Synthesis of tetra(TTF-Crown-ether) Phthalocyanine 6

**General Proceedures:**
Melting points were recorded on a Buchi melting point apparatus and are uncorrected. Microanalysis were performed with a Carbo Erba Ea 1108 instrument at the University of Nijmegen, The Netherlands. Infrared spectra were recorded on an ANADIS reflection mode IR 300 spectrometer on solid state samples. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AC ($^1$H, 300 MHz; $^{13}$C, 75 MHz) and Bruker AM ($^1$H, 400 MHz; $^{13}$C, 100 MHz) spectrometers. All NMR spectra were referenced to internal solvent residue (CDCl$_3$: $^{13}$C = 77.1 ppm) or tetramethysilane (H = 0 ppm). $^{13}$C NMR spectra are reported as the fully proton-decoupled spectra. All spectra were recorded at 300 K ($\pm$ 1K). The following abbreviations for multiplicity are used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; qt, quartet; m, multiplet; br, broad. Signals in the $^1$H spectra arising from the crown ether moiety are reported labelled a,b,c and d starting from the benzene ring and moving sequentially toward the TTF unit. UV-vis spectra were measured on a Varian Cary 50 UV-vis spectrophotometer. Mass spectra were obtained on a MAT900 ESI instrument at the University of Nijmegen. Transmission electron microscopy was carried out on an JEOL TEM 1010 microscope. Column chromatography was performed with the stated solvent systems using Merck silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on Merck silica gel F254 precoated sheets (0.2 mm). All solvents used were purified using standard literature procedures prior to use. Where solvent mixtures were used, the proportions are given by volume. All other chemicals were used as obtained from commercial sources with the exception of the TTF compound which was supplied by the Amabilino group, Institute de Ciència de Materials de Barcelona (CSIC), Campus Universitari, Spain.

**Synthesis of 1,2-bis(2-(2-iodoetoxy)ethoxy)-4,5-dibromobenzene 2**

4,5-Dibromocatechol (2.07 g, 7.75 mmol) was dissolved in bis(2-chloroethyl)ether (20 mls) before nitrogen was bubbled through the solution for 15 min. Potassium carbonate (4 g) was added before the reaction mixture was heated at reflux under nitrogen for 2 days. The reaction mixture was then cooled, washed with water (3 x 100 mls), dried over sodium sulfate and the solvent removed under vacuum to yield an orange oil (quantitative conversion to 1,2-bis(2-(2-chloroetoxy)ethoxy)-4,5-dibromobenzene confirmed by $^1$H NMR). A mixture of the resultant oil (2.02 g, 4.21 mmol) and NaI (2.36 g, 15.7mmol) was refluxed in acetonitrile (20 mL) for 3 hr under a nitrogen atmosphere. After cooling, the reaction mixture was filtered, the solid washed with CHCl$_3$ and the filtrate evaporated. The residue was extracted into CHCl$_3$ (200 mL) and the solution washed with aq NaHSO$_3$ solution (100 mL, 10%), water (100 mL) and dried over MgSO$_4$. The solvent was removed in vacuo after filtration to give a yellow-green oil. The residue was recrystallized twice from methanol to give the product 2 (0.97 g, 1.47 mmol, 35%) as a white solid, m.p. 60 – 62 °C. Found C 25.62; H 2.74. C$_{14}$H$_{18}$O$_4$Br$_2$I$_2$ requires C 25.33; H 2.73 IR (solid): v 3726, 3699, 3625, 3587, 2937, 2867, 2358, 2339, 1581, 1494, 1454, 1348, 1249, 1197, 1113, 1035 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.12 (2H, Ar-H, s), 4.12 (4H, H$_a$, t, J 4.8 Hz), 3.87 - 3.80 (8H, H$_b$, H$_c$, m), 3.27 (4H, H$_d$, t, J 6.8 Hz). $^{13}$C NMR (CDCl$_3$, 50 MHz): δ 148.6, 118.8, 115.4, 72.1, 69.2, 69.1, 42.8 Mass (EI): Calc. 661.7661. Found: 661.7660
TTF-dibromide derivate 4

The diprotected dithiol compound 3 (136.5 mg, 0.18 mmol) was dissolved in dried, degassed DMF (4 mL) and a solution of CsOH.H₂O (64.9 mg, 0.39 mmol) in dried, degassed methanol (1.5 mL) was added dropwise with stirring over a period of 20 min. The solution was then stirred for 1 hr under an argon atmosphere. This solution was added dropwise to a solution of 4 (121.6 mg, 0.18 mmol) in dried and degassed DMF (20 mL) at room temperature and the mixture was stirred overnight under an argon atmosphere. The solvents were removed and dichloromethane (50 mL) was added before the solution was washed with water (50 mL) brine (50 mL), dried over MgSO₄ and the solution was concentrated in vacuo. The residue was purified over silica (CH₂Cl₂:hexane 1:1 changing to 8:2) and recrystallised from acetone to give the product 4 (101 mg, 0.09 mmol, 53%) as an orange solid, m.p. 81 - 83%. Found: C 48.80; H 6.29. C₄₄H₆₈Br₂O₄S₈ requires C 49.05; H 6.32. IR(solid): ν 2915, 2848, 1494, 1452, 1259, 1207, 1103, 1024 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.1 (2H, Ar-H, s), 4.12 - 4.09 (4H, Ha, m), 3.92 - 3.90 (4H, Hc, m), 3.82 (4H, Hb, t, J 6.5 Hz), 3.04 (4H, Hd, t, J 6.5 Hz), 2.82 (4H, 2CH₂-S, t, J 7.2 Hz), 1.63 (4H, 2CH₂, s), 1.26 (36H, 18CH₂, s), 0.89 (6H, 2CH₃, t, J 6.5 Hz). ¹³C NMR (CDCl₃, 75 MHz): δ 148.7, 128.4, 127.8, 118.1, 115.3, 111.2, 108.9, 70.1, 69.7, 69.6, 36.3, 35.7, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 28.5, 22.7, 14.1. HR-MALDI-TOF: calc. 1077.1250, found 1077.0824.

TTF-dicyano derivate 5

The dibromide compound 4 (94.3 mg, 0.09 mmol) and copper(I) cyanide (69.4 mg, 0.77 mmol) were added to dried, degassed DMF (4.5 mL) and pyridine (0.1 mL). The solution was stirred at 150 °C with the exclusion of light under an argon atmosphere for 60 hr. The brown reaction mixture was cooled and then poured into aq ammonia solution (7.5 mL, 25%) which resulted in a green solution. Chloroform (15 mL) was added and air was bubbled through the mixture for 2 hr. The mixture was extracted with chloroform (3×25 mL), the organic layers
were washed with aq ammonia (25 mL, 25%), water (2×25 mL) and brine (25 mL). The solvent was removed from the yellow-orange solution obtained and the residue was purified over silica (dichloromethane), the major fraction collected and solvent removed. The residue was recrystallised from acetone to give the product 5 (37 mg, 0.03 mmol, 31%) as an orange solid, m.p. 127 – 128 °C. Found: C 57.03; H 6.84; N 2.619. C₄₆H₆₈Br₂N₂O₄S₈ requires C 56.98; H 7.07; N 2.89. IR (solid): ν₂₉₁₀, 2₇₆₈, 2₃₉₉, 2₂₄₈, 1₅₈₅, 1₅₅₃, 1₄₂₂, 1₄₁₇, 1₃₃₉, 1₂₉₂, 1₂₂₄, 1₁₃₅, 1₀₇₂, 9₉₃, 9₂₀, 8₇₉, 7₆₉, 7₁₁ cm⁻¹. ¹H NMR (CDCl₃, 300MHz): δ 7.16 (2H, Ar-H, s), 4.13 (4H, Hₐ, t, J 3.9 Hz), 3.86 (4H, Hc, t, J 4.0 Hz), 3.71 (4H, Hb, t, J 6 Hz), 2.95 (4H, H₄, t, J 6 Hz), 2.73 (4H, 2CH₂-S, t, J 7.3 Hz), 1.58 - 1.49 (4H, 2CH₂, m), 1.35 - 1.2 (36H, 18CH₂, m), 0.81 (6H, 2CH₃, t, J 6.6 Hz). ¹³C NMR (CDCl₃, 50MHz): δ 1₅₂.₁, 1₂₈.₆, 1₂₇.₇, 1₁₅.₇, 1₀₈.₈, 1₀₈.₆, ₇₀.₂, ₆₉.₆, ₆₉.₁, 3₆.₂, ₃₅.₈, ₃₁.₉, ₂₉.₇, ₂₉.₆, ₂₉.₅, ₂₉.₃, ₂₉.₁, ₂₈.₅, ₂₂.₆, ₁₄.₁. MALDI-TOF: calc. 9₆₉.₅₇₈₁ found 9₆₈.₂₇₉₃.

**H₂ TTF-Crown Ether Phthalocyanine 6a**

The dicyano compound 5 (42 mg, 0.043 mmol) was added to a solution of lithium hexanolate in hexanol (prepared from 20 mg Li in 2 ml hexanol) under an argon atmosphere and the reaction mixture heated at 130°C with stirring for 3 hr in the absence of light in which time the reaction mixture changed colour from orange to deep green. After cooling, the solvent was evaporated in vacuo, acetic acid (10ml) was added and the solution stirred overnight. The solution was then decanted, chloroform (20 ml) was added and the organic layer was washed with water (3 x 50 ml). The organic layer was dried over sodium sulphate and the solvent removed. The residue was purified by size exclusion column, (biobeads® SX1 with CH₂Cl₂ as the mobile phase) and the front running band collected and the solvent removed. The product was precipitated from hot acetone by the slow addition of methanol to yield 6 as a green solid (4.32 mg, 11 %). ¹H-NMR (CDCl₃, 300 MHz): δ 8.6 (bs, 8H Ar-H), 4.25-3.80 (br m, 48H), 3.10 (br t,16H), 2.82 (br t, 16H), 1.65 (m, 16H), 1.2-1.4 (m, 144H), 0.87 (t, 24H) (inner N-H signals not observed due to aggregation at NMR sample concentrations). ¹³C-NMR (CDCl₃, 75 MHz): δ 2₂₀₂.₂, ₁₉₂.₂, ₁₉₁.₇, ₁₈₇.₀, ₁₇₈.₉, ₁₇₂.₃, ₁₄₀.₁, ₁₂₅.₂, ₁₂₄.₁, ₇₇.₂, ₃₁.₉, ₂₉.₆, ₁₄₅.₄, ₁₃₅₉, ₁₂₇₈, ₁₂₆₁, ₁₂₁₄, ₁₁₂₆, ₁₀₉₉, ₁₀₂₅, ₈₀₀, ₇₄₆ cm⁻¹. UV-Vis (CHCl₃) λ (CHCl₃): ₇₀₁, ₆₆₃, ₆₀₅, ₃₃₁, ₂₈₆ nm.
Aggregation Studies

**Fig. S1.** Left: Plot of absorbance at 613 nm divided by the absorbance at 700 nm as a function of methanol addition to a chloroform solution of 6a (UV-vis spectrum of q-band region showed on right). The critical aggregation concentration of MeOH is around 20%.

Gelation Studies

Pc 6a (1.2 mg) was dissolved in chloroform (1 ml). The solution was filtered and the volume was reduced to 100 µl. The solution was slowly warmed up to 70°C and drop of dioxane was added before the solution was cooled down slowly to 0°C upon which gelation was observed to occur. TEM samples was prepared by inserting the carbon TEM grid on the meniscus of the gelation and visualised by TEM (figure S2) before and after shadowing with Pt (angle of 45°).

**Fig. S2.** Selected examples of TEM images of the helical fibres (2 top pictures) formed from the bilayer structures (2 bottom pictures) produced by the gelation of Pc 6a.
Supplementary Information for manuscript: “Chiral molecular tapes from novel tetra(thiafulvalene-crown-ether)-substituted phthalocyanine building blocks”, Sly et. al. (page 5 of 6)

**Preparation CT- complex of TCNQ with 6**

Pc 6b (0.3 mg) was dissolved in DMSO (100µl) before the addition of TCNQ (0.02 mg of TCNQ was administered from a solution prepared from 5 ml DMSO and 1 mg TCNQ). The solution was stirred for 5 min and evaporated in vacuo. Chloroform (0.2 ml) was added and the sample warmed up and slowly cooled down. Acetonitrile (0.02 ml) was added to completely dissolve the sample for UV-Vis analysis. The IR spectrum of a drop of 6 in DMSO was measured before the addition of one drop of TCNQ in CH₂Cl₂ the resulting IR spectrum showed a new peak at 2179 cm⁻¹ and the absence of any peak 2223 cm⁻¹ when compared to the spectrum of TCNQ in CH₂Cl₂ which showed only the peak at 2223 cm⁻¹ for this region.

![UV-vis spectra of 6b](image)

**Fig. S3.** UV-vis spectra of 6b in the mixture acetonitrile-dichloromethane 1-9 at 20°C no TCNQ (solid line), and addition of excess TCNQ (dotted line).

**Addition of iodine:**

![UV-vis spectra of 6b](image)

**Fig. S4.** UV-vis spectra of 6b upon addition of iodine

**Electrochemistry:** Reference electrode: Ag/AgI; working and counter electrodes: Pt, sweep rate 100mVs⁻¹, supporting electrolyte: nBu₄NPF₆ 0.1 mol/l.
Fig S5. Artistic interpretation of how the self-assembled monolayer formed from the self-association of 6 (as described in Fig S5) forms the unique chiral helical scrolled structures observed. While the overall bulk architecture is apparent, the exact relationship of the monomeric units within the scroll is not yet precisely known. The exact driving force behind the scroll formation is also not currently understood.