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Tetrathiafulvalene-functionalized triptycenes: synthetic protocols and elucidation of intramolecular Coulomb repulsions in the oxidized species

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Abstract—A large selection of triptycenes functionalized with tetrathiafulvalene (TTF) units as well as triptycenes containing extended TTFs as a part of the triptycene core have been synthesized utilizing new triptycene di- and tetraaldehydes as well as bis-, tetrakis- and hexakis(bromomethyl) derivatives. The largest scaffold contains a total of 12 TTFs around the central triptycene core. From spectroelectrochemical and chemical oxidation studies, we have elucidated the extent to which an increasing number of electrostatic interactions among oxidized TTF units exert an influence on the absorption characteristics.

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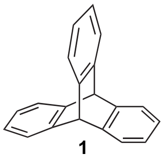
1. Introduction

The geometric features of the triptycene (**1**) skeleton make it appealing for exploitation in supramolecular chemistry.[1] The good electron donor tetrathiafulvalene (TTF) is another attractive molecule for both materials and supramolecular chemistry as it is oxidized reversibly in two one-electron steps.[2] In order to enhance the interactions between individual TTF units and the formation of mixed-valence radical cation salts, several macrocyclic,[3] ladder-like[4] and dendritic[5] TTF oligomers have been prepared during the past 10 years. Some of these molecules are also interesting as host molecules for electron deficient guest molecules. Moreover, oxidation of the TTFs to dications yields species that have a potential to form donor–acceptor complexes with electron rich molecules.[5g,6] We identified the triptycene core as a new and convenient scaffold for TTF oligomers and became interested in elucidating in a systematic manner the relationship between electrostatic interactions between oxidized TTF units and the absorption characteristics.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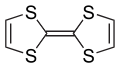
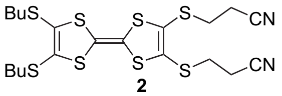

TTF

Synthetically, we benefit from readily available TTF building blocks **2**–**4**. The cyanoethyl group is an efficient protecting group for TTF thiolates as demonstrated by Becher and co-workers.[7] The two cyanoethyl groups of **2** can be removed stepwise by the action of a base such as CsOH or NaOMe, which allows two subsequent thiolate alkylations. In a theoretical study, this stepwise deprotection protocol was explained by an unfavourable Coulombic repulsion between two negatively charged thiolates on the same dithiole ring.[8] Phosphonate esters **3**[9] and phosphonium salt **4**[10] can be subjected to Wittig–Horner reactions.



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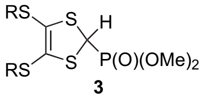

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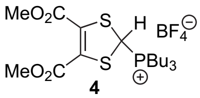
R = Bu: **3a**



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Some of us[11] have recently devised a simple synthesis of triptycene di- and tetracarboxylic acids by oxidation of appropriate methyl precursors. Here, we wish to present the utilization of these compounds in efficient syntheses of

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Keywords: Redox systems; Spectroelectrochemistry; Supramolecular chemistry; Tetrathiafulvalenes; Triptycenes.

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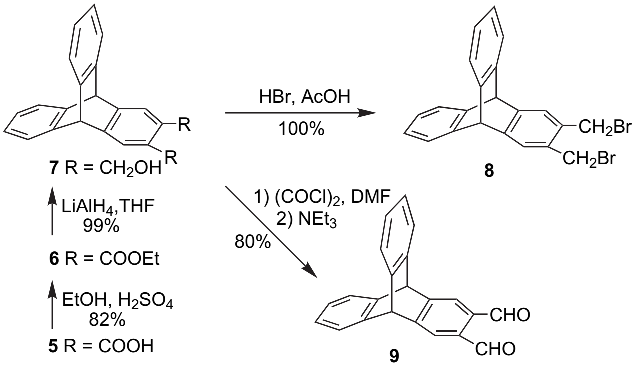
triptycene di- and tetraaldehydes as well as bis-, tetrakis- and hexakis(bromomethyl)triptycenes. The aldehydes are good substrates for the Wittig–Horner reaction with **3** or **4**, whereas the benzylic bromides represent reactive alkylation reagents towards thiolate anions generated from **2**. Hereby, a large selection of triptycenes functionalized with TTF as well as triptycenes containing extended TTFs as a part of the triptycene core have been obtained. Moreover, we have employed the triptycene unit as a core for a 12-TTF macromolecule.

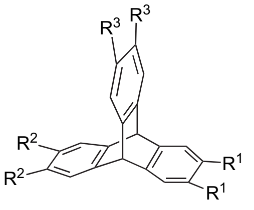
2. Results and discussion

Fischer esterification of the dicarboxylic acid **5** with EtOH gave the diethyl ester **6** (Scheme 1). The two ester groups were reduced with lithium aluminium hydride to provide the diol **7**. Treatment of compound **7** with HBr in acetic acid gave the dibromide **8**. Oxidation of **7** by pyridinium chlorochromate (PPC) gave the phthalide lactone rather than the desired dialdehyde. An analogous lactone formation has been observed in oxidation of 1,2-bis(hydroxymethyl)-benzene.[12] Nevertheless, Swern oxidation of **7** successfully gave the dialdehyde **9**.



Scheme 1.

By similar reactions, the esters **10** and **11**, the alcohol **12** and the bromides **14** and **15** were prepared. The alcohol **13** proved difficult to isolate and was, therefore, used in the ensuing bromination step without purification.

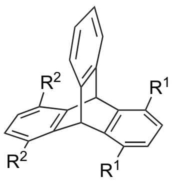


R^1 = R^2 = CO$_2$Et, R^3 = H: **10**
R^1 = R^2 = R^3 = CO$_2$Et: **11**

R^1 = R^2 = CH$_2$OH, R^3 = H: **12**
R^1 = R^2 = R^3 = CH$_2$OH **13**

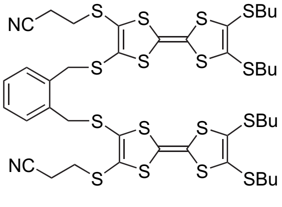
R^1 = R^2 = CH$_2$Br, R^3 = H: **14**
R^1 = R^2 = R^3 = CH$_2$Br: **15**

By a sequence of Fischer esterification, lithium aluminium hydride reduction and PCC oxidation, the new *para*-substituted derivatives **16**–**20** were prepared. The known dibromide **21** was obtained by NBS bromination according to a literature protocol.[13a] The tetrabromide **22** was obtained by analogous NBS bromination of the tetramethyl precursor **23**.[13,14] It should be mentioned that, in general, we experienced problems in obtaining the benzylic bromides analytically pure owing to their limited stabilities.



R^1 = CO$_2$Et, R^2 = H: **16**
R^1 = CH$_2$OH, R^2 = H: **17**
R^1 = R^2 = CH$_2$OH: **18**
R^1 = CHO, R^2 = H: **19**
R^1 = R^2 = CHO: **20**
R^1 = CH$_2$Br, R^2 = H: **21**
R^1 = R^2 = CH$_2$Br: **22**
R^1 = R^2 = CH$_3$: **23**

Triptycenes containing two TTF units were prepared from the dibromides **8** and **21** according to Scheme 2. Compound **2** was selectively deprotected with 1 equiv of caesium hydroxide and the resulting monothiolate was then alkylated in situ with the bromides to afford compounds **24** and **25**. Similarly, we prepared bis-TTFs **26** and **27** based on *o*- and *p*-xylene cores. The tetrabromides **14** and **22** served as precursors for triptycenes **28** and **29** containing four TTF units, while the hexabromide **22** was converted to the triptycene **30**.



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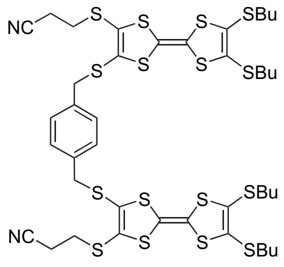

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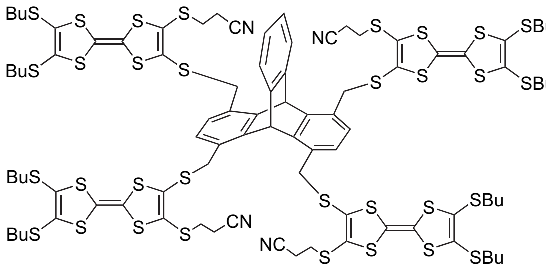

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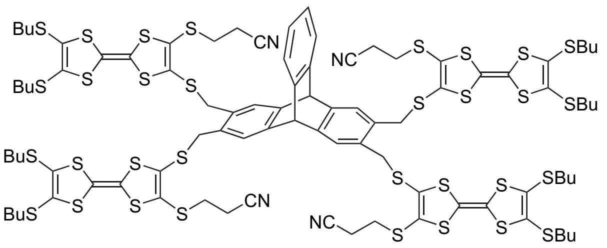

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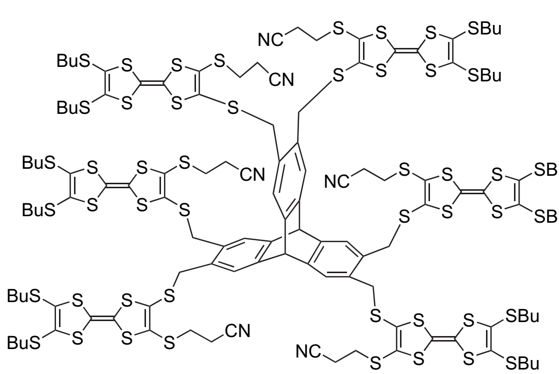

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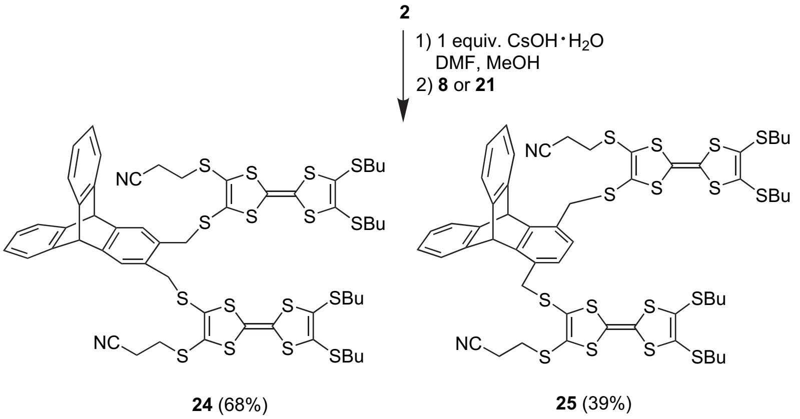
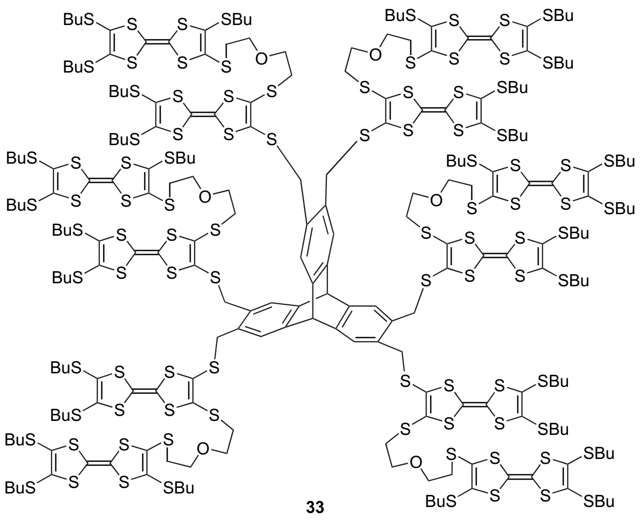


Scheme 2.

Selective monodeprotection of **2** with 1 equiv of caesium hydroxide and subsequent alkylation with butyl bromide gave compound **31** (Scheme 3). Deprotection and alkylation with an excess of bis(2-iodoethyl) ether gave compound **32**. With this reactive TTF-halide in hand, we decided to prove the synthetic usefulness of the remaining cyanoethyl groups of compounds **24**–**30**.

As an illustrative example, compound **30** was deprotected with caesium hydroxide and the resulting hexathiolate was then treated with an excess of the iodide **32** to provide the dendritic 12-TTF **33** in a yield of 64%.



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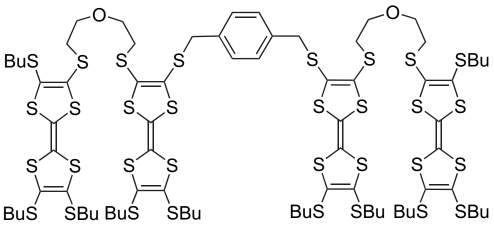
Similarly, the simple ladder compound **34** was obtained by deprotection of **27** followed by alkylation with **32**.



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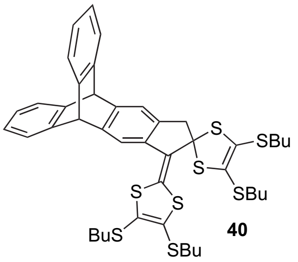
Treatment of **2** with 2 equiv of caesium hydroxide generated a dithiolate, which was then alkylated using an appropriate amount of the di-, tetra- and hexabromide **8**, **14** and **15** to afford the triptycenes **35**, **36** and **37**, respectively (Scheme 4).

The triptycene-extended TTFs **38** and **39** were prepared by treating the phosphonate ester **3a** (prepared from the dithiolium tetrafluoroborate in analogy with a literature procedure[4]) with butyllithium followed by the aldehydes **9** and **19**, respectively (Scheme 5).

The *ortho*-substituted triptycene **38** was purified using basic alumina as the adsorbent for column chromatography. Employing silica gel instead, isomeric compound **40** was obtained in 70% yield. A similar conversion was also observed for simple *o*-phenylene-extended TTFs.[15] Application of the same synthetic protocol in the reaction of terephthalaldehyde with **3a** afforded the *p*-phenylene-extended TTF **41**. Related phenylene-extended TTFs were previously reported by Gorgues and co-workers.[10]



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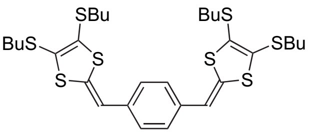

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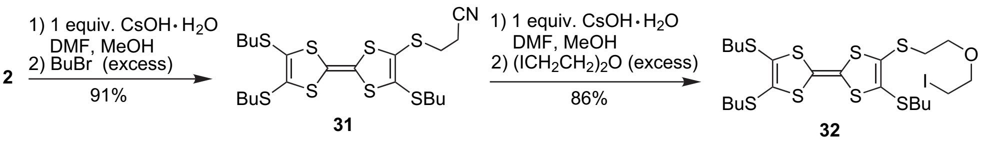
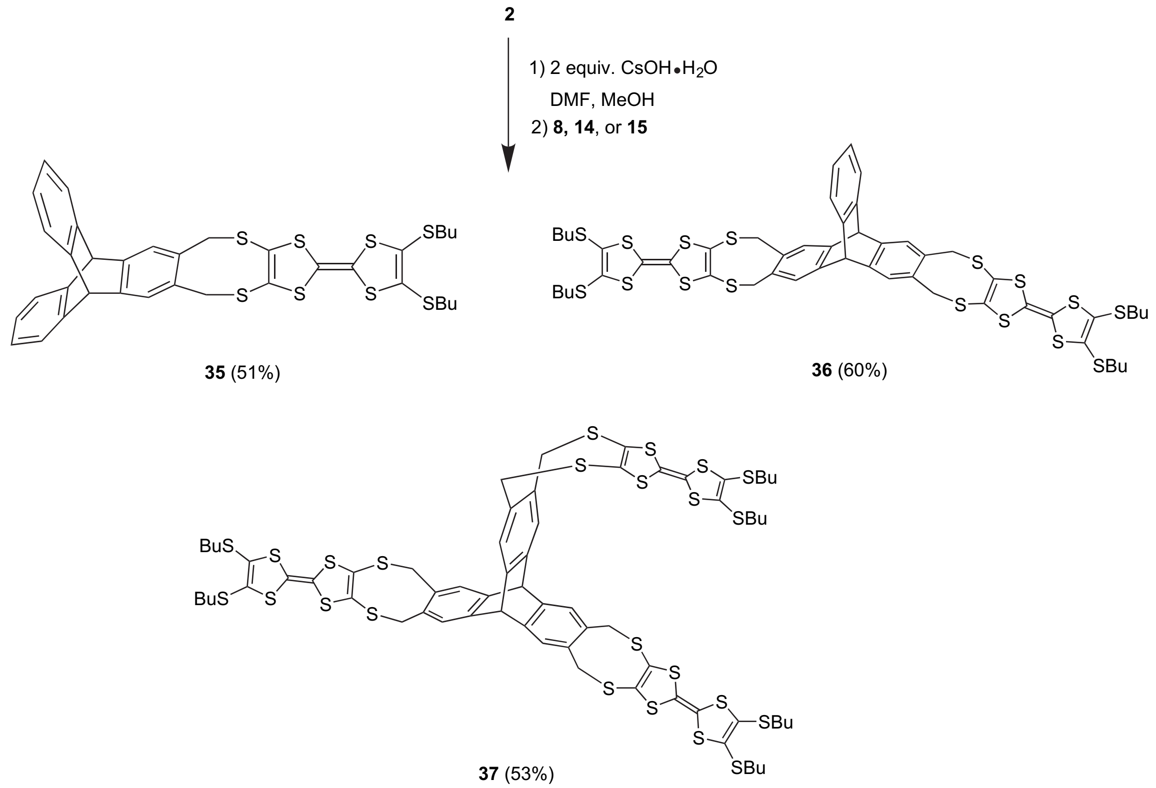
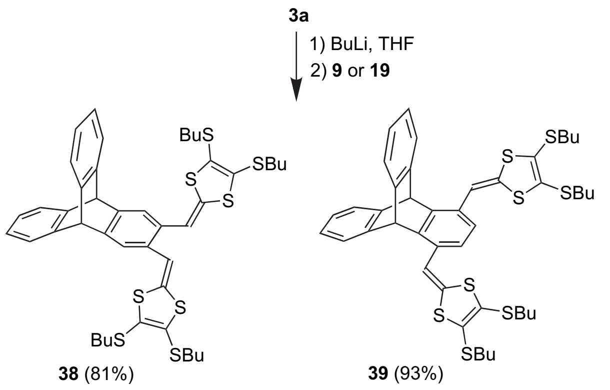


Scheme 3.



Scheme 4.

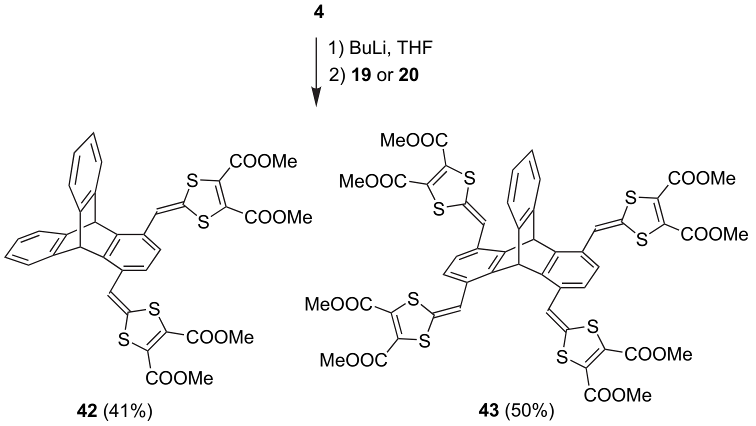


Scheme 5.

The phosphonium salt **4** was deprotonated with butyllithium and then treated with the dialdehyde **19** or tetraaldehyde **20** to provide triptycene-extended TTFs **42** and **43**, respectively (Scheme 6). The PM3-optimized structure of **43** obtained using the Gaussian 03 program package[16] is shown in Figure 1. The donor-functionalized cavity has dimensions characterized by sulfur–sulfur distances of 6.1 Å (S1–S3), 9.3 Å (S2–S4), 10.8 Å (S3–S5) and 6.1 Å (S4–S6).

2.1. Electrochemistry

The redox properties of the triptycene-TTFs were studied by cyclic voltammetry and differential pulse voltammetry. The data are summarized in Table 1; two representative cyclic



Scheme 6.

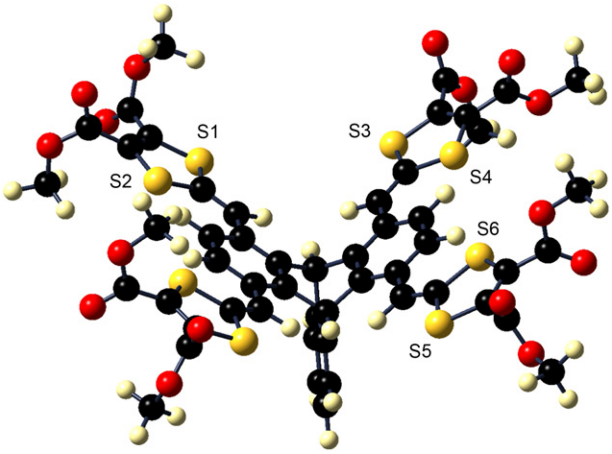


Figure 1. PM3-optimized structure of compound **43**.

Table 1. Potentials[a] obtained from cyclic voltammetric (CV) and differential pulse voltammetric (DPV) data

Compound	CV[b]		DPV	
	E^1_{ox}	E^2_{ox}	E^1_{ox}	E^2_{ox}
24	0.12	0.45	0.10	0.43
25	0.13	0.46	0.11	0.44
26	0.12	0.44	0.10	0.42
27	0.11	0.45	0.10	0.43
28	0.12	0.47	0.11	0.46
29	0.12	0.46	0.10	0.44
30	0.10	0.43	0.08	0.42
33	0.07	0.40	0.06	0.39
34	0.06	0.38	0.06	0.38
35	0.04	0.48	0.03	0.47
36	0.05	0.48	0.03	0.46
37	0.08	0.45	0.06	0.44
39	0.20[c]	0.45[c]	0.13	0.37
41	0.15[c]	0.47[c]	0.10	0.39
42	0.45[c]	0.82[c]	0.38	0.74
43	0.50[c]	0.84[c]	0.42	0.76

[a] All the potentials were determined in CH_2Cl_2 using Ag/Ag^+ as a reference electrode, Pt as the counter electrode, and glassy carbon as the working electrode. Supporting electrolyte: 0.1 M NBu_4PF_6. All values are reported against Fc^+/Fc.

[b] Scan rate 100 mV s^{-1}. Half-wave potentials.

[c] Irreversible redox process. Anodic peak potential.

voltammograms are shown in Figure 2. Compounds **25–30** and **33–37** were all oxidized in two reversible steps and, accordingly, the TTFs behaved in all cases as independent redox centres. In contrast, oxidation steps of compounds based on dithiafulvene (**39** and **41–43**) were irreversible.

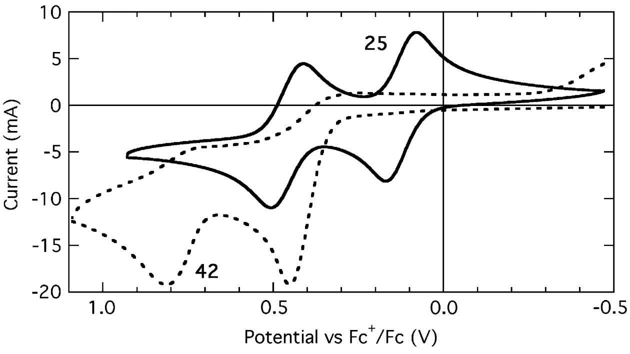


Figure 2. Cyclic voltammograms of compounds **25** and **42** in CH_2Cl_2 (0.1 M Bu_4NPF_6). Scan rate 100 mV s^{-1}.

The TTF derivatives displaying reversible redox processes can tentatively be divided into three groups. Compounds **35–37** all possess doubly linked units **2**. These have their first and second oxidation potentials around +0.05 and +0.48 V versus Fc^+/Fc, respectively. The second group includes compounds **33** and **34**, which have a twinned TTF unit attached to each substitution site of the scaffold. Even though the substitution pattern for the TTFs in the bis-unit is slightly different, neither CV nor DPV reveals any differences, i.e., again only two oxidation steps are observed. For these compounds, the first oxidation is around +0.06 V and the second oxidation is somewhat easier than for the aforementioned group, namely around +0.40 V. The last and largest group contains the benzene and triptycene derivatives where all substitution sites are occupied by singly linked TTF units, **24–30**. In this group the first oxidation seems slightly more difficult than in the other groups (around +0.12 V), while the second oxidation is in between the first and second groups, at +0.45 V.

As the number of electrons transferred in each oxidation step corresponds to the total number of TTF units (confirmed by spectroelectrochemistry, vide infra), the diffusion coefficients (*D*) for selected TTF compounds were calculated relative to that of ferrocene (D_{Fc}) employing the peak currents. The results are listed in Table 2. As expected, the D/D_{Fc} ratio decreases with increasing size of the molecule. Thus, the 12-TTF macromolecule **33** is characterized by the smallest diffusion coefficient. The diffusion coefficient of compound **35** is almost twice that of compound **36**, which is reasonable as the former is almost half the size of the latter. Finally, we note that the diffusion coefficient of the *para*-substituted triptycene **25** is somewhat smaller than that of the *ortho*-substituted triptycene **24**. These two compounds have identical molecular weights but obviously differ in shape.

2.2. Spectroelectrochemistry

The absorption spectra of the neutral, radical cation and dication states of compounds **24–27**, **30** and **31** and **33–36** were measured in CH_2Cl_2. The absorption maxima of the characteristic transition(s) are collected in Table 3, and as an example the full spectra of compounds **30**, **31** and **33** are shown in Figure 3. Two absorptions are observed for the TTF radical cations and are both assigned as intrinsic absorptions.[17]

Notably, isosbestic points are observed during the oxidations, and the resulting absorption spectra are indicative of only radical cation absorptions after the first oxidation and only dication absorptions after the second oxidation. Thus, with no exception among the prepared compounds, all the TTFs are oxidized simultaneously in both oxidation steps. This observation suggests that no disproportionation takes place.

Table 2. Diffusion coefficients (*D*) relative to that of ferrocene (D_{Fc}) obtained from electrochemical experiments

Compound	**24**	**25**	**26**	**27**	**30**	**31**	**33**	**34**	**35**	**36**
D/D_{Fc}	0.30	0.20	0.26	0.26	0.04	1.06	0.02	0.12	0.43	0.22

Solvent: 0.1 M Bu_4NPF_6 in CH_2Cl_2.

Table 3. Absorption peaks from spectroelectrochemistry

Compound	Neutral λ_{max} (nm)	Radical cation[a] λ_{max} (nm)		Dication[a] λ_{max} (nm)
24	331	453	825	703
25	331	452	820	701
26	332	453	824	698
27	332	453	826	697
30	331	448	811	704
31	331	455	842	707
33	333	441	802	701
34	333	450	821	704
35	336	449	802	695
36	337	450	798	696

Solvent: 0.1 M Bu_4NPF_6 in CH_2Cl_2.

[a] Oxidation state of each individual TTF unit in the molecule.

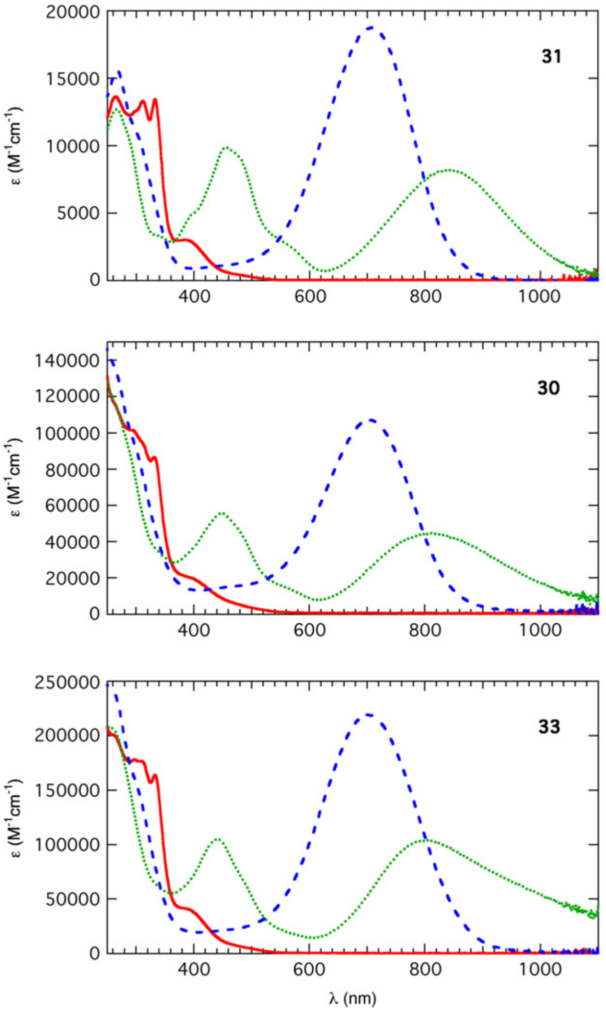
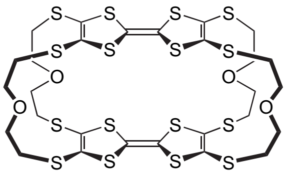


Figure 3. Spectroelectrochemistry of $(TTF)_n$ compounds **31** (n=1), **30** (n=6) and **33** (n=12) in CH_2Cl_2 (0.1 M Bu_4NPF_6). Red solid curves: neutral $(TTF)_n$; green dotted curves: singly oxidized TTF units $[(TTF)_n^{n(\bullet+)}]$; blue dashed curves: doubly oxidized TTF units $[(TTF)_n^{n(2+)}]$.

Again, compounds **35** and **36** with doubly linked TTFs are somewhat different from the other compounds, as the peak in the neutral state is slightly red-shifted (≈450 cm^{-1}) relative to the reference compound **31** while a blue-shift is observed in the oxidized states: ≈620 cm^{-1} and ≈240 cm^{-1} for the low and high energy bands, respectively, for the radical cation and ≈240 cm^{-1} for the dication. Of the mono-linked TTF derivatives, the 12-TTF macromolecule **33** shows the largest blue-shift of the radical cation bands, by ≈590 and ≈700 cm^{-1} relative to that of **31**$^{\bullet+}$, and to some extent the 6-TTF **30** follows this trend (blue-shifts of ≈450 and ≈340 cm^{-1}). A measurable blue-shift is also found for the dication absorption. In general, however, the dication absorptions are much less influenced by the number of TTF units and the substitution patterns. The data indicate increased electrostatic interactions between TTF radical cations when proceeding along a progression where the number of TTF units protruding from the central core is increased (Fig. 4). This observation might be explained by a larger destabilization of the excited state relative to the ground state on account of different charge distributions (the low energy absorption is likely a HDOMO–SOMO transition[18]). For comparison, Bryce and co-workers[5d] investigated a $(TTF)_{21}$-glycol dendrimer and observed absorptions at 425 and 800 nm for the 21-TTF radical cations in the molecule. Thus, the mere addition of further TTF units does not induce a substantial blue-shift in the lowest-energy absorption as the many TTF units are not constrained in a small volume of space. It should be emphasized that the substitution pattern is obviously of importance too, as compounds **35** and **36**, containing only one and two TTFs, respectively, show radical cation absorptions also around 800 nm. A significant blue-shift can be observed by simply forcing two TTF units close together in a rigid structure. The bis-TTF *belt*-type molecule **44** linked by four glycol linkers (identical to those in **33**) presents an example of such a compound that was investigated previously.[19] It exhibits a lowest-energy absorption at 660 nm for the radical cation absorptions. This blue-shifted value is most likely a result of the enhanced electrostatic interactions enforced by the rigid structure as compared to the more flexible dendritic structures.



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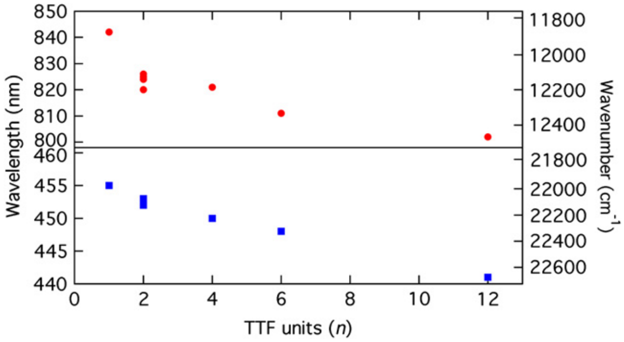

Figure 4. Plot of the radical cation absorption (top, low energy band (●), bottom, high energy band (■)) as a function of the number n of TTF units (data for compounds **24**–**27**, **30**, **31**, **33** and **34**). The oxidized species correspond to $(TTF)_n^{n(\bullet+)}$.

2.3. Chemical oxidation

By chemical oxidation, we find that the TTF units of compound **33** can be oxidized sequentially. Thus, treatment of

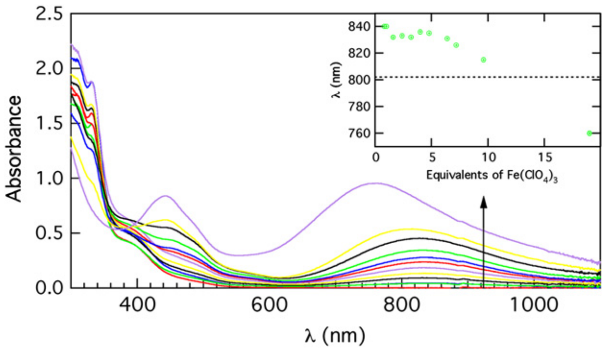

Figure 5. Chemical oxidation of compound **33** (1×10^{-5} M in solvent mixture CH_2Cl_2–CH_3CN 4:1) with $Fe(ClO_4)_3$. The arrow indicates increasing number of $Fe(ClO_4)_3$ equivalents (0, 0.8, 1.0, 1.6, 2.4, 3.2, 4.0, 4.8, 6.4, 7.2, 9.6, 19). Inset shows the lowest-energy absorption maximum of the radical cationic species. The dotted line is the value obtained by spectroelectrochemistry for all 12 TTF units oxidized.

a dilute solution (10^{-5} M) of **33** with increasing number of equivalents of $Fe(ClO_4)_3$ leads to a gradual increase of the absorptions assigned to TTF radical cations and a concomitant decrease of those assigned to neutral TTF units (Fig. 5). Interestingly, we find that the lowest-energy absorption maximum is almost constant (ca. 835 nm) until addition of 5 equiv of $Fe(ClO_4)_3$, whereafter a blue-shift gradually begins. Thus, the maximum is at ca. 815 nm after adding 10 equiv of $Fe(ClO_4)_3$. This observation is in agreement with an increasing number of electrostatic interactions as the total number of radical cations is increased and hence in agreement with the above observations on a series of oligo-TTFs. From the spectroelectrochemical data, we found that $\mathbf{33}^{12(\bullet+)}$ (i.e., the species where all TTFs exist as radical cations) absorbs at 802 nm. Yet, after adding more equivalents of the chemical oxidant, the observed blue-shift may in part be induced by an overlap between the radical cation absorption band and an emerging absorption band from TTF dications. In fact, spectral resolution into components of neutral, radical cation and dication absorptions, obtained from spectroelectrochemistry, reveals that the addition of 19 equiv of oxidant results in a mixture of neutral, radical cation and dication TTF units in an approximate (±5) ratio of 25:60:15. Sequential monitoring of the oxidation from radical cation to dication is complicated by the broad and overlapping absorption bands of the species. However, adding a large excess of $Fe(ClO_4)_3$ leads to complete oxidation of all TTF radical cations to dications.

3. Conclusions

Efficient syntheses of new triptycene building blocks have been developed. These compounds have been employed in the synthesis of a large selection of triptycene-TTF scaffolds. The largest such scaffold, compound **33**, contains a total of 12 TTF units. Spectroelectrochemical studies reveal that each individual TTF in this compound is oxidized at the same potential. Chemical oxidation, however, can be performed to a certain extent stepwise. Compared to smaller scaffolds containing fewer TTF units, it is shown that electrostatic interactions between TTF radical cations are of importance for the spectroscopic properties of the oxidized species of **33**. However, from a comparison with a 'limiting case', the rigid *belt*-type molecule **44** previously investigated, it can be inferred that the macromolecule still possesses sufficient flexibility to diminish the repulsive Coulomb interactions. This branched molecule as well as the triptycene derivative **43** containing two extended TTF units may in particular be of interest for future host–guest applications.

4. Experimental

4.1. General experimental procedures

Thin-layer chromatography (TLC) was carried out using aluminium sheets pre-coated with silica gel 60F (Merck 5554). Column chromatography was carried out using silica gel 60 (Merck 9385, 0.040–0.063 mm). Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian instrument. Samples were prepared using deuterated solvents ($CDCl_3$, DMSO-d_6, CD_2Cl_2) purchased from Cambridge Isotope Labs. Fast atom bombardment (FAB) spectra were obtained on a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode using 3-nitrobenzyl alcohol (NBA) as matrix. EIMS spectra were recorded on a ZAB-EQ (VG-Analytical) instrument. Microanalyses were performed at the Microanalytical Laboratory in the Department of Chemistry, University of Copenhagen. UV/vis spectra were recorded on a Cary 50 (Varian Inc.) with pure solvent as baseline. Cyclic voltammetry and differential pulse voltammetry were measured using a CHI630B potentiostat (CH Instruments, TX) equipped with a glassy carbon working electrode and a Pt wire counter electrode. All potentials are expressed relative to that of Fc^+/Fc (0.31 V vs SCE[20]) and were measured in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte; scan rate 0.1 V s^{-1}. The same instrument was used for the spectroelectrochemical experiments in a 1-mm absorption cuvette (Quartz, Starna), except that the counter electrode was separated from the solution by a glass frit, and the working electrode exchanged for a Pt grid (mesh 400). Setting the potential at ca. 0.1 V more oxidative value than the peak potentials found from cyclic voltammetry, the UV/vis spectra of the neutral and cationic species were recorded on a Cary 50 (Varian Inc.).

Synthesis of 1,4,5,8-tetramethyltriptycene, triptycene-1,4,5,8-tetracarboxylic acid, triptycene-2,3,6,7-tetracarboxylic acid and triptycene-2,3,6,7,14,15-hexacarboxylic acid was as previously described.[21] For alternative syntheses of dialkyl triptycene-2,3-dicarboxylates (alkyl=methyl), see Ref. 22.

4.2. Compound 5

This compound was prepared by a $KMnO_4$ oxidation[11] of 2,3-dimethyltriptycene.[23] To a refluxing solution of 2,3-dimethyltriptycene (100 mg, 0.35 mmol) in a mixture of pyridine (5 mL) and water (3 mL) was added $KMnO_4$ (1.01 g, 6.37 mol) portionwise over 24 h. After cooling to rt, the precipitated MnO_2 was filtered off and washed with 1% aq solution of KOH (15 mL). The filtrate was evaporated on a rotatory evaporator to approximately one third of its original volume and then acidified to pH 1 with 3 M HCl. The precipitated product was collected by filtration and dried under vacuum at 60 °C. Analytical sample was further recrystallized from acetone–water and dried in vacuo to yield a white powder. Yield: 105 mg (87%); mp 313–314 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ=5.82 (s, 2H, H-9,10), 7.03 (m, 4H, H-6,7,14,15), 7.47 (m, 4H, H-5,8,13,16), 7.75 (s, 2H, H-1,4), 13.03 (br s, 2H, CO_2H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ=52.26 (CH-9,10), 123.72 (CH-1,4), 124.15 (CH-5,8,13,16), 125.54 (C-6,7,14,15), 130.22 (C-2,3), 144.59 (C-8a,10a,11,12), 148.28 (C-4a,9a), 168.62 (C=O). MS (EI): *m*/*z* (%)=324 (79) [M^+-H_2O], 280 (15), 252 (100). Anal. Calcd for $C_{22}H_{14}O_4\cdot 1/2H_2O$: C, 75.21; H, 4.30. Found: C, 75.52; H, 4.03.

4.3. Triptycene-1,4-dicarboxylic acid

This compound was prepared as described for **5** using 1,4-dimethyltriptycene[24] (500 mg, 1.77 mmol) and $KMnO_4$ (5.04 g, 31.87 mmol) as the starting materials. Yield: 540 mg (89%); mp 348–350 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ=6.76 (s, 2H, H-9,10), 7.03 (m, 4H, H-6,7,14,15), 7.45 (m, 4H, H-5,8,13,16), 7.56 (s, 2H, H-2,3), 13.41 (br s, 2H, CO_2H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ=49.48 (CH-9,10), 124.38 (CH-5,8,13,16), 125.70 (CH-6,7,14,15), 126.06 (CH-2,3), 129.87 (C-1,4), 144.75 (C-8a,10a,11,12), 147.74 (C-4a,9a), 167.91 (C=O). MS (EI): *m*/*z* (%)=342 (100) [M^+], 324 (21), 296 (51), 279 (38), 252 (62). Anal. Calcd for $C_{22}H_{14}O_4\cdot 1/4CH_3C(O)CH_3$: C, 76.57; H, 4.38. Found: C, 76.68; H, 4.17.

4.4. Compound 6

A mixture of triptycene-2,3-dicarboxylic acid **5** (1.63 g, 4.76 mmol) and concd H_2SO_4 (7 mL) in ethanol (50 mL) was refluxed for 7 days. After cooling to rt, the reaction mixture was concentrated and water (50 mL) was added. It was extracted with dichloromethane (3×50 mL), the organic phase was washed with brine (50 mL), dried over $MgSO_4$ and evaporated to dryness. An analytical sample was further recrystallized from toluene–heptane to give **6** as white crystals. Yield: 1.55 g (82%); mp 154–155 °C. R_f=0.20 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.32 (t, 6H, *J*=7.2), 4.31 (q, 4H, *J*=7.2), 5.49 (s, 2H), 7.02 (m, 4H), 7.39 (m, 4H), 7.72 (d, 2H, *J*=1.2). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.24, 53.94, 61.64, 124.06, 124.07, 125.75, 129.63, 144.10, 148.69, 167.69. MS (FAB): *m*/*z*=399 (91) [$M+H^+$], 353 (100), 325 (74). Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.14; H, 5.41.

4.5. Compound 7

A suspension of $LiAlH_4$ (170 mg, 4.4 mmol) in dry THF (20 mL) was stirred under argon at rt. A solution of diethyl triptycene-2,3-dicarboxylate **6** (440 mg, 1.1 mmol) in dry THF (5 mL) was added and the reaction mixture was stirred for 3 h. Then ethyl acetate (30 mL) was added and the mixture was extracted with water (100 mL). The water phase was extracted with ethyl acetate (3×50 mL). Combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4 and evaporated in vacuo. The product was obtained as a white foam. An analytical sample was further recrystallized from dichloromethane–hexane to give **7** as white needles. Yield: 345 mg (99%); mp 224–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.58 (br s, 2H), 4.63 (s, 4H), 5.44 (s, 2H), 6.98 (m, 4H), 7.27–7.39 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=53.83, 64.11, 123.78, 125.36, 125.41, 136.46, 145.03, 145.89. HRMS (FAB): *m*/*z*= 314.1312 [M^+]; calcd for $C_{22}H_{18}O_2$: 314.1307.

4.6. Compound 8

A solution of 2,3-bis(hydroxymethyl)triptycene **7** (200 mg, 0.32 mmol) in glacial acetic acid (10 mL) was stirred at rt. A solution of HBr in acetic acid (30%, 8 mL) was added and the reaction mixture was stirred overnight. After removal of the solvent in vacuo, the crude product was redissolved in dichloromethane and passed through a pad of silica gel. Evaporation to dryness afforded the product as a yellowish powder. Yield: 279 mg (100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.58 (s, 4H), 5.42 (s, 2H), 7.01 (m, 4H), 7.37–7.40 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.37, 53.70, 123.94, 125.60, 126.40, 133.49, 144.60, 146.78.

4.7. Compound 9

A solution of oxalyl chloride (61 μL, 0.70 mmol) in dry dichloromethane (0.8 mL) was stirred under argon at −60 °C. A solution of DMSO (99 μL, 1.40 mmol) in dry dichloromethane (0.2 mL) was added dropwise and the reaction mixture was stirred for 30 min. Then a solution of 2,3-bis(hydroxymethyl)triptycene **7** (100 mg, 0.32 mmol) in dichloromethane–DMSO (0.5 mL to 20 μL) was added and stirring was continued for 30 min. After addition of another portion of DMSO (1 mL), in order to dissolve the precipitate, the reaction mixture was further stirred for 1 h. Then triethylamine (0.79 mL, 5.65 mmol) was added, the reaction mixture was stirred at −60 °C for 20 min, and then allowed to warm to rt for 2 h. Ice-cold water (20 mL) was added and then the mixture was extracted with dichloromethane (3×20 mL), the organic phase was dried over $MgSO_4$ and evaporated to dryness. Column chromatography on a silica gel column in EtOAc–heptane (1:2, R_f=0.27) afforded the product as a white powder. Yield: 79 mg (80%); mp 252–253 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.62 (s, 2H), 7.06 (m, 4H), 7.44 (m, 4H), 7.97 (s, 2H), 10.47 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=54.14, 124.27, 125.69, 126.08, 134.55, 143.54, 151.66, 191.78. HRMS (FAB): *m*/*z*= 310.0994 [M^+]; calcd for $C_{22}H_{14}O_2$: 310.0994.

4.8. Compound 10

A mixture of triptycene-2,3,6,7-tetracarboxylic acid (1.19 g, 2.8 mmol) and concd H_2SO_4 (7 mL) in dry ethanol (50 mL) was refluxed for 8 days. After cooling to rt, the reaction mixture was concentrated and water (40 mL) was added. The mixture was extracted with dichloromethane (3×40 mL), the organic phase was washed with brine (40 mL), dried over $MgSO_4$ and evaporated to dryness. Chromatography on a silica gel column in EtOAc–cyclohexane (1:3 → 1:1, R_f=0.45) afforded the product as a white powder. An analytical sample was further recrystallized from toluene–heptane to give **10** as white crystals. Yield: 700 mg (47%); mp 160–161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.33 (t, 12H, *J*=7.2), 4.32 (q, 8H, *J*=7.2), 5.58 (s, 2H), 7.03 (m, 2H), 7.39 (m, 2H), 7.74 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$):

δ=14.20, 53.56, 61.71, 124.32, 124.37, 126.19, 130.09, 142.84, 147.31, 167.37. MS (FAB): *m/z*=543 [M+H$^+$]. Anal. Calcd for $C_{32}H_{30}O_8$: C, 70.83; H, 5.57. Found: C, 70.89; H, 5.45.

4.9. Compound 11

A mixture of triptycene-2,3,6,7,14,15-hexacarboxylic acid (0.93 g, 1.8 mmol) and concd H_2SO_4 (5 mL) in dry ethanol (50 mL) was refluxed for 6 days. After cooling to rt, the reaction mixture was concentrated and water (50 mL) was added. The mixture was extracted with dichloromethane (3×50 mL), the organic phase was washed with brine (50 mL), dried over $MgSO_4$ and evaporated to dryness. Chromatography on a silica gel column in EtOAc–heptane (1:1, R_f=0.31) afforded the product as a white solid. Yield: 215 mg (17%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.33 (t, 18H, *J*=7.2), 4.32 (q, 12H, *J*=7.2), 5.66 (s, 2H), 7.76 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.21, 53.24, 61.86, 124.71, 130.59, 146.06, 167.11. HRMS (FAB): *m/z*=686.2348 [M$^+$]; calcd for $C_{38}H_{38}O_{12}$: 686.2363.

4.10. Compound 12

A suspension of $LiAlH_4$ (337 mg, 8.88 mmol) in dry THF (20 mL) was stirred under argon at rt. A solution of tetraethyl triptycene-2,3,6,7-tetracarboxylate **10** (600 mg, 1.11 mmol) in dry THF (5 mL) was added and the reaction mixture was stirred for 20 h. Then ethyl acetate (50 mL) was carefully added and the mixture was extracted with water (75 mL). The water phase was extracted with ethyl acetate (3×50 mL). The combined organic extracts were washed with brine (75 mL), dried over $MgSO_4$ and evaporated in vacuo. The product was obtained as a white powder. Yield: 400 mg (97%); mp 278–280 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=4.42 (d, 8H, *J*=5.4), 4.92 (t, 4H, *J*=5.4), 5.61 (s, 2H), 6.97 (m, 2H), 7.42 (m, 2H), 7.44 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=52.24, 60.27, 122.62, 123.34, 124.68, 135.91, 143.86, 145.61. HRMS (FAB): *m/z*=374.1529 [M$^+$]; calcd for $C_{24}H_{22}O_4$: 374.1518.

4.11. Compound 14

A solution of 2,3,6,7-tetrakis(hydroxymethyl)triptycene **12** (100 mg, 0.27 mmol) in glacial acetic acid (5 mL) was stirred at rt. A solution of HBr in acetic acid (30%, 7 mL) was added and the reaction mixture was stirred overnight. After removal of the solvent in vacuo, the crude product was redissolved in dichloromethane and passed through a pad of silica gel (R_f=0.73 (CH_2Cl_2)). Evaporation to dryness afforded the product as a yellowish powder. Yield: 165 mg (99%); mp 264–266 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.58 (s, 8H), 5.41 (s, 2H), 7.05 (m, 2H), 7.35–7.43 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.09, 53.24, 124.13, 125.94, 126.54, 133.88, 143.87, 145.98. MS (FAB): *m/z*=545, 547 [M$^+$−Br].

4.12. Compound 15

A suspension of $LiAlH_4$ (100 mg, 2.61 mmol) in dry THF (15 mL) was stirred under argon at rt. A solution of hexaethyl triptycene-2,3,6,7,14,15-hexacarboxylate **11** (200 mg, 0.29 mmol) in dry THF (5 mL) was added and the reaction mixture was stirred overnight. The reaction was quenched with ethyl acetate and water, and the solvents were evaporated in vacuo. A solution of HBr in acetic acid (30%, 20 mL) was added to the crude alcohol **13** and the suspension was stirred for 48 h. After removal of the solvent in vacuo, the crude product was suspended in dichloromethane and passed through a pad of silica gel. Chromatography on a silica gel column in dichloromethane–cyclohexane (1:1, R_f=0.41) afforded the desired product as a yellowish powder. Yield: 60 mg (26%); mp >320 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.57 (s, 12H), 5.39 (s, 2H), 7.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.85, 52.76, 126.69, 134.27, 145.20.

4.13. Compound 16

A mixture of triptycene-1,4-dicarboxylic acid (490 mg, 1.43 mmol) and concd H_2SO_4 (3 mL) in dry ethanol (20 mL) was refluxed for 5 days. After cooling to rt, the reaction mixture was concentrated and water (40 mL) was added. The mixture was extracted with dichloromethane (3×40 mL), the combined organic phases were washed with brine (40 mL), dried over $MgSO_4$ and evaporated to dryness. An analytical sample was further recrystallized from toluene–heptane to give **16** as white crystals. Yield: 450 mg (79%); mp 202–203 °C. R_f=0.46 (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.48 (t, 6H, *J*=6.9), 4.48 (q, 4H, *J*=6.9), 6.82 (s, 2H), 7.03 (m, 4H), 7.46 (m, 4H), 7.59 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.37, 49.92, 61.34, 124.28, 125.57, 125.98, 129.01, 144.67, 148.72, 166.65. MS (FAB): *m/z*=399 [M+H$^+$]. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.33; H, 5.58.

4.14. Compound 17

A suspension of $LiAlH_4$ (152 mg, 4.0 mmol) in dry THF (20 mL) was stirred under argon at rt. A solution of diethyl triptycene-1,4-dicarboxylate **16** (400 mg, 1.0 mmol) in dry THF (10 mL) was added and the reaction mixture was stirred overnight. Then ethyl acetate (30 mL) was added and the mixture was extracted with water (100 mL). The water phase was extracted with ethyl acetate (3×50 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$ and evaporated in vacuo. An analytical sample was further recrystallized from dichloromethane–heptane to give **17** as a white powder. Yield: 315 mg (100%); mp 267–269 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=4.73 (d, 4H, *J*=5.4), 5.16 (t, 2H, *J*=5.7), 5.92 (s, 2H), 6.94 (s, 2H), 6.98 (m, 4H), 7.44 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=48.74, 60.79, 123.66, 124.74, 135.15, 143.33, 145.43 (2C). HRMS (FAB): *m/z*=314.1310 [M$^+$]; calcd for $C_{22}H_{18}O_2$: 314.1307.

4.15. Tetramethyl triptycene-1,4,5,8-tetracarboxylate

To a stirred suspension of triptycene-1,4,5,8-tetracarboxylic acid (432 mg, 1.00 mmol) in dichloromethane (40 mL) was added diazomethane (30 mL, 0.75 M solution in diethyl ether) in 5 mL portions over 1 h at 0 °C. The resulting mixture was stirred at 0 °C for 3 h and then for 12 h at rt. After evaporation of the solvents, the residue was resuspended in chloroform and filtered. Chloroform was removed in vacuo and the crude product was crystallized from toluene–hexane to give white crystals. Yield: 444 mg (91%); mp 302–303 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ=4.04 (s, 12H, CH_3O), 7.08 (m, 2H, H-14,15), 7.56 (m, 2H, H-13,16), 7.60 (s, 4H, H-2,3,6,7), 7.92 (s, 2H, H-9,10). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=46.29 (CH-9,10), 52.38 (CH_3O), 124.93 (CH-13,16), 126.06 (C-14,15), 126.46 (CH-2,3,6,7), 129.72 (C-1,4,5,8), 143.96 (C-11,12), 147.64 (C-4a,8a,9a,10a), 166.90 (CO). MS (EI): *m/z* (%)=486 (100) [M]$^+$. Anal. Calcd for $C_{28}H_{22}O_8$: C, 69.13; H, 4.56. Found: C, 68.92; H, 4.54.

4.16. Compound 18

A suspension of $LiAlH_4$ (100 mg, 2.64 mmol) in dry THF (15 mL) was stirred under argon at rt. A suspension of tetramethyl triptycene-1,4,5,8-tetracarboxylate (160 mg, 0.33 mmol) in dry THF (10 mL) was added and the reaction mixture was stirred for 22 h at rt and then refluxed for 3 h. After cooling, ethyl acetate (50 mL) was carefully added and the mixture was extracted with water (50 mL). The water phase was extracted with ethyl acetate (3×50 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The product was obtained as a white powder. Yield: 120 mg (98%); mp 255–257 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=4.76 (m, 8H), 5.17 (t, 4H, *J*=5.4), 6.21 (s, 2H), 6.93 (s, 4H), 6.96 (m, 2H), 7.45 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=44.97, 60.92, 123.70 (2C), 124.60, 135.21, 143.51, 145.57. MS (EI): *m/z* (%)=374 (78) [M$^+$]. HRMS (FAB): *m/z*=374.1501 [M$^+$]; calcd for $C_{24}H_{22}O_4$: 374.1518.

4.17. Compound 19

To a suspension of PCC (720 mg, 3.34 mmol) in dichloromethane (12 mL) was added a suspension of 1,4-bis-(hydroxymethyl)triptycene **17** (300 mg, 0.95 mmol) in dichloromethane (9 mL) and the reaction mixture was stirred for 3.5 h. It was filtered through a pad of silica gel and evaporated to dryness to give **18** as a white solid. Yield: 230 mg (78%); mp >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 6.92 (s, 2H), 7.06 (m, 4H), 7.55 (m, 4H), 7.67 (s, 2H), 10.64 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=46.59, 124.41, 125.65, 125.90, 133.19, 144.01, 149.21, 192.72. HRMS (FAB): *m/z*=310.0998 [M$^+$]; calcd for $C_{22}H_{14}O_2$: 310.0994.

4.18. Compound 20

To a suspension of PCC (262 mg, 1.21 mmol) in dichloromethane (5 mL) was added a suspension of 1,4,5,8-tetrakis(hydroxymethyl)triptycene **18** (60 mg, 0.16 mmol) in dichloromethane (5 mL) and the reaction mixture was stirred for 5.5 h. It was filtered through a pad of silica gel and then chromatographed on a silica gel column in dichloromethane (R_f=0.06) to give **20** as a white solid after evaporation to dryness. Yield: 16 mg (27%); mp >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=7.12 (m, 2H), 7.69 (m, 2H), 7.72 (s, 4H), 7.99 (s, 2H), 10.67 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=41.03, 125.22, 125.97, 126.23, 133.83, 142.88, 147.80, 192.08. HRMS (FAB): *m/z*= 367.0948 [M+H$^+$]; calcd for $C_{24}H_{15}O_4$: 367.0970.

4.19. Compound 22

To a solution of 1,4,5,8-tetramethyltriptycene (245 mg, 0.78 mmol) in carbon tetrachloride (30 mL) was added *N*-bromosuccinimide (550 mg, 3.12 mmol) and the resulting mixture was irradiated with 500 W lamp and refluxed for 2 h. After filtration, dichloromethane (50 mL) was added and the organic phase was extracted with cold NaOH solution (5%, 3×20 mL), washed with brine and dried ($MgSO_4$). Purification of the product was achieved by column chromatography on silica gel using 5% ethyl acetate in cyclohexane as eluent (R_f=0.19). Yield: 205 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.70 (d, 4H, *J*=10.5), 4.98 (d, 4H, *J*=10.5), 6.23 (s, 2H), 7.00 (s, 4H), 7.05 (m, 2H), 7.56 (m, 2H).

4.20. Compound 24

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (224 mg, 0.41 mmol) was dissolved in dry DMF (20 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (69 mg, 0.42 mmol) in dry methanol (3 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid 2,3-bis(bromomethyl)triptycene **8** (90 mg, 0.20 mmol) was added and stirring was further continued for 2 h. The mixture was evaporated to dryness and chromatographed on a silica gel column using EtOAc–heptane (1:4, R_f=0.16) as eluent. The product was obtained as an orange oil. Yield: 170 mg (65%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.85 (m, 12H), 1.39 (m, 8H), 1.56 (m, 8H), 2.23 (t, 4H, *J*=6.6), 2.89 (m, 12H), 4.19 (s, 4H), 5.46 (s, 2H), 7.01 (m, 4H), 7.34 (s, 2H), 7.41 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=13.34, 13.43, 17.55, 20.87, 20.93, 30.80, 31.31, 31.34, 35.14, 35.19, 37.00, 52.40, 108.69, 111.67, 118.45, 123.68, 125.14, 125.85, 126.73, 127.35, 128.34, 128.89, 131.50, 144.64, 144.99. MS (FAB): *m/z*=1272 [M$^+$]. Anal. Calcd for $C_{56}H_{60}N_2S_{16}$: C, 52.79; H, 4.75; N, 2.20. Found: C, 53.14; H, 4.54; N, 2.01. UV/vis (toluene): λ_{max} (ε)=294 (26,100), 310 (25,800), 332 (25,500), 390 nm (5500, shoulder).

4.21. Compound 25

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (410 mg, 0.75 mmol) was dissolved in dry DMF (30 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (134 mg, 0.80 mmol) in dry methanol (5 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid 1,4-bis(bromomethyl)triptycene **21** (165 mg, 0.38 mmol) was added and stirring was continued for 3 h. The mixture was evaporated to dryness and chromatographed on a silica gel column using EtOAc–cyclohexane (1:9) as eluent. The product was obtained as a red oil. An analytical sample was further purified by precipitation from EtOAc–heptane mixture. Yield: 185 mg (39%); mp 126–127 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.80 (t, 6H, *J*=7.2), 0.87 (t, 6H, *J*=7.2), 1.37 (m, 8H), 1.53 (m, 8H), 2.02 (t, 4H, *J*=7.2), 2.53 (t, 4H, *J*=7.2), 2.86 (t, 8H, *J*=7.1), 4.40 (s, 4H), 6.04 (s, 2H), 6.86 (s, 2H), 6.99 (m, 4H), 7.52 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=13.31, 13.38, 17.08, 20.89 (2C), 30.59, 31.29 (2C), 35.12 (2C), 37.05, 48.90, 109.58, 110.36, 118.35, 124.01, 124.90, 126.07, 126.92, 127.19, 127.49, 129.80, 130.80, 144.69, 144.96. MS (FAB): *m/z*=1272 [M$^+$]. Anal. Calcd for $C_{56}H_{60}N_2S_{16}$: C, 52.79; H, 4.75; N, 2.20. Found: C, 53.00; H, 4.45; N, 2.11. UV/vis (toluene): λ_{max} (ε)=297 (27,500), 310 (28,000), 331 (27,000), 392 nm (5300).

4.22. Compound 26

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (275 mg, 0.50 mmol) was dissolved in dry DMF (20 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (85 mg, 0.51 mmol) in dry methanol (3 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid α,α'-dibromo-*o*-xylene (66 mg, 0.25 mmol) was added and stirring was further continued overnight. The mixture was evaporated to dryness and chromatographed on a silica gel column using EtOAc–heptane (1:4, R_f=0.13) as eluent. The product was obtained as a red oil. An analytical sample was further purified by precipitation from dichloromethane–methanol mixture to give orange crystals. Yield: 190 mg (69%); mp 75–77 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.88 (t, 12H, J=6.9), 1.39 (m, 8H), 1.54 (m, 8H), 2.66 (t, 4H, J=6.9), 2.86 (m, 8H), 2.98 (t, 4H, J=6.9), 4.30 (s, 4H), 7.27 (m, 2H), 7.32 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=13.39, 13.41, 17.96, 20.87, 20.93, 30.93, 31.25, 31.30, 35.10, 35.20, 37.16, 108.80, 110.74, 118.58, 126.94, 127.17, 127.42, 128.12, 129.25, 130.73, 134.88. MS (FAB): m/z=1096 [M$^+$]. Anal. Calcd for $C_{42}H_{52}N_2S_{16}$: C, 45.95; H, 4.77; N, 2.55. Found: C, 46.18; H, 4.73; N, 2.47. UV/vis (toluene): λ_{max} (ε)=310 (29,300), 332 (28,500), 390 nm (5900).

4.23. Compound 27

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (547 mg, 1.00 mmol) was dissolved in dry DMF (40 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (170 mg, 1.05 mmol) in dry methanol (5 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid α,α'-dibromo-*p*-xylene (132 mg, 0.50 mmol) was added and stirring was continued for 1 h. The orange precipitate was filtered off, washed with methanol and dried under vacuum. Recrystallization from toluene–hexane afforded orange crystals. Yield: 525 mg (96%); mp 145–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.94 (m, 12H), 1.45 (m, 8H), 1.63 (m, 8H), 2.36 (t, 4H, J=7.6), 2.83 (m, 12H), 4.04 (s, 4H), 7.29 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.78, 18.39, 21.80, 31.36, 31.90, 36.13, 40.42, 107.75, 113.18, 117.77, 126.25, 127.82, 128.05, 129.63, 132.05, 136.63. MS (FAB): m/z= 1096 [M$^+$]. Anal. Calcd for $C_{56}H_{60}N_2S_{16}$: C, 45.95; H, 4.77; N, 2.55. Found: C, 45.44; H, 4.54; N, 2.47. UV/vis (toluene): λ_{max} (ε)=311 (29,000), 332 (28,200), 391 nm (5900).

4.24. Compound 28

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (490 mg, 0.90 mmol) was dissolved in dry DMF (40 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (151 mg, 0.90 mmol) in dry methanol (5 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid 1,4,5,8-tetrakis(bromomethyl)triptycene **22** (140 mg, 0.22 mmol) was added and stirring was continued overnight. The mixture was evaporated to dryness and chromatographed on a silica gel column using EtOAc–heptane (1:3, R_f=0.17) as eluent. The product was obtained as a red oil. An analytical sample was further purified by precipitation from EtOAc–heptane mixture. Yield: 120 mg (23%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.86 (m, 24H), 1.38 (m, 16H), 1.54 (m, 16H), 2.31 (t, 8H, J=6.9), 2.67 (t, 8H, J=6.9), 2.86 (t, 16H, J=6.9), 4.47 (d, 4H, J=12.9), 4.62 (d, 4H, J=12.9), 6.29 (s, 2H), 6.96 (s, 4H), 7.02 (m, 2H), 7.58 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=13.39 (2C), 17.56, 20.88, 20.95, 30.76, 31.28 (2C), 35.09, 35.21, 37.39, 54.87, 108.99, 110.45, 118.40, 126.66, 126.84, 126.95, 127.27, 129.68, 130.69, 144.10 (2C). MS (FAB): m/z=2293 [M$^+$]. Anal. Calcd for $C_{92}H_{106}N_4S_{32}$: C, 48.17; H, 4.66; N, 2.44. Found: C, 48.25; H, 4.48; N, 2.29. UV/vis (toluene): λ_{max} (ε)=297 (56,100, shoulder), 310 (56,900), 332 (53,300), 392 nm (10,900).

4.25. Compound 29

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (350 mg, 0.64 mmol) was dissolved in dry DMF (30 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (110 mg, 0.64 mmol) in dry methanol (5 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid 2,3,6,7-tetrakis(bromomethyl)triptycene **14** (100 mg, 0.16 mmol) was added and stirring was continued overnight. The mixture was evaporated to dryness and chromatographed on a silica gel column using EtOAc–heptane (1:3) as eluent. The product was obtained as a red oil. An analytical sample was further purified by precipitation from EtOAc–heptane mixture. Yield: 207 mg (56%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.86 (m, 24H), 1.39 (m, 16H), 1.57 (m, 16H), 2.37 (t, 8H, J=6.6), 2.64 (m, 8H), 2.88 (m, 16H), 4.20 (s, 8H), 5.37 (s, 2H), 7.03 (m, 2H), 7.33 (s, 4H), 7.39 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ=13.38, 13.44, 17.74, 20.90, 20.96, 30.84, 31.29, 31.35, 35.17 (2C), 37.15, 54.87, 108.66, 111.35, 118.45, 126.00, 126.76, 127.35, 128.08, 128.78, 131.66, 144.09, 144.54. MS (FAB): m/z=2293 [M$^+$]. Anal. Calcd for $C_{92}H_{106}N_4S_{32}$: C, 48.17; H, 4.66; N, 2.44. Found: C, 48.35; H, 4.52; N, 2.34. UV/vis (toluene): λ_{max} (ε)=297 (60,300), 309 (59,700), 332 (56,500), 390 nm (12,100, shoulder).

4.26. Compound 30

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (102 mg, 0.185 mmol) was dissolved in dry DMF (10 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (31 mg, 0.185 mmol) in dry methanol (2 mL) was added via syringe over 0.5 h. The reaction mixture was stirred for another 0.5 h, then solid 2,3,6,7,14,15-hexakis(bromomethyl)triptycene **15** (25 mg, 0.031 mmol) was added and stirring was continued overnight. The mixture was evaporated to dryness and passed through a pad of silica gel using dichloromethane as eluent (R_f=0.11). The product obtained after evaporation of the solvent as a red oil was further purified by precipitation from EtOAc–heptane mixture. Yield: 89 mg (87%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.87 (m, 36H), 1.39 (m, 24H), 1.56 (m, 24H), 2.46 (t, 12H, J=6.9), 2.74 (t, 12H, J=6.9), 2.88 (m, 24H), 4.20 (s, 12H), 5.30 (s, 2H), 7.32 (s, 6H). ^{13}C NMR: not stable enough in solution. MS (FAB): m/z=3314 [M+H$^+$]. Anal. Calcd for $C_{128}H_{152}N_6S_{48}$: C, 46.39; H, 4.62; N, 2.54. Found: C, 46.70; H, 4.63; N, 2.33. UV/vis (toluene): λ_{max} (ε)=298 (97,000), 308 (95,000, shoulder), 331 (86,300), 386 nm (19,500, shoulder).

4.27. Compound 31

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (1.50 g, 2.72 mmol) was dissolved in dry DMF (120 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (479 mg, 2.85 mmol) in dry methanol (15 mL) was added via syringe over 30 min. The reaction mixture was stirred for further 30 min, and then neat 1-bromobutane (745 mg, 5.44 mmol) was added and stirring was continued for 3 h. The resulting solution was evaporated to dryness and the residue was subjected to column chromatography on silica gel (10% ethyl acetate in heptane) yielding orange oil, which solidified upon standing. Yield: 1.37 g (91%); mp 49–51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (m, 9H), 1.44 (m, 6H), 1.63 (m, 6H), 2.70 (t, 2H, J=7.5), 2.83 (m, 6H), 3.03 (t, 2H, J=7.5). ^{13}C NMR (300 MHz, $CDCl_3$): δ=13.54, 13.58, 13.59, 18.71, 21.64 (3C), 31.26, 31.75 (2C), 31.79, 36.00 (2C), 36.05, 108.28, 112.40, 117.54, 121.86, 127.64, 127.96, 133.75. MS (FAB): m/z=553 [M$^+$]. Anal. Calcd for $C_{21}H_{31}NS_8$: C, 45.53; H, 5.64; N, 2.53. Found: C, 45.76; H, 5.54; N, 2.46.

4.28. Compound 32

2,3,6-Tris(butylthio)-7-(2-cyanoethylthio)tetrathiafulvalene **31** (750 mg, 1.35 mmol) was dissolved in dry DMF (30 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (249 mg, 1.49 mmol) in dry methanol (4 mL) was added via syringe over 10 min. The reaction mixture was stirred for further 30 min, and then a large excess of di(2-iodoethyl) ether (4.4 g, 13.5 mmol) was added and stirring was continued for 3 h. The resulting solution was evaporated to dryness and the residue was passed through a pad of silica gel using dichloromethane as eluent. Further purification was achieved by column chromatography on silica gel eluting with gradient starting at 5% and ending at 30% dichloromethane in heptane (R_f=0.06 (30% CH_2Cl_2 in heptane)). Yield: 810 mg (86%). ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.88 (m, 9H), 1.39 (m, 6H), 1.54 (m, 6H), 2.86 (m, 6H), 3.04 (t, 2H, J=6.3), 3.31 (t, 2H, J=6.3), 3.65 (m, 4H). ^{13}C NMR (300 MHz, DMSO-d_6): δ=13.38 (3C), 20.86 (3C), 31.28 (3C), 35.00, 35.11 (2C), 68.78 (2C), 70.70 (2C), 109.56, 109.74, 126.66, 127.01, 127.06, 127.47. MS (FAB): m/z=698 [M$^+$]. Anal. Calcd for $C_{22}H_{35}IOS_8$: C, 37.81; H, 5.05. Found: C, 38.49; H, 5.11.

4.29. Compound 33

TTF derivative **30** (45 mg, 13.6 μmol) was dissolved in dry DMF (5 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (18 mg, 109 μmol) in dry methanol (1 mL) was added via syringe over 10 min, and the reaction mixture was stirred for 1 h at rt. Then neat TTF derivative **32** (115 mg, 163 μmol) was added and stirring was continued overnight. The solvent was removed under reduced pressure and the oily residue was purified by column chromatography on silica gel using ethyl acetate in heptane (10–20%) as eluent (R_f=0.34 (20% EtOAc in heptane)). Yield: 56 mg (64%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ=0.92 (m, 90H), 1.44 (m, 60H), 1.61 (m, 60H), 2.66 (t, 18H, J=6.0), 2.84 (m, 60H), 2.98 (t, 18H, J=6.3), 3.45 (t, 18H, J=6.3), 3.59 (t, 18H, J=6.0), 4.20 (s, 12H), 7.33 (s, 6H). Triptycene bridgehead singlet is probably concealed within solvent residual signal. ^{13}C NMR (75 MHz, CD_2Cl_2): δ=14.00, 14.11, 22.26, 30.26, 32.42, 36.28, 36.65, 70.35, 126.83, 128.47. Remaining signals are not visible or separated. MS (FAB): m/z=6420 [M$^+$]. Anal. Calcd for $C_{242}H_{338}O_6S_{96}$: C, 45.26; H, 5.31. Found: C, 45.80; H, 5.14. UV/vis (toluene): λ_{max} (ε)=290 (175,500, shoulder), 300 (177,800), 323 (160,900), 380 nm (40,500, shoulder).

4.30. Compound 34

TTF derivative **27** (50 mg, 45.5 μmol) was suspended in dry DMF (5 mL) and nitrogen was passed through the suspension for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (16 mg, 95.6 μmol) in dry methanol (1 mL) was added via syringe over 10 min. The reaction mixture was stirred for 1 h at rt, while all the solid material dissolved. Then neat TTF derivative **32** (134 mg, 191 μmol) was added and stirring was continued overnight. The solvent was removed under reduced pressure and the oily residue was purified by column chromatography on silica gel using ethyl acetate in heptane (5–10%) as eluent (R_f=0.13 (10% EtOAc in heptane)). Yield: 82 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93 (m, 30H), 1.43 (m, 20H), 1.62 (m, 20H), 2.83 (m, 24H), 2.98 (t, 4H, J=6.3), 3.56 (t, 4H, J=6.6), 3.63 (t, 4H, J=6.6), 4.01 (s, 4H), 7.27 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.80, 21.83, 31.93, 31.99, 35.62, 36.16, 40.52, 69.92, 69.99, 109.35, 109.72, 111.00, 111.43, 126.07, 127.87, 127.97, 128.03, 129.53, 129.84, 136.31. MS (FAB): m/z=2132 [M$^+$]. UV/vis (toluene): λ_{max} (ε)=301 (63,800), 322 (59,800), 380 nm (14,300, shoulder).

4.31. Compound 35

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (75 mg, 0.14 mmol) was dissolved in dry DMF (20 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (57 mg, 0.34 mmol) in dry methanol (2 mL) was added via syringe over 10 min. The reaction mixture was stirred for 0.5 h, then solid 2,3-bis(bromomethyl)triptycene **8** (60 mg, 0.14 mmol) was added and stirring was further continued for 2 h. It was evaporated to dryness, dissolved in dichloromethane and filtered through a pad of silica gel using dichloromethane as eluent (R_f=0.73). The product was obtained as an orange oil. An analytical sample was further purified by precipitation from dichloromethane–methanol mixture. Yield: 79 mg (81%); mp 213–215 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.91 (t, 6H, J=7.4), 1.42 (m, 4H), 1.59 (m, 4H), 2.78 (t, 4H, J=7.2), 4.13 (s, 4H), 5.38 (s, 2H), 6.97 (m, 4H), 7.20 (s, 2H), 7.35 (m, 4H). ^{13}C NMR: not stable enough in solution. MS (FAB): m/z=722 [M$^+$]. HRMS (FAB): m/z=722.0425 [M$^+$]; calcd for $C_{36}H_{34}S_8$: 722.0426. Anal. Calcd for $C_{36}H_{34}S_8$: C, 59.79; H, 4.74.

Found: C, 59.83; H, 4.58. UV/vis (toluene): λ_{max} (ε)=290 (14,900, shoulder), 338 (13,900), 400 nm (2800, shoulder).

4.32. Compound 36

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (176 mg, 0.32 mmol) was dissolved in dry DMF (50 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (118 mg, 0.70 mmol) in dry methanol (5 mL) was added via syringe over 10 min. The reaction mixture was stirred for 0.5 h, then solid 2,3,6,7-tetra(bromomethyl)triptycene **14** (100 mg, 0.16 mmol) was added and stirring was further continued overnight. The resulting suspension was filtered through a pad of silica gel and washed with methanol until the filtrate was colourless. The solid product was then dissolved and eluted using dichloromethane (R_f=0.76). Dark yellow crystals were obtained upon evaporation and precipitation from a dichloromethane–methanol mixture. Yield: 115 mg (60%); mp 231–232 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.86 (t, 12H, J=7.2), 1.38 (m, 8H), 1.50 (m, 8H), 2.81 (t, 8H, J=7.2), 4.20 (d, 4H, J=12.9), 4.33 (d, 4H, J=12.9), 5.58 (s, 2H), 6.92 (m, 2H), 7.30 (s, 4H), 7.41 (m, 2H). Low *s*/*n* ratio due to poor solubility. ^{13}C NMR: not soluble enough to obtain a spectrum. MS (FAB): *m*/*z*=1190 [M$^+$]. Anal. Calcd for $C_{52}H_{54}S_{16}$: C, 52.39; H, 4.57. Found: C, 52.54; H, 4.56. UV/vis (toluene): λ_{max} (ε)=296 (30,100), 338 (28,100), 400 nm (4400, shoulder).

4.33. Compound 37

2,3-Bis(butylthio)-6,7-bis(2-cyanoethylthio)tetrathiafulvalene **2** (51 mg, 92.4 µmol) was dissolved in dry DMF (10 mL) and nitrogen was passed through the solution for 0.5 h. A degassed solution of $CsOH\cdot H_2O$ (34 mg, 203 µmol) in dry methanol (2 mL) was added via syringe over 10 min. The reaction mixture was stirred for 0.5 h, then solid 2,3,6,7,14,15-hexa(bromomethyl)triptycene **15** (25 mg, 30.8 µmol) was added and stirring was further continued overnight. The resulting suspension was filtered through a pad of silica gel and washed with methanol until the filtrate was colourless. The solid product was then dissolved and eluted using dichloromethane (R_f=0.79). Orange crystals were obtained upon evaporation and precipitation from a dichloromethane–methanol mixture. Yield: 27 mg (53%); mp 219–222 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ=0.86 (t, 18H, J=6.9), 1.37 (m, 12H), 1.50 (m, 12H), 2.79 (m, 12H), 4.22 (s, 12H), 5.56 (s, 2H), 7.28 (s, 6H). Low *s*/*n* ratio due to poor solubility. ^{13}C NMR: not soluble enough to obtain a spectrum. MS (FAB): *m*/*z*=1660 [M$^+$]. Anal. Calcd for $C_{68}H_{74}S_{24}$: C, 49.17; H, 4.49. Found: C, 49.43; H, 4.37. UV/vis (toluene): λ_{max} (ε)=298 (46,300), 337 (40,100), 400 nm (7300, shoulder).

4.34. Compound 38

A solution of the phosphonate **3a** (188 mg, 0.48 mmol) in dry THF (7 mL) was stirred under argon at −78 °C. A solution of butyllithium (1.6 M in hexanes, 0.30 mL, 0.48 mmol) was added dropwise via syringe for 5 min. The reaction mixture was stirred for 15 min and then a solution of triptycene-2,3-dicarboxaldehyde **9** (50 mg, 0.16 mmol) in dry THF (3 mL) was added dropwise for 10 min. The reaction mixture was stirred at −78 °C for 1 h and at rt for 3 h. Evaporation to dryness and column chromatography on basic alumina in dichloromethane–heptane (1:1) afforded the product as an orange oil. Yield: 110 mg (81%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ=0.91 (t, 6H, J=6.9), 0.93 (t, 6H, J=6.9), 1.43 (m, 8H), 1.61 (m, 8H), 2.78 (t, 4H, J=7.2), 2.82 (t, 4H, J=7.2), 5.44 (s, 2H), 6.37 (s, 2H), 7.02 (m, 4H), 7.40 (s, 2H), 7.42 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ=13.94, 13.97, 22.20, 22.25, 32.32, 32.48, 36.28, 36.36, 54.22, 112.76, 122.14, 124.21, 125.19, 125.89, 127.95, 131.85, 134.40, 144.24, 145.53. MS (FAB): *m*/*z*=835 [M+H]$^+$. HRMS (FAB): *m*/*z*=834.1686 [M$^+$]; calcd for $C_{44}H_{50}S_8$: 834.1678. UV/vis (toluene): λ_{max} (ε)=348 (22,400), 394 nm (21,100).

When the column chromatography was performed using silica gel instead of basic alumina, compound **40** was isolated in 70% yield as a red oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ=0.89–1.01 (m, 12H), 1.38–1.73 (m, 16H), 2.63–2.73 (m, 2H), 2.84–2.98 (t, 8H, J=7.3), 3.90 (s, 2H), 5.40 (s, 1H), 5.49 (s, 1H), 7.01 (m, 4H), 7.23 (s, 1H), 7.36–7.44 (m, 4H), 7.54 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ=14.04, 22.20, 22.31, 32.43, 32.69, 36.26, 36.66, 36.77, 58.66, 71.34, 118.19, 120.31, 121.91, 124.03, 124.14, 125.57, 125.85 (2C), 126.30, 132.35, 133.48, 136.49, 137.79, 144.80, 145.49, 145.72 (2C). MS (FAB): *m*/*z*=835 [M+H]$^+$. Anal. Calcd for $C_{44}H_{50}S_8$: C, 63.26; H, 6.03. Found: C, 63.20; H, 5.96.

4.35. Compound 39

A solution of the phosphonate **3a** (188 mg, 0.48 mmol) in dry THF (7 mL) was stirred under argon at −78 °C. A solution of butyllithium (1.6 M in hexanes, 0.30 mL, 0.48 mmol) was added dropwise via syringe for 5 min. The reaction mixture was stirred for 15 min, and then a solution of triptycene-1,4-dicarboxaldehyde **19** (50 mg, 0.16 mmol) in dry THF (3 mL) was added dropwise for 10 min. The reaction mixture was stirred at −78 °C for 1 h and at rt for 2.5 h. It was evaporated to dryness and chromatographed on basic alumina using dichloromethane–heptane (1:2) as eluent. The product was obtained as an orange oil from dichloromethane–methanol. Yield: 125 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, 6H, J=7.2), 0.97 (t, 6H, J=7.2), 1.35–1.75 (m, 16H), 2.77 (t, 4H, J=7.2), 2.88 (t, 4H, J=7.2), 5.68 (s, 2H), 6.88 (s, 2H), 6.99 (m, 4H), 7.05 (s, 2H), 7.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.78, 13.81, 21.80, 21.90, 31.84, 32.03, 35.88, 35.93, 50.23, 110.78, 122.54, 123.94, 125.33, 126.79, 129.96, 134.21, 142.76, 145.07. MS (FAB): *m*/*z*=835 [M+H$^+$]. Anal. Calcd for $C_{44}H_{50}S_8$: C, 63.26; H, 6.03. Found: C, 63.24; H, 5.88. UV/vis (toluene): λ_{max} (ε)=365 (21,100, shoulder), 403 nm (25,500).

4.36. Compound 41

A solution of the phosphonate **3a** (200 mg, 0.51 mmol) in dry THF (7 mL) was stirred under argon at −78 °C. A solution of butyllithium (1.5 M in hexanes, 0.34 mL, 0.51 mmol) was added dropwise via syringe for 5 min. The reaction mixture was stirred for 15 min, and then a solution of terephthalaldehyde (23 mg, 0.17 mmol) in dry THF (3 mL) was added dropwise. The reaction mixture was stirred at

−78 °C for 1 h and at rt for 2 h. It was evaporated to dryness and chromatographed on a silica gel column using dichloromethane–cyclohexane (1:1) as eluent (R_f=0.65). It was then triturated with hexane and yellow crystalline material was thus obtained. An analytical sample was recrystallized from dichloromethane–methanol to form yellow needles. Yield: 88 mg (78%); mp 66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.95 (t, 6H, J=7.3), 0.96 (t, 6H, J=7.3), 1.40–1.53 (m, 8H), 1.60–1.73 (m, 8H), 2.85 (t, 8H, J=7.3), 6.46 (s, 2H), 7.22 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.77, 21.83, 31.86, 31.99, 35.85, 35.97, 114.15, 124.94, 127.00, 127.75, 132.12, 133.83. MS (FAB): m/z=658 [M$^+$]. Anal. Calcd for $C_{30}H_{42}S_8$: C, 54.66; H, 6.42. Found: C, 54.31; H, 6.09. UV/vis (toluene): λ_{max} (ε)=406 (34,700), 427 nm (34,300).

4.37. Compound 42

A suspension of the phosphonium salt **4** (180 mg, 0.35 mmol) in dry THF (7 mL) was stirred under argon at −78 °C. A solution of butyllithium (1.6 M in hexanes, 0.22 mL, 0.35 mmol) was added dropwise via syringe for 5 min. The reaction mixture was stirred for 1 h, and then a solution of triptycene-1,4-dicarboxaldehyde **19** (50 mg, 0.16 mmol) in dry THF (3 mL) was added dropwise for 10 min. The reaction mixture was stirred at −78 °C for 1 h, then allowed to warm to rt and stirred for 16 h. Evaporation to dryness and column chromatography on neutral alumina in dichloromethane–heptane (2:1) followed by crystallization from dichloromethane–heptane afforded the product as orange crystals. Yield: 47 mg (41%); mp 263–265 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.81 (s, 6H), 3.89 (s, 6H), 5.62 (s, 2H), 6.83 (s, 2H), 7.00 (m, 4H), 7.03 (s, 2H), 7.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=50.40, 53.37, 53.58, 112.26, 122.65, 124.02, 125.48, 129.63, 130.27, 131.20, 133.10, 143.36, 144.75, 159.93, 160.37. HRMS (FAB): m/z=714.0522 [M$^+$]; calcd for $C_{36}H_{26}O_8S_4$: 714.0511. UV/vis (toluene): λ_{max} (ε)=380 nm (24,700).

4.38. Compound 43

A suspension of the phosphonium salt **4** (110 mg, 0.216 mmol) in dry THF (7 mL) was stirred under argon at −78 °C. A solution of butyllithium (1.6 M in hexanes, 0.14 mL, 0.216 mmol) was added dropwise via syringe for 5 min. The reaction mixture was stirred for 1 h, and then a solution of triptycene-1,4,5,8-tetracarboxaldehyde **20** (13 mg, 0.036 mmol) in dry THF (3 mL) was added dropwise during 10 min. The reaction mixture was stirred at −78 °C for 1 h and at rt for 2 h. Evaporation to dryness and filtration through a short column of neutral alumina in dichloromethane afforded the product as an orange oil. An analytical sample was crystallized from dichloromethane–heptane to form **43** as orange crystals. Yield: 21 mg (50%); mp 202–204 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ=3.77 (s, 12H), 3.85 (s, 12H), 5.86 (s, 2H), 6.83 (s, 4H), 7.03 (m, 2H), 7.05 (s, 4H), 7.44 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=47.11, 111.96, 123.42, 124.74, 126.11, 129.94, 131.13, 131.67, 134.57, 143.61, 144.46, 160.25, 160.61. HRMS (FAB): m/z=1173.9971 [M$^+$]; calcd for $C_{52}H_{38}O_{16}S_8$: 1173.9926. UV/vis (toluene): λ_{max} (ε)=368 nm (38,900).

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Supplementary data

Spectroelectrochemical absorption spectra of compounds **24–27** and **34–36**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.020.

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