Pergamon

Tetrahedron 56 (2000) 3385–3390

TETRAHEDRON

Synthesis and Characterisation of Tetrathiafulvalenyl- and Ferrocenyl-Triphenylenes

Graeme Cooke,[a,*] Abdulla Radhi,[a] Neville Boden,[b] Richard J. Bushby,[b] Zhibao Lu,[b]
Sarah Brown[b] and Sarah L. Heath[c,†]

[a]*School of Applied and Molecular Sciences, University of Northumbria at Newcastle, Ellison Building, Newcastle-upon-Tyne NE1 8ST, UK*
[b]*School of Chemistry and SOMS Centre, University of Leeds, Leeds LS2 9JT, UK*
[c]*Department of Chemistry, The University, Sheffield S3 7HF, UK*

Received 2 March 2000; accepted 23 March 2000

Abstract—The synthesis, electrochemistry and mesogenic properties of novel tetrathiafulvalenyl- and ferrocenyl-triphenylenes are described. In all cases the juxtaposition of the hexa-alkyloxytriphenylene with a tetrathiafulvalene or ferrocene unit failed to give rise to derivatives displaying a discotic mesophase. Solution electrochemistry of derivatives **7** and **13** has revealed an interaction occurs between the dicationic state of the TTF moiety and the triphenylene nucleus. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The chemistry of tetrathiafulvalene (TTF)[1] and ferrocene[2] derivatives has been at the forefront of attention over the last 25 years regarding the development of redox-active supramolecules with advanced material applications. As the bulk physical properties of these molecules invariably depend upon the supramolecular architecture of these systems, an enormous amount of effort has been directed towards the production of highly organised single crystals[3] and thin films.[4] As an alternative strategy to create highly ordered self-annealing supramolecules, recent attention has focused upon the synthesis of liquid crystalline derivatives bearing the TTF[5] and ferrocene[2] units. Although the study of TTF, and in particular, ferrocene based nematic and calamitic liquid crystals has proved to be a fertile field of study over the last few years, remarkably few examples of discotic liquid crystalline derivatives have been reported.[5f,h,i] This is particularly surprising as appropriately functionalised disc-like molecules have the propensity of forming columnar structures, which are reminiscent of the segregated stacking observed in anisotropic molecular conductors. In particular, the attachment of these units to a hexa-alkyloxytriphenylene moiety due to their propensity of forming highly conducting 1D conductors, make such systems prime synthetic targets.[6] In the present work, we report the synthesis and properties of the first examples of tetrathiafulvalenyl- and ferrocenyl-hexa-alkyloxytriphenylenes. Supramolecular formulations of this type are particularly exciting as there is a possibility that suitably functionalised derivatives may display a thermotropic discotic liquid crystalline phase.[7] Furthermore, the juxtaposition of redox-active molecules with differing ionisation potentials such as the TTF-triphenylenes described here, may give rise to novel redox controllable supramolecular architectures[8] with electrochemical switching applications.[9]

Results and Discussion

The triphenylene building blocks **3** and **4** were prepared from alcohols **1**[10] and **2**[11] by a K_2CO_3 catalysed Williamson's reaction with 6-bromohexan-1-ol. Triphenylenes **7** and **8** were then prepared in good yield by a DCC/DMAP esterification of compound **3** with **5**[12] or **6** in CH_2Cl_2 at 25°C (Scheme 1).

When similar reactions were attempted using alcohol **4** with either **5** or **6** in CH_2Cl_2 or THF, the *N*-acyl ureas **9** and **10** were the exclusive products from the reactions. *N*-Acyl ureas are the known side products formed during the activation of carboxyl groups with DCC.[13] The low solubility of alcohol **4** in both of the aforementioned solvents, apparently promotes the rearrangement of the *O*-acyl urea formed from the initial reaction of the carboxy- derivatives with DCC, to the *N*-acyl urea derivative. To circumvent the problems of preparing **13** and **14** using the DCC/DMAP esterification procedures, we investigated the use of fluorocarbonyl-TTF **11**[14] and fluorocarbonyl-ferrocene **12**,[15] which we have shown previously to be versatile and effective reagents for

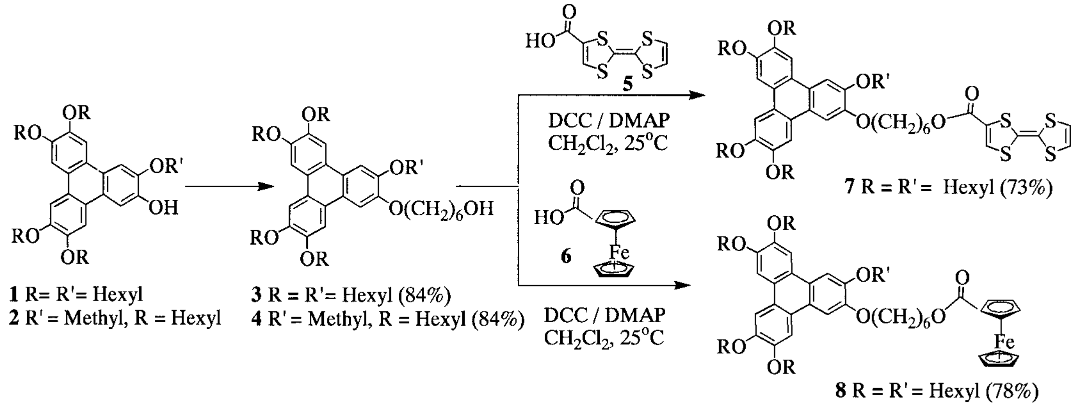
---

Keywords: tetrathiafulvalene; ferrocenes; triphenylene; electrochemistry; molecular modelling.

* Corresponding author. Tel.: +44-191-227-3554; fax: +44-191-227-3519; e-mail: graeme.cooke@unn.ac.uk

† Present address: Department of Chemistry, University of York, Heslington, York YO10 5DD, UK.

PII: S0040-4020(00)00250-7



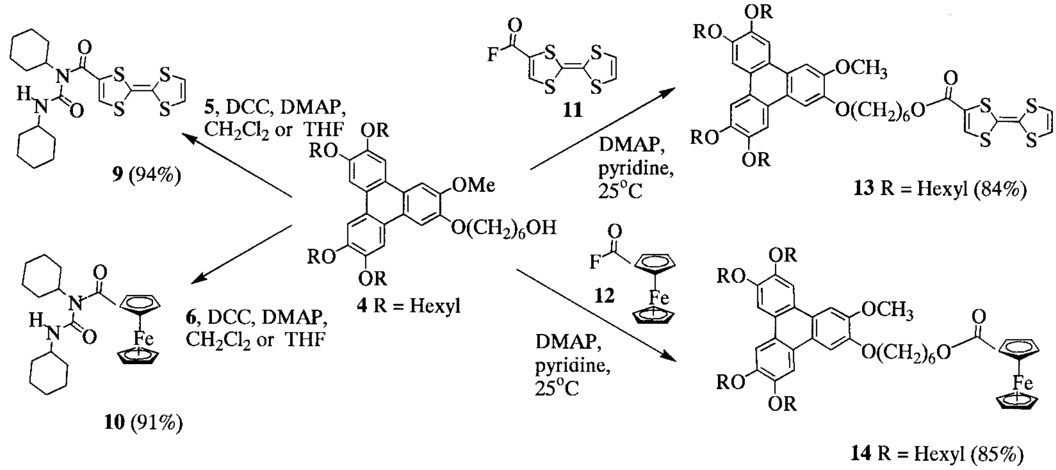
Scheme 1.

preparing carboxylic esters. Derivatives **11** and **12** proved to be very effective reagents for preparing **13** and **14**, indeed, in accordance with previous work carried out in our laboratory, the addition of DMAP to the reaction mixture results in high yields of the desired esters (Scheme 2).

X-Ray quality crystals of **10** were obtained from a toluene solution by slow evaporation of the solvent, the molecular structure of this compound is provided in Fig. 1a and b. Fig. 1a confirms the proposed formation of the *N*-acyl urea derivative via a rearrangement of the *O*-acyl derivative. Fig. 1b shows that the molecules form a dimer in the solid-state, held together by hydrogen bonds formed between the N–H of the urea and the carbonyl of the acyl-ferrocene moiety (H2AB-O1A and H2AA-O1B). The hydrogen bond length is 2.028 Å in each case. An interesting feature of the dimer architecture is that the carbonyl group of the central urea moiety plays no part in hydrogen bonding process, presumably due to steric hindrance of the neighbouring cyclohexyl-moieties.

There is currently a considerable interest in producing multi-functional macromolecular supramolecules bearing redox-active moieties. Within this remit, the development of dendrimer architectures bearing pendent TTF[16] and ferrocene[17] units is a burgeoning field of study. Here, we describe the synthesis of new prototype structures in which we have a triphenylene nucleus bearing six ferrocene units.[18] The hexahydroxy-triphenylene derivative **15**[19] was reacted with excess bromohexan-1-ol in the presence of potassium carbonate to yield the hexa-hexylhydroxytriphenylene **16** in good yield. Compound **17** was synthesised in moderate yield by reacting an eight molar excess of **6** with **16** in pyridine (Scheme 3).

We have investigated the solution electrochemistry of these derivatives using cyclic voltammetry. The oxidation potentials are presented in Table 1. The triphenylene precursors **3**, **4** and **16** all displayed a single reversible oxidation at 1.07 V due to the formation of the radical cation species by a one electron oxidation.[20] The ferrocenyl-triphenylenes **8** and **14** each gave rise to two oxidation waves due to the formation of the ferrocenium and the triphenylene radical cation species, respectively. The voltammogram of derivative **17** displays a single oxidation peak at 0.76 V for the ferrocene moieties. In accordance with previously reported CV data for hexaferrocene systems, the relative intensity ratio of six between the pseudo-reversible anodic and cathodic waves for **17**, confirms the presence of the six ferrocene units.[21] The oxidation of the ferrocene derivatives **8**, **14** and **17** occurred at comparable potentials to that of acylferrocenes, indicating that central triphenylene core has no influence on the oxidation of the ferrocene units. The tetrathiafulvalenyl-triphenylenes, on the other hand, gave rise to two reversible



Scheme 2.

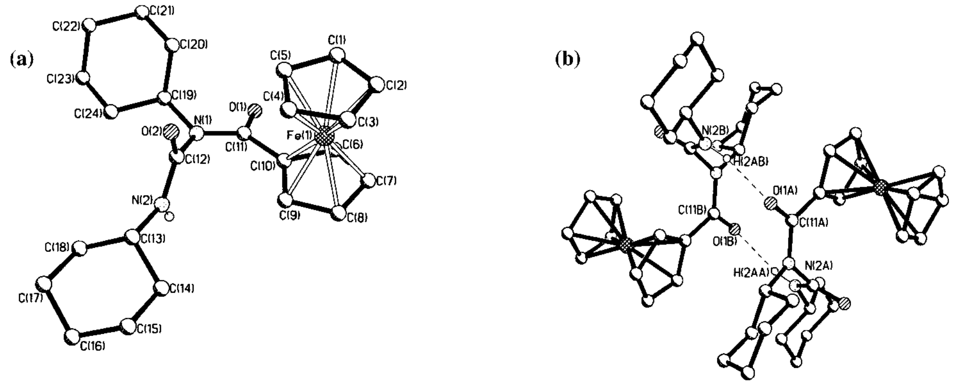
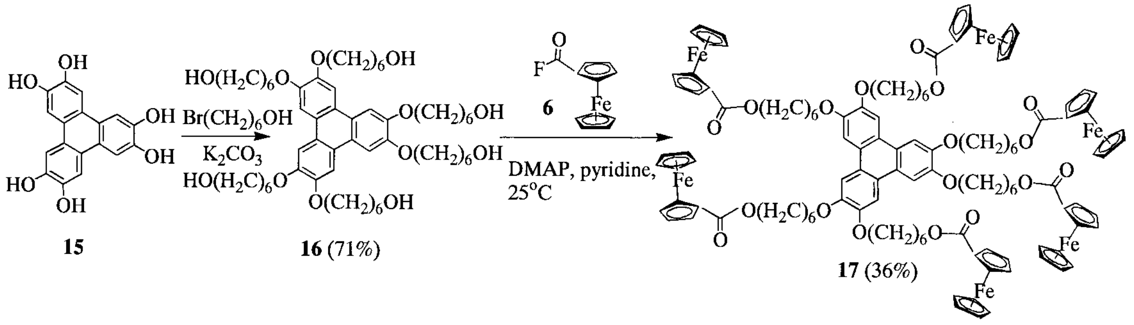


Figure 1. (a) X-Ray structure of **10**. (b) Hydrogen bonded dimer of **10**.



Scheme 3.

Table 1. Cyclic voltammetry data. (In volts, 0.5 M TBA PF_6/CH_2Cl_2 vs. Ag/AgCl, scan rate 100 mV s^{-1}. Working and counter electrodes: Pt)

Compound	$E_{\frac{1}{2}}{}^1$	$E_{\frac{1}{2}}{}^2$	$E_{\frac{1}{2}}{}^3$
3	1.07		
4	1.07		
7	0.53	0.98	1.13
8	0.76	1.06	
9	0.55	0.96	
10	0.70		
13	0.54	0.98	1.13
14	0.74	1.06	
16	1.07		
17	0.76	1.06	
18	0.54	0.89	

oxidation waves due to the sequential formation of the TTF radical cation ($TTF^{+\cdot}$) and dication (TTF^{++}) states, and a pseudo-reversible wave due to the formation of the triphenylene radical cation species. The oxidation waves caused by the formation of triphenylene radical cation species occur at slightly higher potentials that the non-TTF functionalised precursors **3** and **4**. Furthermore, the half wave potential due to the formation of the TTF^{++} is at a higher potential than that observed for the non-triphenylene functionalised 4-methoxycarbonyl-TTF **18** (0.98 V rather than 0.89 V). The oxidation potential due to the formation of the $TTF^{+\cdot}$ species in derivatives **7** and **13**, appear to be unaffected by the presence of the triphenylene nucleus. This result is in accordance with previously reported results,

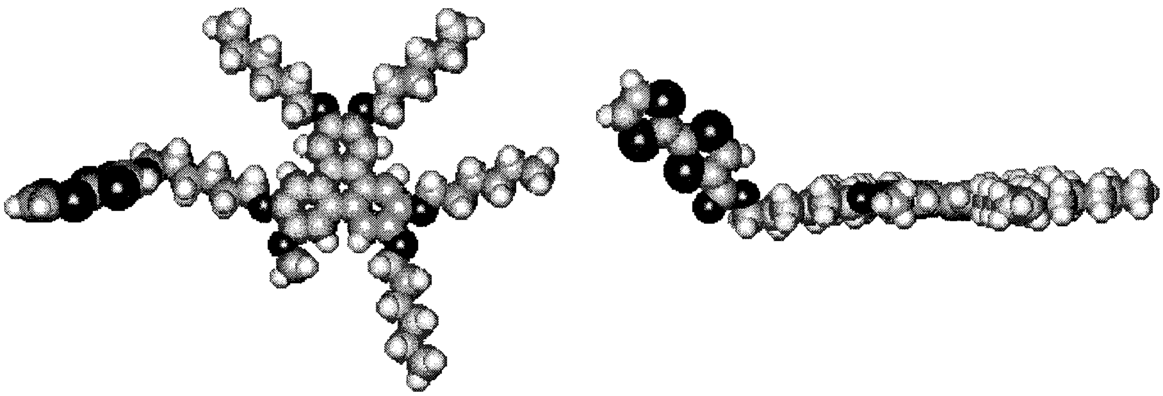


Figure 2. MM+ Energy minimised structure of **13**.

which described the ability of the electrochemically generated electron deficient TTF^{++}, and not TTF$^{+\cdot}$, to complex with electron rich macrocyclic polyether 1,5,-dinaphtho-[38]crown-10.[8] Addition of an equimolar amount of **18** to a CV cell containing **3** or **4**, resulted in similar shifts of the redox waves, thereby indicating both intra- and intermolecular charge-transfer complexation occurs in solution.

We have modelled molecule **13** using the MM+ forcefield,[22] which revealed a low energy structure whereby no observable interaction occurs between the triphenylene and TTF units (Fig. 2). This supports our extensive ^{1}H NMR studies performed on derivatives **7** and **13** and **18**, which has shown that the spectra of the TTF protons were identical in each case, which argues against an interleaving of the TTF and triphenylene units in solution. Furthermore, the ferrocene protons of ^{1}H NMR spectra of systems **8**, **14** and **17** are essentially the same as that of methoxycarbonylferrocene, thereby indicating that edge-to-face/CH-π interaction of the ferrocene protons with the phenyl rings of the triphenylene nucleus does not occur in solution.[23]

We have investigated the mesogenic properties of the new compounds using polarised microscopy and differential scanning calorimetry. In all cases the addition of the TTF and ferrocene units to the non-liquid crystalline triphenylene cores of molecules of **3**, **4** and **16**, failed to promote the formation of a discotic mesophase.

In conclusion, we have synthesised the first examples of tetrathiafulvalenyl- and ferrocenyl-triphenylenes. ^{1}H NMR and modelling studies have indicated that no interaction between the neutral TTF and ferrocene units of these moieties and triphenylene nucleus are observed in solution. However, CV studies have revealed an interaction between the dication of the TTF units of **7** and **13** and the triphenylene core. The addition of the TTF and ferrocene units to triphenylene building blocks **3**, **4** and **16** failed to transform the non-discotic hydroxy-functionalised triphenylenes into derivatives displaying a liquid crystal phase. Studies are underway in our laboratories to synthesise new tetrathiafulvalenyl- and ferrocenyl-triphenylene derivatives to further investigate the redox controlled complexation behaviour and to help coax the derivatives into forming a discotic mesophase.

Experimental

General

All new compounds gave satisfactory microanalyses. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. CV measurements were recorded on a BAS 50 W electrochemical workstation.

2-(6-Hydroxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 3. **1** (0.5 g, 0.67 mmol), 6-Bromohexan-1ol (0.12 g, 0.67 mmol) and K_2CO_3 (20 g) were heated under reflux in absolute ethanol (200 mL) for 48 h. The resulting mixture was filtered whilst hot, and the ethanol was removed under vacuum. The crude mixture was then purified using chromatography (SiO_2/CH_2Cl_2) to afford **3** as a white solid (0.47 g, 84%). Mp 68–70°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 4.23 (t, 12H, *J*=7 Hz), 3.69 (t, 2H, *J*=7 Hz), 1.95 (m, 12H, *J*=7 Hz), 1.57–1.41 (m, 36H, *J*=7 Hz), 0.94 (t, 15H, *J*=7 Hz). MS (FAB) *m*/*z*=845 (M$^+$). Found: C, 76.80; H, 10.00%. Calcd for $C_{54}H_{84}O_7$ C, 76.69; H, 9.94%.

2-(6-Hydroxyhexyloxy)-3-methoxy-6,7,10,11-tetrahexyloxytriphenylene 4. Compound **4** was prepared analogously to compound **3** using **2** (0.5 g, 0.74 mmol), 6-bromohexan-1ol (0.13 g, 0.74 mmol) and K_2CO_3 (20 g) to afford **4** as a white solid (0.48 g, 84%). Mp 78–81°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 4.23 (t, 10H, *J*=7 Hz), 4.10 (s, 3H), 3.69 (t, 2H, *J*=7 Hz), 1.94 (m, 12H, *J*=7 Hz), 1.57–1.41 (m, 28H, *J*=7 Hz), 0.93 (t, 12H, *J*=7 Hz). MS (FAB) *m*/*z*=775 (M$^+$). Found: C, 75.80; H, 9.60%. Calcd for $C_{49}H_{74}O_7$ C, 75.87; H, 9.56%.

2-(6-Tetrathiafulvalenylcarboxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 7. To a stirred solution of **3** (0.5 g, 0.59 mmol), **5** (0.15 g, 0.59 mmol) in dry CH_2Cl_2 (25 mL) at 25°C were added DCC (0.24 g, 1.18 mmol) and DMAP (0.07 g, 0.59 mmol). The resulting solution was stirred for 48 h, then water (50 mL) was added. The organic layer was separated, dried ($MgSO_4$), filtered and concentrated under vacuum to yield a crude mixture. Column chromatography (SiO_2, CH_2Cl_2/hexane 50/50) afforded **7** as a yellow/orange solid (0.46 g, 73%). Mp 52–54°C ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.83 (s, 6H), 7.29 (s, 1H), 6.23 (s, 2H), 4.23 (t, 12H, *J*=7 Hz), 1.94 (m, 12H, *J*=7 Hz), 1.80 (t, 2H, *J*=7 Hz), 1.58–1.41 (m, 36H, *J*=7 Hz), 0.94 (t, 15H, *J*=7 Hz). MS (FAB) *m*/*z*=1074 (M$^+$). Found: C, 68.20; H, 8.19%. Calcd for $C_{61}H_{86}O_8S_4$ C, 68.16; H, 8.00%.

2-(6-Ferrocenylcarboxyhexyloxy)-3,6,7,10,11-pentahexyloxytriphenylene 8. Compound **8** was prepared analogously to **7** using **3** (0.5 g, 0.59 mmol), **6** (0.14 g, 0.59 mmol), dry CH_2Cl_2 (25 mL), DCC (0.24 g, 1.18 mmol) and DMAP (0.07 g, 0.59 mmol). Compound **8** was afforded as a yellow solid (0.49 g, 78%). Mp 40–41°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 4.78 (t, 2H, *J*=1 Hz), 4.33 (t, 2H, *J*=1 Hz), 4.23 (t, 12H, *J*=7 Hz), 4.15 (s, 5H), 1.94 (m, 12H, *J*=7 Hz), 1.80 (t, 2H, *J*=7 Hz), 1.58–1.40 (m, 36H, *J*=7 Hz), 0.94 (t, 15H, *J*=7 Hz). MS (FAB) *m*/*z*=1056 (M$^+$). Found: C, 73.90; H, 8.98%. Calcd for $C_{65}H_{92}FeO_8$ C, 73.86; H, 8.71%.

1,3-Dicyclohexyl-1-tetrathiafulvalenyl-urea 9. To a stirred solution of **4** (0.46 g, 0.59 mmol) and **5** (0.14 g, 0.59 mmol) in THF (or CH_2Cl_2) (50 mL) at 25°C was added DCC (0.24 g, 1.18 mmol) and DMAP (0.07 g, 0.59 mmol). The solution was stirred for 24 h, then water (50 mL) was added, and the organic layer was separated, dried ($MgSO_4$), filtered and concentrated under vacuum. The crude product was purified using chromatography (SiO_2, CH_2Cl_2) to yield an orange solid (0.25 g, 94%). Mp 140–143°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.31 (s, 2H), 6.04 (d, 1H), 4.10 (m, 1H, *J*=4 Hz), 3.64 (m, 1H, *J*=4 Hz), 1.61 (m, 12H, *J*=9 Hz), 1.24 (m, 8H, *J*=7 Hz). MS (FAB) *m*/*z*=454 (M$^+$). Found: C, 52.84; H, 5.65%. Calcd for $C_{20}H_{26}N_2O_2S_4$ C, 52.86; H, 5.73%.

1,3-Dicyclohexyl-1-ferrocenyl-urea 10. Compound **10** was prepared analogously to **9** using **4** (0.46 g, 0.59 mmol), **6** (0.14 g, 0.59 mmol), THF (or CH_2Cl_2) (50 mL), DCC (0.24 g, 1.18 mmol), DMAP (0.07 g, 0.59 mmol) to yield **10** as a yellow solid (0.24 g, 91%). Mp 169–173°C ^1H NMR (270 MHz, $CDCl_3$) δ 6.45 (d, 1H), 4.74 (t, 2H, J=1 Hz), 4.34 (t, 2H, J=1 Hz), 4.25 (m, 1H, J=4 Hz), 4.21 (s, 5H), 3.53 (m, 1H, J=4 Hz), 1.80 (m, 12H, J=9 Hz), 1.31 (m, 8H, J=8 Hz). MS (FAB) m/z=436 (M^+). Found: C, 66.19; H, 7.65%. Calcd for $C_{24}H_{32}N_2FeO_2$ C, 66.06; H, 7.34%.

Crystal data for compound 10. $C_{24}H_{32}FeN_2O_2$, M_W= 436.37, triclinic, space group P-1, a=10.117(2) Å, b=10.678(2) Å, c=11.777(2) Å, α=104.554(4)°, β= 108.486(3)°, γ=108.259(3)°, V=1055.5(4) Å^3, Z=2, D_c= 1.373 mg/m^3, F(000)=464, MoKα (λ=0.71073 Å). Crystal dimension, 0.32×0.27×0.23 mm^3 (red block). Intensity data were collected at 150 K on a Bruker SMART-CCD diffractometer using graphite monochromated MoKα (λ= 0.71073 Å). A total of 4851 independent reflections were measured in range 1.98–28.34°. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL NT)[24] to $R1$=0.0327 (for 4256 $F>4\sigma(F)$); wR_2=0.0865, S=1.043 for all 4851 unique data and 262 refined parameters with allowance for the thermal anisotropy of all non-hydrogen atoms. Further details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK.

2-(6-Tetrathiafulvalenylcarboxyhexyloxy)-3-methoxy-6,7,10,11-tetrahexyloxytriphenylene 13. Triphenylene **4** (0.3 g, 0.39 mmol), **11** (0.1 g, 0.39 mmol) and DMAP (0.05 g, 0.39 mmol) were stirred in dry pyridine (20 mL) for 24 h. The pyridine was removed under vacuum and the resulting solid was partitioned between CH_2Cl_2 and water (50 mL; 50 mL). The organic layer was separated, dried ($MgSO_4$), filtered and evaporated to give a crude product which was purified using chromatography (SiO_2, CH_2Cl_2) to afford **13** as an orange solid (0.34 g, 84%). Mp 76–78°C. ^1H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 7.30 (s, 1H), 6.25 (s, 2H), 4.23 (t, 10H, J=7 Hz), 4.09 (s, 3H), 1.94 (m, 12H, J=7 Hz), 1.80 (t, 2H, J=7 Hz), 1.77–1.40 (m, 28H, J=7 Hz), 0.93 (t, 12H, J=7 Hz). MS (FAB) m/z=1004 (M^+). Found: C, 66.89; H, 7.59%. Calcd for $C_{56}H_{76}O_8S_4$ C, 66.93; H, 7.57%.

2-(6-Ferrocenylcarboxyhexyloxy)-3-methoxy-6,7,10,11-tetrahexyloxytriphenylene 14. Compound **14** was prepared analogously to **13** using **4** (0.3 g, 0.39 mmol), **12** (0.09 g, 0.39 mmol) DMAP (0.05 g,0.39 mmol) and dry pyridine (20 mL) to yield **14** as a yellow solid (0.33 g, 85%). Mp 42–44°C. ^1H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 4.78 (t, 2H, J=1 Hz), 4.33 (t, 2H, J=1 Hz), 4.23 (t, 10H, J=7 Hz), 4.16 (s, 5H), 4.09 (s, 3H), 1.94 (m, 12H, J=7 Hz), 1.81 (t, 2H, J=7 Hz), 1.68 −1.40 (m, 28H, J=7 Hz), 0.93 (t, 12H, J=7 Hz). MS (FAB) m/z=986 (M^+). Found: C, 73.08; H, 8.38%. Calcd for $C_{60}H_{82}FeO_8$ C, 73.02; H, 8.32%.

2,3,6,7,10,11-Hexa-6-(hydroxyhexyloxy)-triphenylene 16. **15** (0.5 g, 1.5 mmol), 6-Bromohexan-1ol (1.68 g, 9.3 mmol) and K_2CO_3 (20 g) were heated under reflux in absolute ethanol (200 mL) for 72 h. The resulting mixture was filtered whilst hot, and the ethanol was removed under vacuum. The crude mixture was then purified using chromatography (SiO_2/CH_2 Cl_2/MeOH 80/20) to afford **16** as a brown semi-solid (0.98 g, 71%). ^1H NMR (270 MHz, $CDCl_3$) δ 7.98 (s, 6H), 4.38 (t, 6H, J=7 Hz), 4.24 (t, 12H, J=7 Hz), 3.43 (m, 12H, J=7 Hz), 1.81 (m, 12H, J=7 Hz), 1.49 (m, 36H, J=7 Hz). MS (FAB) m/z=925 (M^+). Found: C, 69.99; H, 9.10%. Calcd for $C_{54}H_{84}O_{12}$ C, 70.12; H, 9.09%.

2,3,6,7,10,11-Hexa-6-(ferrocenylcarboxyhexyloxy)-triphenylene 17. To a stirred solution of triphenylene **16** (0.1 g, 0.11 mmol) and DMAP (0.11 g, 0.86 mmol) in dry pyridine (20 mL) at 5°C was added a solution of **11** (0.2 g, 0.86 mmol) in pyridine (5 mL) over 5 h. The resulting solution was stirred for 24 h, and then the solvent was removed under vacuum and the resulting solid was partitioned between CH_2Cl_2 and water (50 mL/50 mL). The organic layer was separated, dried ($MgSO_4$), filtered and evaporated to give a crude product which was purified using chromatography (SiO_2, CH_2Cl_2) to afford **17** as a brown semi-solid (0.09 g, 36%). ^1H NMR (270 MHz, $CDCl_3$) δ 7.84 (s, 6H), 4.78 (t, 12H, J=1 Hz), 4.34 (t, 12H, J=1 Hz), 4.24 (t, 12H, J=7 Hz), 4.16 (s, 30H), 1.99 (m, 12H, J=7 Hz), 1.80 (t, 12H, J=7 Hz) 1.67 (m, 36H, J=7 Hz). MS (FAB) m/z=2197 (M^+). Found: C, 65.86; H, 6.00%. Calcd for $C_{120}H_{132}Fe_6O_{18}$ C, 65.57; H, 6.01%.

Acknowledgements

The author thanks the Royal Society of Chemistry and the Royal Society for financial support and the EPSRC National Mass Spectrometry Service Centre, Swansea for performing FAB mass spectral analysis. S. L. H. would like to thank the Royal Society for the award of a University Research Fellowship.

References

1. Garin, J. *Adv. Heterocycl. Chem.* **1995**, *62*, 249–304.
2. *Ferrocenes*, Togni, A., Hayashi, T. Eds.; VCH: New York, 1995.
3. Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481–1496.
4. Bryce, M. R. *Chem. Soc. Rev.* **1991**, *29*, 355–390.
5. (a) Mueller-Westerhoff, U. T.; Nazzal, A.; Cox, R. J.; Giroud, A.-M. *J. Chem. Soc., Chem. Commun.* **1980**, 497–498. (b) Babeau, A.; Tinh, N. H.; Gasparoux, H.; Polycarpe, C.; Torreilles, E.; Giral, L. *Mol. Cryst. Liq. Cryst. Sci Technol.* **1982**, *72*, 171–176. (c) Chanh, N. B.; Cotrait, M.; Gautlier, J.; Haget, Y.; Tinh, N. H.; Polycarpe, C.; Torreilles, E. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **1983**, *101*, 129–141. (d) Polycarpe, C.; Torreilles, E.; Giral, L.; Babeau, A.; Tinh, N. H.; Gasparoux, H. *J. Heterocycl. Chem.* **1984**, *21*, 1741–1745. (e) Frenzel, S.; Arndt, S.; Gregorious, R. M.; Mullen, K. *J. Mater. Chem.* **1995**, *5*, 1529–1537. (f) Cook, M. J.; Cooke, G.; Jafari-Fini, A. *Chem. Commun.* **1996**, 1925–1926. (g) Andreu, R.; Barbera, J.; Garin, J.; Orduna, J.; Seranno, J. L.; Sierra, T.; Leriche, P.; Salle, M.; Riou, A.; Jubault Gorgues, A. *Synth. Met.* **1997**, *86*, 1869–1870. (h) Andreu, R.; Garin, J.; Orduna, J.; Barbera, J.; Seranno, J. L.; Sierra, T.; Salle, M.; Gorgues, A. *Tetrahedron* **1998**, *54*, 3895. (i) Bissell, R. A.; Boden. N.; Bushby,

R. J.; Fishwick, C. W. G.; Holland. E.; Movaghar, B.; Ungar, G. *Chem. Commun.* **1998**, 113–114. (j) Andreu, R.; Barbera, J.; Garin, J.; Orduna, J.; Seranno, J. L.; Sierra, T.; Leriche, P.; Salle, M.; Riou, A.; Jubault, M.; Gorgues, A. *J. Mater. Chem.* **1998**, *8*, 881–887.

6. Boden, N.; Bushby, R. J.; Clements, J.; Luo, R. *J. Mater. Chem.* **1995**, *5*, 1741–1748.

7. Janietz, D. *J. Mater. Chem.* **1998**, *8*, 265–274.

8. Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951–3957.

9. Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 333–337.

10. Cooke, G.; Hell, F.; Violini, S. *Synth. Commun.* **1997**, *27*, 3745–3748.

11. Boden, N.; Bushby, R. J.; Cammidge, A. N.; Martin, P. S. *J. Mater. Chem.* **1995**, *5*, 1857–1860.

12. Garin, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489–493.

13. Toniolo, T.; Valle, G.; Crisma, M.; Morretto, V.; Izbedski, J.; Pelka, J.; Schnieder, C. H. *Helv. Chim. Acta* **1990**, *73*, 626–633.

14. Cooke, G.; Rotello, V. M.; Radhi, A. *Tetrahedron Lett.* **1999**, *40*, 8611–8613.

15. Gallow, T. H.; Rodrigo, J.; Cleary, K.; Cooke, G.; Rotello, V. M. *J. Org. Chem.* **1999**, *64*, 3745–3746.

16. Bryce, M. R.; Devonport, W.; Goldenberg, L. M.; Wang, C. *Chem. Commun.* **1998**, 945–951.

17. Newkome, G. R.; He, E.; Moorfield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746.

18. The reaction of eight equivalents of **11** with **16** gave small amounts of 2,3,6,7,10,11-hexa-6-(tetrathiafulvalenylcarboxyhexyloxy)-triphenylene. However, an analytically pure sample of this compound could not be obtained.

19. Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851–858.

20. Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749–4750.

21. Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460–2462.

22. As implemented in HyperChem 5.1, Hypercube Inc., Gainesville, Florida.

23. (a) Moriuchi, T.; Ikeda, I.; Hirao, T. *Organometallics* **1995**, *14*, 3578–3580. (b) Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1542–1544.

24. Sheldrick, G. M. SHELXL97, an integrated system for solving and refining crystal structures from diffraction data, University of Göttingen, Germany, 1997.