, J. Cano, M. A. Flores, EP 01500020.1 **2001**.

[17] G. M. Sheldrick, SHELXL-97, Program for the Solution and the refinement of Crystal Structures, Universität Göttingen, Germany, **1997**.

Tetrathiafulvaleno-Annelated Porphyrins[**]

Jan Becher,* Thomas Brimert, Jan O. Jeppesen, Jens Z. Pedersen, Roman Zubarev, Thomas Bjørnholm, Niels Reitzel, Torben R. Jensen, Kristian Kjaer, and Eric Levillain

Dedicated to Professor Michael P. Cava
on the occasion of his 75th birthday

Porphyrins are of fundamental importance in biological systems and are currently in focus for applications in supramolecular[1] and materials chemistry, for which the porphyrin chromophore has been extensively modified to enhance the desired properties.[2] Langmuir–Blodgett (LB) films[3] of porphyrin derivatives have been studied because of their optical, magnetic, and electrical properties.[4] Tetrathiafulvalene (TTF) is able to exist in three different stable redox states (TTF, $\mathrm{TTF}^{+\bullet}$, and TTF^{2+}). For this reason TTF derivatives have found widespread use[5] in materials chemistry. Since the first TTF charge-transfer complex with metallic behavior was reported[5a] a huge number of TTF radical-cation salts have been studied resulting in the discovery of organic superconductivity in some of these systems.[5a] Although there have been some attempts to combine TTF chemistry with porphyrin chemistry, the direct combination of these two major fields has so far been unsuccessful, most likely on account of the lack of an appropriate pyrrolo-TTF unit. Some of us recently developed an efficient synthesis of the parent pyrrolo[3,4-*d*]-TTF ring system using a nonclassical and simple pyrrole synthesis.[6] With this building block at hand, we decided to prepare the first examples of single molecules in which the intriguing optical and metal-ion binding properties of the

---

[*] Prof. J. Becher, Dr. T. Brimert, M. Sc. J. O. Jeppesen,
Dr. J. Z. Pedersen, Prof. R. Zubarev
Department of Chemistry
Odense University (University of Southern Denmark)
Campusvej 55, 5230, Odense M (Denmark)
Fax: (+45) 66-15-87-80
E-mail: jbe@chem.sdu.dk

Prof. T. Bjørnholm, N. Reitzel
Nano-Science Center, Department of Chemistry
University of Copenhagen
Universitetsparken 5, 2100, Copenhagen Ø (Denmark)

Dr. T. R. Jensen, Dr. K. Kjaer
Condensed Matter Physics and Chemistry Department
Risø National Laboratory
Building 108, Post Office Box 49, 4000 Roskilde (Denmark)

Dr. E. Levillain
Ingénierie Moléculaire et Matériaux Organiques
CNRS UMR 6501, Université d'Angers, 49045 Angers (France)

[**] We gratefully acknowledge financial support from Carlsbergfondet and Bengt Lundquists Minnesfond for a post-doctoral position to T. B., the University of Odense for a Ph.D. scholarship to J. O. J. and the French Embassy Copenhagen for a travel grant to J. B. We thank HASYLAB at DESY, Hamburg for beam time at beam line BW1 and DANSYNC for financial support. The gift of Jan Skov Peterson's FORTRAN program LSQREFL is gratefully acknowledged. Finally, we thank Prof. K. S. Murray, University of Monash, Australia for helpful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

1433-7851/01/4013-2497 $ 17.50+.50/0

porphyrin molecule have been coupled with the favorable redox properties of the TTF moiety. The direct annelation of the porphyrin core with four TTF units situated at the periphery gives a porphyrin in which the annulene π-electron system is extended by direct conjugation with TTF units.

Here, we report 1) two synthetic routes to the first tetrathiafulvaleno-annelated fully conjugated porphyrins **5a**, **b**, 2) preliminary physical characterization of these novel porphyrin systems, and 3) structural studies of the porphyrin **5a** obtained from Langmuir films.

Our approach to the porphyrins **5a**, **b** is outlined in Scheme 1 (**5a** and **5b** refer to the mixtures **5ai** and **5aii**, and **5bi** and **5bii**, respectively). Vilsmeier formylation of the pyrrolo-TTF[6b] **1** under standard conditions produced the formylpyrrolo-TTF **2** in 96% yield. Reduction of the formyl group proceeded quantitatively to give the alcohol **3**. Treatment of **3** with *p*-toluenesulfonic acid (TsOH) in EtOH (RT, 1 min) gave a dark green precipitat of **4a** in quantitative yield (Scheme 1, Route A). The plasma desorption mass spectrum (PD-MS) of this compound[7] featured a peak at $m/z = 1837.5$, which corresponds with the porphyrinogen **4a** ($M^{+\bullet} = 1839.2$). Furthermore, small peaks at $m/z = 2299.3$ and 2757.0 were observed indicating the formation of cyclic pentapyrrole ($M^{+\bullet} = 2299.0$) and cyclic hexapyrrole ($M^{+\bullet} = 2758.8$), respectively.[8] When the cyclization was carried out in benzene, precipitation of **4a** was avoided, and subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was performed in a one-pot reaction to afford **5a** in 89% yield (oxidation occurred spontaneously when a solution of **4a** was left standing a few days under ambient conditions). This resulted in a pitch black solid, purified by chromatography. The PD-MS of this product (Figure 1) featured a peak at $m/z = 1833.3$, corresponding to the porphyrin **5a** ($M^{+\bullet} = 1833.1$). Stirring the pyrrolo-TTF **1** with paraformaldehyde ($(HCHO)_n$) or benzaldehyde and a catalytic amount of TsOH in THF at room temperature, produced the porphyrinogens **4a**, **b** (Scheme 1, Route B) in excellent yields (70–80%). These intermediates could be either isolated and purified by chromatography, or directly oxidized with DDQ in THF yielding **5a**, **b**, respectively.[9]

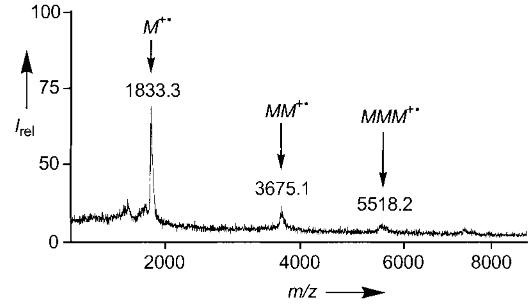
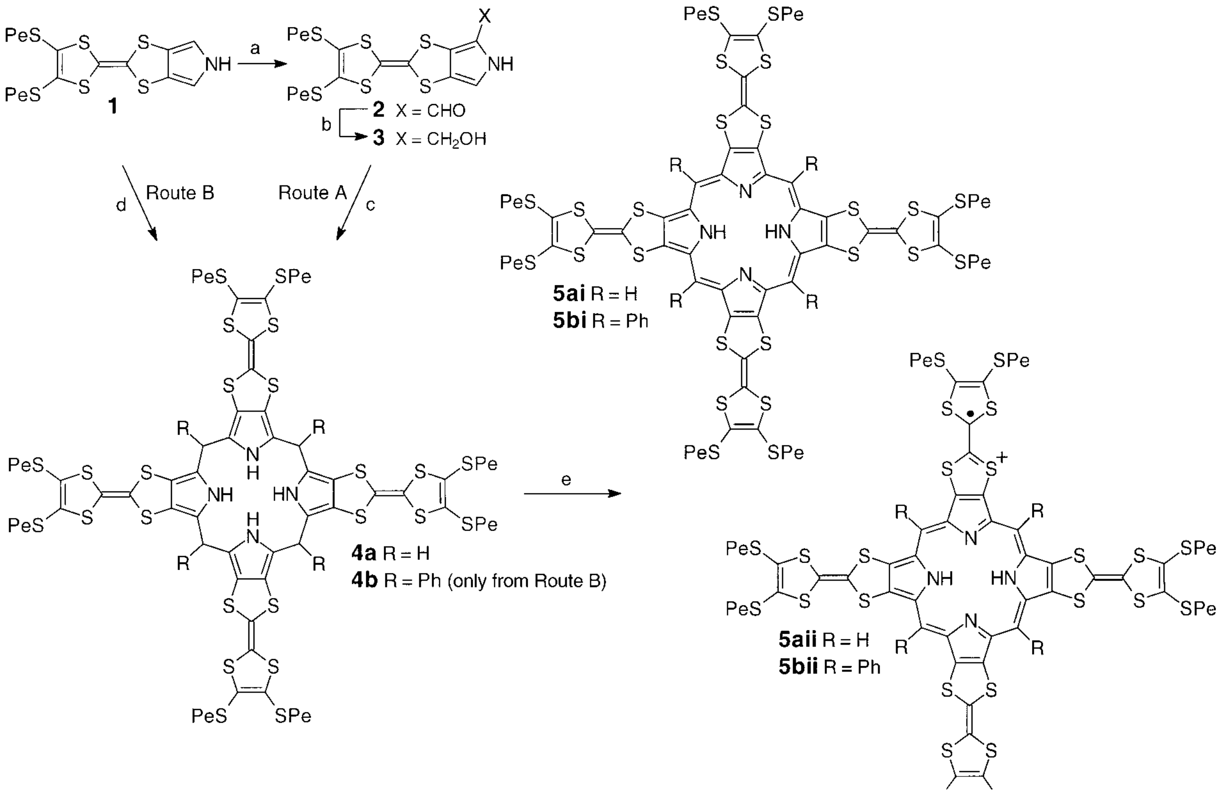


Figure 1. PD-MS spectrum of the porphyrin **5a**.

High resolution matrix-assisted laser-desorption/ionization mass spectra (MALDI-MS) of **4b**, **5a**, and **5b** showed the exact masses, $m/z = 2140.239$, 1830.076, and 2134.203, respec-



Scheme 1. Synthesis of the porphyrins **5a**, **b**: a) DMF/$POCl_3$, 96%; b) $NaBH_4$/THF, RT, quantitative; c) TsOH(cat.)/EtOH or $C_6H_6 \rightarrow$ **4a**; d) $(HCHO)_n$ or PhCHO/TsOH(cat.)/THF, RT, 18 h; e) DDQ/C_6H_6 or THF $\rightarrow$ **5a** 89% from **3**, Route A (one-pot), **5a** 48% from **1**, Route B (one-pot), **5b** 55% from **1**, Route B (one-pot). Pe = n-C_5H_{11}.

tively, corresponding to $C_{100}H_{116}N_4S_{24}^{+\bullet}$, $C_{76}H_{94}N_4S_{24}^{+\bullet}$, and $C_{100}H_{110}N_4S_{24}^{+\bullet}$ (calcd masses $M^{+\bullet} = 2140.2492$, 1830.0770, and 2134.2022). Electron paramagnetic resonance (EPR) spectroscopy revealed strong signals, arising from radicals, as broad singlets without any detectable hyperfine structure at $g = 2.0084$ and 2.0044 for **5a** and **5b**, respectively, either used neat or in CH_2Cl_2 solution. The linewidths and *g*-values are consistent with the presence of a TTF radical cation.[10] Quantitative EPR measurements in CH_2Cl_2 showed that the isolated product **5a** contained 19% unpaired spin,[11] indicating that compound **5a** consist of a mixture of the neutral porphyrin (**5ai**) and the radical cation porphyrin (**5aii**) in a ratio of approximately 4:1 (Scheme 1). Solution oxidation potentials (vs Ag/AgCl) obtained from cyclic voltammograms (CVs) of compound **1** recorded in CH_2Cl_2 revealed two pairs of reversible redox waves at $E^1_{1/2} = 0.48$ V and $E^2_{1/2} = 0.93$ V. The porphyrinogen **4b** gave a CV that is fully analogous with that of a nonconjugated tetra-TTF,[12] showing two pairs of reversible oxidation waves at $E^1_{1/2} = 0.49$ V and $E^2_{1/2} = 0.87$ V, whereas the porphyrins **5a** and **5b** showed CVs with reversible waves $E^1_{1/2} = 0.63$ V, $E^2_{1/2} = 1.10$ V and $E^1_{1/2} = 0.58$ V, $E^2_{1/2} = 0.96$ V for **5a** and **5b**, respectively.[13] Thin layer cyclic voltammetry[14] (TLCV) and the deconvoluted voltammograms of both **5a** (Figure 2) and **5b** revealed that the first oxidation waves actually correspond to two one-electron processes with $\Delta E < 100$ mV, whereas the second wave involves a one-step two-electron process. Thus, first a radical cation is formed, which is then closely followed by the formation of a dication (probably as a biradical). Finally, a tetracation is formed. These results suggest the presence of an isolated electron-withdrawing 18 π-electron porphyrin ring system in which the pyrrolo *c*-bonds in two of the TTF units are included in the 18 π-electron ring system. Therefore, those two TTF units do not show the electrochemical characteristics of a normal TTF unit and hence only a total of four electrons are removed during oxidation of the neutral porphyrin. Furthermore, the deconvoluted voltammograms of compound **5a** (Figure 2b) and **5b** showed one reversible wave at $E_{1/2} = -1.3$ V (1 electron), which could be assigned to the first reduction of the porphyrin ring system. The ^1H NMR spectra (250 MHz) of compound **5a** and **5b** recorded in $CDCl_3$ at 298 K featured only very broad peaks, which could be explained by the presence of radicals or slow tumbling resulting from aggregation in solution. Evidence for aggregation is observed in the PD-MS (Figure 1) of **5a**, which revealed small peaks at $m/z = 3675.1$ and 5518.2. These peaks can not be explained by the presence of cyclic polypyrroles of higher order. Instead, we suggest that the porphyrins aggregate together in the gas phase forming dimers ($MM^{+\bullet} = 3666.1$) and trimers ($MMM^{+\bullet} = 5499.2$).

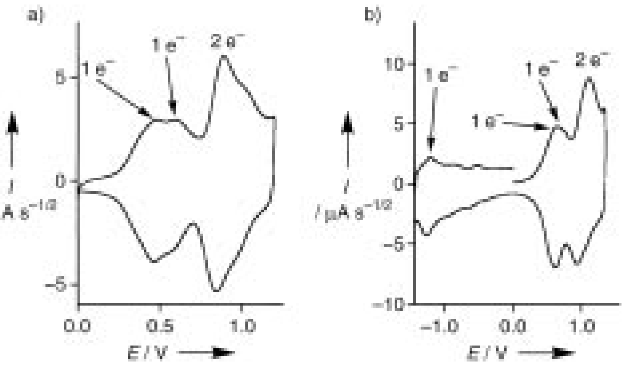


Figure 2. Deconvoluted voltammograms (vs Ag/AgCl) of a solution of **5a** (1.00 mM) in CH_2Cl_2/nBu_4NPF_6 (0.4 M) on platinum electrode; a) scan rate 0.1 V s^{-1}, b) scan rate = 0.2 V s^{-1}.[14]

Information about the packing of the porphyrin **5a** at an air–water interface comes from X-ray diffraction studies of Langmuir films. Compound **5a** spreads readily from $CHCl_3$ solutions on water resulting in formation of a well-defined thin film. Compression on a Langmuir trough reveals a compression isotherm[7] with a onset in the pressure rise at a mean molecular area, mma = 50 Å^2 and a collapse at 35 Å^2 corresponding to a lateral pressure, $\pi = 40$ mN m^{-1}. X-ray diffraction[7] studies using synchrotron X-rays[15] on a Langmuir film compressed to a nominal mean molecular area of 48 Å^2 ($\pi = 5$ mN m^{-1}) reveal a broad Bragg peak (possibly split) corresponding to a repeat distance of 23–27 Å and coherence length of $\xi = 50$–60 Å indicating weak lateral order in the thin film. Model independent fits[16] to the X-ray reflectivity measured on the same film reveal an electron-density profile along the surface normal (ρ(z)) corresponding to a 60 Å thick film with a mean electron density relative to water $\rho/\rho_{water} = 1.18$. The rms (root mean square) film rough-

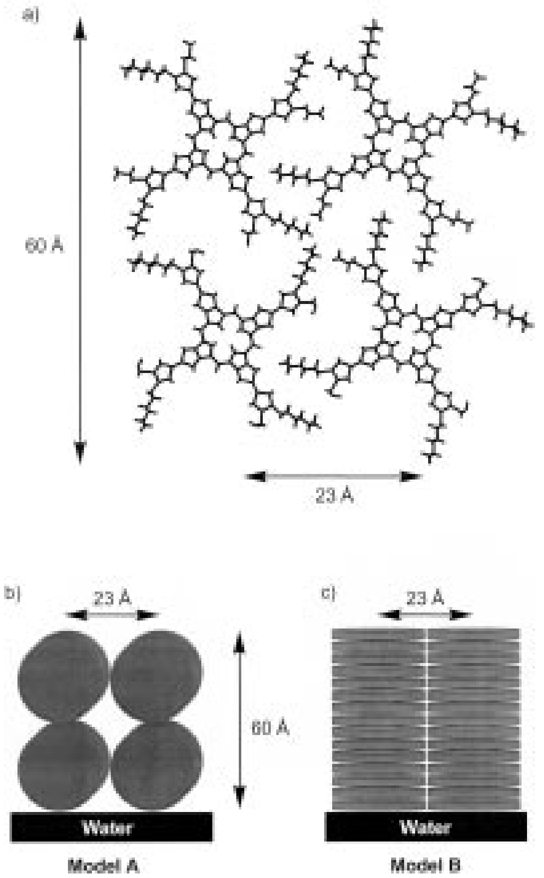


Figure 3. Proposed structure of the porphyrin **5a** deduced from X-ray diffraction studies using synchrotron X-rays on a Langmuir film of **5a**. Details are given in the text.

ness σ = 7 Å towards the film–air interface. Measurements by atomic force microscopy[7] (AFM) on films transferred to mica by horizontal dipping show smooth films with occasional 50 Å deep defects. Based on this limited structural data we propose the structural model depicted in Figure 3a in which the four peripheral thioalkyl substituted TTF moieties interdigitate to fill space. The in-plane repeat distance of 23–27 Å agrees well to the resulting edge-to-edge close-packed arrangement (Figure 3a). Two orientations of stacks of these molecules are in accordance with the data. In one model (Model A, Figure 3b) stacks run along the water surface in two layers, in the other (Model B, Figure 3c) stacks of approximately 15 molecules run along the surface normal. The measured thickness of 60 Å corresponds roughly to the thickness of model A. Indirect information about the repeat distance along the normal to the porphyrin plane ($d_{\pi\text{-stack}}$) may be deduced by assuming a rectangular unit cell and by using the measured electron density of the film $\rho/\rho_{\text{water}} = 1.18$[17] or the area per molecule (Model A). In both cases we obtain $d_{\pi\text{-stack}} = 3.5-4.2$ Å, which agrees with the typical stacking distances between π-stacked TTF molecules. Diffraction studies of bulk samples could not reveal any long-range order and attempts to grow single crystals of the compounds presented here have so far failed.

Further work is aimed at complete physical characterization and understanding of these novel porphyrin ring systems, together with further functionalization and generation of mono, bis-, and tris-(tetrathiafulvaleno)-annelated porphyrins and their metal complexes.

Experimental Section

2: $POCl_3$ (0.23 g, 1.50 mmol) was added to anhydrous DMF under an atmosphere of nitrogen and stirred at room temperature for 10 min. A solution of the pyrrolo-TTF[6b] **1** (0.45 g, 1.01 mmol), dissolved in anhydrous DMF (5 mL) was added dropwise and the mixture became dark violet. The mixture was stirred for another 20 min, whereupon an aqueous solution of NaOAc (10%, 20 mL; Ac = acetyl) and H_2O (20 mL) were added. The resulting slurry was stirred for 10 min and the solid collected, redissolved in Me_2CO (100 mL) and concentrated under vacuum. The crude product was dissolved in CH_2Cl_2 (50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the resulting yellow powder was subjected to column chromatography (SiO_2, EtOAc). The yellow band ($R_f = 0.5$) was collected and the solvent evaporated affording the aldehyde **2** (0.46 g, 96%) as yellow needles: M.p. 139.5–140.5 °C; ^1H NMR (CD_3SOCD_3, 250 MHz, 298 K): $\delta = 0.84$ (t, $J = 7.1$ Hz, 6H), 1.20–1.40 (m, 8H), 1.55 (m, 4H), 2.84 (t, $J = 7.0$ Hz, 4H), 7.25 (s, 1H), 9.51 (s, 1H), 12.44 (br s, 1H); ^{13}C NMR (CD_3SOCD_3): $\delta = 13.8$, 21.6, 28.9, 29.9, 35.4, 109.4, 118.7, 120.1, 120.8, 125.0, 126.7, 126.9, 177.6; MS (EI): m/z (%) = 475 $[M]^+$ (100); IR (KBr): $\tilde{\nu} = 1645$ cm^{-1} (C=O); elemental analysis calcd (%) for $C_{19}H_{25}NOS_6$ (475.77): C 47.97, H 5.30, N 2.94, S 40.43; found C 48.08, H 5.35, N 3.03, S 40.28.

5a (Route A, one-pot reaction): $TsOH \cdot H_2O$ (20 mg, 0.11 mmol) was added to a solution of the hydroxymethylpyrrolo-TTF **3** (0.54 g, 1.13 mmol) in C_6H_6 (20 mL). The reaction mixture was stirred at room temperature and monitored by thin layer chromatography (TLC). After approximately 3 min, all of the starting material **3** had been consumed and DDQ (0.19 g, 0.84 mmol) was added in one portion. The reaction mixture was stirred for another 30 min and the solvent removed under vacuum to afford a pitch-black residue. The crude product was purified by column chromatography (SiO_2, gradient of CH_2Cl_2/MeOH 1:0 → 19:1) affording the porphyrin **5a** (0.46 g, 89%) as a black powder: M.p. no visible melting 25–250 °C; ^1H NMR ($CDCl_3$, 250 MHz, 298 K): $\delta = 0.91$ (br s, 24H), 1.37 (br s, 32H), 1.64 (br s, 16H), 2.84 (br s, 16H); MS(PD): $m/z = 1833.3$ $[M]^+$ 3675.1 $[MM]^+$, 5518.2 $[MMM]^+$; HiResMALDI-MS: $m/z = 1830.0764$ (calcd for $C_{76}H_{94}N_4S_{24}^{+\bullet} = 1830.0770$); UV/Vis ($CH_2Cl_2$): λ_{max} (ε [M^{-1}cm^{-1}]) 297 (43000), 393 nm (33000); elemental analysis calcd (%) for $C_{76}H_{94}N_4S_{24}$ (1833.05): C 49.80, H 5.17, N 3.06; found C 50.12, H 5.43, N 3.23.

Received: January 17, 2001 [Z16440]

---

[1] J. N. H. Reek, A. E. Rowan, R. de Gelder, P. T. Beurskens, M. J. Crossley, S. De Feuter, F. de Scryver, R. J. M. Nolte, *Angew. Chem.* **1997**, *109*, 396–399; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 361–363.

[2] a) K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, **1975**; b) D. Dolphin, *The Porphyrins*, *Vol. 8*, Academic Press, New York, **1978**; c) *The Porphyrin Handbook*, *Vol. 1* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**.

[3] a) M. C. Petty, *Langmuir-Blodgett Films. An Introduction*, Cambridge University Press, Cambridge, **1996**, pp. 1–234; b) T. Bjørnholm, T. Hassenkam, N. Reitzel, *J. Mater. Chem.* **1999**, *9*, 1975–1990.

[4] a) H. Chou, C.-T. Chen, K. F. Stork, P. W. Bohn, K. S. Suslick, *J. Phys. Chem.* **1994**, *98*, 383–385; b) E. Dalcanale in *Comprehensive Supramolecular Chemistry*, *Vol. 10* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, D. Reinhoudt), Pergamon, Oxford, **1996**, chap. 20; c) J. B. Peng, G. A. Lawrie, G. T. Barnes, I. R. Gentle, G. J. Foran, M. J. Crossley, Z. Huang, *Langmuir* **2000**, *16*, 7051–7055.

[5] For TTF reviews, see a) *Organic Superconductors including Fullerenes* (Eds.: J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geise, H. H. Wang, A. M. Kini, M.-H. Wangbo), Prentice-Hall, Engelwood Cliffs, **1992**, pp. 1–210; b) G. Schukat, E. Fanghänel, *Sulfur Rep.* **1996**, *18*, 1–294; c) M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589–598; d) M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153–164.

[6] a) J. O. Jeppesen, K. Takimiya, F. Jensen, J. Becher, *Org. Lett.* **1999**, *1*, 1291–1294; b) J. O. Jeppesen, K. Takimiya, F. Jensen, T. Brimert, K. Nielsen, N. Thorup, J. Becher, *J. Org. Chem.* **2000**, *65*, 5794–5805.

[7] A PD-MS spectrum of compound **4a** and a Langmuir–Blodgett compression isotherm of the porphyrin **5a**, together with a description of the AFM and XRD measurements on **5a** are available in the Supporting Information.

[8] The formation of cyclic polypyrroles (pentamer, hexamer etc.) from condensation of pyrroles have been reported, see: J.-I. Setsune, Y. Katakami, N. Iizuna, *J. Am. Chem. Soc.* **1999**, *121*, 8957–8958, and refs. therein.

[9] If the pentyl groups are interchanged with methyl groups the porphyrins are virtually insoluble.

[10] F. Wudl, G. M. Smith, E. J. Hufnagel, *J. Chem. Soc. Chem. Commun.* **1970**, 1453–1454.

[11] The radical content was determined at room temperature through double integration of the EPR signal and comparison with aknown standard, the stable radical 2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl measured under identical experimental conditions. All attempts to obtain the neutral porphyrin **5ai** exclusively by chemical reduction of the paramagnetic mixture of the neutral porphyrin **5ai** and the radical cation porphyrin **5aii**, was unsuccessful.

[12] J. Lau, J. Becher, *Synthesis* **1997**, 1015–1020.

[13] CV was performed using 0.89, 0.84, 1.10, and 0.75 mM solutions of **1**, **4b**, **5a**, and **5b**, respectively, in anhydrous CH_2Cl_2 with nBu_4NPF_6 (0.10 M) as supporting electrolyte and Ag/AgCl as reference electrode at a scan rate of 0.1 V s^{-1}.

[14] TLCV of **5a** (0.93 mM) + dichloronaphthoquinone (1.88 mM) + nBu_4NPF_6 (0.45 M) in deoxygenated CH_2Cl_2, platinum electrode = 0.0314 cm^2, scan rate = 5 mV s^{-1}, layer = close to 20 μm.

[15] J. Als-Nielsen, D. Jacquemain, K. Kjaer, F. Leveiller, M. Lahav, L. Leiserowitz, *Phys. Rep.* **1994**, *246*, 251–313.

[16] J. S. Pedersen, I. W. Hamley, *J. Appl. Crystallogr.* **1994**, *27*, 36–49.

[17] This value corresponds to a mass density $\rho = 1.2$ g cm^{-3} $= M_W V^{-1} N_A^{-1}$ (M_W = molecular weight, V = unit cell volume, N_A = Avogadros constant).