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Synthesis of highly functionalized BEDT-TTF analogues incorporating 1,4-dithiin rings from 1,8-diketones

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ABSTRACT

Employment of 1,8-diketone ring formation reaction led to the synthesis of tetrathiafulvalene derivatives having diphenyl-1,4-dithiin ring together with dihydroxyl, dimethyl, MEM and diphenylthiophene groups. Spectroelectrochemistry of ET and its fully unsaturated analogue **4** was compared. While both displayed nearly similar behaviours, ET started to precipitate as the second oxidation potential is reached. CV studies indicated that the fully unsaturated **4** and tetraphenyldithiophene **20** have the highest oxidation potentials, while diphenyldithiindimethylthio **16** displayed the lowest oxidation potentials. CV measurements indicated that the combination of dithiin and hydroxyl groups help lowering the oxidation potentials. It is surprising that while the presence of dithiin ring results in higher oxidation potentials, hydroxyl groups lower the potentials. Single crystal structure of **13**, having both dithiin and 1,4-dithiepine rings, was examined and it was observed that dithiin and dithiepine rings form angles of 20.52° and 25.65° with the planar TTF core in cis form as both rings bent about their S···S axis to give a boat conformation.

1. Introduction

Since the discovery of superconductivity of β-(BEDT-TTF)$_2$I$_3$ with a transition temperature of 1.4 K at atmospheric pressure, there has been great deal of effort to improve and understand the properties of related multi-sulfur π-donors.[1] Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) **1** is among the most widely used and derivatized electron donor molecules for the synthesis of organic materials, which show electrical conductivity, semi conductivity and, at very low temperatures, superconductivity.[2,3]

It appears that two important features, a highly ordered crystal structure of the charge transfer salts and the extension of the donor molecules, are the central points to improve the properties of ET.[2b] Studies to implement such properties to a single molecule by molecular design have led to the development of various advanced materials,[4,2b,c] including analogues having different potential applications such as nonlinear optics,[5] liquid crystals,[6] dendrimers,[7–9] phthalocyanines,[7,8] polymers[10] and supramolecular switches.[11]

So far, extension has mostly been demonstrated in the middle of the molecule with an increased conjugation, which would allow the system to have an extended delocalization of the dication formed in the TTF moiety after reaching the second oxidation state.[2b] However, although there are some examples of introduction of conjugation at the peripheral ethylene groups, such an exploration has remained limited.[12] There are two reasons for this, lack of convenient methods and, at first sight, extension in TTF core looks more useful as the dication forms in the TTF moiety. On the other hand, it could equally be important to explore any expansion at the peripheries since such compounds have now been accepted as useful electron donors and find various applications.[4b,13]

Recently, we have reported a convenient method for synthesizing fused 1,4-dithiin rings with various functional groups **2**.[14] It involves an interesting ring formation reaction from 1,8-diketone with Lawesson's reagent (LR) **3** or P_4S_{10}. Employment of this reaction led to the synthesis of the dithiin **5** and its coupling resulted in, to our best knowledge, the first example of BEDT-TTF analogue having the highest conjugation at the peripheries.[15,16]

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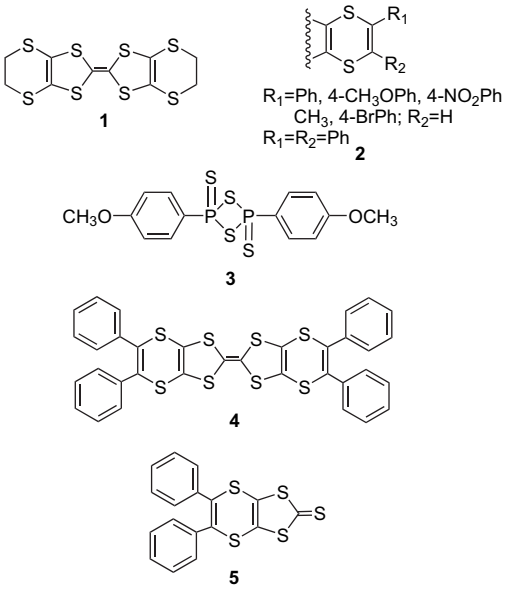
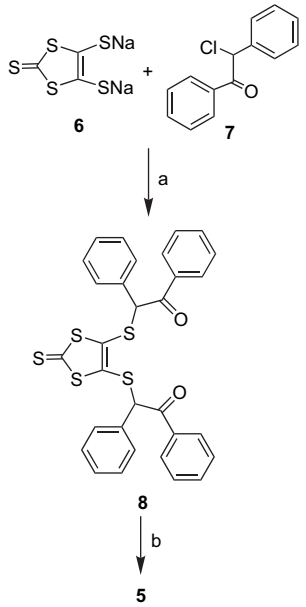


In our previous studies, we developed mono,[17] di, tri and tetra hydroxyl analogues of BEDT-TTF[18] to introduce hydrogen bonding functionalities into the radical cation salts, which could provide the charge transfer salts with highly ordered crystal structures. We report here, in addition to the fully unsaturated tetraphenyl ET analogue (TPhET) **4**, the synthesis and properties of the analogues having dimethoxyethoxymethyldiphenyldithiin **13**, diphenyldithiindithiomethyl **16**, dihydroxydiphenyldithiin **21**, dimethoxyethoxymethyldiphenylthiophene **19** and dihydroxydiphenylthiophene **22** groups at the peripheries.

2. Results and discussion

2.1. Synthesis

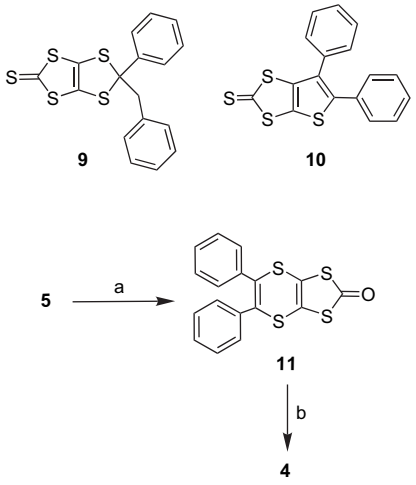
Synthesis of **4** was achieved by employing the 1,8-diketone ring formation reaction on BEDT-TTF **1**.[14,16] The readily available dianion **6**[19] was reacted with desyl chloride **7** in dry THF at room temperature, which gave the 1,8-diketone **8** (Scheme 1) in 90% yield. The



Scheme 1. Reagents and conditions: (a) THF (dry), rt, 3 h; (b) P_4S_{10}, toluene (dry), N_2, reflux, dark, 3 h.

ring closure reaction was then performed using P_4S_{10} in dry toluene under a nitrogen atmosphere and in the dark, which was completed in 3 h. As it was reported earlier,[16] this reaction gave three products; benzylphenyldithiole **9** (trace), thiophene **10** (20%) and 1,4-dithiin **5** (65%), structures of which were confirmed by X-ray single crystal diffraction analysis.[20]

The thione sulfur atom of 5,6-diphenyl[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione **5** was converted to oxygen with mercuric acetate to obtain **11**, which was then subjected to self-coupling (Scheme 2) and couplings with the reaily available precursors such as MEM protected dihydroxymethyldithiolodithiepinone **12**[18b] and dimethylthiodithiolone **15** (Scheme 3).[21]

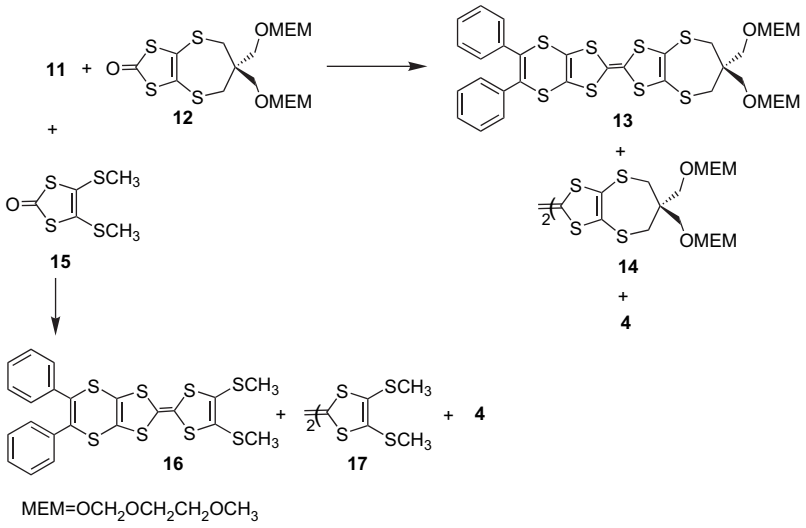


Scheme 2. Reagents and conditions: (a) $Hg(OAc)_2$, AcOH; (b) $P(OEt)_3$, N_2, reflux.

The coupling reactions were performed in neat triethylphosphite at 110 °C for 2 h (Schemes 2 and 3). While the self-coupling reaction yielded **4** in 90% as the only product, the coupling reactions with **12** and **15** produced mixtures of self and cross-couplings (Scheme 3). Thus, the reaction of **11** with **12** gave a mixture of cross-coupled **13** and self-coupled products **14**[18b] and **4**, and the reaction with **15** produced, in the same way, a mixture of cross-coupled **16** and self-coupled products **17**[21] and **4**. Their separation was successfully achieved by column chromatography.

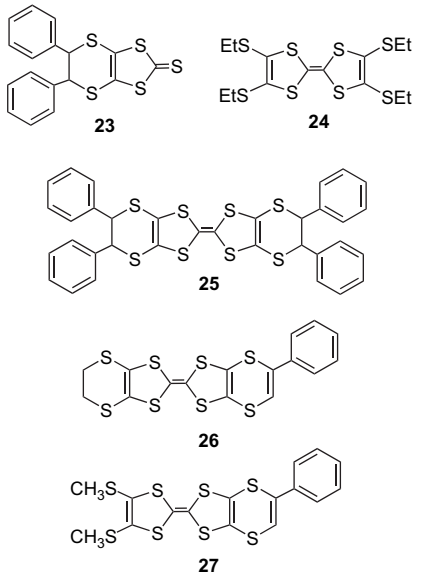
In the same way, the thione sulfur atom of 5,6-diphenylthieno[3,2-*d*][1,3]dithiole-2-thione **10** was converted to oxygen using mercuric acetate to obtain **18**, coupling reaction of which with dihydroxymethyldithiolodithiepinone **12** gave three coupling products, cross-coupled **19** and self-coupled products **20**[15b] and **14** (Scheme 4). Removal of MEM protecting groups of **13** and **19** was carried out in acid (20% HCl/THF, 1:1) to obtain diphenyldihydroxy ET analogues **21** and **22**, respectively (Scheme 5). In a previous study, it was reported that when saturated analogue **23** was subjected to a coupling reaction, rather than self-coupled **25**, tetrakis(ethylthio)tetrathiafulvalene **24** was obtained.[15a,c] On the other hand, in our case, coupling of **11** smoothly gave fully unsaturated analogue of ET with four phenyls at the peripheries. Moreover, ET analogues having dithiin rings with one phenyl group, **26** and **27** were obtained in our previous studies without any problem.[14b] These results suggest that the unsaturated dithiin ring contributes to the stability of the molecule through conjugation.

Attempts for the self or cross-couplings of **28** having a benzylphenyldithole ring, obtained through the reaction of **9** with mercury acetate, with **15**, unfortunately did not yield any products as **29** and **30**, respectively, except many spots on TLC, which could not be identified (Scheme 6). A possible explanation could be the presence of a quaternary benzylic carbon, which is susceptible to any



Scheme 3. Reagents and conditions: $P(OEt)_3$, N_2, reflux.

nucleophilic attack, which can easily be performed by triethylphosphite and the resultant product can end up with various side reactions.

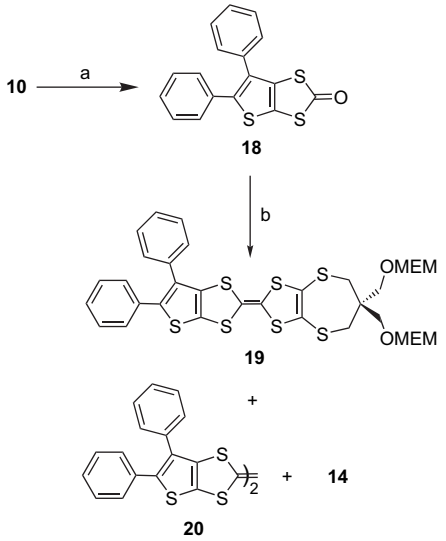


Mono aryl analogues **34**–**36** having dihydoxy groups were prepared following the usual methodology to compare the CV measurements of both diaryl and mono aryl compounds (Scheme 7). The readily available mono aryl dithiins **31**[14b] were coupled with the MEM protected dihydroxyl **12** in refluxing $P(OEt)_3$. Chromatographic separation of the resultant crude product yielded three compounds, cross-coupled **33** and self-coupled products **32** and **14**. Removal of the MEM protecting group of **33** was carried out in acid (20% HCl/THF, 1:1) to obtain phenyldihydroxy ET analogues **34**–**36**.

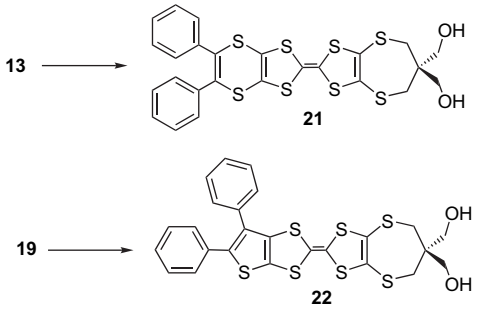
2.2. X-ray crystallography

The X-ray structure and molecular packing of **13** are shown in Figures 1 and 2, respectively. Some selected geometric parameters are given in Table 1.

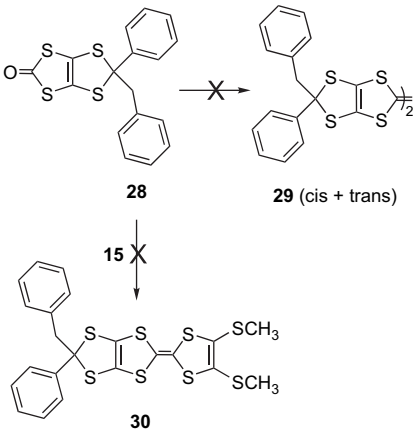
The angle between the best planes of the dithiolane rings of **13** is 48.6(6)°. The calculated puckering parameters show that both dithiolane rings are in an envelope conformation on C1 [Q=0.243(15) Å, φ=34(4)°] and C1′[Q=0.275(15) Å, φ=214(3)°].[22] The dithiine ring is bent about the S···S axis to give a boat conformation with the S atoms at the apices [Q=0.702(13) Å, θ=90(3)°, φ=181(2)°]. The dihedral angle between S2/C2/C3/S3 and C2/C3/C4/C5 is 30.0(6)°. The seven membered ring fused to one of the dithiolane rings also deviates from planarity and the angle between S2′/C2′/C3′/S3′ and S4′/C2′/C3′/S5′ is 1.4(3)°. The phenyl groups make dihedral angles



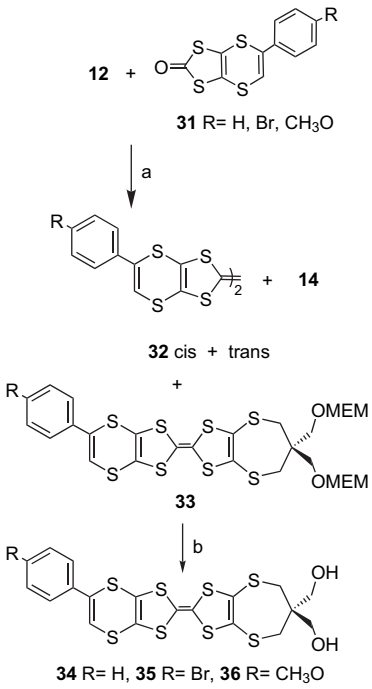
Scheme 4. Reagents and conditions: (a) $Hg(OAc)_2$, AcOH; (b) **12**, $P(OEt)_3$, N_2, reflux.



Scheme 5. Reagents and conditions: THF/HCl (1:1), rt.



Scheme 6.



Scheme 7. Reagents and conditions: (a) $P(OEt)_3$, N_2, reflux; (b) THF/HCl (1:1), rt.

of 41.6(9)° and 73.3(7)° with the best plane of the dithiin ring [C2/C3/C4/C5].

As depicted in Figure 3. the mean heterocycle of the molecule is not planar. Each moiety in the mean heterocycle, S2–C1–S3–C1′–

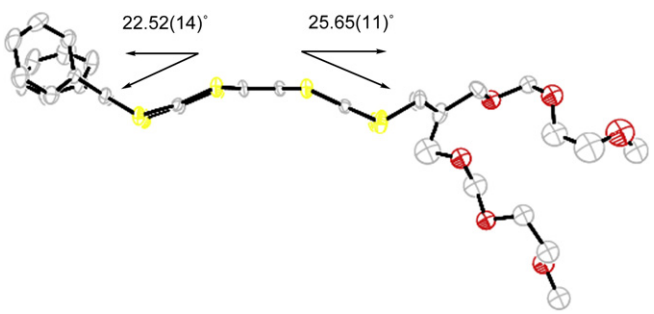


Figure 1.

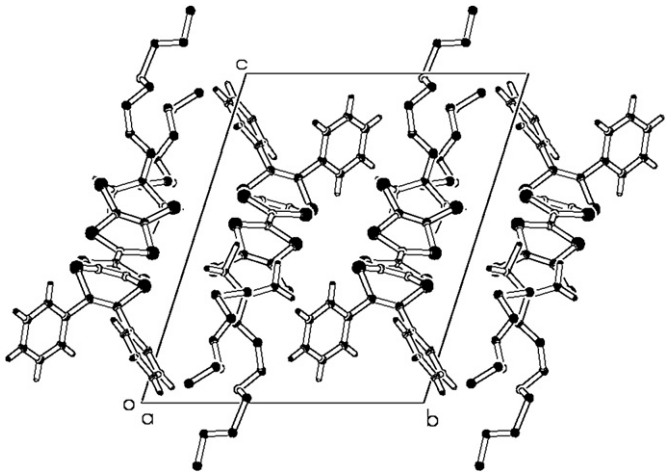


Figure 2.

Table 1
Selected geometric parameters for **13** (Å, °)

S2′–C1′	1.754(18)
S2′–C2′	1.767(19)
S3′–C1′	1.754(17)
S3′–C3′	1.759(18)
S5–C3	1.738(17)
S5–C4	1.792(18)
S4–C2	1.752(17)
S4–C5	1.801(18)
S2–C2	1.746(18)
S2–C1	1.760(17)
S3–C1	1.754(17)
S3–C3	1.774(18)
S4′–C2′	1.738(18)
S4′–C18	1.81(2)
S5′–C20	1.76(2)
S5′–C3′	1.761(17)
C1–C1′	1.35(2)
C4–C5	1.33(2)
C3′–C2′	1.33(2)
C3–C2	1.34(2)
S5–C4–C5–C6	174.9(16)
C12–C4–C5–S4	176.6(15)

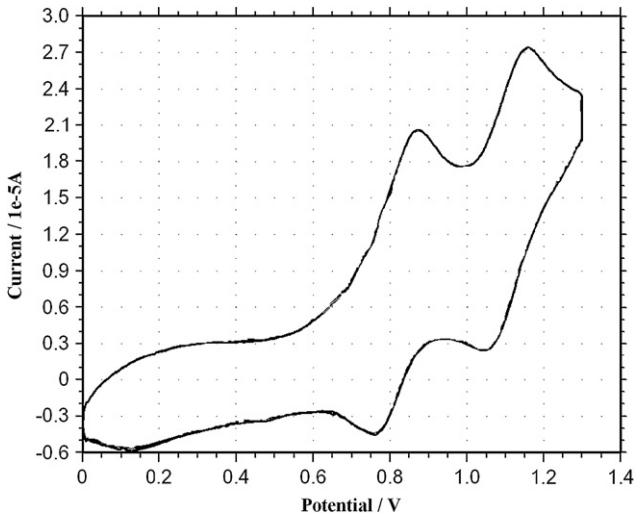


Figure 3. CV of **4** (1.0×10^{-3} M) in 0.1 M $TBABF_4/CH_2Cl_2$ with a scan rate of 100 mV s^{-1}, Pt working, Pt counter and Ag/Ag^+ reference electrodes.

S2′–S3′ (Line 1), S2–S3–C2–C3–S4–S5 (Line 2) and S2–S3′–C2′–C3′–S4′–S5′ (Line 3) can be assumed planar, independently. Maximum deviations from planarity are 0.028(5) Å for S3 for Line 1, −0.073(18) Å for C2 for Line 2 and 0.021(6) Å for S5′ for Line 3. The angle between Line 1 and Line 2 is 20.52(14)° and the angle between Line 1 and Line 3 is 25.65(11)°.

The packing arrangement of **13** is shown in Figure 2. As usual in this type of compounds, packing appears to be governed by short S···S interactions. Two especially short S···S contacts, S5···S5′ (1−*x*, −*y*, 1−*z*) 3.473(4) Å and S2···S2′ (1−*x*, 1−*y*, 1−*z*) 3.576(4) Å, are less than that (3.6 Å) predicted from traditional Van der Waals radii. Some other close S···S contacts are S4···S4′ (−*x*, 1−*y*, 1−*z*) 3.601(4) Å and S3′···S5 (1+*x*, *y*, *z*) 3.731(4) Å. The intramolecular close contacts are S2···S2′ 3.273(7) Å and S3···S3′ 3.261(7) Å.

2.3. Cyclic voltammetry (CV) measurements

Oxidation potentials of the new organosulfur donors **4**, **13**, **16**, **19**, **20**–**22** and **34**–**36** were measured by cyclic voltammetry and compared with the data for ET **1**, along with the analogues **26**, **27** and **37**, reported previously[14b,18b] (Table 2). The measurements were performed in acetonitrile containing $NaClO_4$. CV measurements showed that while the ET analogue having diphenyldithiin ring and dimethyl groups **16** had the lowest oxidation potentials, the analogues, TPhET **4** and tetraphenyldithiophene **20** displayed the highest oxidation potentials. It seems that the presence of four phenyl groups at the peripheries do not help easy oxidation, as well as the presence of thiophene rings, since all the molecules having diphenylthiophene showed higher oxidation potentials, i.e., **19**, **20** and **22**. On the other hand, the compounds having diphenyldithiindihydroxyl and diphenyldithiindiMEM groups **13** and **21**, respectively, join the lowest oxidation potential group compared with ET **1**. As these ET analogues showed lower oxidation potentials, they were compared with similar molecules having dithiins with one aryl group such as phenyl **34**, 4-BrPh **35** and 4-MeOPh **36**. Contrary to the diphenyldithiindiMEM **13** and diphenyldihydroxyl **21**, these analogues displayed slightly higher oxidation potentials except **36** having electron donating methoxy group, which showed a slightly lower oxidation potential than ET. Interestingly, **26** having an ethylene peripheral on one side and a phenyldithiin on the other side showed higher oxidation potentials, the dihydroxyl **37**,[18b] on the other side displayed lower oxidation potential compared with ET.

Considering the CV results discussed above, the ET analogues having diphenyldithiin or phenyldithiin rings and dithiomethyl groups, **16** and **27**, respectively, have lower oxidation potentials as well as the analogues having diphenyldithiin rings and hydroxyl and MEM groups. Contrarily, having two diphenyldithiin rings put the oxidation potentials higher. Similarly, diphenylthiophene rings do not contribute to lower the oxidation potentials.

It could be concluded that (i) the presence of bis(diphenyldithiin) and bis(diphenylthiophene) rings do not make the oxidations easier; (ii) the combination of diphenyldithiin and dimethylthio lower the oxidation potential; (iii) the presence of hydroxyl groups, in general lower the oxidation potential (typical example could be the comparison of **26** and **37**); (iii) also the combination of diphenyldithiin and dihydroxyl groups lower the oxidation potentials.

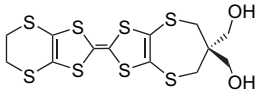


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Table 2
In ca. 1 mM AcCN solutions, $NaClO_4$ (0.1 M) versus Ag/AgCl, 100 mV s^{-1}

	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)
1	0.46	0.71
4	0.72	1.03
13	0.44	0.70
16	0.36	0.59
19	0.60	0.84
20	0.72	1.06
21	0.41	0.63
22	0.57	0.80
26	0.66	0.96
27	0.49	0.63
34	0.49	0.74
35	0.50	0.76
36	0.42	0.70
37	0.42	0.70

2.4. Spectroelectrochemical studies

To the best of our knowledge, this is the first spectroelectrochemical report of an ET analogue involving a comparison with ET. Spectroelectrochemical experiments of both ET **1** and TPhET **4** were performed in CH_2Cl_2 solution as ET has better solubility, containing 0.1 M $TBABF_4$. First and second oxidation potentials of ET and TPhET were recorded as 0.79, 1.15 V and 0.86, 1.14 V, respectively. Neutral UVs of ET and TPhET showed absorptions at 236, 321 and 347 nm (Fig. 4) and 241, 300 and 339 nm (Fig. 5), respectively.

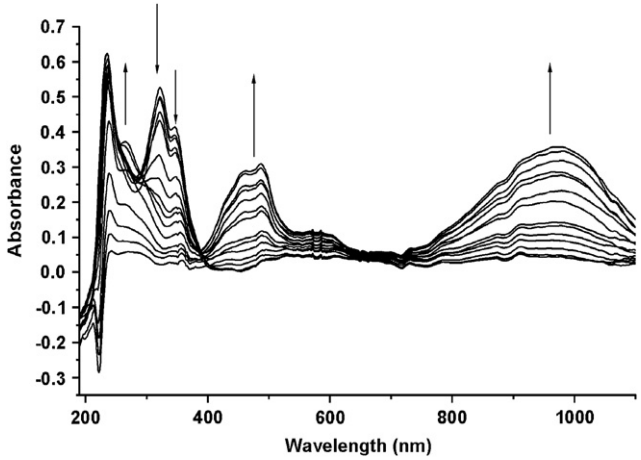

Figure 4. UV–vis spectroelectrochemistry of ET **1** (1.0×10^{-3} M) in CH_2Cl_2 (0.1 M $TBABF_4$). Oxidation on a platinum grid.

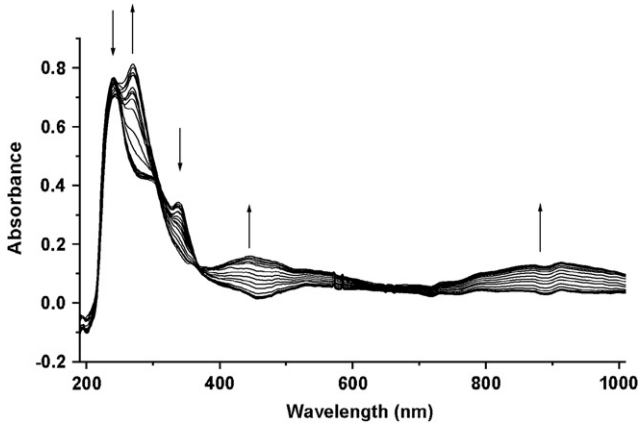

Figure 5. UV–vis spectroelectrochemistry of fully unsaturated tetraphenyl ET (TPhET) **4** (1.0×10^{-3} M) in CH_2Cl_2 (0.1 M $TBABF_4$). Oxidation on a platinum grid.

On gradual increase of potential, the absorption bands of ET at 321 and 347 nm started to go down as the potential approached to the first oxidation state, 0.79 V, and three new bands between 388 and 534 nm, 534 and 629 nm and 719 and 1100 nm emerged due to the formation of cation radical $\mathbf{1}^{+\bullet}$, forming an isobestic point at 388 nm (Fig. 4). When the potential reached to the second oxidation state, 1.15 V, a new band at 266 nm, possibly due to the formation of the dication $\mathbf{1}^{2+}$, started to appear. Unfortunately, only the emergence of the new band could be observed as the precipitation of the material in the cell took place, so the behaviour of ET at higher potentials could not be obtained.

Although the neutral TPhET showed almost similar absorption bands with the neutral ET, its bands at 300 and 339 nm appeared with lower intensities (Fig. 5). Similarly, on gradual increase of potential, three new bands between 372 and 517 nm, 517 and 631 nm and a third band between 725 and 1069 nm appeared as the potential approached to the first oxidation potential, 0.86 V. On contrary to ET, while the band at 241 nm showed a small decrease, the band at 339 nm went down completely and the band at 300 nm remained constant. An isobestic point at 372 nm formed. As the second oxidation state, 1.15 V, was approached a new band at 270 nm started to appear and reached maximum at the second oxidation potential. No precipitation was observed and no change of the bands emerged during the first oxidation state. It is not clear if the bands belong to the cation radical $\mathbf{1}^{+\bullet}$ could remain unchanged as the second oxidation state of ET is approached.

TPhET shows almost similar spectroelectrochemical behaviour with ET with the exception that ET displays stronger absorption peaks in neutral and oxidation states. The advantage TPhET has is that it does not precipitate at the second oxidation potential.

In conclusion, synthesis of ET analogues incorporating combinations of dithiin and thiophene rings and dihydroxyl groups has been achieved, employing a 1,8-diketone ring formation reaction. To our best knowledge, for the first time, a spectroelectrochemical comparison of ET with its fully unsaturated analogue has been performed, which showed that both have a comparable spectroelectrochemistry.

The CV measurements indicated that as TPhET **4** has the higher oxidation potentials, functionalization of ET with the combinations of dithiin ring and dimethylthio, and dithiin ring and dihydroxyl help to lower the oxidation potentials. It would appear that the presence of the dithiin ring on its own, as in **26**, does not lower the oxidation potentials. On the other hand, the presence of dihydroxy groups alone help to lower the oxidation potentials of ET.

3. Experimental section

3.1. General

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (250 MHz) or solvent as the internal standard for ^{13}C (67.8 MHz) unless otherwise stated. Mass spectra were recorded at an ionizing voltage of 70 eV. Chromatography was performed on flash silica gel (Merck) and TLC was carried out on 0.2 mm silica gel plates. All reagents and solvents were commercial grade (Aldrich) and purified according to established convention.

3.2. 5,5′-6,6′-Tetraphenyl-2,2′bi([1,3]dithiolo[4,5-*b*][1,4]dithiinylidene) 4

Compound **11**[16] (1 g, 2.8 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under a N_2 atmosphere at 110 °C for 3 h. $(EtO)_3P$ was then evaporated under reduced pressure. The residue was recrystallized from methanol to give the title compound **4** (0.86 g, 90%) as a yellow powder. Mp 248–250 °C. ^1H NMR ($CDCl_3$) δ 7.14–7.30 (20H, m); ^{13}C NMR ($CDCl_3$) δ 128.4 (*C*-t), 128.8 (*C*-t), 129.6 (*C*-t), 134.2 (*C*-q), 135.3 (*C*-q), 136.8 (*C*-q); UV (CH_3CN, nm) 237, 296, 338; HRMS (EI) calculated for $C_{34}H_{20}S_8$ M^+ *m*/*z* 683.933075, found 683.932946. Anal. Calcd for $C_{34}H_{20}S_8$: C, 59.65; H, 2.92. Found: C, 60.03; H, 2.83.

3.3. 5,6-Diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione 5

A mixture of **8** (6 g, 10 mmol) and P_4S_{10} (5 g, 11.5 mmol) was refluxed in dry toluene (100 mL) under a N_2 atmosphere and in dark until the starting material was consumed, which took nearly 3 h. The solvent was then evaporated under reduced pressure and the residue was separated by column chromatography, eluting with hexane/CH_2Cl_2 (3:1) to give the title compound **5** (brown powder, 2.4 g, 65%), **10** (brown powder, 0.7 g, 20%) and **9** (trace) as first, second and third fractions, respectively. Compound **5**. Mp 113–114 °C. ^1H NMR ($CDCl_3$) δ 7.09–7.34 (10H, m); ^{13}C NMR ($CDCl_3$) δ 128.6 (*C*-t), 128.7 (*C*-t), 129.5 (*C*-t), 130 (*C*-q), 134.7 (*C*-q), 136.2 (*C*-q), 213.9 (*C*=S); IR (KBr, cm^{-1}) 1080 (C=S); UV (CH_3CN, nm) 392; HRMS (EI) calculated for $C_{17}H_{10}S_5$ M^+ *m*/*z* 373.938609, found 373.9397. Anal. Calcd for $C_{17}H_{10}S_5$: C, 54.54; H, 2.67. Found: C, 54.85; H, 2.29.

3.4. 2-[5-(2-Oxo-1,2-diphenylethylsulfanyl)-2-thioxo-1,3-dithiol-4-ylsulfanyl]-1,2-diphenyl-1-ethanone 8

To the solution of dianion **6** (5 g, 20 mmol) in dry THF (50 mL) under a N_2 atmosphere and in an ice bath was added a solution of desyl chloride **7** (9.5 g, 40 mmol) in dry THF (30 mL) dropwise from a dropping funnel, and the mixture was stirred for 3 h at room temperature. The yellow precipitate was filtered, washed with cold ethanol and dried to give the title compound **8**, which was used for the next step without further purification (9.9 g, 85%). Mp 158–159 °C. ^1H NMR ($CDCl_3$) δ 7.95 (2H, d, *J*=8.1 Hz, Ph), 7.86 (2H, d, *J*=7.0 Hz, Ph), 7.20–7.58 (16H, m, Ph), 6.09 (1H, s), 5.85 (1H, s); EIMS *m*/*z* 586.9 (M^++1). Anal. Calcd for $C_{31}H_{22}O_2S_5$: C, 63.48; H, 3.75. Found: C, 63.10; H, 3.92.

3.5. 5-Benzyl-5-phenyl-[1,3]dithiolo[4,5-*d*][1,3]dithiole-2-thione 9

A mixture of **8** (3 g, 5 mmol) and P_4S_{10} (2.5 g, 5.6 mmol) was refluxed in dry toluene (50 mL) under a N_2 atmosphere until the starting material was consumed, which took nearly 3 h. The solvent was then evaporated under reduced pressure and the residue was separated by column chromatography, eluting with hexane/CH_2Cl_2 (2:1) to give the title compound **9** as a brown powder (0.17 g, 25%) and **10** as a brown powder (0.5 g, 30%) as first and second fractions, respectively. Compound **9**. Mp 128–129 °C. ^1H NMR ($CDCl_3$) δ 7.13–7.26 (8H, m), 6.95 (2H, d, *J*=7 Hz), 3.76 (2H, s); ^{13}C NMR ($CDCl_3$) δ 50.75 (CH_2), 86.34 (*C*-t), 127.0, 127.6, 127.8, 128.5, 128.85, 129.6, 134.5 (*C*-q), 139.5 (*C*-q), 205 (*C*=S); IR (KBr, cm^{-1}) 1080 (C=S); UV (CH_3CN, nm) 426; EIMS *m*/*z* 375.5 (M^+). Anal. Calcd for $C_{17}H_{12}S_5$: C, 54.25; H, 3.19. Found: C, 53.90; H, 2.82. *5,6-Diphenylthieno[3,2-d][1,3]dithiole-2-thione* ***10***.[15b] Mp: 156–157 °C. ^1H NMR ($CDCl_3$) δ 7.25–7.37 (10H, m), ^{13}C NMR ($CDCl_3$) 128.5, 128.6, 128.8, 129, 129.1, 129.6, 132.6, 133.9, 140, 143.9, 213 (*C*=S); IR (KBr, cm^{-1}) 1080 (C=S); UV (CH_3CN, nm) 398; EIMS *m*/*z* 342 (M^+). Anal. Calcd for $C_{17}H_{10}S_4$: C, 59.64; H, 2.92. Found: C, 60.10; H, 2.59.

3.6. 5,6-Diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one 11

A mixture of **5** (2 g, 5.5 mmol) dissolved in $CHCl_3$ (20 mL), mercuric acetate (5 g, 15 mmol) and glacial acetic acid (20 mL) was stirred at room temperature for 1 h. The mixture was filtered through Celite and the filtrate was extracted with sodium

carbonate solution (2×50 mL) and water (2×50 mL). The organic layer was dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure to give the title compound **11** (1.6 g, 80%) as a light yellow powder. Mp 116–118 °C. ^{1}H NMR ($CDCl_3$) δ 7.12–7.20 (10H, m); ^{13}C NMR ($CDCl_3$) δ 120.5 (*C*-q), 128.37, 128.5, 130.6, 134.55 (*C*-q), 136.5 (*C*-q), 192 (*C*=O); IR (KBr, cm^{-1}) 1690 (*C*=O); UV (CH_3CN, nm) 3010; HRMS (EI) calculated for $C_{17}H_{10}S_4O$ M^+ *m*/*z* 357.96145, found 357.96915. Anal. Calcd for $C_{17}H_{10}OS_4$: C, 56.98; H, 2.79. Found: C, 57.31; H, 2.52.

3.7. 6,6-Bis(2-methoxyethoxymethyl)-6,7-dihydro-2-(5,6-diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine 13

A mixture of oxo compound **11** (0.5 g, 1.4 mmol) and MEM protected oxo derivative **12**[18b] (0.65 g, 1.4 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under a N_2 atmosphere at 110 °C for 3 h. $(EtO)_3P$ was distilled off and the residue was separated by column chromatography eluting with hexane/ethyl acetate (1:1). The second fraction gave the title compound **13** (0.16 g, 30%) as an orange powder. Mp 185–187 °C. ^{1}H NMR ($CDCl_3$) δ 7.12–7.22 (10H, m), 4.7 (4H, s), 3.72 (4H, s), 3.61–3.64 (4H, m), 3.51–3.54 (4H, m), 3.38 (6H, s), 2.75 (4H, s); ^{13}C NMR ($CDCl_3$) δ 29.7 (*C*-t), 37.0 (*C*-t), 44.2 (S–CH_2), 59.0 (O–CH_3), 64.5 (O–CH_2, br), 69.6 (O–CH_2CH_2–O), 71.7 (O–CH_2CH_2–O), 95.8 (O–CH_2–O), 122.5 (C-q), 128.3, 128.6, 128.8, 129.6 (C-q), 135.2 (C-q), 136.8 (C-q); EIMS *m*/*z* 785.3 (M^+). Anal. Calcd for $C_{33}H_{36}O_6S_8$: C, 50.51; H, 4.59. Found: C, 50.25; H, 4.70.

3.8. 2-(4,5-Bis(methylthio)-1,3-dithiol-2-ylidene)-5,6-diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiine 16

A mixture of oxo compounds **11** (1 g, 2.8 mmol) and **15** (0.63 g, 2.8 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under a N_2 atmosphere at 110 °C for 3 h. $(EtO)_3P$ was distilled off and the residue was separated by column chromatography eluting with hexane/CH_2Cl_2 (25:1). The third fraction gave the title compound **16** (0.26 g, 35%) as a brown powder. Mp 165–168 °C. ^{1}H NMR ($CDCl_3$) δ 7.09–7.22 (10H, m), 2.42 (6H, s); ^{13}C NMR ($CDCl_3$) δ 19.2 (CH_3), 122.5 (*C*-q), 128.3, 128.6, 128.8, 129.5 (*C*-q), 129.6 (C-q), 135.21 (*C*-q), 136.8 (*C*-q); HRMS (EI) calculated for $C_{22}H_{16}S_8$ M^+ *m*/*z* 535.90177, found 535.89645. Anal. Calcd for $C_{22}H_{16}S_8$: C, 49.25; H, 2.98. Found: C, 49.12; H, 2.72.

3.9. 5,6-Diphenylthieno[3,2-*d*][1,3]dithiol-2-one 18

A mixture of **10** (2 g, 5.84 mmol) dissolved in $CHCl_3$ (20 mL), mercuric acetate (5 g, 15 mmol) and glacial acetic acid (20 mL) was stirred at room temperature for 1 h. The mixture was filtered through Celite and the filtrate was extracted with aq sodium carbonate solution (2×50 mL) and water (2×50 mL). The organic layer was dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure to give the title compound **18** (1.33 g, 70%) as a white powder. Mp 162–163 °C. ^{1}H NMR ($CDCl_3$) δ 7.17–7.36 (10H, m); ^{13}C NMR ($CDCl_3$) δ 121.5 (*C*-q), 128.31, 128.7, 129.1, 129.2, 129.6, 132.6, 134.55 (*C*-q), 140.0 (*C*-q), 196.0 (*C*=O); IR (KBr, cm^{-1}) 1690 (*C*=O); EIMS *m*/*z* 326.5 (M^+). Anal. Calcd for $C_{17}H_{10}OS_3$: C, 62.57; H, 3.06. Found: C, 62.20; H, 2.81.

3.10. 2-(5,6-Diphenylthieno[2,3-*d*][1,3]dithiol-2-yliden)-6,6-di(2-methoxyethoxymethoxymethyl)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepine 19

A mixture of oxo compound **18** (0.5 g, 1.5 mmol) and MEM protected oxo derivative **12** (0.70 g, 1.5 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under a N_2 atmosphere at 110 °C for 3 h. $(EtO)_3P$ was distilled off and the residue was separated by column chromatography eluting with hexane/ethyl acetate (1:1). The second fraction gave the title compound **19** (0.17 g, 30%) as an orange powder. Mp 182–184 °C. ^{1}H NMR ($CDCl_3$) δ 7.26–7.32 (10H, m), 4.50 (4H, s), 3.73 (4H, s), 3.66 (4H, t), 3.63 (4H, t), 3.39 (6H, s), 2.76 (4H, s); ^{13}C NMR ($CDCl_3$) δ 29.7 (*C*-t), 37.0 (*C*-t), 44.3 (S–CH_2), 59.1 (O–CH_3), 67.0 (O–CH_2, br), 69.7 (O–CH_2CH_2–O), 71.7 (O–CH_2CH_2–O), 95.8 (O–CH_2–O), 114.6 (C-q), 117.3 (*C*-q), 122.5 (*C*-q), 128.3, 128.8, 129.6 (*C*-q), 135.2 (*C*-q), 136.8 (*C*-q); HRMS (EI) calculated for $C_{33}H_{36}O_6S_7$ M^+ *m*/*z* 752.05569, found. 752.05482. Anal. Calcd for $C_{33}H_{36}O_6S_7$: C, 52.65; H, 4.78. Found: C, 52.88; H, 4.45.

3.11. 2-(5,6-Diphenyl[1,3]ditholo[4,5-*b*][1,4]dithiin-2-yliden)-6-hydroxymethyl-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-6-ylmethanol 21

To a solution of **13** (0.25 g, 0.32 mmol) in THF (10 mL) was added dropwise 20% aq HCl (5 mL). The mixture was stirred at room temperature for 2 days. It was then neutralized with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 mL). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure to give the title compound **21** (0.15 g, 75%) as an orange powder. Mp 185–187 °C. ^{1}H NMR ($CDCl_3$) δ 7.00 (10H, s), 5.03 (2H, s), 3.82 (4H, br s), 2.29 (4H, s); ^{13}C NMR ($CDCl_3$) δ 36.8 (*C*-q), 44.3 (S–CH_2), 64.5 (O–CH_2), 122.5, 125.5, 128.3, 129.5, 132.0, 135.3, 136.8, 135.7; EIMS *m*/*z* 607.8 (M^+). Anal. Calcd for $C_{25}H_{20}O_2S_8$: C, 49.34; H, 3.28. Found: C, 49.11; H, 3.52.

3.12. 2-(5,6-Diphenylthieno[2,3-*d*][1,3]dithiol-2-yliden)-6-hydroxymethyl-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-6-ylmethanol 22

To a solution of **19** (0.25 g, 0.33 mmol) in THF (10 mL) was added dropwise 20% aq HCl (5 mL). The mixture was stirred at room temperature for 2 days. It was then neutralized with solid sodium carbonate. The THF layer was decanted and the remaining material was extracted with THF (30 mL). The combined THF solutions were dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure to give the title compound **22** (0.14 g, 75%) as an orange powder. Mp 177–179 °C. ^{1}H NMR ($CDCl_3$) δ 7.05 (10H, s), 3.9 (4H, br s), 2.70 (4H, s); EIMS *m*/*z* 574.9 (M^+). Anal. Calcd for $C_{25}H_{20}O_2S_7$: C, 52.08; H, 3.47. Found: C, 52.30; H, 3.15.

3.13. 6,6-Bis(2-methoxyethoxymethyl)-2-(5-phenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-6,7-dihydro-5*H*-2-(5,6-diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin 33 (R=H)

A mixture of oxo compounds **31** (0.30 g, 1.06 mmol) and **12** (0.48 g, 1.04 mmol) was heated in freshly distilled $(EtO)_3P$ (20 mL) under a N_2 atmosphere at 110 °C for 3 h. $(EtO)_3P$ was distilled off and the residue was separated by column chromatography eluting with initially hexane/CH_2Cl_2 (3:1) mixture to separate **32** and then with the mixture of ethylacetate/hexane (3:1) to separate **33** and **14** as the second and third fractions, respectively. Compound **33** (R=H) (0.20 g, 27%) yellow powder. ^{1}H NMR ($CDCl_3$) δ 7.44–7.50 (2H, m, Ph), 7.25–7.29 (3H, m, Ph), 6.59 (1H, s, =C*H*), 4.69 (4H, s, 2×OCH_2O), 3.52–3.58 (8H, m, 4×OCH_2), 3.45–3.50 (4H, m, 2×OCH$_2$CH_2O), 3.39 (6H, s, 2×OCH_3), 2.75 (4H, s, 2×SCH_2); HRMS (EI) calculated for $C_{27}H_{32}O_6S_8$ M^+ *m*/*z* 709.0235, found 709.0238.

The following were similarly produced.

3.14. 6,6-Bis(2-methoxyethoxymethyl)-2-(5-(4-bromo phenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-6,7-dihydro-5*H*-2-(5,6-diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin 33 (R=Br)

Column chromatography eluting with ethylacetate/hexane (3:1) gave the self-coupled **32** as the first fraction, the cross-coupled **33** as the second fraction and the cross-coupled **14** as the third fraction. Compound **33** (R=Br) (29%) yellow powder. ^{1}H NMR ($CDCl_3$) δ 7.46 (2H, d, J=8.6 Hz, Ph), 7.37 (2H, d, J=8.6 Hz, Ph), 6.59 (1H, s, =C*H*), 4.67 (4H, s, 2×OCH_2O), 3.63–3.58 (8H, m, 4×OCH_2), 3.55–3.51 (4H, m, 2×OCH_2), 3.37 (6H, s, 2×OCH_3), 2.73 (4H, s, 2×SCH_2); FABMS m/z 788 (M^++1).

3.15. 6,6-Bis(2-methoxyethoxymethyl)-2-(5-(4-methoxy phenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-6,7-dihydro-5*H*-2-(5,6-diphenyl-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin 33 (R=OCH$_3$)

Column chromatography eluting with ethylacetate/hexane (3:1) gave the self-coupled **32** as the first fraction, the cross-coupled **33** (R=OCH$_3$) as the second fraction and the cross-coupled **14** as the third fraction.

Compound **33** (R=OCH$_3$) (40%) yellow powder. ^{1}H NMR ($CDCl_3$) δ 7.47 (2H, d, J=8.4 Hz, Ph), 6.87 (2H, d, J=8.4 Hz, Ph), 6.46 (1H, s, =C*H*), 4.70 (4H, s, 2×OCH_2O), 3.71 (3H, s, OCH_3), 3.63–3.58 (8H, m, 4×OCH_2), 3.55–3.51 (4H, m, 2×OCH_2), 3.36 (6H, s, 2×OCH_3), 2.72 (4H, s, 2×SCH_2); FABMS m/z 739 (M^++1).

The following were similarly produced as **21**.

3.16. [6-(Hydroxymethyl)-2-(5-phenyl[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-6-yl]methanol 34

Column chromatography eluting with ethylacetate/hexane (3:1) gave the title compound **34** (43%). Mp 182–184 °C. Yellow powder. ^{1}H NMR (DMSO-d_6) δ 7.62–7.57 (2H, m, Ph), 7.43–7.40 (3H, m, Ph), 7.21 (1H, s, =C*H*), 4.61 (2H, br, O*H*), 3.55 (4H, d, J=5.2 Hz, 2×OCH_2), 2.72 (4H, s, 2×SCH_2); FABMS m/z 532 (M^+). Anal. Calcd for $C_{19}H_{16}O_2S_8$: C, 42.85; H, 3.00. Found: C, 42.83; H, 2.98.

3.17. [2-[5-(4-Bromophenyl)[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene]-6-(hydroxymethyl)-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4]dithiepin-6-yl]methanol 35

Column chromatography eluting with ethylacetate/hexane (3:1) gave the title compound **35** (35%). Mp 130–131 °C. Yellow powder. ^{1}H NMR (DMSO-d_6) δ 7.62 (2H, d, J=8.7 Hz, Ph), 7.54 (2H, d, J=8.7 Hz, Ph), 7.29 (1H, s, =C*H*), 4.61 (2H, br, O*H*), 3.55 (4H, d, J=4.8 Hz, 2×OCH_2), 2.75 (4H, s, 2×SCH_2); ^{13}C NMR (DMSO-d_6) δ 138.5 (*C*H=), 135.2 (*C*=), 134.0 (*C*H=), 132.1 (*C*=), 129.0 (*C*=), 123.0 (*C*H=), 121.7 (*C*H=), 62.0 (br, *C*OH), 45.1 (*C*S), 36.3 (*C*=); EIMS m/z 611 (M^+). Anal. Calcd for $C_{19}H_{15}BrO_2S_8$: C, 37.31; H, 2.45. Found: C, 37.45; H, 2.71.

3.18. {6-(Hydroxymethyl)-2-[5-(4-methoxyphenyl) [1,3]dithiolo[4,5-*b*][1,4]dithiin-2-ylidene]-6,7-dihydro-5*H*-[1,3]dithiolo[4,5-*b*][1,4] dithiepin-6-yl}methanol 36

Column chromatography eluting with ethylacetate/hexane (3:1) gave the title compound **36** (34%). Mp 140–144 °C. Yellow powder. ^{1}H NMR (THF-d_8) δ 7.40 (2H, d, J=8.8 Hz, Ph), 6.79 (2H, d, J=8.8 Hz, Ph), 6.62 (1H, s, =C*H*), 4.65 (2H, br, O*H*), 3.68 (3H, s, OCH_3), 3.52 (4H, d, J=4.8 Hz, 2×OCH_2), 2.76 (4H, s, 2×SCH_2); ^{13}C NMR (THF-d_8, 67.5 MHz) δ 142.5 (*C*H=), 130.0 (*C*H=), 129.3 (*C*=), 128.7 (*C*H=), 122.6 (*C*H=), 118.0 (*C*H=), 117.2 (*C*=), 115.0 (*C*=), 64.8 (br, *C*OH), 55.6 (OCH_3), 46.2 (*C*S), 37.5 (*C*); HRMS calculated for $C_{20}H_{18}O_3S_8$ M^+ m/z 561.9008, found 561.9021. Anal. Calcd for $C_{20}H_{18}O_3S_8$: C, 42.70; H, 3.20. Found: C, 42.80; H, 3.29.

3.19. X-ray structure determination

Specimen of suitable quality and size of **13** was mounted on a fibreglass and used for intensity data collection. The X-ray diffraction data of **13** was collected using a CAD4 single crystal diffractometer. Graphite monochromated Mo Kα radiation (λ=0.71073 Å) was generated at 50 kV and 40 mA. The data sets were corrected for Lorentz and polarization effects. Psi-scan absorption correction was applied for **13**. The structure was solved by direct methods program SHELXS-97[23] and refined by the full-matrix least-squares method based on F^2 using SHELXL-97.[24] The structure solution revealed disorder in the side chains connected to the C19 atom. To prevent abnormal bond lengths and angles, geometric restraints were applied to the neighbouring atomic distances. Two components of the disordered atoms were located in difference maps. The disordered atoms were refined isotropically and the occupation factors converged at 0.702(12) and 0.298(12) for each component. The hydrogen atoms were positioned geometrically and refined using a riding model. The calculations were carried out with the PLATON[25] and PARST97.[26]

3.20. Crystal data and refinement parameters

$C_{33}H_{10}O_6S_8$, Triclinic, $P\bar{1}$, a=9.375(2) Å, b=13.122(3) Å, c=15.918(5) Å, α=72.06(2)°, β=86.80(3)°, γ=83.294(17)°, volume=1849.8(8) Å^3, Z=2, D_c=1.363 Mg m^{-3}, μ=0.523 mm^{-1}, θ_{max}=26.3°, 7759 measured and 3026 unique (R_{int}=0.0578) reflections, $R1$ (obsd)=0.1001 and $wR2$ (all data)=0.357, ρ_{max}/ρ_{min}=1.901/−1.032 e Å^{-3}. CCDC reference number: 266306.

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