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Tetrathiafulvalene Porphyrins

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Abstract: Four tetrathiafulvalene (TTF)-annulated porphyrins **1**–**4** were synthesized and characterized. All contain a tetraphenylporphyrin (TPP) core onto which four, two, or one TTF subunits were annulated. Absorption and fluorescence spectroscopic studies together with electrochemical investigations reveal that interactions between the porphyrin system and the annulated TTF units take place in solution. The annulation of one or more TTF units to the porphyrin core has a profound effect on the reduction potentials associated with this latter framework, with positive shifts in the range of 0.105 to 0.355 V and 0.200 to 0.370 V for the first and second reduction potential, respectively, compared to the corresponding processes in the model compound TPP, **18**. The redox potentials for the first oxidation of the TTF units are considerably shifted in **4** ($\Delta E_{ox}{}^{1} = +0.285$ V) and **2** ($\Delta E_{ox}{}^{1} = -0.140$ V), whereas for **1** and **3** these potentials remain within the region expected for a normal TTF unit. Considerable changes in the second oxidation potential associated with the TTF subunits were seen for **2** ($\Delta E_{ox}{}^{1} = -0.085$) and **3** ($\Delta E_{ox}{}^{1} = -0.175$). The emission spectra of **1**–**4** revealed that the porphyrin fluorescence is almost quenched in the neutral state of the TTF-annulated porphyrins, a finding that is consistent with substantial electron transfer taking place from the TTF subunits to the porphyrin core. Oxidation of the TTF unit(s) ($\mathrm{TTF} \rightarrow \mathrm{TTF}^{\bullet +}$) present in **1**–**4** leads to the emission intensity being restored.

Keywords: electrochemistry · electron transfer · porphyrinoids · supramolecular chemistry · tetrathiafulvalenes

Introduction

Porphyrins and related tetrapyrrolic macrocycles,[1] classic “pigments of life”, are found in a large variety of biological systems (e.g., bacterial photosynthetic system, cytochrome P450, cytochrome C, hemoglobin).[2] Not surprisingly, therefore, porphyrins and metalloporphyrins have been incorporated into a large number of electron- and energy-transfer model systems and have also been used to create artificial light-harvesting antenna,[3] photosynthetic reaction centers, photonic wires,[4] and redox switches.[5] Likewise, the redox-active tetrathiafulvalene[6] (TTF) unit has been the subject of extensive investigation because it is able to exist in three different stable redox states (TTF, $\mathrm{TTF}^{\bullet +}$, and TTF^{2+}). Indeed, TTF derivatives[7] have found widespread use in materials chemistry. Since the first TTF charge transfer (CT) complex with metallic behavior was reported,[8] a huge number of TTF radical-cation salts have been studied, work that has been stimulated in part by the discovery that some of the systems in question display organic superconductivity.[8] During the last few years TTF and its derivatives have also been used to prepare a number of intriguing molecular and supramolecular systems, including chemical sensors,[9] charge-separating ligands,[10] artificial muscles,[11] molecular shuttles,[12] chemical springs,[13] and synthetic switches.[14] Although there have been some attempts to combine TTF chemistry with porphyrin chemistry,[15] the direct combination of these two all-important building blocks into the same molecular system in which the TTF

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units are directly annulated to the porphyrin core has only recently been achieved[16–18] by the Odense and Angers groups, and only after the development[19] of a fused monopyrrolo-TTF (MPTTF) precursor. However, the chemistry of these hybrid systems has yet to be extensively explored.

One of the reasons why compounds containing both porphyrin and TTF entities are of interest is that compounds containing both a chromophore and a redox site incorporated into a single molecule can act as chemical sensors. In fact, a multitude of porphyrin systems functionalized with redox groups,[15e,20] such as ferrocene,[21] have been prepared with such an objective in mind. In many cases, the utility of these compounds as chemical sensors has been limited by a lack of suitable communication between the redox group and the porphyrin core. Recently, some of us described[16] the synthesis of tetraTTF-porphyrins, such as **1** depicted in Figure 1, as well as a monoTTF-porphyrin bearing *p*-cyanophenyl substituents in the four *meso*-positions.[17] In these systems, the TTF units were annulated directly to the C-bonds of the porphyrin core, giving an annulene-like π-electron system in which the electronic character was "extended" by direct conjugation with the TTF units. However, it turned out that the system wherein the central porphyrin ring was annulated with four TTF units (compound **1**) was isolated as a mixture of the neutral porphyrin **1** and its corresponding radical-cation porphyrin $\mathbf{1}^{\cdot+}$ in a ratio of approximately 4:1; this rendered the ^{1}H NMR spectroscopic and photophysical features almost impossible to deconvolute.[16] In the case of the monoTTF-porphyrin appended with *p*-cyanophenyl groups, electrochemical and photophysical investigations revealed an absence of significant interactions between its constituent subunits in the ground state. However, substantial electron transfer from the TTF donor to the porphyrin chromophore was observed to occur in the excited state of the corresponding monoTTF-porphyrin. Thus, preliminary experiments[17] reveal that the emission intensity can be changed by oxidation of the TTF unit.

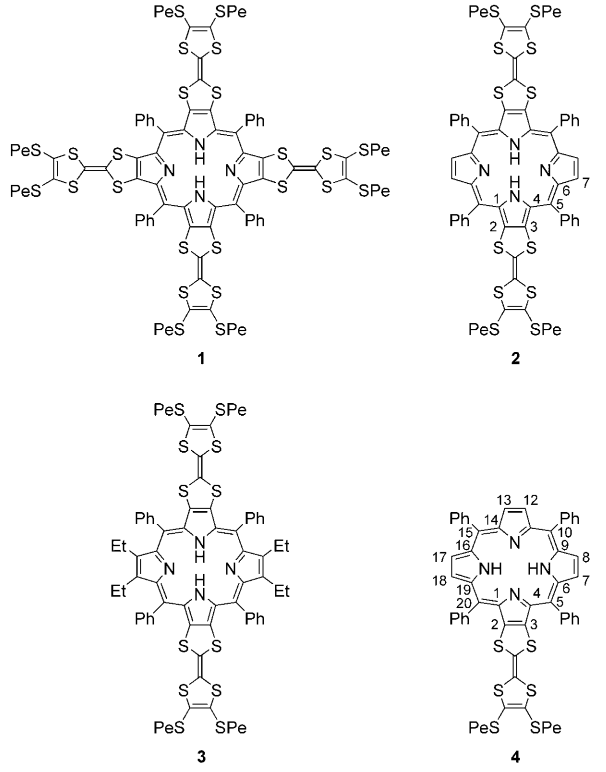


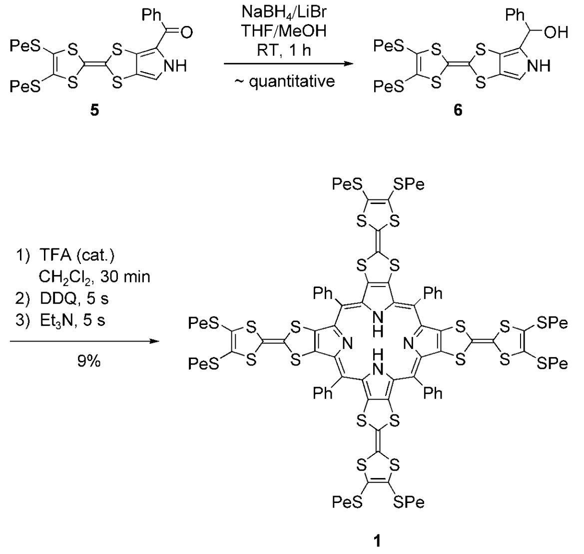
Figure 1. Structural formulae (Pe = n-C_5H_{11}) of the tetraTTF-porphyrin **1**, the bisTTF-porphyrins **2** and **3**, and the monoTTF-porphyrin **4**.

To elucidate further the effect of annulating TTF units directly onto a central porphyrin chromophore, and motivated by a desire to understand more fully the physical properties of the resulting systems, we decided to investigate (Figure 1) a series of neutral TTF-annulated porphyrins containing four, two, and one TTF units. Here, we describe the synthesis of four different TTF-porphyrins, namely, 1) the tetraTTF-porphyrin **1**, 2) the bisTTF-porphyrins **2** and **3**, and 3) the monoTTF-porphyrin **4**, and present the results of mass spectrometric, ^{1}H NMR spectroscopic, X-ray crystallographic, electrochemical, and photophysical studies of these four systems.

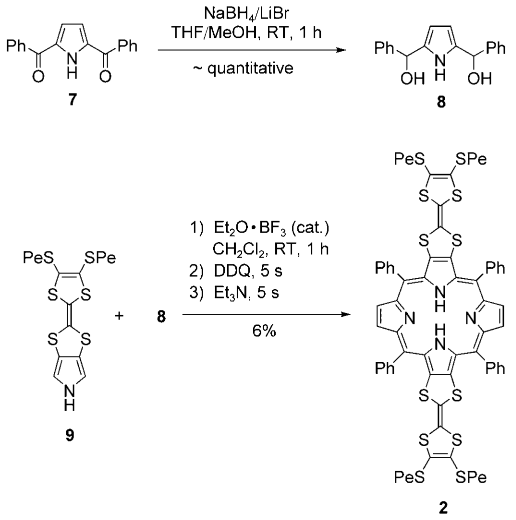
Results and Discussion

Synthesis: The synthesis of the monopyrrolo-tetrathiafulvalene (MPTTF) derivative[22] **5**, 2,5-bisbenzoylpyrrole[23] (**7**), and the MPTTF derivative[19b] **9** have already been reported. Here, we describe the synthesis of the TTF-porphyrins **1–4** (see Figure 1).

The synthesis of the tetraTTF-annulated porphyrin **1** is outlined in Scheme 1. The monobenzoyl-MPTTF **5** was effectively[24] reduced to the corresponding alcohol **6** by using an excess of $NaBH_4$ and LiBr in a THF/MeOH (3:1) solvent mixture. However, all attempts to isolate the product **6** by



Scheme 1. Synthesis of the tetraTTF-porphyrin **1** (Pe = n-C_5H_{11}).

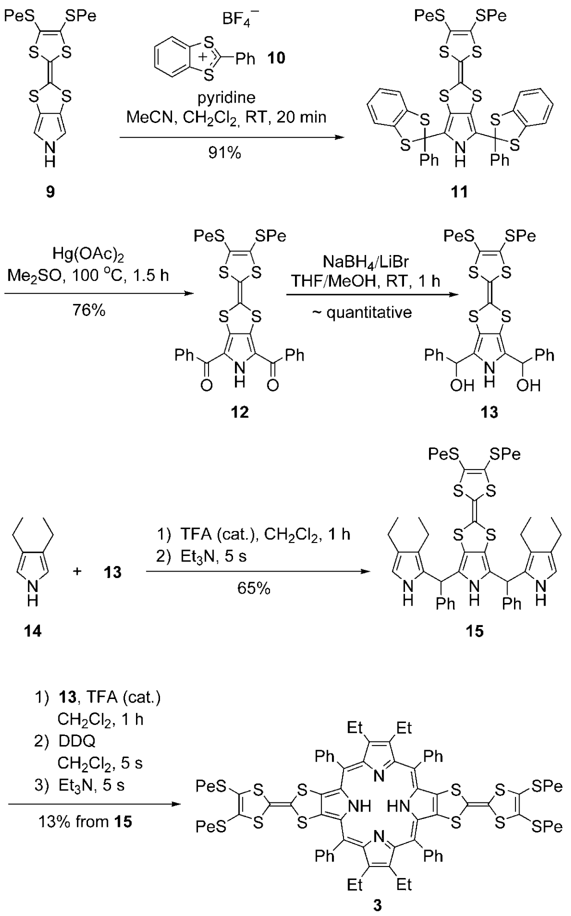


Scheme 2. Synthesis of the bisTTF-porphyrin **2** (Pe = n-C_5H_{11}).

column-chromatographic purification failed. Instead, the alcohol **6** was subjected to a standard non-acidic workup[25] and subsequently cyclized into the corresponding porphyrinogen (structure not shown) by addition (Scheme 1) of a catalytic amount of trifluoroacetic acid (TFA) to a CH_2Cl_2 solution of the alcohol **6**. Matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometry and TLC analysis were used to monitor qualitatively the crude, unpurified, reaction mixture for the disappearance of the starting material **6** and the formation of the presumed porphyrinogen product. After 30 min this conversion was deemed complete, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added, followed by an immediate addition of triethylamine (Et_3N). This afforded the neutral tetraTTF-porphyrin **1** as a dark-purple solid in 9 % yield after column-chromatographic purification.[26]

The synthesis of the bisTTF-annulated porphyrin **2** is illustrated in Scheme 2. The two benzoyl groups in **7**[23] were reduced (Scheme 2) by using an excess of $NaBH_4$ and LiBr in an anhydrous THF/MeOH (3:1) solvent mixture to give the corresponding diol **8** in quantitative yield. The diol **8** was rather unstable as inferred from TLC analysis. It was, therefore, used without any purification other than being subjected to a non-acidic aqueous workup. The bisTTF-annulated porphyrin **2** was obtained as a purple solid in 6 % yield by stirring a mixture of the MPTTF derivative **9**, the diol **8**, and a catalytic amount of $Et_2O{\cdot}BF_3$ in anhydrous CH_2Cl_2 for 1 h followed by first oxidation with three equivalents of DDQ for 5 s and then treatment with excess Et_3N.

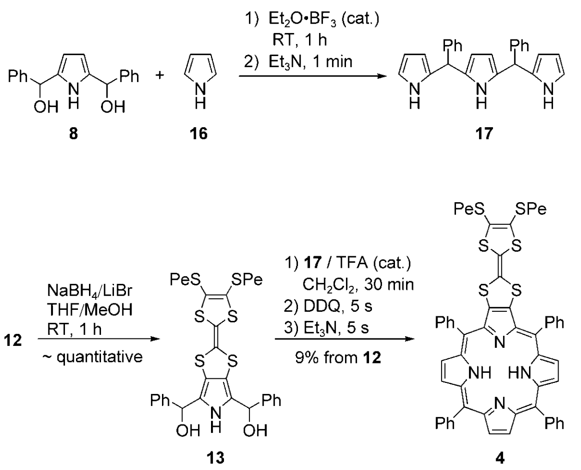
The bisTTF-annulated porphyrin **3** was synthesized as outlined in Scheme 3. Initially, starting from the MPTTF derivative **9**,[19b] 2-phenyl-1,3-benzodithiol-2-ylium tetrafluoroborate (**10**), and pyridine (1:3:3), the 2,5-bisbenzoditholyl functionalized MPTTF **11** was obtained as a yellow solid in 91 % yield. Removal of the protecting groups in **11** using an excess of mercury(II) acetate ($Hg(OAc)_2$) at 100 °C in Me_2SO gave the corresponding 2,5-bisbenzoyl functionalized



Scheme 3. Synthesis of the bisTTF-porphyrin **3** (Pe = n-C_5H_{11}).

MPTTF **12** in 76 % yield. Subsequently, the two carbonyl groups in **12** were reduced in near-quantitative yield by using an excess of $NaBH_4$ and LiBr in a solvent mixture consisting of THF/MeOH (3:1). This afforded the diol **13** as an unstable solid after a non-acidic aqueous workup.[27] Treating diol **13** with ten equivalents of 3,4-diethylpyrrole (**14**)[28] and a catalytic amount of TFA in anhydrous CH_2Cl_2 for 1 h, followed by neutralization with Et_3N, gave the functionalized MPTTF **15** as a yellow oil in 65 % yield after column chromatography. This compound was used without any further purification. Finally, the bisTTF-annulated porphyrin **3** was synthesized using a 3+1 approach[29] that involved stirring a catalytic amount of TFA, the functionalized MPTTF **13**, and the functionalized MPTTF **15** for 1 h in CH_2Cl_2 followed by oxidation with DDQ for 5 s and subsequent neutralization with Et_3N. This produced the bisTTF-porphyrin **3** as a purple solid in 13 % yield.

The monoTTF-annulated porphyrin **4** was also synthesized using the 3+1 approach[29] as shown in Scheme 4. Stirring the diol **8** dissolved in neat pyrrole (**16**) with a catalytic amount of $Et_2O{\cdot}BF_3$ for 1 h, followed by neutralization with Et_3N, gave the tripyrrane[30] **17** as a colorless solid. Cyclization was accomplished by stirring the functionalized MPTTF **13** and the tripyrrane **17** together with a catalytic amount of TFA for 30 min in CH_2Cl_2 followed by oxidation with DDQ



Scheme 4. Synthesis of the monoTTF-porphyrin **4** (Pe = n-C_5H_{11}).

for 5 s and subsequent neutralization with Et_3N; this afforded the monoTTF-porphyrin **4** as a purple solid in 9 % yield.

Mass-spectrometric characterization: High-resolution matrix-assisted laser-desorption/ionization mass-spectrometric (HiResMALDI-MS) analysis of **1**, **2**, and **4** produced peaks with exact masses of m/z 2134.1950, 1374.2235, and 994.2393, respectively, corresponding to the expected molecular ions $M^{\bullet +}$ (calcd masses $M^{\bullet +} = 2134.2022$, 1374.2243, and 994.2354, respectively). These were the dominant peaks in all cases. The HiResMALDI-MS spectrum of **3** gave rise to a major peak at m/z 1487.4453, corresponding to MH^+ (calcd mass $MH^+ = 1487.3579$).

^{1}H NMR spectroscopic studies: The ^{1}H NMR spectra (300 MHz) of the TTF-porphyrins **1**–**4** were recorded in $CDCl_3$ at 298 K and exhibited in all four cases sharp lines. This finding provides important support for the conclusion that, in contrast to what proved true previously in the case of **1**,[16] under the present reaction conditions products **1**–**4** were obtained as the neutral porphyrins (as indicated in Schemes 1–4) free of any radical species.[31,32]

The ^{1}H NMR spectrum of the monoTTF-porphyrin **4** was characterized by a 2 H singlet at $\delta = 8.74$ ppm and a 4 H AB system ($J = 5.0$ Hz) at $\delta = 8.75$ and 8.89 ppm, a feature that was assigned to the $H_{12,13}$ and $H_{7,18/8,17}$ protons (Figure 1), respectively. The resonances for the two inner-ring NH protons were observed as a broad 2 H singlet at $\delta = -2.94$ ppm, as would be expected given the strong shielding effect of the conjugated porphyrin π system.

The ^{1}H NMR spectrum of the bisTTF-porphyrin **2** featured a singlet, integrating to 4 H, at a chemical shift of $\delta = 8.74$ ppm; this feature was assigned to the resonances associated with the H_7 protons (Figure 1), whereas the resonances for the two inner-ring NH protons were observed as a broad 2 H singlet at $\delta = -3.15$ ppm.

The ^{1}H NMR spectra of the tetraTTF-porphyrin **1** and the bisTTF-porphyrin **3** each featured a broad singlet integrating to 2 H at $\delta = -3.03$ and -2.88 ppm, respectively. These peaks were assigned to the two inner-ring NH protons. The remaining aromatic and aliphatic protons in the TTF-porphyrins **1**–**4** all appeared at the expected chemical-shift values (see Experimental Section).

X-ray diffraction analysis: Diffraction-grade single crystals[33] of the bisTTF-porphyrin **3** were grown by slow diffusion of a MeOH layer into a CH_2Cl_2 solution containing **3**. The resulting structure (Figure 2a) revealed a non-planar solid-state structure (Figure 2b). The distortion from planarity is ascribed to the high degree of peripheral substitution with four ethyl groups, four sulfur atoms (two TTF units), and four phenyl rings in the *meso*-positions. The structure exhibits a saddle-like conformation (Figure 2b), wherein the pyrrole subunits are substantially tilted and the core atoms deviate considerably from the mean macrocyclic plane. In the packing diagram of **3** (Figure 2c), two molecules of **3** are paired, as reflected in several short S···S interactions in the solid state.

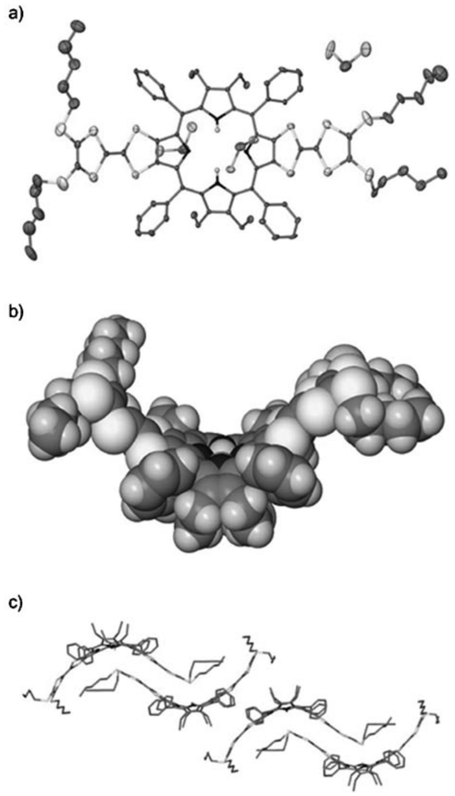


Figure 2. X-ray crystal structure of the bisTTF-porphyrin **3**; a) top view showing the three co-crystallized CH_2Cl_2 molecules found per unit of **3**, b) space-filling representation (side view) showing the saddle conformation, and c) partial packing diagram.

Electrochemical investigations: Electrochemical studies involving the TTF-porphyrins **1**–**4** were carried out in a glove box in THF solution at room temperature using cyclic voltammetry (CV). In these studies the main focus was on oxidation processes involving the TTF unit and reduction processes ascribable to the porphyrin core. To facilitate analysis of the data, the MPTTF derivative **9** and tetraphenylporphyrin (TPP, **18**)[34] were studied under conditions analogous to those used to study the TTF porphyrins **1**–**4**. Deconvoluted voltammograms of these latter species are shown in Figure 3 and the resulting redox potentials are summarized in Table 1, along with those for the model compounds MPTTF **9** and TPP **18**. A more detailed discussion of each TTF-porphyrin follows.

Table 1. Electrochemical data[a] for the TTF-porphyrins **1**–**4** and for the model compounds **9** and **18**, as determined by cyclic voltammetry.

	Porphyrin[b]		TTF[b]	
Compound	E_{red}^2 [V]	E_{red}^1 [V]	E_{ox}^1 [V]	E_{ox}^2 [V]
9			−0.010[c]	+0.445[c]
18	−2.010[c]	−1.675[c]		
4	−1.640[c]	−1.340[c]	+0.275[c]	+0.500[c]
2	−1.810[c]	−1.570[c]	−0.150[c], −0.020[c]	+0.360[d]
3	−1.770[c]	−1.510[c]	+0.030[d]	+0.270[d]
1	−1.660[c]	−1.320[c]	+0.080,[e] +0.150,[e] +0.250,[e] +0.400,[e] +0.510[e]	

[a] Nitrogen-purged THF, RT; tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 0.1 M) and a platinum disk were used as the supporting electrolyte and working electrode, respectively; potential values in V vs. Fc/Fc$^+$ couple. [b] Unit involved in the observed processes. [c] Reversible and monoelectronic processes. [d] Reversible and dielectronic processes. [e] See text for further details.

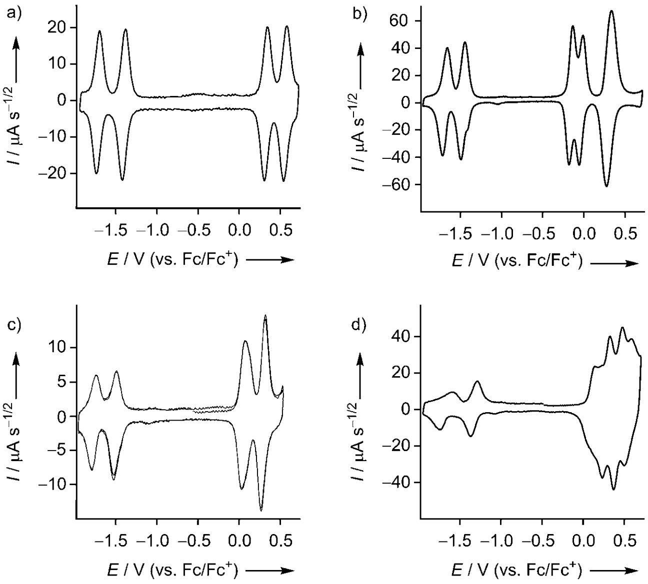


Figure 3. Deconvoluted voltammograms (vs. Fc/Fc$^+$) recorded on THF/n-Bu$_4$NPF$_6$ (0.1 M) solutions of a) the monoTTF-porphyrin **4**, b) the bisTTF-porphyrin **2**, c) the bisTTF-porphyrin **3**, and d) tetraTTF-porphyrin **1** using a platinum electrode with a scan rate of 0.1 V s^{-1}.

*MonoTTF-porphyrin **4***: For the monoTTF-porphyrin **4**, the redox processes (Figure 3a) at −1.340 and −1.640 V vs. Fc/Fc$^+$ can be assigned to the first and second one-electron reduction of the porphyrin ring system, respectively. Although clearly identifiable as being analogous, these reductions are substantially shifted relative to the first (−1.675 V vs. Fc/Fc$^+$) and second (−2.010 V vs. Fc/Fc$^+$) reduction processes of the model compound TPP **18**. The redox processes at +0.275 (one electron) and +0.500 V (one electron) vs. Fc/Fc$^+$ can be associated with the first and second oxidation of the TTF unit, respectively. As compared with the model compound MPTTF **9**, the first and second oxidation processes of **4** are shifted to more positive potentials ($\Delta E_{ox}^1 = +0.285$ and $\Delta E_{ox}^2 = +0.055$ V). The relatively large positive shift observed for the first TTF-centered oxidation in **4** can most likely be ascribed to the presence of an electron-withdrawing 18 π-annulene porphyrin ring system or by more direct electronic involvement of the TTF unit within the delocalization pathway of the 18 π-annulene system. The second oxidation of **4**, however, is close to that of the model compound MPTTF **9**.[19b] Such an observation is consistent with little direct electronic interaction between the TTF unit and the porphyrin ring. However, it could reflect the fact that the putative interaction is blocked after the first oxidation.

*BisTTF-porphyrin **2***: The CV of the bisTTF-annulated porphyrin **2** features (Figure 3b) two one-electron reduction waves at −1.570 and −1.810 V vs. Fc/Fc$^+$, respectively. The oxidation processes associated with the TTF units in **2** are observed at −0.150 (one electron), −0.020 (one electron), and +0.360 V (two electrons) vs. Fc/Fc$^+$. In this case, it is important to note that the ratio of the intensities of the two first-oxidation waves and of the first reduction wave is consistent with the proposed structure, namely the presence of two TTF units per porphyrin ring. It is also noteworthy that the first-oxidation signals for each of the two TTF units are separated from one another. Such a finding is best interpreted[35] in terms of intramolecular interactions taking place between the two TTF units in the mono-oxidized form of **2** (i.e., $\mathbf{2}^{\bullet+}$). Compared with the MPTTF model compound **9**, the first-oxidation process (i.e., $\mathbf{2} \rightarrow \mathbf{2}^{\bullet+}$) of the first TTF unit in **2** is shifted to a more negative potential ($\Delta E_{ox}^1 = -0.140$ V), whereas the first-oxidation process (i.e., $\mathbf{2}^{\bullet+} \rightarrow \mathbf{2}^{2\bullet/2+}$) of the second TTF unit in **2** only is slightly shifted ($\Delta E_{ox}^2 = -0.010$ V). We interpret these observations in terms of an electronic communication between the two TTF units in **2** that is made possible as the result of their being annulated directly onto the porphyrin core.

*BisTTF-porphyrin **3***: For the bisTTF-annulated porphyrin **3**, the first-oxidation processes (i.e., $\mathbf{3} \rightarrow \mathbf{3}^{\bullet+}$ and $\mathbf{3}^{\bullet+} \rightarrow \mathbf{3}^{2\bullet/2+}$) were observed in the CV (Figure 3c) as a broad peak centered around +0.030 V. Such an observation is consistent with the first-oxidation process (i.e., $\mathbf{3} \rightarrow \mathbf{3}^{\bullet+}$) of the first TTF unit and the first-oxidation process (i.e., $\mathbf{3}^{\bullet+} \rightarrow \mathbf{3}^{2\bullet/2+}$) of the second TTF unit occurring at different potentials. However, the separation between these two presumed oxidation processes proved too small to be resolved under the conditions of the experiment. In addition, a comparison between the oxidation potentials of the related compounds **2** and **3** reveals that the first-oxidation processes of compound **3** (+0.030 V) appear at more positive potentials relative to compound **2** (−0.150 and −0.020 V). Taken together, these results might indicate that the electronic communication between the two TTF units in compound **3** is much less pronounced than the electronic communication in compound **2**. The most likely explanation for this difference is that the periphery of compound **3** is substituted with additional four ethyl groups relative to compound **2**. This higher degree of substitution in compound **3** produces a non-planar structure as confirmed by its X-ray crystal structure (see above), with a concomitant reduction in the electronic communication between the two TTF units in the case of compound **3**.

*TetraTTF-porphyrin **1***: The tetraTTF-annulated porphyrin **1** displays numerous redox processes. Because **1** contains four TTF units, it was expected that a total of eight electrons could be removed readily from **1**. In fact, the electrochemical behavior in the oxidative region is rather complex because all the oxidation waves coalesce and appear within a sharp potential range. Nevertheless, at least five oxidation processes (+0.080, +0.150, +0.250, +0.400 and +0.510 V vs. Fc/Fc$^+$) were observed (Figure 3d). All of these potentials are in the region expected for oxidation of the TTF units. The two one-electron reduction processes of the porphyrin ring system appear (Figure 3d) at higher potentials (−1.320 and −1.660 V vs. Fc/Fc$^+$) than those recorded for the model system **18**.

Photophysical studies: The photophysical properties of the mono-, bis-, and tetraTTF-porphyrins **1**–**4** and the model compounds MPTFF **9** and TPP **18** were studied in solutions of air-equilibrated THF at room temperature. The absorption spectra of the TTF-porphyrins **1**–**4** were comparable to the sum of the spectra of their constituents, as defined by model compounds **9** and **18**. This observation rules out a significant interaction between the TTF and porphyrinic chromophores of **1**–**4** in the ground state. In the visible region of the absorption spectra, the expected strong Soret bands appear (Figure 4 and Table 2) at 420, 430, 441, and 440 nm for **4**, **2**, **3**, and **1**, respectively. Based on this progression, it is evident that the Soret band shifts to longer wavelength as the porphyrin core becomes more substituted. In addition to the Soret bands, two or three Q-type bands are seen in the visible region between 483 and 605 nm (Table 2) and can be ascribed to the porphyrin core present in the TTF-porphyrins **1**–**4**. Likewise, weak absorptions between 250 and 350 nm are seen in the UV region of the absorption spectra and reflect the presence of the TTF subunits.

Diamagnetic porphyrins are well known[1] to display a strong fluorescence-emission feature in the 600–800 nm spectral region. However, a comparison of the emission spectra of the monoTTF-porphyrin **4** (Figure 4b) and TPP **18** (Figure 4a) reveals that the fluorescence of the porphyrin core in **4** is quenched by >90 % relative to this latter unsubstituted model compound.[36] This observation provides support for the proposal that substantial electron transfer, from the TTF donor to the porphyrin acceptor, occurs following photoexcitation of **4**. It was expected that removal of one electron from the TTF unit (TTF→TTF$^{\bullet+}$) in the monoTTF-porphyrin **4** would prevent the TTF unit from acting as an electron donor and that consequently, it would not act to quench the porphyrin emission. The net result would be a (re)generation of the porphyrin emission. To test this hypothesis, an oxidation experiment was carried out that involved the addition of increasing amounts of the chemical oxidant FeCl$_3$ to a THF solution of **4**. It was observed (Figure 5) that the fluorescence intensity increased as the amount of added FeCl$_3$ increased. This finding thus provides support for the notion that the porphyrin emission can indeed be (re)generated, at least in part, by oxidizing the

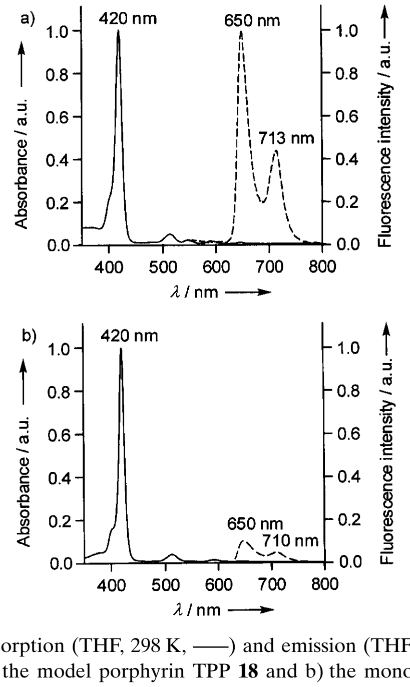


Figure 4. Absorption (THF, 298 K, ——) and emission (THF, 298 K, -----) spectra of a) the model porphyrin TPP **18** and b) the monoTTF-porphyrin **4**. Excitation was performed at 420 nm (Soret band) for **18** and **4**. Note that the fluorescence intensity is much weaker for **4** than for **18**.

Table 2. Photophysical data for TTF-porphyrins **1**–**4** and for the model porphyrin **18**.

Cpd.	Soret band [nm][a]	Soret band ε [L mol^{-1} cm^{-1}][a]	Q bands [nm][a]	Fluorescence [nm]
4	420	186000	520, 610	650, 710[b]
2	430	625000	520, 590	680, 740[b]
3	441	261000	483, 538, 605	701, 783[b]
1	440	696000	525, 550	710, 770[b]
18	420	460000	512, 546, 590, 648	650, 713[c]

[a] Absorption maxima (THF, 298 K) of **1**–**4**. [b] Emission maxima (THF, 298 K) of **1**–**4** after addition of the oxidant FeCl$_3$. Note that, compared to the TPP control, **18**, the fluorescence intensity of **1**–**4** is weak. [c] Emission maxima (THF, 298 K) of **18**. Excitation of the porphyrins was carried out at their respective Soret bands.

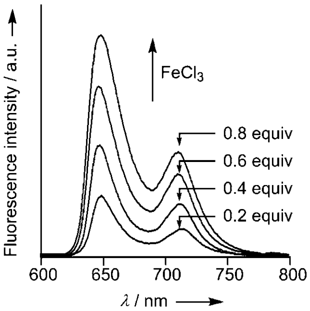


Figure 5. Emission (THF, 298 K) spectra of the monoTTF-porphyrin **4** recorded upon addition of increasing amounts of the chemical oxidant FeCl$_3$. Excitation was performed at 420 nm. The Soret band was omitted from the plotted spectra for clarity.

TTF unit to the corresponding TTF$^{\bullet+}$ radical cation.[37] The emission maxima of compounds **1**–**3** together with those for compounds **4** and **18** are summarized in Table 2. It is evident that the emission maxima shifts to longer wavelengths as the porphyrin core becomes more substituted.

Spectroelectrochemical investigations: Spectroelectrochemistry[38] has proven to be a very powerful tool for monitoring the formation of the TTF radical cation (TTF$^{\bullet+}$) and TTF dication (TTF^{2+}) during electrochemical oxidation. In the case of the bisTTF-porphyrin **2**, spectroelectrochemical analysis (Figure 6) reveals the formation of a species with two structured absorption bands with maxima at 450 and 810 nm, respectively, as the voltage is stepped from -0.2 to $+0.3$ V; such features are characteristic of a TTF radical cation.[38] Increasing the voltage further leads (Figure 6) to a decrease in these bands along with a concomitant increase in the intensity of the band centered around $\lambda_{max} = 680$ nm, a spectral feature that can be assigned to the presence of a TTF dication. It is thus proposed that the species produced is **2**$^{4+}$, that is, TTF^{2+}-porphyrin-TTF^{2+}.

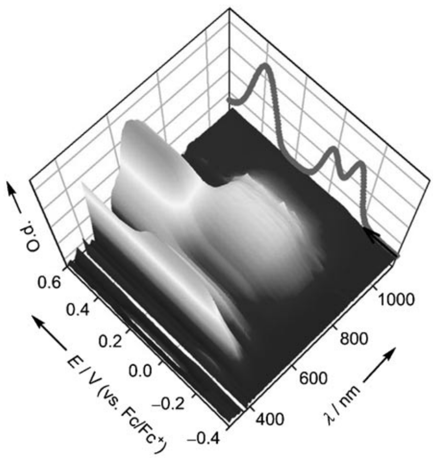


Figure 6. UV/Vis/NIR spectroelectrochemistry of the bisTTF-porphyrin **2** recorded in THF at 298 K.

Conclusion

Herein we have reported the clean synthesis of TTF-annulated porphyrins that permits the annulated derivatives **1**–**4** to be prepared free of any apparent radical impurities. This finding provides support for the notion that preparative pathway matters and that the radical impurities seen previously in the sample of **1**, synthesized using the prior procedure, were just that, namely impurities, as opposed to an intrinsic feature of the molecule. A single-crystal X-ray diffraction analysis of **3** revealed that the porphyrin macrocycle adopts a non-planar saddle-like conformation in the solid state. Photophysical studies carried out in solution show that in TTF-porphyrins **1**–**4** there are no significant interactions between the constituent chromophore subunits in the ground state. However, substantial electron transfer from the TTF units to the porphyrin chromophore takes place in the excited state(s) generated upon photoexcitation of these four compounds, as evidenced by 1) a greater than 90% quenching of the fluorescence relative to what is seen in the model compound TPP **18** and 2) the observation that the porphyrin emission of **1**–**4** can be partly (re)generated upon oxidation of the TTF unit. In the case of the bis-TTF-porphyrin **2**, electrochemical studies provide support for the presence of intramolecular interactions between the two TTF units in the mono-oxidized form (i.e., **2**$^{\bullet+}$). This finding thus supports the conclusion that following oxidation, the two TTF units are able to communicate electronically through the intervening porphyrin core. These systems thus serve as potential prototypes for molecular transistors or diodes, in which the extent of through-molecular-device communication depends on an external output. A further novel feature of the present series of compounds, especially **1** and **2**, is that, by applying appropriate potentials, they can be made to hold several electrons, or even more effectively, holes within a small molecular space. This could make them of interest in charge-storage applications or in catalyst development.

Experimental Section

General methods: All reactions were carried out under an atmosphere of anhydrous nitrogen or argon unless otherwise stated. THF was distilled from sodium-benzophenone immediately prior to use or dried by passage through two columns of activated alumina. MeOH was distilled from Mg and I$_2$. CH$_2$Cl$_2$ was distilled from CaH$_2$ immediately prior to use. DMF and MeCN were allowed to stand over molecular sieves (4 Å) for at least three days before use. Benzoylchloride was distilled under reduced pressure. CDCl$_3$ was purchased in bottles from Cambridge Isotope Inc., and stored over K$_2$CO$_3$ to remove the small amount of acid contained in this solvent. Lithium bromide was dried overnight at approximately 200 °C in vacuo. All other reagents were obtained from commercial sources and used as received. The MPTTF derivatives **5**[22] and **9**[19b] were prepared according to literature procedures. Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kiselgel 60 F254 0.2-mm thickness precoated TLC plates, which were inspected by UV light prior to development with iodine vapor. Column chromatography was performed using Merck Kiselgel 60 (0.040–0.060 mm, 230–400 mesh ASTM). Melting points (M.p.) were determined by using a Büchi melting-point apparatus or a Mel-Temp II melting-point apparatus; in both cases the values reported are uncorrected. ^{1}H NMR spectra were recorded by using a Gemini-300BB instrument at 300 MHz at 298 K, using the deuterated solvent to achieve locking and TMS or the residual solvent as an internal standard. ^{13}C NMR spectra were recorded at 75 MHz at 298 K, using broad-band decoupling. The chemical shifts are given in ppm relative to TMS. Infrared (IR) spectra were recorded by using a Perkin–Elmer 580 spectrophotometer. High-resolution Fourier transform matrix-assisted laser-desorption/ionization mass spectrometry (HiRes-FT-MALDI-MS) was performed by using an IonSpec 4.7 tesla Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid (DHB) matrix. Absorption spectra were recorded at RT by using a Shimadzu UV-1601PC instrument. Cyclic voltammetry was carried out in a three-electrode cell equipped with a platinum millielectrode and a platinum wire counter-electrode. A silver wire served as a quasi-reference electrode, and its potential was checked against the ferrocene/ferricinium couple (Fc/Fc^+) before and after each experiment. The concentration of the examined compounds was ≈0.4 mM and the electrolytic media consisted of THF and contained 0.1 M $n\mathrm{Bu_4NPF_6}$. All experiments were performed at RT in a glove box containing anhydrous, oxygen-free (1 ppm) argon. Electrochemical experiments were carried out by using an EGG PAR 273A potentiostat with positive-feedback compensation. On the basis of repetitive measurements, absolute errors on potentials were found to be around 5 mV. The setup used for the UV-visible and fluorescence spectroelectrochemical experiments has been described previously.[38] The conversion time of the cell was less than 1 s at 20 μm and less than 100 s at 200 μm. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

Compound 1: Powdered sodium borohydride (0,76 g, 20.0 mmol) was added in small portions over a period of 30 min to a stirred solution of the MPTTF derivative **5** (0.55 g, 1.0 mmol) and anhydrous lithium bromide (1.74 g, 20.0 mmol) in anhydrous THF (60 mL) and anhydrous MeOH (20 mL) at RT, causing a slow color change from orange to yellow. After stirring for 1 h at RT, H_2O (200 mL) was added and the mixture was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were washed with H_2O (100 mL) and dried ($MgSO_4$). Concentration in vacuo gave a yellow solid containing the alcohol **6**, which was dissolved in anhydrous CH_2Cl_2 (50 mL) before trifluoroacetic acid (≈10 μL) was added causing a slow color change to brown. The reaction mixture was stirred for 30 min at RT. This was followed by the addition of DDQ (0.17 g, 0.75 mmol) in one portion to yield a black reaction mixture. After stirring for 5 s, Et_3N (≈0.1 mL) was added and the entire mixture was immediately filtered through a pad of alumina (40 mL), which was washed with CH_2Cl_2 (≈100 mL) until the filtrate was colorless. The combined organic filtrates were washed with H_2O (2×100 mL) and dried ($MgSO_4$). Concentration in vacuo gave a black solid that was purified by column chromatography (silica gel: cyclohexane/CH_2Cl_2 7:2). The black band ($R_f=0.2$) was collected and concentrated to give compound **1** (49 mg, 9%) as an analytically pure, purple solid. M.p. 276–280 °C. Recrystallization from CH_2Cl_2/MeOH gave **1** as small purple needles. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=-3.03$ (s, 2H), 0.94 (t, $J=7.0$ Hz, 24H), 1.27–1.59 (m, 32H), 1.65 (p, $J=7.2$ Hz, 16H), 2.82 (t, $J=7.4$ Hz, 16H), 7.80–7.92 (m, 16H), 7.96–8.03 ppm (m, 4H); ^{13}C NMR (CDCl, 75 MHz): $\delta=14.1$, 22.4, 29.6, 30.9, 36.5, 117.4, 127.9, 129.5, 130.8, 132.9, 138.9 ppm, four signals are overlapping or missing; IR (KBr): $\tilde{\nu}=2954$, 2926, 2855, 1630, 1456, 1441, 1053, 882, 767, 755, 698 cm^{-1}; UV/Vis (THF, 298 K): λ_{max} (ε) = 440 nm (696000 L mol^{-1} cm^{-1}); HiRes-FT-MALDI-MS: m/z: calcd for $C_{100}H_{110}N_4S_{24}{}^+$: 2134.2022; found: 2134.1950; elemental analysis calcd (%) for $C_{100}H_{110}N_4S_{24}$ (2137.55): C 56.19, H 5.19, N 2.62, S 36.00; found: C 56.41, H 5.19, N 2.69, S 36.16.

Compound 2: Powdered sodium borohydride (1.29 g, 34 mmol) was added in small portions over a period of 30 min to a stirred solution of compound **7** (0.47 g, 1.7 mmol) and anhydrous lithium bromide (1.47 g, 17 mmol) in anhydrous THF (60 mL) and anhydrous MeOH (20 mL) at RT. After stirring for 1 h at RT, H_2O (200 mL) was added and the mixture was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were washed with H_2O (2×100 mL) and dried ($MgSO_4$). Evaporation of the solvent gave (quantitative) the 2,5-bis(hydroxymethylphenyl)pyrrole (**8**) as a colorless solid that proved sufficiently pure for further use as described below.

$BF_3{\cdot}OEt_2$ (≈10 μL) was added to a solution of the MPTTF derivative **9** (0.31 g, 0.70 mmol) and 2,5-bis(hydroxymethylphenyl)pyrrole (**8**) (0.20 g, 0.70 mmol) in anhydrous CH_2Cl_2 (100 mL), causing a color change from yellow to brown. The reaction mixture was stirred for 1 h at RT. This was followed by the addition of DDQ (0.24 g, 1.05 mmol) in one portion, which caused the reaction mixture to become black. After stirring for 5 s, Et_3N (≈0.1 mL) was added and the entire mixture was immediately filtered through a pad of alumina (40 mL), which was washed with CH_2Cl_2 (≈100 mL) until the filtrate was colorless. The combined organic filtrates were washed with H_2O (2×50 mL) and dried ($MgSO_4$). Concentration in vacuo gave a black solid that was purified by column chromatography (silica gel: cyclohexane/CH_2Cl_2 3:1). The black band ($R_f=0.2$) was collected and concentrated. This afforded compound **2** (29 mg, 6%) as an analytically pure, purple solid. M.p. 264–266 °C. Recrystallization from CH_2Cl_2/MeOH gave **2** as small purple needles. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=-3.15$ (s, 2H), 0.93 (t, $J=7.1$ Hz, 12H), 1.27–1.48 (m, 16H), 1.64 (p, $J=7.2$ Hz, 8H), 2.81 (t, $J=7.4$ Hz, 8H), 7.75–7.84 (m, 8H), 7.84–7.94 (m, 4H), 8.00–8.07 (m, 8H), 8.74 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=14.1$, 22.4, 29.6, 30.8, 36.4, 106.9, 118.9, 123.9, 127.9, 128.3, 128.5, 129.4, 133.5, 138.8, 140.5, 142.2, 145.9 ppm; IR (KBr): $\tilde{\nu}=2954$, 2926, 2855, 1630, 1474, 1441, 1062, 797, 750, 700 cm^{-1}; UV/Vis (THF, 298 K): λ_{max} (ε) = 430 nm (625000 L mol^{-1} cm^{-1}); HiRes-FT-MALDI-MS: m/z: calcd for $C_{72}H_{70}N_4S_{12}{}^+$: 1374.2243; found: 1374.2235; elemental analysis calcd (%) for $C_{72}H_{70}N_4S_{12}$ (1376.15): C 62.84, H 5.13, N 4.07, S 27.96; found: C 62.93, H 5.13, N 4.18, S 27.82.

Compound 11: The MPTTF derivative **9** (0.59 g, 1.32 mmol) and 2-benzyl-1,3-benzodithiolium tetrafluoroborate (**10**) (1.04 g, 3.3 mmol) were dissolved in a mixture of anhydrous CH_2Cl_2 (5 mL) and MeCN (15 mL) before anhydrous pyridine (0.26 g, 0.27 mL, 3.3 mmol) was added to the brown solution. This produced a dark-brown solution. The reaction mixture was stirred for 20 min at RT (after approximately 10 min a yellow precipitate was formed), whereupon CH_2Cl_2 (200 mL) was added and the mixture was washed with first H_2O (100 mL), then a saturated aqueous solution of $NaHCO_3$ (2×100 mL), and finally H_2O (100 mL). After being dried ($MgSO_4$), concentration gave a yellow solid, which was purified by column chromatography (silica gel: cyclohexane/CH_2Cl_2 2:1). The yellow band ($R_f=0.45$) was collected and concentrated to give compound **11** (1.08 g, 91%) as an analytically pure yellow solid. M.p. 172–175 °C. Recrystallization from CH_2Cl_2/MeOH gave compound **11** as yellow needles. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=0.90$ (t, $J=7.1$ Hz, 6H), 1.25–1.42 (m, 8H), 1.60 (p, $J=7.2$ Hz, 4H), 2.76 (t, $J=7.4$ Hz, 4H), 7.01–7.08 (m, 4H), 7.14–7.20 (m, 4H), 7.19–7.25 (m, 6H), 7.64–7.71 (m, 4H), 8.58 ppm (brs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=14.0$, 22.2, 29.4, 30.7, 36.2, 53.4, 120.9, 121.6, 122.6, 122.9, 125.4, 126.5, 127.3, 128.2, 128.6, 129.1, 137.2, 138.3 ppm; IR (KBr): $\tilde{\nu}=2954$, 2926, 2855, 1444, 1259, 1207, 1118, 740, 693 cm^{-1}; HiRes-FT-MALDI-MS: m/z: calcd for $C_{44}H_{41}NS_{10}{}^+$: 903.0446; found: 903.0438; elemental analysis calcd (%) for $C_{44}H_{41}NS_{10}$ (904.46): C 58.43, H 4.57, N 1.55, S 35.45; found: C 58.61, H 4.57, N 1.44, S 35.69.

Compound 12: Mercury(II) acetate (3.14 g, 9.84 mmol) was added in one portion to a yellow solution of compound **11** (1.48 g, 1.64 mmol) in Me_2SO (100 mL) producing a dark-green mixture. The reaction mixture was stirred at 100 °C for 1.5 h (after approximately 10 min, the reaction mixture became red), whereupon the reaction mixture was treated with an aqueous solution of potassium iodide (10% solution in H_2O, 200 mL) and extracted with CH_2Cl_2 (4×100 mL). The organic phases were combined, filtered through a layer of Celite (50 mL), washed with first an aqueous solution of potassium iodide (10% solution in H_2O, 100 mL), followed by a saturated aqueous solution of $NaHCO_3$ (100 mL), and then finally H_2O (100 mL). After drying ($MgSO_4$), concentration in vacuo gave a dark solid, which was purified by column chromatography (silica gel: CH_2Cl_2/cyclohexane 3:1). The dark-purple band ($R_f=0.3$) was collected and concentrated providing compound **12** (0.82 g, 76%) as a pure, dark-purple solid. M.p. 55–60 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=0.90$ (t, $J=6.9$ Hz, 6H), 1.23–1.42 (m, 8H), 1.61 (p, $J=7.3$ Hz, 4H), 2.78 (t, $J=7.3$ Hz, 4H), 7.48–7.58 (m, 4H), 7.60–7.68 (m, 2H), 7.75–7.84 (m, 4H), 9.83 ppm (brs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=13.9$, 22.1, 29.4, 30.6, 36.2, 113.5, 117.0, 126.1, 127.5, 128.2, 129.1, 130.4, 133.1, 136.4, 184.3 ppm; IR (KBr): $\tilde{\nu}=2954$, 2926, 2855, 1620, 1493, 1463, 1446, 1317, 1278, 734, 710 cm^{-1}; UV/Vis ($CHCl_3$, 298 K): λ_{max} $(\varepsilon)=539$ nm (2700 L mol^{-1}cm^{-1}); HiRes-FT-MALDI-MS: *m*/*z*: calcd for $C_{32}H_{33}NO_2S_6{}^+$: 655.0830; found: 655.0804; elemental analysis calcd (%) for $C_{32}H_{33}NO_2S_6$ (656.01): C 58.59, H 5.07, N 2.14, S 29.33; found: C 58.75, H 5.08, N 2.09, S 29.44.

Compound 3: Powered sodium borohydride (0.23 g, 6.1 mmol) was added in small portions over a period of 30 min to a stirred solution of the MPTTF derivative **12** (0.26 g, 0.40 mmol) in anhydrous THF (50 mL) and anhydrous MeOH (25 mL) at RT, causing a color change from dark-purple to yellow. After stirring for 1 h at RT, CH_2Cl_2 (100 mL) was added and the mixture was washed with H_2O (3×100 mL) before being dried ($MgSO_4$). Evaporation of the solvent gave the bis(hydroxymethylphenyl)-MPTTF **13** as a yellow solid in quantitative yield. This product was used without further purification.

The bis(hydroxymethylphenyl)-MPTTF **13** (0.13 g, 0.20 mmol) and 3,4-diethylpyrrole (**14**) (0.25 g, 2.0 mmol) were dissolved in anhydrous CH_2Cl_2 (5 mL) and trifluoroacetic acid (≈10 μL) was added causing a color change from yellow to brown. The reaction mixture was stirred for 1 h at RT, whereupon Et_3N (1 drop) and CH_2Cl_2 (50 mL) were added. The mixture was then washed with H_2O (2×50 mL) before being dried ($MgSO_4$). Concentration in vacuo gave a yellow solid that was purified by column chromatography (silica gel: hexanes/CH_2Cl_2 2:1). The yellow band ($R_f=0.15$) was collected and concentrated to give compound **15** (0.11 g, 65%) as a yellow oil, a product that was used immediately for the next step. The bis(hydroxymethylphenyl)-MPTTF **13** (0.13 g, 0.20 mmol) and compound **15** (0.11 g, 0.13 mmol) were dissolved in anhydrous CH_2Cl_2 (5 mL), whereupon trifluoroacetic acid (≈10 μL) was added; this caused a color change from yellow to brown. The reaction mixture was stirred for 1 h at RT, followed by the addition of DDQ (34 mg, 0.15 mmol) in one portion, which caused the reaction mixture to become black. After stirring for 5 s, Et_3N (≈0.1 mL) was added, and the entire mixture was immediately filtered through a pad of alumina (40 mL), which was washed with CH_2Cl_2 (≈100 mL) until the filtrate was colorless. The combined organic filtrates were washed with H_2O (2×50 mL) and dried ($MgSO_4$). Concentration in vacuo gave a black solid that was subjected to column chromatography (silica gel: hexanes/CH_2Cl_2 1:1). The black band ($R_f=0.3$) was collected and concentrated to give compound **3** (25 mg, 13%) as an analytically pure, purple solid. M.p. 232–234 °C. Recrystallization from CH_2Cl_2/MeOH gave **3** as small purple needles suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=-2.88$ (s, 2H), 0.72 (t, $J=7.3$ Hz, 12H), 0.87 (t, $J=7.1$ Hz, 12H), 1.25–1.40 (m, 16H), 1.56 (p, $J=7.4$ Hz, 8H), 2.63 (q, $J=7.4$ Hz, 8H), 2.73 (t, $J=7.4$ Hz, 8H), 7.70–7.80 (m, 8H), 7.80–7.90 (m, 4H), 8.10–8.18 ppm (m, 8H); UV/Vis (THF, 298 K): λ_{max} $(\varepsilon)=441$ (261000 L mol^{-1}cm^{-1}); HiRes-FT-MALDI-MS: *m*/*z*: calcd for $C_{80}H_{86}N_4S_{12}+H^+$: 1487.3574; found: 1487.4453; elemental analysis calcd (%) for $C_{80}H_{86}N_4S_{12}\cdot{}^1/_2\,CH_2Cl_2$ (1488.36): C 63.16, H 5.73, N 3.66, S 25.14; found: C 63.31, H 5.79, N, 3.50, S 24.10.

Compound 4: Powdered sodium borohydride (0.30 g, 8.0 mmol) was added in small portions over a period of 30 min to a stirred solution of compound **7** (0.11 g, 0.4 mmol) and anhydrous lithium bromide (0.69 g, 8.0 mmol) in anhydrous THF (30 mL) and anhydrous MeOH (10 mL) at RT. After stirring for 1 h at RT, H_2O (200 mL) was added and the mixture was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were washed with H_2O (2×100 mL) and dried ($MgSO_4$). Evaporation of the solvent gave 2,5-bis(hydroxymethylphenyl)pyrrole (**8**) as a colorless oil. This oil was dissolved in neat pyrrole (20 mL) and then $Et_2O\cdot BF_3$ (≈10 μL) was added. The resulting reaction mixture was stirred for 1 h at RT, whereupon Et_3N (≈0.05 mL) was added and the remaining pyrrole was removed by using an oil pump. This provided the tripyrrane **17** as a colorless semi-solid that proved sufficiently pure for further use (see below).

Powdered sodium borohydride (0.29 g, 7.6 mmol) was added in small portions over a period of 30 min to a stirred solution of **12** (0.25 g, 0.38 mmol) and anhydrous lithium bromide (0.66 g, 7.6 mmol) in anhydrous THF (60 mL) and anhydrous MeOH (20 mL) at RT, causing a color change from purple to yellow. After stirring for 1 h at RT, H_2O (200 mL) was added and the mixture was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were washed with H_2O (100 mL) and dried ($MgSO_4$). Evaporation of the solvent gave the MPTTF diol **13** as a yellow solid in quantitative yield. This latter product was then dissolved in anhydrous CH_2Cl_2 (50 mL) together with the tripyrrane **17** (prepared as described above). Trifluoroacetic acid (≈10 μL) was then added, which produced a slow color change from yellow to brown. The reaction mixture was stirred for 30 min at RT, followed by addition of DDQ (86 mg, 0.38 mmol) in one portion, which caused the reaction mixture to become black. After stirring for 5 s, Et_3N (≈0.1 mL) was added and the entire mixture was immediately filtered through a pad of alumina (40 mL), which was washed with CH_2Cl_2 (≈100 mL) until the filtrate was colorless. The combined organic filtrates were washed with H_2O (2×50 mL) and dried ($MgSO_4$). Concentration in vacuo gave a black solid that was subjected to column chromatography (silica gel: cyclohexane/CH_2Cl_2 2:1). The black band ($R_f=0.25$) was collected and concentrated to afford compound **4** (35 mg, 9%) as an analytically pure, purple solid. M.p. 264–265 °C. Recrystallization from CH_2Cl_2/MeOH then provided **4** in the form of small purple needles. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=-2.94$ (s, 2H), 0.93 (t, $J=7.1$ Hz, 6H), 1.26–1.47 (m, 8H), 1.64 (p, $J=7.1$ Hz, 4H), 2.82 (t, $J=7.3$ Hz, 4H), 7.67–7.84 (m, 10H), 7.84–7.94 (m, 2H), 8.02–8.10 (m, 4H), 8.14–8.23 (m, 4H), 8.74 (s, 2H), 8.75 and 8.89 ppm (AB q, $J=5.0$ Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=14.1$, 22.4, 29.6, 30.8, 36.4, 118.2, 121.0, 126.9, 127.9, 128.0, 128.2, 128.2, 128.7, 129.3, 139.6, 134.1, 134.6, 140.8, 142.0 ppm, seven signals overlapping or missing; UV/Vis (THF, 298 K): λ_{max} $(\varepsilon)=420$ nm (186000 L mol^{-1}cm^{-1}); HiRes-FT-MALDI-MS: *m*/*z*: calcd for $C_{58}H_{50}N_4S_6{}^+$: 994.2354; found: 994.2393; elemental analysis calcd (%) for $C_{58}H_{50}N_4S_6$ (995.44): C 69.98, H 5.06, N 5.63, S 19.33; found: C 69.56, H 5.32, N 5.64, S 19.03.

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[1] *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**.

[2] L. Stryer, *Biochemistry*, 4th ed., W. H. Freeman, New York, **1995**.

[3] a) P. G. Van Patten, A. P. Shreve, J. S. Lindsey, R. J. Donohoe, *J. Phys. Chem. B* **1998**, *102*, 4209–4216; b) A. Ambroiser, J. Li, L. Yu, J. S. Lindsey, *Org. Lett.* **2000**, *2*, 2563–2566; c) R. Takahashi, Y. Kobuke, *J. Am. Chem. Soc.* **2003**, *125*, 2372–2373; d) C. Ikeda, A. Satake, Y. Kobuke, *Org. Lett.* **2003**, *5*, 4935–4938; e) Y. Kuramochi, A. Satake, Y. Kobuke, *J. Am. Chem. Soc.* **2004**, *126*, 8668–8669; f) I. V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D. F. Docian, J. S. Lindsey, D. Holten, *J. Am. Chem. Soc.* **2004**, *126*, 2664–2665; g) T. S. Balaban, *Acc. Chem. Res.* **2005**, *38*, 612–623; h) F. Hajjaj, Z. S. Yoon, M.-C. Yoon, J. Park, A. Satake, D. Kim, P. Kobuke, *J. Am. Chem. Soc.* **2006**, *128*, 4612–4623; i) F. D'Souza, S. Gadde, D.-M. S. Islam, C. H. Wijesinghe, A. L. Schumacher, M. E. Zandler, Y. Araki, O. Ito, *J. Phys. Chem. A* **2007**, *111*, 8552–8560; j) J. Yu, S. Mathew, B. S. Flavel, M. R. Johnston, J. G. Shapter, *J. Am. Chem. Soc.* **2008**, *130*, 8788–8796.

[4] a) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, *35*, 57–69; b) D. Kim, A. Osuka, *Acc. Chem. Res.* **2004**, *37*, 735–745; c) A. Harriman, S. A. Rostron, A. Khatyr, R. Zressel, *Faraday Discuss.* **2006**, *131*, 377–391.

[5] a) M. P. O'Neil, M. P. Niemczy, W. A. Svec, D. Gosztola, G. L. Gaines, M. R. Wasielewski, *Science* **1992**, *257*, 63–65; b) M. Harm-

janz, H. S. Gill, M. J. Scott, *J. Am. Chem. Soc.* **2000**, *122*, 10476–10477.

[6] a) J. Becher, J. O. Jeppesen, K. Nielsen, *Synth. Met.* **2003**, *133–134*, 309–315; b) J. O. Jeppesen, J. Becher, *Eur. J. Org. Chem.* **2003**, 3245–3266; c) *TTF Chemistry* (Eds.: J.-i. Yamada, T. Sugimoto), Kodansha, Tokyo, **2004**; d) special issue on molecular conductors, *Chem. Rev.* **2004**, *104*, 4887–5782.

[7] a) M. R. Bryce, *J. Mater. Chem.* **2000**, *10*, 589–598; b) J. L. Segura, N. Martín, *Angew. Chem.* **2001**, *113*, 1416–1455; *Angew. Chem. Int. Ed.* **2001**, *40*, 1372–1409; c) G. Schukat, E. Fanghänel, *Sulfur Rep.* **2003**, *24*, 1–282; d) T. Otsubo, K. Takimiya, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 43–58.

[8] *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.

[9] a) F. Le Derf, E. Levillain, G. Trippé, A. Gorgues, M. Sallé, R.-M. Sebastían, A.-M. Caminade, J.-P. Majoral, *Angew. Chem.* **2001**, *113*, 230–233; *Angew. Chem. Int. Ed.* **2001**, *40*, 224–227; b) G. Trippé, E. Levillain, F. Le Derf, A. Gorgues, M. Sallé, J. O. Jeppesen, K. Nielsen, J. Becher, *Org. Lett.* **2002**, *4*, 2461–2464; c) K. A. Nielsen, J. O. Jeppesen, E. Levillain, J. Becher, *Angew. Chem.* **2003**, *115*, 197–201; *Angew. Chem. Int. Ed.* **2003**, *42*, 187–191; d) K. A. Nielsen, W.-S. Cho, J. O. Jeppesen, V. M. Lynch, J. Becher, J. L. Sessler, *J. Am. Chem. Soc.* **2004**, *126*, 16296–16297; e) H. Lu, W. Xu, D. Zhang, C. Chen, D. Zhu, *Org. Lett.* **2005**, *7*, 4629–4632; f) K. A. Nielsen, W.-S. Cho, J. Lyskawa, E. Levillain, V. M. Lynch, J. L. Sessler, J. O. Jeppesen, *J. Am. Chem. Soc.* **2006**, *128*, 2444–2451; g) K. A. Nielsen, W.-S. Cho, G. Sarova, B. M. Petersen, A. D. Bond, J. Becher, F. Jensen, D. M. Guldi, J. L. Sessler, J. O. Jeppesen, *Angew. Chem.* **2006**, *118*, 7002–7007; *Angew. Chem. Int. Ed.* **2006**, *45*, 6848–6853; h) K. A. Nielsen, G. H. Sarova, L. Martín-Gomis, F. Fernández-Lázaro, P. C. Stein, L. Sanguinet, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos, J. O. Jeppesen, *J. Am. Chem. Soc.* **2007**, *129*, 460–462, i) K. A. Nielsen, L. Martín-Gomis, G. H. Sarova, L. Sanguinet, D. E. Gross, F. Fernández-Lázaro, P. C. Stein, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos, J. O. Jeppesen, *Tetrahedron* **2008**, *64*, 8449–8463.

[10] N. Martín, L. Sánchez, D. M. Guldi, *Chem. Commun.* **2000**, 113–114.

[11] Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C.-M. Ho, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759.

[12] a) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433–444; b) J. O. Jeppesen, J. Becher, J. F. Stoddart, *Org. Lett.* **2002**, *4*, 557–560; c) Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, J. R. Heath, *ChemPhysChem* **2002**, *3*, 519–525; d) T. Yamamoto, H.-R. Tseng, J. F. Stoddart, V. Balzani, A. Credi, F. Marchioni, M. Venturi, *Collect. Czech. Chem. Commun.* **2003**, *99*, 1488–1514; e) J. O. Jeppesen, S. Nygaard, S. A. Vignon, J. F. Stoddart, *Eur. J. Org. Chem.* **2005**, 196–220; f) S. Nygaard, K. C.-F. Leung, I. Aprahamian, T. Ikeda, S. Saha, B. W. Laursen, S.-Y. Kim, S. W. Hansen, P. C. Stein, A. H. Flood, J. F. Stoddart, J. O. Jeppesen, *J. Am. Chem. Soc.* **2007**, *129*, 960–970.

[13] S. Nygaard, Y. Liu, P. C. Stein, A. H. Flood, J. O. Jeppesen, *Adv. Funct. Mater.* **2007**, *17*, 751–762.

[14] a) C. Farren, C. A. Christensen, S. FitzGerald, M. R. Bryce, A. Beeby, *J. Org. Chem.* **2002**, *67*, 9130–9139; b) G. Zhang, D. Zhang, X. Guo, D. Zhu, *Org. Lett.* **2004**, *6*, 1209–1212; c) S. Nygaard, B. W. Laursen, A. H. Flood, C. N. Hansen, J. O. Jeppesen, J. F. Stoddart, *Chem. Commun.* **2006**, 144–146; d) J. W. Choi, A. H. Flood, D. W. Steuerman, S. Nygaard, A. B. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. DeIonno, A. J. Peters, J. O. Jeppesen, K. Xu, J. F. Stoddart, J. R. Heath, *Chem. Eur. J.* **2006**, *12*, 261–279.

[15] Only a few papers on molecular systems including both TTF and porphyrin units have been reported so far; see for instance: a) P. A. Liddell, G. Kodis, L. de la Garza, J. L. Bahr, A. L. Moore, T. A. Moore, D. Gust, *Helv. Chim. Acta* **2001**, *84*, 2765–2783; b) S.-i Sadaike, K. Takimiya, Y. Aso, T. Otsubo, *Tetrahedron Lett.* **2003**, *44*, 161–165; c) S. Saha, E. Johansson, A. H. Flood, H.-R. Tseng, J. I. Zink, J. F. Stoddart, *Chem. Eur. J.* **2005**, *11*, 6846–6858; d) M. Di Valentin, A. Bisol, G. Agostini, P. A. Liddell, G. Kodis, A. L. Moore, T. A. Moore, D. Gust, D. Carbonera, *J. Phys. Chem. B* **2005**, *109*, 14401–14409; e) X. Xiao, W. Xu, D. Zhang, H. Xu, H. Lu, D. Zhu, *J. Mater. Chem.* **2005**, *15*, 2557–2561; f) Y. Liu, C. Wang, M. Li, S. Lv, G. Lai, Y. Shen, *J. Porphyrins Phthalocyanines* **2007**, *11*, 729–735; g) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi, A. Credi, *J. Am. Chem. Soc.* **2007**, *129*, 12159–12171.

[16] J. Becher, T. Brimert, J. O. Jeppesen, J. Z. Pedersen, R. Zubarev, T. Bjørnholm, N. Reitzel, T. R. Jensen, K. Kjaer, E. Levillain, *Angew. Chem.* **2001**, *113*, 2565–2568; *Angew. Chem. Int. Ed.* **2001**, *40*, 2497–2500.

[17] H. Li, J. O. Jeppesen, E. Levillain, J. Becher, *Chem. Commun.* **2003**, 846–847.

[18] The synthesis of tetrakisTTF-annulated phthalocyanines have recently been reported, see: C. Loosli, C. Jia, S.-X. Liu, M. Haas, M. Dias, E. Levillain, A. Neels, G. Labat, A. Hauser, S. Decurtins, *J. Org. Chem.* **2005**, *70*, 4988–4992.

[19] 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*, 5797–5805.

[20] a) A. D. Hamilton, H.-D. Rubin, A. B. Bocarsly, *J. Am. Chem. Soc.* **1984**, *106*, 7255–7257; b) K. Araki, L. Angnes, H. E. Toma, *Adv. Mater.* **1995**, *7*, 554–559; c) C. Policar, I. Artuad, D. Mansuy, *Inorg. Chem.* **1996**, *35*, 210–216; d) J. L. Sessler, V. L. Capuano, A. K. Burrell, *Inorg. Chim. Acta* **1993**, *204*, 93–101; e) A. Harriman, R. Ziessel, *Chem. Commun.* **1996**, 1707–1716.

[21] a) E. S. Schmidt, T. S. Calderwood, T. C. Bruice, *Inorg. Chem.* **1986**, *25*, 3718–3720; b) A. K. Burrell, W. Campbell, D. L. Officer, *Tetrahedron Lett.* **1997**, *38*, 1249–1252; c) P. D. W. Boyd, A. K. Burrell, W. M. Campbell, P. A. Cocks, K. C. Gordon, G. B. Jameson, D. L. Officer, Z. Zhao, *Chem. Commun.* **1999**, 637–638; d) A. K. Burrell, W. M. Campbell, D. L. Officer, S. M. Scott, K. C. Gordon, M. R. McDonald, *J. Chem. Soc. Dalton Trans.* **1999**, 3349–3354; e) D. T. Gryko, F. Zhao, A. A. Yasseri, K. M. Roth, D. F. Bocian, W. G. Kuhr, J. S. Lindsey, *J. Org. Chem.* **2000**, *65*, 7356–7362; f) S. W. Rhee, B. B. Park, Y. Do, J. Kim, *Polyhedron* **2000**, *19*, 1961–1966; g) S. Woo Rhee, Y. H. Na, Y. Do, J. Kim, *Inorg. Chim. Acta* **2000**, *309*, 49–56; h) M. C. Hodgson, A. K. Burrell, P. D. W. Boyd, P. J. Brothers, C. E. F. Rickard, *J. Porphyrins Phthalocyanines* **2002**, *6*, 737–747; i) A. Auger, A. J. Muller, J. C. Swarts, *Dalton Trans.* **2007**, 3623–3633; j) M. Schmittel, R. S. K. Kishore, J. W. Bats, *Org. Biomol. Chem.* **2007**, *5*, 78–86.

[22] K. A. Nielsen, K. R. Larsen, J. O. Jeppesen, unpublished results.

[23] a) M. Barbero, S. Cadamuro, I. Degani, R. Fochi, A. Gatti, V. Regondi, *J. Org. Chem.* **1988**, *53*, 2245–22; b) M. Barbero, S. Cadamuro, I. Degani, S. Dughera, R. Fochi, A. Gatti, C. Prandi, *Gazz. Chim. Ital.* **1990**, *120*, 619–627; c) S. Cadamuro, I. Degani, R. Fochi, A. Gatti, L. Piscopo, *J. Chem. Soc. Perkin Trans. 1* **1993**, 2923–2943.

[24] Support for the proposed conversion of the monobenzoyl-MPTTF derivative **5** to the corresponding alcohol **6** came from the fact that a color change from orange to yellow was observed to take place during the reaction. In addition, TLC analysis revealed the presence of only one new product with a lower R_f value than the starting material **6**.

[25] A ^{1}H NMR spectroscopic examination carried out revealed spectral features consistent with the proposed complete reduction of the carbonyl group in **5** and the formation of the corresponding alcohol **6**. Although the alcohol **6** can be handled for a few hours, significant decomposition is seen within one day.

[26] Some of us have previously reported (ref. [16]) that the tetraTTF-annulated porphyrin **1** can be synthesized by stirring the MPTTF derivative **9**, benzaldehyde, and a catalytic amount of *p*-toluenesulfoic acid (PTSA) in THF at RT for 18 h followed by DDQ oxidation. However, this method gives rise to a mixture of the neutral porphy-

rin **1** and the corresponding radical-cation porphyrin $\mathbf{1}^{\bullet +}$ in a ratio of approximately 4:1. Unfortunately, in our hands this mixture proved impossible to separate by any means. The ^{1}H NMR spectrum of this porphyrin mixture recorded in $CDCl_3$ at 298 K featured only very broad peaks, an observation consistent with the presence of radicals or slow tumbling resulting from aggregation in solution. The radical-cation nature of the porphyrin mixture was confirmed (ref. [16]) by quantitative electron paramagnetic resonance (EPR) spectroscopy. This porphyrin mixture (**1** and $\mathbf{1}^{\bullet +}$) was isolated as a stable pitch-black residue after column-chromatographic purification over silica gel using CH_2Cl_2/MeOH (19:1) as the eluent. Attempts to obtain the neutral tetraTTF-porphyrin **1** by chemical reduction of this radical mixture ($\mathbf{1}+\mathbf{1}^{\bullet +}$) proved unsuccessful (ref. [16]). The big difference in color and eluent (cyclohexane/CH_2Cl_2 7:2) used for the column-chromatographic purification of the neutral tetraTTF-porphyrin **1** reported here compared to the radical mixture of tetraTTF-porphyrins ($\mathbf{1}+\mathbf{1}^{\bullet +}$) reflects the different physical properties of these ostensibly similar tetraTTF-porphyrin products. Note the high stability of both the neutral product **1**, whose synthesis is detailed in this report, and the radical-cation porphyrin mixture prepared earlier. Unfortunately, as noted above, efforts to interconvert these ostensibly similar materials proved unsuccessful.

[27] A color change from deep-purple to yellow took place during the reduction, an observation that we take as indicative that the starting material **12** is being converted to the product **13**. Based on TLC analysis, it was inferred that the diol **13** was unstable; therefore, no specific purification of this species was attempted.

[28] J. L. Sessler, A. Mozaffari, M. R. Johnson, *Org. Synth.* **1992**, *70*, 68–77.

[29] a) A. Boudif, M. Momenteau, *J. Chem. Soc. Perkin Trans. 1* **1996**, 1235–1242; b) T. D. Lash, *Chem. Eur. J.* **1996**, *10*, 1197–1200; c) J. L. Sessler, J. W. Genge, A. Urbach, P. Sansom, *Synlett* **1996**, 187–188.

[30] a) P.-Y. Heo, K. Shin, C.-H. Lee, *Tetrahedron Lett.* **1996**, *37*, 197–200; b) P.-Y. Heo, C.-H. Lee, *Bull. Korean Chem. Soc.* **1996**, *17*, 515–520; c) C. Brückner, E. D. Sternberg, R. W. Boyle, D. Dolphin, *Chem. Commun.* **1997**, 1689–1690; d) C. Bucher, D. Seidel, V. Lynch, V. Král, J. L. Sessler, *Org. Lett.* **2000**, *2*, 3103–3106; e) J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, J. S. Lindsey, *Org. Process Res. Dev.* **2003**, *7*, 799–812.

[31] Further support for this conclusion comes from the finding that no radical signals could be seen using conventional EPR spectroscopy.

[32] As a result of the presumed presence of an oxidized radical species (i.e., $\mathbf{1}^{\bullet +}$), the ^{1}H NMR spectrum of a sample of **1** obtained using the previously published procedure (ref. [16]) featured broad lines.

[33] X-ray crystal-structure determination of **3**: Crystals of the bisTTF-porphyrin **3**, suitable for X-ray diffraction, were grown by slow diffusion of a MeOH layer into a CH_2Cl_2 solution containing **3**. Crystallographic data: $C_{83}H_{92}C_{16}N_4S_{12}$, $M_r=1743.03$, triclinic, $P\bar{1}$, dark-brown plates, crystal size $=0.42\times 0.40\times 0.06$ mm^3, $Z=2$, $a=13.3526(2)$, $b=16.2106(3)$, $c=21.3553(4)$ Å, $\alpha=93.017(1)$, $\beta=92.291(1)$, $\gamma=111.631(1)°$, $V=4282.16(13)$ Å^3, $T=153$ K, $\lambda=0.71073$, $\rho_{calcd}=1.352$ g cm^{-3}, $\mu(Mo_{K\alpha})=0.539$ mm^{-1}, $F(000)=1824$, θ range $=2.94$ to $27.50°$, reflections $=30910$, parameters $=19182$, $R1$ $[I>2\sigma(I)]=0.0891$, w$R_2=0.1437$, GOF $=1.836$. The data were collected by using a Nonius Kappa CCD diffractometer. A total of 467 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 124 seconds per frame. Data reduction was performed using DENZO-SMN (DENZO-SMN **1997**). Z. Otwinowski, W. Minor, *Methods Enzymol.* **2007**, *276* 307–326). The structure was solved by direct methods using SIR97 (SIR97, a program for crystal structure solution: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119) and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97 (G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1994**). The hydrogen atoms on carbon were calculated in ideal positions with isotropic-displacement parameters set to $1.2\times U_{eq}$ of the attached atom ($1.5\times U_{eq}$ for methyl hydrogen atoms). The hydrogen atoms on the pyrrole nitrogen atoms, N2 and N4, were observed in a ΔF map and refined with isotropic-displacement parameters. The anisotropic-displacement parameters for the four pentyl-group carbon atoms were restrained to be approximately isotropic in the final stages of the refinement. The function, $\Sigma w(|F_o|^2-|F_c|^2)^2$, was minimized, in which $w=1/[(\sigma(F_o))^2+(0.02*P)^2]$ and $P=(|F_o|^2+2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.155, with $R(F)$ equal to 0.0891 and a goodness of fit, $S,=1.87$. Definitions used for calculating R(F), R_w(F^2), and the goodness of fit, S, gave the following: $R_w(F^2)=\{\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$, in which w is the weight given to each reflection. $R(F)=\{\Sigma(|F_o|-|F_c|)/\Sigma|F_o|\}$ for reflections with $F_o>4(\sigma(F_o))$. $S=[\Sigma w(|F_o|^2-|F_c|^2)^2/(n-p)]^{1/2}$, in which n is the number of reflections and p is the number of refined parameters. The data were checked for secondary extinction effects, but no correction was applied. Neutral atom-scattering factors and values used to calculate the linear-absorption coefficient are from the International Tables for X-ray Crystallography: International Tables for X-ray Crystallography, *Vol. C*, Tables 4.2.6.8 and 6.1.1.4 (Ed.: A. J. C. Wilson), Kluwer Academic Press, Boston, **1992**. CCDC 697641 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[34] Y. Terazono, D. Dolphin, *J. Org. Chem.* **2003**, *68*, 1892–1900.

[35] a) K. Takimiya, Y. Aso, F. Ogura, T. Otsubo, *Chem. Lett.* **1995**, 735–736; b) K. Takimiya, A. Oharuda, Y. Aso, F. Ogura, T. Otsubo, *Chem. Mater.* **2000**, *12*, 2196–2204.

[36] G. Zhang, D. Zhang, X. Guo, D. Zhu, *Org. Lett.* **2004**, *6*, 1209–1212.

[37] Attempts to reverse the process (i.e., $TTF^{\bullet +}\rightarrow TTF$) through the addition of chemical reductants proved unsuccessful.

[38] a) H. Laurent, A. Said, E. Levillain, J. Roncali, A. Emge, P. Baeuerle, *J. Phys. Chem. B* **1998**, *102*, 7776–7781, and references therein; b) H. Spanggaard, J. Prehn, M. B. Nielsen, E. Levillain, M. Allain, J. Becher, *J. Am. Chem. Soc.* **2000**, *122*, 9486–9494.

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