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Synthesis of 4,6-Disubstituted Thianthrenes; X-Ray Crystal Structures of 4,6-diphenylthianthrene and 1-tetrathiafulvalenylnaphthalene

James M. Lovell, Roy L. Beddoes, and John A. Joule*

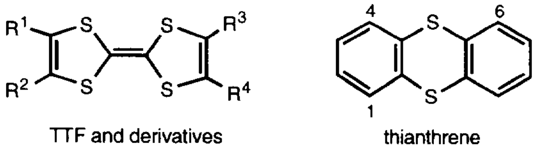
Chemistry Department, University of Manchester, Manchester M13 9PL, U. K.

Key Words: thianthrene 5-oxide lithiation; *ipso*-displacement of aromatic silicon with Br; Pd(0)-coupling.

Abstract: Lithiation of thianthrene 5-oxide, then trapping with chlorotrimethylsilane gave 4-mono-, 4,6-di-, **4b**, and 4,6,9-tri-TMS derivatives. Reduction of oxide **4b** to the thianthrene followed by reaction with bromine gave 4,6-dibromothianthrene which coupled smoothly with phenylboronic acid producing 4,6-diphenylthianthrene, **5c**. The crystal structures of **5c** and of 4-(1-naphthalenyl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole were determined.

INTRODUCTION

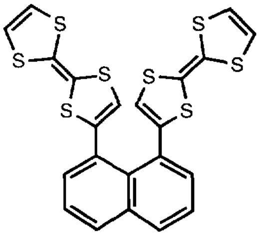
Tetrathiafulvalene (TTF itself has $R^1=R^2=R^3=R^4=H$) and structural analogues thereof play a central role in the structures of many 'organic metals'. In such materials, molecules of TTF (or its derivatives) align themselves in the crystalline state to allow intermolecule electronic communication and thence conduction after oxidation ('doping').[1] Many of the more exciting derivatives have further sulfur, or selenium, atoms[2] to facilitate multi-dimensional electronic communication. The utility of TTF derivatives lies in the ability of the nucleus to be easily oxidised, *i.e.* to lose an electron, generating a delocalised radical-cation, and thence the possibility for intermolecular electron hopping from a non-oxidised molecule to an adjacent radical cation.



TTF and derivatives

thianthrene

In conducting organic crystals, molecules are arranged according to the imperfectly understood, and certainly unpredictable, rules of crystal packing. We are engaged on a programme of synthesis aimed at the production of molecules in which, for the generation of situations suitable for electronic interaction, less reliance is placed on these unpredictable factors, *i.e.* where, in the molecular architecture of the substance, there are already small distances between components and thus the opportunity for electronic interaction[3] in more than one dimension.[2a,4] The thianthrene[5] system seems to us an ideal building block for such substances, since it has two sulfur atoms and is known to undergo an easy one-electron oxidation to generate the thianthrene radical cation chemically,[6] electrochemically,[7] or photochemically.[8] We sought means for the installation of other sulfur-containing units – for example thianthrenes or tetrathiafulvalenes – at positions on the thianthrene nucleus which are sufficiently close that we could envisage intramolecular electronic communication – our target was 4,6-disubstitution. Whilst our work was in progress, the syntheses of naphthalene and 1,6-methano[10]annulene derivatives (**1**) and (**2**) carrying TTF units at *peri*-type positions were reported;[9] naphthalenes with other aromatic units at 1,8-positions had been described previously[10] and the orientations of those substituents, in the crystalline state of some of these, determined.[10a,c,e] In each of these cases the two aromatic substituent rings were approximately parallel to each other and subtended angles of 63°,[10a] 57°,[10c] and 70°[10e] respectively to the planar naphthalene. Recently, the synthesis of 1,8-bis[(9-anthryl)methoxy]-9,10-anthraquinone (**3**) has been described; this molecule was shown to co-crystallise with tetracyanoquinodimethane (TCNQ) in such a way as to place a molecule of TCNQ between the two aromatic donors on the pillaring anthraquinone.[11]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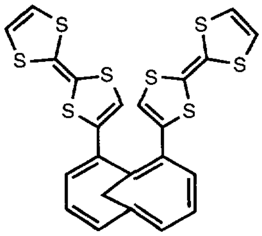
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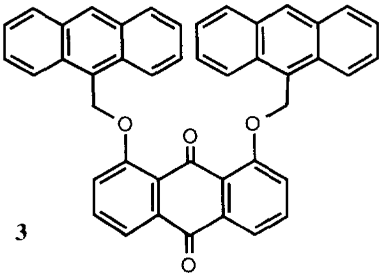
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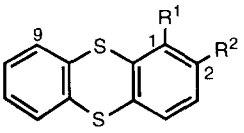
RESULTS

The thianthrene substitution pattern chosen as a target – 4,6-disubstitution – is not easy to achieve. Lithiation adjacent to ring sulfur has been long known,[12] but our attempts to force disubstitution, on either side of the same ring heteroatom, were unsuccessful. It seemed possible that the influence of a suitable[13] 1-substituent might direct lithiation to the 9-position. Thianthren-1-ylcarboxylic acid (**4a**)[12] was converted *via* its acid chloride (**4b**) into the *N,N*-diethylamide (**4c**); unfortunately, lithiation of (**4c**) and quenching produced the undesired result – 2-trimethylsilyl derivative (**4d**) cleanly. After we had completed this study, it was reported[14] that lithiation of a dibenzothiophen carrying a 1-*t*-butoxycarbamate comparably proceeded at C-2, though a second paper described[15] the (predominant) C-8-lithiation of 1-formyldibenzofuran *via* assistance from an aldehyde/dimethylamine adduct.

4	R^1	R^2
a	CO_2H	H
b	CO.Cl	H
c	$CO.NEt_2$	H
d	$CO.NEt_2$	$SiMe_3$

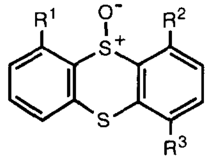


4,6-Dilithiation of thianthrene 5,5-dioxide allowed the synthesis of the corresponding 4,6-diacid,[16] but the use of such a strategy appeared unsuitable for our purposes since the methods available for subsequent double deoxygenation would not have been compatible with our aims. We were encouraged by a report[17] of the dilithiation of thianthrene 5-oxide, in which subsequent reaction with disulfides, a diselenide, sulfur and chlorotrimethylsilane were reported to afford mixtures of 4-mono- and 4,6-disubstituted thianthrene 5-oxides.

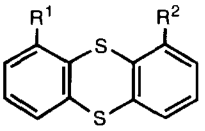
Like the sulfone, the sulfoxide unit must increase the acidity of the 4- and 6-hydrogen atoms inductively and may also assist by intramolecular co-ordination to the metal.

In our hands, and using various ratios of thianthrene 5-oxide to lithium diisopropylamide (LDA) we were also unable to obtain 4,6-disubstituted products cleanly. Our optimal conditions (2.7 mol equivalents of LDA followed by 2.7 mol equivalents of chlorotrimethylsilane) provided, after a straightforward chromatographic separation, 4-trimethylsilylthianthrene 5-oxide (**5a**) (28%), 4,6-bis(trimethylsilyl)thianthrene 5-oxide (**5b**) (41%) and 1,4,6-tris(trimethylsilyl)thianthrene 5-oxide (**5c**) (11%). Attempts to produce halogenated thianthrene 5-oxides directly, after lithiation, by reaction with iodine, 1,2-diiodoethane, or 1-iodoperfluorohexane gave moderate yields of 4-iodothianthrene 5-oxide (**5d**) but only an unworkably low yield of diiodo-derivative (**5e**).

5	R^1	R^2	R^3
a	H	$SiMe_3$	H
b	$SiMe_3$	$SiMe_3$	H
c	$SiMe_3$	$SiMe_3$	$SiMe_3$
d	I	H	H
e	I	I	H



6	R^1	R^2
a	$SiMe_3$	$SiMe_3$
b	Br	Br
c	Ph	Ph
d	TTF	TTF



Attempted replacement of the silicon substituents of sulfoxide (**5b**) with halogen failed. Reasoning that this resulted from inhibition to electrophilic addition adjacent to the sulfoxide grouping, it was removed, by reaction with acetyl chloride in the presence of potassium iodide, giving (**6a**) in high yield.[18] Reaction of bis(trimethylsilyl)thianthrene (**6a**) with bromine at room temperature now provided the desired 4,6-dibromothianthrene (**6b**) in high yield.

The coupling of dihalide (**6b**) with phenylboronic acid, as a model, proceeded in good yield producing 4,6-diphenylthianthrene (**6c**) using tetrakis(triphenylphosphine)palladium(0) as a catalyst. Crystals were produced and an X-ray analysis carried out which showed, as illustrated in the two alternative perspective Chem3D™ drawings in Figure 1, and in the projection of crystal packing, Figure 2, that the two phenyl substituents are each at approximately the same angle (54.6° and 56.6°) to the benzene rings to which they are attached, and consequently make an angle of 55.8° with respect to each other. The 'butterfly' angle between the two benzene rings ('wings') of the thianthrene is 124.7° which can be compared with typical values[5,19] of 128-130° for simpler thianthrenes.

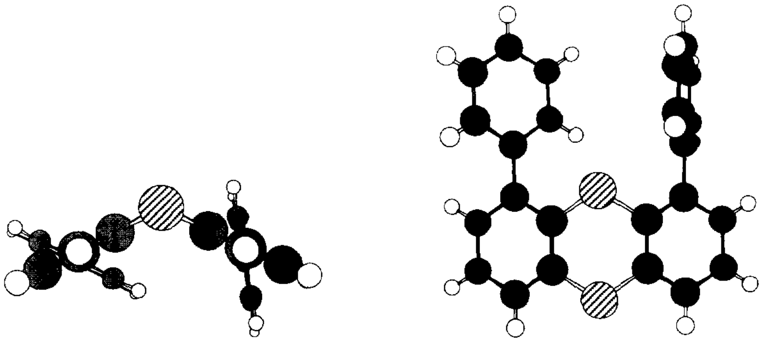


Figure 1 Chem3D™ drawings of 4,6-diphenylthianthrene (**6c**)

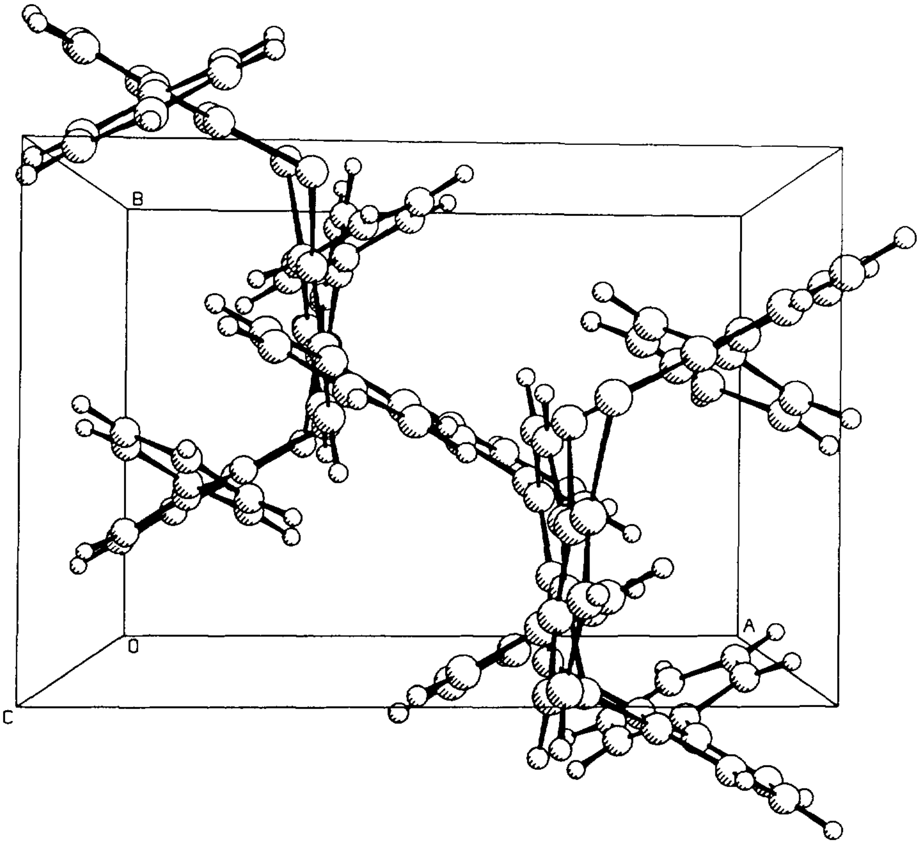


Figure 2 Molecular packing in crystal of 4,6-diphenylthianthrene (**6c**).

The coupling of 4,6-dibromothianthrene with tributylstannyltetrathiafulvalene, prepared by lithiation then reaction with chlorotributylstannane, proceeded using catalysis with tetrakis(triphenylphosphine)palladium(0) but only in modest yield producing (**6d**). Unfortunately suitable crystals could not be produced and it is therefore not possible to comment on the orientation of the two TTF units on the pillaring thianthrene. The results of electrochemical studies on (**6d**) will be reported elsewhere. However, for comparison, we have determined the crystal structure (Figure 2) of 4-(1-naphthalenyl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole (1-tetrathiafulvalenylnaphthalene) (**7**),[9] prepared by coupling 1-bromonaphthalene with tributylstannyl-tetrathiafulvalene using tetrakis(triphenylphosphine)palladium(0) as catalyst.

The angle between the two ring systems in 1-tetrathiafulvalenylnaphthalene is 49.4°. It is interesting that the TTF unit is substantially bowed: about the S-S axes, for the two rings, the departures from planarity are 13.8° and 12.5° respectively, where the anticipated geometry[4b,20] for such a unit is planar. The explanation for this effect must derive either from an intramolecular electronic interaction between the heterocyclic system and its attached naphthalene or *via* intermolecular interactions in the crystal lattice. The relative dispositions of the two ring systems make the first of these suggestions untenable, however the observed packing may provide support for the second postulate (Figure 3 shows a projection in the AB plane). Table 1 shows the nearest approaches (<3.7Å) of the sulfur atoms of a TTF unit to carbons of naphthalene and TTF units close by in the lattice. The

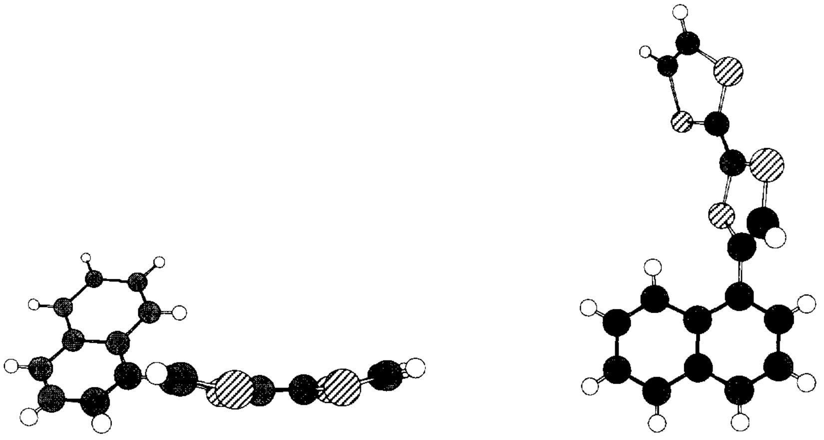
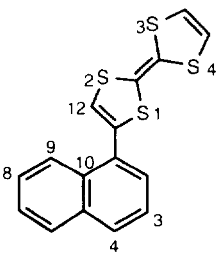


Figure 3 Chem3D™ drawings of 1-tetrathiafulvalenylnaphthalene (**7**)

closest intermolecular S-S approach is 4.03. TTF units have been incorporated into cyclophanes where the molecular geometry demands distortion from planarity – departures of as much as 50° were found.[4b] Departure from TTF planarity in mono-substituted derivatives has also been noted before[21] – in TTFs carrying thioester and thioamide substitutents the pairs of rings showed fold angles of 3.1, 4.9; 1.2, 9.3; 6, 12; and 22.8° and 13.9°, with the greatest deviation from planarity displayed by a ring carrying C(S)NHMe. It seems that a TTF moiety in a molecule in the crystalline state is relatively easily distorted from planarity, according to other influences in the lattice including the possibility for the formation of hydrogen bonds and Van der Waals interactions.

atom	atom	distance (Å)
S-1	C-3	3.554
S-2	C-4'	3.615
S-3	C-8'	3.593
S-4	C-9"	3.553
S-4	C-10"	3.655
S-4	C-12"	3.596

Table 1 Close intermolecular approaches (< 3.7Å) between S atoms of a particular molecule and C atoms in nearby molecules in crystals of 1-tetrathiafulvalenylnaphthalene (numbering shown on **7**) (primes indicate different molecules)



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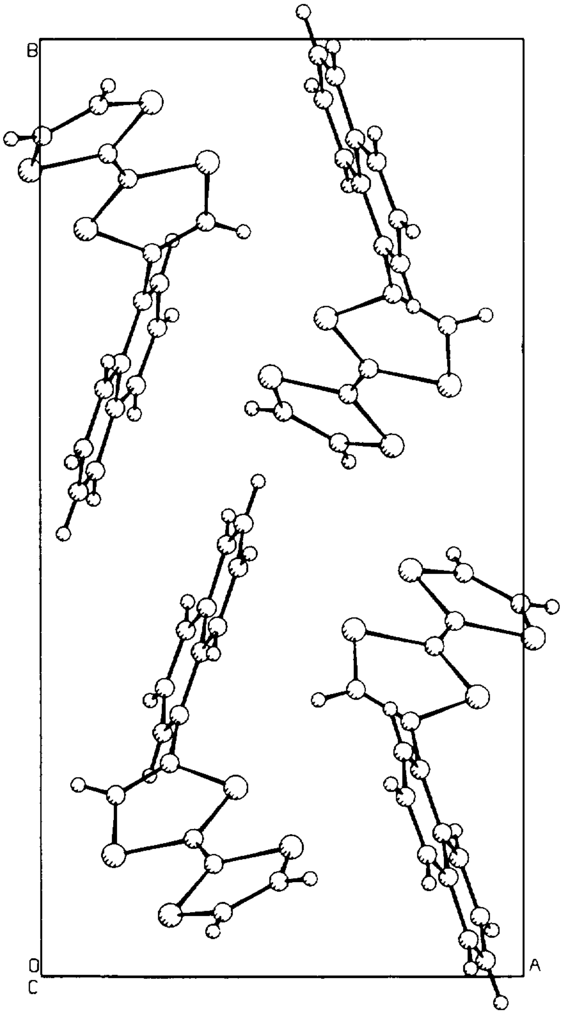

Figure 4 Projection of packing in crystal of 1-tetrathiafulvalenylnaphthalene (**7**) on the AB plane

ACKNOWLEDGEMENTS

We thank the University of Manchester for Duncan Campbell and Sir Samuel Hall studentships (JML) and the SERC which provided support towards the cost of consumables for part of this work.

EXPERIMENTAL

Thianthren-1-ylcarbonyl chloride (4b) and *N,N*-diethylthianthren-1-ylcarboxamide (4c). A mixture of thianthren-1-ylcarboxylic acid[12] (**4a**) (100 mg, 0.385 mmol) and $SOCl_2$ (5 ml) was heated at reflux for 1 h. After cooling to r.t. the solvent was removed *in vacuo* to give thianthren-1-ylcarbonyl chloride, **4b**, as a yellow crystalline solid (96 mg, 83%) which was used without further purification, m.p. 110-111 °C, ν_{max} (film): 3055, 1748, 1390, 1222, 1185, 930, 748 and 691 cm^{-1}; λ_{max} (log ε_{max}) (DCM) 252 (4.43), 292 (3.67) and 364 (3.30) nm; δ_H (300 MHz, $CDCl_3$): 7.26-7.60 (5H, m, Ar-H), 7.75 (1H, d, *J* 7.8, 4-H), and 8.14 (1H, d, *J* 7.9, 2-H); δ_C (75 MHz, $CDCl_3$): 166.05, 140.32, 136.76, 135.42, 134.37, 134.16, 133.91, 132.02, 129.17, 128.61, 128.53, 128.15, and 126.87; *m/z* (e.i.) 278 and 280 (M^+, 32, 15%), 243 (35%), and 50 (100%). Accurate m.s.: $C_{13}H_7{}^{35}ClOS_2$ requires *m/z* 277.9627, peak at *m/z* 277.9626. To a stirred solution of thianthren-1ylcarbonyl chloride (**4b**) (96 mg, 0.345 mmol) in CH_2Cl_2 (10 ml) at room temperature was added Et_2NH (5 ml). Stirring was continued for a further 1 h and then the solution was shaken with aq HCl (3M), aq sat $NaHCO_3$ then dried ($MgSO_4$). Concentration of the organic phase gave *N,N*-diethylthianthren-1-ylcarboxamide, (**4c**) (88 mg, 82%), of sufficient purity for further reactions, m.p. 105-107 °C, ν_{max} (film): 3500, 2974, 2933, 1631, 1428, 1289, and 750 cm^{-1}; λ_{max} (log ε_{max}) (DCM) 260 (4.54) nm; δ_H (300 MHz, $CDCl_3$): 1.05 (3H, t, *J* 7.1, CH_3), 1.39 (3H, t, *J* 7.1, CH_3), 3.15 (2H, m, CH_2), 3.68 (2H, m, CH_2), 7.20-7.35 (4H, m, Ar-H), and 7.49-7.54 (3H, m, Ar-H); δ_C (75 MHz, $CDCl_3$): 168.42, 137.64, 136.89, 135.97, 134.90, 132.76, 129.02, 128.84, 128.74, 127.93, 127.84, 127.48, 125.17, 42.87, 39.05, 14.13, and 12.77; *m/z* (c.i.) 333 (MNH_4^+, 18%), 316 (MH^+, 100%), and 74 (30%). Accurate m.s.: $C_{17}H_{17}NOS_2$ requires *m/z* 315.0752, peak at *m/z* 315.0750.

2-Trimethylsilyl-*N,N*-diethylthianthren-1-ylcarboxamide (4d). To a stirred solution of *N,N*-diethylthianthren-1-yl-carboxamide (**4c**) (55 mg, 0.175 mmol) and Me_3SiCl (27 µl, 0.213 mmol) in THF (10 ml) at -78 °C under an atmosphere of argon was added *t*-butyllithium (0.12 ml, 1.7M solution in pentane, 0.21 mmol). The clear colourless solution was allowed to warm to r.t. and quenched with saturated aq NH_4Cl (10 ml). Solvent was removed *in vacuo* and the residue was extracted with Et_2O (2 x 10 ml). The ethereal extracts were combined and washed with H_2O (1 x 10 ml) and brine (1 x 10 ml), dried ($MgSO_4$) and solvent removed *in vacuo*. Chromatography on SiO_2 with EtOAc-light petroleum (b.p. 40-60 °C) (20 : 80) as the eluent yielded the title compound (**4d**) as a clear colourless oil (47 mg, 70%), ν_{max} (film): 2973, 2935, 2898, 2876, 1632, 1451, 1281, 1248, 1101, 856, 843, and 751 cm^{-1}; λ_{max} (log ε_{max}) (DCM) 264 (4.60) nm; δ_H (200 MHz, $CDCl_3$): 0.26 (9H, s, $SiMe_3$), 1.01 (3H, t, *J* 7.2, CH_3), 1.41 (3H, t, *J* 7.2, CH_3), 2.90-3.25 (2H, m, 1 x NCH_2CH_3) 3.30-3.50 (1H, m, 1 x $NCHHCH_3$), 3.75-3.95 (1H, m, 1 x $NCHHCH_3$), 7.18-7.29 (2H, m, Ar-H), and 7.38-7.50 (4H, m, Ar-H); δ_C (50 MHz, $CDCl_3$): 169.41, 142.77, 137.89, 137.26, 136.50, 135.61, 134.47, 132.60, 129.54, 129.07, 128.33, 128.23, 43.73, 39.41, 14.09, 12.97, and 0.38; *m/z* (e.i.) 387 (M^+, 40%), 372 (100%) and 49 (67%); Accurate m.s.: $C_{20}H_{25}NOSiS_2$ requires *m/z* 387.1147, peak at *m/z* 387.1143.

4,6-Bis(trimethylsilyl)thianthrene 5-oxide (5b), 4-trimethylsilylthianthrene 5-oxide (5d), and 4,6,9-tris(trimethylsilyl)thianthrene 5-oxide (5c). To a stirred solution of thianthrene-5-oxide (250 mg, 1.08 mmol) in THF (10 ml) was added lithium diisopropylamide mono(tetrahydrofuran) (1.80 ml of a 1.5M solution in C_6H_{12}, 2.70 mmol) dropwise at -78 °C under an atmosphere of argon. After stirring for 3 hours at

-78 °C, Me_3SiCl (0.342 ml, 2.70 mmol) was added and the reaction was allowed to warm to room temperature overnight then treated with water (5 ml). The solvent was removed *in vacuo* and the residue was extracted with Et_2O (3 x 10 ml). The combined organic extracts were washed with water (2 x 10 ml), brine (10 ml), dried ($MgSO_4$), and solvent removed *in vacuo*. Flash chromatography on SiO_2 with EtOAc-light petroleum (b.p. 40-60 °C) (25 : 75) as the eluent yielded firstly 1,4,6-tris(trimethylsilyl)thianthrene 5-oxide (**5c**) (54 mg, 11 %), as a colourless oil, R_f 0.53, ν_{max} (film): 2954, 1408, 1324, 1250, 1190, 1132, 1033, 843, 760, and 692 cm^{-1}; λ_{max} (log ε_{max}) (DCM) 248 (4.31), 282 (3.89), and 338 (3.60) nm; δ_H (300 MHz, $CDCl_3$): 0.54 (9H, s, $SiMe_3$), 0.63 (18H, s, 2 x $SiMe_3$), 7.47 (1H, dd, *J* 7.55 and 7.6, 8-H), 7.67 (2H, s, 2-H and 3-H), 7.69 (1H, dd, *J* 7.6 and 1.2, 9-H), and 7.80 (1H, dd, *J* 7.7 and 1.2, 7-H); δ_C (75 MHz, $CDCl_3$): 145.17, 144.07, 141.69, 141.62, 140.35, 136.18, 134.70, 134.40, 133.49, 130.11, 129.82, 1.57, and -0.01; *m/z* (e.i.) 448 (M^+, 7%), 433 (100%), and 73 (92%); *m/z* (c.i.) 449 (MH^+, 77%) and 90 (100%); Accurate m.s.: $C_{21}H_{32}OS_2Si_3$ requires *m/z* 448.1202, peak at *m/z* 448.1191; then 4-trimethylsilylthianthrene 5-oxide (**5a**) (93 mg, 28 %), as a colourless oil, R_f 0.40, : λ_{max} (log ε_{max}) (DCM) 244 (4.25), 288 (3.71), and 328 (3.37) nm; ν_{max} (KBr): 3056, 1437, 1250, 1118, 1078, 1058, 1037, 844, and 755 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.52 (9H, s, $SiMe_3$), 7.37-7.66 (5H, m, Ar-H), 7.60-7.70 (1H, m, Ar-H), and 7.90-8.00 (1H, m, Ar-H); *m/z* (e.i.) 304 (M^+, 5%) and 289 (100%); *m/z* (c.i.) 322 (MNH_4^+, 10%) and 305 (MH^+, 100%); Accurate m.s.: $C_{15}H_{16}OS_2Si$ requires *m/z* 304.0412, peak at *m/z* 304.0413; and finally 4,6-bis(trimethylsilyl)thianthrene 5-oxide (**5b**) (166 mg, 41 %) as a white crystalline solid, R_f 0.21, m.p. 213-214 °C, λ_{max} (log ε_{max}) (EtOH) 246 (4.10), 296 (3.53), and 338 (3.43) nm; ν_{max} (KBr): 2952, 1547, 1364, 1247, 1023, 845, 786, and 760 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 0.60 (18H, s, 2 x $Si(CH_3)_3$), 7.48 (2H, dd, *J* 7.56 and 7.6, 2-H and 8-H), 7.67 (2H, dd, *J* 7.4 and 1.2, 1-H and 9-H), and 7.76 (2H, dd, *J* 7.8 and 1.2, 3-H and 7-H); δ_C (200 MHz, $CDCl_3$): 144.40, 141.12, 134.22, 134.00, 130.14, 129.55, 1.46; *m/z* (c.i.) 394 (MNH_4^+, 2%) and 377 (MH^+, 100%); Elemental analysis: C, 57.5; H, 6.5; S 17.3% Calc. for $C_{18}H_{24}OS_2Si_2$, C, 57.4; H, 6.4; S, 17.0%.

4,6-Bis(trimethylsilyl)thianthrene (6a). To a stirred solution of 4,6-bis(trimethylsilyl)thianthrene 5-oxide, **5b** (1.67 g, 4.44 mmol) and AcCl (3.80 ml, 53.2 mmol) in Me_2CO (75 ml), KI (17.00 g, 102 mmol) was added. After stirring at r.t. for 10 min, solvent was removed *in vacuo* and the residue was extracted with Et_2O (2 x 20 ml). The extract was washed with H_2O (2 x 20 ml) and aq. $Na_2S_2O_3$ solution (1M, 1 x 20 ml), dried ($MgSO_4$), and solvent removed *in vacuo* to afford 4,6-bis(trimethylsilyl)thianthrene (**6a**) (1.50 g, 94%) which was used without further purification. An analytical sample was crystallized from EtOH, m.p. 95-96 °C, λ_{max} (log ε_{max}) (EtOH) 266 (4.45) nm; ν_{max} (KBr): 2957, 1364, 1249, 1128, 840, and 756 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 0.51 (18H, s, 2 x $Si(CH_3)_3$), 7.26 (2H, dd, *J* 7.6 and 7.4, 2-H and 8-H), 7.47 (2H, dd, *J* 7.4 and 1.3, 1-H and 9-H), and 7.53 (2H, dd, *J* 7.6 and 1.3, 3-H and 7-H); δ_C (75 MHz, $CDCl_3$): 142.42, 139.82, 134.35, 134.04, 129.60, 126.70, and 0.62; *m/z* (e.i.) 360 (M^+, 100%), 345 (30%), 329 (25%) 257 (20%), and 73 (48%); Accurate m.s.: $C_{18}H_{24}S_2Si_2$ requires *m/z* 360.0858, peak at *m/z* 360.0867.

4-Iodothianthrene 5-oxide (5d) and 4,6-diiodothianthrene 5-oxide (5e). To a stirred solution of thianthrene-5-oxide (500 mg, 2.16 mmol) in THF (10 ml) at -78 °C under an atmosphere of argon was added, dropwise over 5 min, lithium diisopropylamide mono(tetrahydrofuran) (3.60 ml of a 1.5M solution in C_6H_{12}, 5.40 mmol). Once addition was complete, stirring at -78 °C was continued for a further 3 h. Perfluorohexyl iodide (1.17 ml, 5.40 mmol) was then added dropwise and the reaction was allowed to warm to room temperature overnight. Removal of solvent *in vacuo* gave a brown oil. Chromatography on SiO_2 with EtOAc-light petroleum (b.p. 40-60 °C) (4 : 6) as the eluent yielded a mixture of 4-iodothianthrene 5-oxide and 4,6-diiodothianthrene 5-oxide which were separated by HPLC using C_6H_{14}-EtOAc (2 : 1) as the eluent to give, in the order collected, 4,6-diiodothianthrene 5-oxide (**5e**) (63 mg, 6%), m.p. 248-250 °C, λ_{max} (log ε_{max}) (DCM) 250 (4.15), 304 (3.68), and 342 (3.45) nm; ν_{max} (film): 1545, 1424, 1191, 1025, 790, and 778 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 7.18 (2H, dd, *J* 7.9 and 7.8, 2-H and 8-H), 7.78 (2H, dd, *J* 7.9 and 1.1, 1-H and 9-H), and 7.92 (2H, dd, *J* 7.8 and 1.1, 3-H and 7-H); *m/z* (c.i.) 502 (MNH_4^+, 10%), 485 (MH^+, 15%), and 160 (100%); Accurate m.s.: $C_{12}H_6I_2OS_2$ requires *m/z* 483.7950, peak at *m/z* 483.7944; then 4-iodothianthrene 5-oxide (**5d**) (409 mg, 53%), m.p. 189-190 °C, λ_{max} (log ε_{max}) (DCM) 248 (4.37), 294 (3.89), and 334 (3.65) nm; ν_{max} (KBr): 3045, 1559, 1422, 1054, 1031, and 754 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 7.14 (1H, dd, *J* 7.9 and 7.8, 2-H), 7.44-7.60 (2H, m, Ar-H), 7.70-7.81 (2H, m, Ar-H), 7.91 (1H, dd, *J* 7.8 and 1.0, 1-H), and 8.01-8.08 (1H, m, 3-H); *m/z* (c.i.) 376 (MNH_4^+, 10%), 359 (MH^+, 100%), 310 (20%), and 233 (25%); Accurate m.s.: $C_{12}H_7IOS_2$ requires *m/z* 357.8983, peak at *m/z* 357.8979.

4,6-Dibromothianthrene (6b). Bromine (1.0 ml, 19.5 mmol) was added to a solution of 4,6-bis(trimethylsilyl)thianthrene (**6a**) (700 mg, 1.94 mmol) in CCl_4 (15 ml) and the resulting red solution was stirred at r.t. for 2.5 h. Solvent and excess Br_2 were removed *in vacuo* and the residue was crystallized from PhMe/C_6H_{14} to give pure 4,6-dibromothianthrene (**6b**) (520 mg, 72%), as pale tan needles, m.p. 181-183 °C, λ_{max} (log ε_{max}) (DCM) 250 (4.27) and 268 (4.32) nm; ν_{max} (film): 1551, 1386, 782, and 767 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 7.14 (2H, dd, *J* 7.8 and 7.8, 2-H and 8-H), 7.45 (2H, dd, *J* 7.8 and 1.1, 1-H and 9-H), and 7.57 (2H, dd, *J* 7.8 and 1.1, 3-H and 7-H); δ_C (75 MHz, $CDCl_3$): 123.35, 127.43, 128.74, 131.94, 136.42, and 136.64; *m/z* (e.i.) 372, 374, 376 (M^+, 35, 65, 40%), and 214 (100%); Elemental analysis: C, 38.7; H, 1.8; Br, 42.2; S, 17.0% Calc. for $C_{12}H_6Br_2S_2$: C, 38.5; H, 1.6; Br, 42.7; S, 17.1%.

4,6-Diphenylthianthrene (6c). 4,6-Dibromothianthrene (**6b**) (100 mg, 0.267 mmol) and $(Ph_3P)_4Pd$ (19 mg, 0.016 mmol) were stirred together in $(CH_2OMe)_2$ (10 ml) under N_2 for 10 min at r.t. Phenylboronic acid (98 mg, 0.802 mmol) was added, immediately followed by aq. $NaHCO_3$ (1M, 1.60 ml, 1.6 mmol). The reaction mixture was heated at reflux for 4 h, with vigorous stirring under N_2. Solvent was removed *in vacuo*, H_2O (15 ml) was added and the residue was extracted with Et_2O (3 x 10 ml). The combined extracts were washed with H_2O, brine then dried ($MgSO_4$). After removal of the solvent *in vacuo*, the product was purified by flash chromatography on SiO_2 with C_6H_{14} as the eluent to yield 4,6-diphenylthianthrene (**6c**) (67 mg, 68%) as a white crystalline solid, m.p. 176-177 °C, λ_{max} (log ε_{max}) (DCM) 240 (4.24) and 260 (4.46) nm; ν_{max} (film): 3050, 2360, 1443, 1382, 1101, 754, and 697 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 7.18-7.39 (14H, m, Ar-H), and 7.62 (2H, dd, *J* 7.2 and 1.8, 1-H and 9-H); δ_C (75 MHz, $CDCl_3$): 142.96, 139.93, 137.88, 135.08, 133.90, 133.64, 129.46, 129.09, 128.72, 128.56, 128.46, 128.14, 128.00, 127.80, 127.44, and 127.34; *m/z* (c.i.) 386 (MNH_4^+, 100%) and 369 (MH^+, 40%); Accurate m.s.: $C_{24}H_{16}S_2$ requires *m/z* 368.0693, peak at *m/z* 368.0694.

A colourless tabular, monoclinic crystal was taken for X-ray analysis, dimensions 0.25 x 0.55 x 0.60 mm. 17 reflections for unit cell determination ($78.77 < 2\theta < 79.78°$). Lattice parameters a = 11.254 (2)Å, b = 7.7204 (6)Å, c = 20.950 (2)Å, β = 97.51 (1)°, V = 1804.7 (4)$Å^3$. Space group $P2_1/c$ (#14), Z value = 4, D_{calc}

= 1.356 g/cm^3, F_{000} = 768, $\mu_{(CuK\alpha)}$ = 26.33 cm^{-1}, temperature = 27 ± 1 °C. 3081 reflections measured, 2917 of which were unique. Final R = 0.041, R_w = 0.057.[22,23]

Tributyltetrathiafulvalenylstannane. To a stirred solution of tetrathiafulvalene (250 mg, 1.22 mmol) in Et_2O (20 ml) at -78 °C under an atmosphere of argon was added lithium diisopropylamide mono-tetrahydrofuran (0.90 ml of a 1.6M solution in C_6H_{12}, 1.35 mmol) dropwise over a period of 5 min. After stirring for a further 30 min, Bu_3SnCl (0.36 ml, 1.35 mmol) was added dropwise to the yellow slurry. The resulting clear orange solution was stirred for a further 2 h at -78 °C and 1 h at r.t. before quenching with saturated aq. NH_4Cl (10 ml). The aqueous layer was separated and the ethereal phase was washed with H_2O (3 x 10 ml), dried ($MgSO_4$), and solvent removed *in vacuo*. The crude product was dissolved in C_6H_{14} (20 ml) and washed with MeCN (3 x 15 ml) to give tributylstannyltetrathiafulvalene (262 mg, 43 %), as an orange oil of sufficient purity to be used in later reactions, λ_{max} (log ε_{max}) (EtOH) 308 (4.03), 320 (4.02), 368 (3.19), and 448 (2.57) nm; ν_{max} (film): 2956, 2925, 2852, 1462, 1377, 1075, 861, and 796 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 0.97-1.80 (27H, m, $SnBu_3$), 6.54 (1H, s, 5-H) and 6.66 (2H, d, *J* 0.82, 4'-H and 5'-H); δ_C (75 MHz, $CDCl_3$): 123.92, 120.28, 28.52, 27.66, 13.74, and 11.40; *m/z* (e.i.) 494 ($^{120}M^+$, 8%), 203 (20%), 177 (15%), 146 (100%), 103 (22%), and 57; Accurate m.s.: $C_{18}H_{30}S_4{}^{120}Sn$ requires *m/z* 494.0252, peak at *m/z* 494.0240.

4,6-Bis(tetrathiafulvalenyl)thianthrene (6d). 4,6-Dibromothianthrene (**6b**) (100 mg, 0.267 mmol) and $(Ph_3P)_4Pd$ (62 mg, 0.054 mmol) were stirred together in PhMe (10 ml) for 10 min at r.t. under an atmosphere of argon. A solution of tributylstannyltetrathiafulvalene (554 mg, 1.12 mmol) in PhMe (10 ml) was then added and the solution was heated at reflux for 5 h. After cooling, the reaction mixture was filtered through a short column of SiO_2 using PhMe as eluent. Removal of solvent *in vacuo* yielded an orange solid that was purified by chromatography on SiO_2 with EtOAc-light petroleum (b.p. 40-60 °C) (20 : 80) as the eluent yielding 4,6-bis(tetrathiafulvalenyl)thianthrene (**6d**) (27 mg, 16%) as an orange solid, m.p. 214-216 °C, λ_{max} (log ε_{max}) (DCM) 272 (4.30), 310 (4.27), 322 (4.27), and 402 (3.51) nm; ν_{max} (film): 2955, 1110, 1092, and 802 cm^{-1}; δ_H (300 MHz, d_6-DMSO): 6.77 (2H, d, *J* 6.4, tetrathiafulvalenyl-4'(5')-H), 6.86 (2H, d, *J* 6.4, tetrathiafulvalenyl-5'(4')-H), 7.04 (2H, s, tetrathiafulvalenyl-5-H), 7.52 (2H, dd, *J* 7.4 and 7.6, thianthrenyl-2- and -8-H), 7.58 (2H, dd, *J* 7.6 and 1.6, thianthrenyl-5- and -7-H), and 7.79 (2H, dd, *J* 7.4 and 1.6, thianthrenyl-1- and -9-H); δ_C (75 MHz, d_6-DMSO): 136.95, 134.25, 133.10, 130.98, 129.57, 128.56, 121.28, 120.10, 119.95, 111.38, and 108.96; *m/z* (f.a.b.) 620 (M^+); Accurate m.s.: $C_{24}H_{12}S_{10}$ requires *m/z* 619.8146, peak at *m/z* 619.8138.

4-(1-Naphthalenyl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole (7). 1-Bromonaphthalene (161 mg, 0.78 mmol) and $(Ph_3P)_4Pd$ (90 mg, 0.078 mmol) were stirred together in PhMe (10 ml) for 10 minutes at r.t. under an atmosphere of argon. A solution of tributylstannyltetrathiafulvalene (383 mg, 0.78 mmol) in PhMe (10 ml) was then added and the solution was heated at reflux for 3 h. After cooling, the reaction mixture was washed with H_2O (3 x 10 ml), dried ($MgSO_4$) and solvent removed *in vacuo* to give the crude product. Purification by flash chromatography on alumina with PhMe-C_6H_{14} (1:9) as the eluent yielded 4-(1-naphthalenyl)-2-(1,3-dithiol-2-ylidene)-1,3-dithiole (**7**) (69 mg, 27%) as an orange solid, m.p. 120-121 °C, λ_{max} (log ε_{max}) (DCM) 269 (4.53), 320 (4.34), and 417 (3.61) nm; ν_{max} (film): 3062, 2357, 796, 773, and 656 cm^{-1}; δ_H (200 MHz, $CDCl_3$): 6.34 (2H, s, 4'- and 5'-H), 6.53 (1H, s, 5-H), 7.22-7.30 (4H, m, Ar-H), and 7.41-7.54 (3H, m, Ar-

H); *m/z* (e.i.) 330 (M^+, 100%) and 152 (50%); *m/z* (c.i.) 331 (MH^+, 100%); Accurate m.s.: $C_{16}H_{10}S_4$ requires *m/z* 329.9665, peak at *m/z* 329.9675.

The sample examined by X-ray analysis was an orange tabular orthorhombic crystal, dimensions 0.13 x 0.26 x 0.55 mm. 15 reflections for unit cell determination ($76.61 < 2\theta < 79.77^\circ$). Lattice parameters a = 10.058 (1)Å, b = 19.470 (6)Å, c = 7.422 (1)Å, V = 1453.6 (5)$Å^3$. Space group $P2_12_12_1$ (#19), Z value = 4, D_{calc} = 1.510 g/cm^3, F_{000} = 680, $\mu_{(CuK\alpha)}$ = 57.94 cm^{-1}, temperature = 22 ± 1 °C. 1302 reflections collected. Final R = 0.046, R_w = 0.060.[22,23]

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22 The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

23 Supplementary data available: tables of positional parameters, bond lengths, and bond angles.

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