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Thiaheterohelicenes 1. Synthesis of Unsubstituted Thia[5]-, [9]- and [13]heterohelicenes

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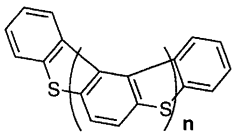
The unsubstituted thiaheterohelicenes, 5,8-dithia[5]helicene, **1**, 5,8,11,14-tetrathia[9]helicene, **2**, and 5,8,11,14,17,20-hexathia[13]helicene, **3**, have been prepared. The key reaction was the oxidative photolysis of 1,2-diaryl-substituted ethenes which were prepared by Wittig–Horner or McMurry reactions.

In order to investigate the donor properties of a series of thiahelicenes[1] and derived conducting solids[2] we have prepared the unsubstituted thiaheterohelicenes, **1–3** depicted in Fig. 1.



1 : n = 1
2 : n = 3
3 : n = 5

Fig. 1.

We have made extensive use of the classical routes to these structures as developed by Wynberg.[3–5] In some cases we investigated several strategies in order to obtain the desired structures. All helicenes reported are 'benzene capped' in order to avoid thiophene-like polymerisation[6] of the molecules in the their use as donors. In the present work we used lithiation of the acidic 2-position of thiophenes to obtain important intermediates. Another key reaction was the 6π photocyclisation of 1,2-diarylethenes followed by *in situ* oxidation with iodine. This reaction was used to obtain the final helicenes and also to obtain several intermediates. Note that when 1,2-bis(thiophen-2-yl)ethene structures are photocyclised in this manner the problem of formation of two geometrical isomers as encountered in similar preparations of carbohelicenes[7] is avoided.

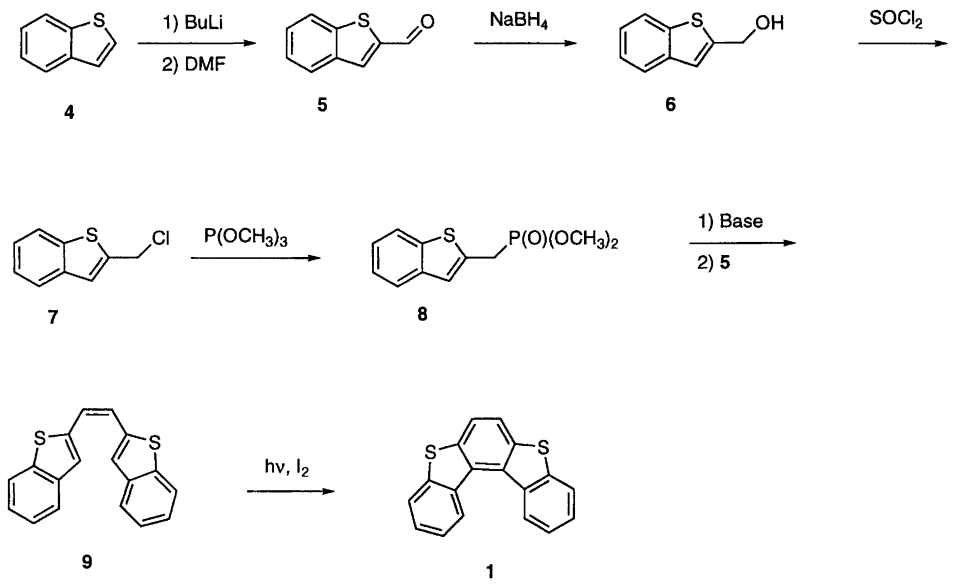
Results and discussion

5,8-Dithia[5]helicene, **1**, was prepared as outlined in Scheme 1.

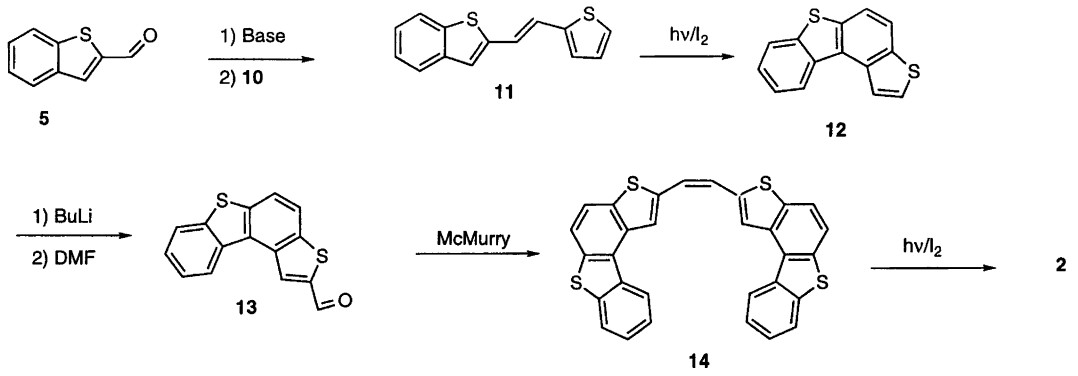
Benzo[*b*]thiophene **4** was lithiated with BuLi and then treated with DMF (*N*,*N*-dimethylformamide). After aqueous work-up the aldehyde **5** was obtained. This aldehyde was reduced to the alcohol **6**, which was treated with $SOCl_2$ to give 2-chloromethylbenzo[*b*]thiophene **7**. Compound **7** when treated with $P(OCH_3)_3$ gave the phosphonate ester **8**. Horner–Wittig coupling of compounds **5** and **8** gave the ethylene **9** as a mixture of *Z* and *E* isomers. Oxidative photolysis of the isomer mixture gave the derived 5,8-dithia[5]helicene **1**. The procedure is essentially equivalent to the reported procedure[3] but utilises Horner–Wittig coupling, which facitates the work-up procedure. The sequence serves as an example of the preparation of a [5]helicene though coupling of symmetrical ethenes.

5,8,11,14-Tetrathia[9]helicene, **2**, was prepared by two alternative procedures. We found the most efficient (see Scheme 2) to be the following: Compound **5** was Wittig–Horner coupled with the phosphonate ester **10** to give the unsymmetrical ethene **11**. Oxidative photolysis of compound **11** gave compound **12**. Lithiation of **12** and treatment with DMF followed by aqueous work-up gave the aldehyde **13**. McMurry coupling of **13** gave the symmetrical ethene **14**. Oxidative photocyclisation gave the desired helicene 5,8,11,14-tetrathia[9]helicene **2**. 5,8,11,14-Tetrathia[9]helicene, **2**, was also prepared by an alternative sequence (see Scheme 3). The phosphonate **10** and thiophene-2-carbaldehyde were coupled to give 1,2-bis(thiophen-2-yl)ethene **15**. Oxidative photolysis of **15** gave the thienobenzothiophene **16** which was dilithiated and treated with DMF. Aqueous work-up gave the dialdehyde **17**. The dialdehyde **17** was then Wittig–Horner coupled with compound **8** to yield the ethene **18**. Double oxidative photolysis gave the helicene **2**.

It was generally most advantageous to use McMurry coupling[8,9] to obtain intermediate ethenes. The helicenes obtained in this manner consist of an uneven number of condensed benzene and thiophene units. We thus pre-



Scheme 1.



Scheme 2.

ferred to couple oxo compounds directly to give a central 1,2-diaryl substituted ethene unit rather than to use sequences of Wittig–Horner reactions of two different compounds. The latter strategy normally required more steps.

The preparation of 5,8,11,14,17,20-hexathia[13]-helicene **3** illustrates this. The McMurry route (see Scheme 4) utilised, however, in the first step a Wittig–Horner coupling of **13** and **10** to yield the ethene **19**. Oxidative photolysis of **19** gave **20**, which was lithiated and treated with DMF. Aqueous work-up gave the aldehyde **27**. Compound **27** was McMurry coupled to give the ethene **22**. The final step was oxidative photolysis of compound **22** to give **3**.

Alternatively compound **13** was reduced to **23** (see Scheme 5). Compound **23** was treated with $SOCl_2$ to give **24**. Compound **24** was converted into the phosphonate ester **25** and coupled with **17** in a Wittig–Horner reaction to give **26**. Subsequent double oxidative photolysis gave the desired helicene **3**.

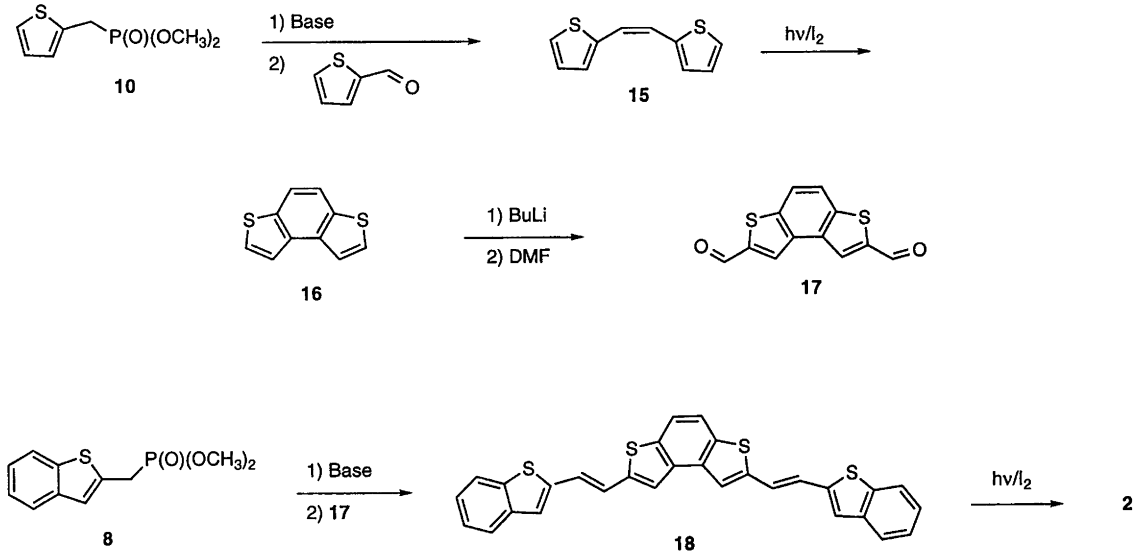
Conclusions

It was found that the most efficient strategy in the preparation of thiaheterohelicenes was to use symmetrical ethenes as intermediates. This strategy generally involves fewer steps.

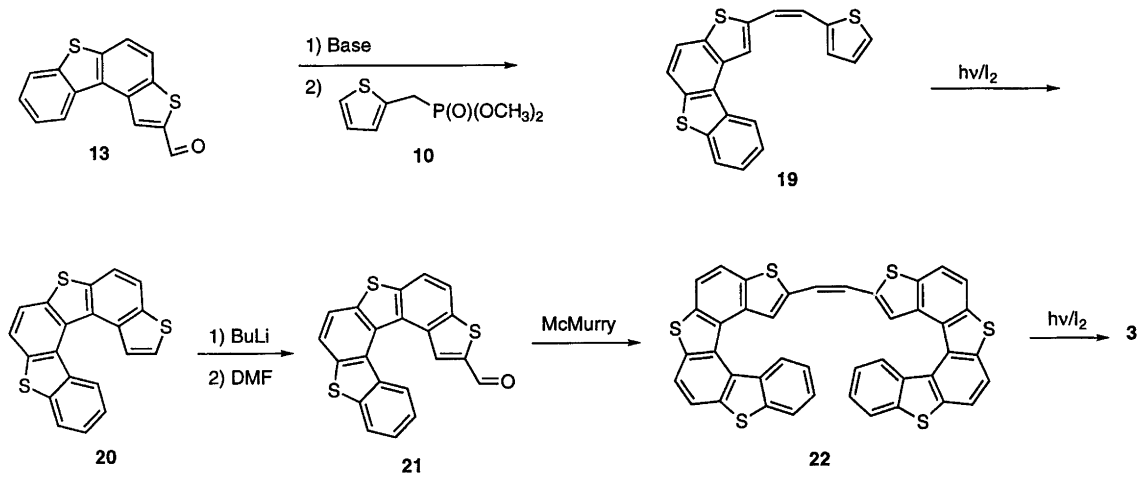
Experimental

All compounds gave analytical results (C,H,N) within $\pm 0.3\%$ of the theoretical values unless otherwise indicated. Generally ^1H NMR and mass spectrometry was used to check the identity of new compounds. In some cases ^1H NMR spectra were not obtained owing to limited solubility of the compounds.

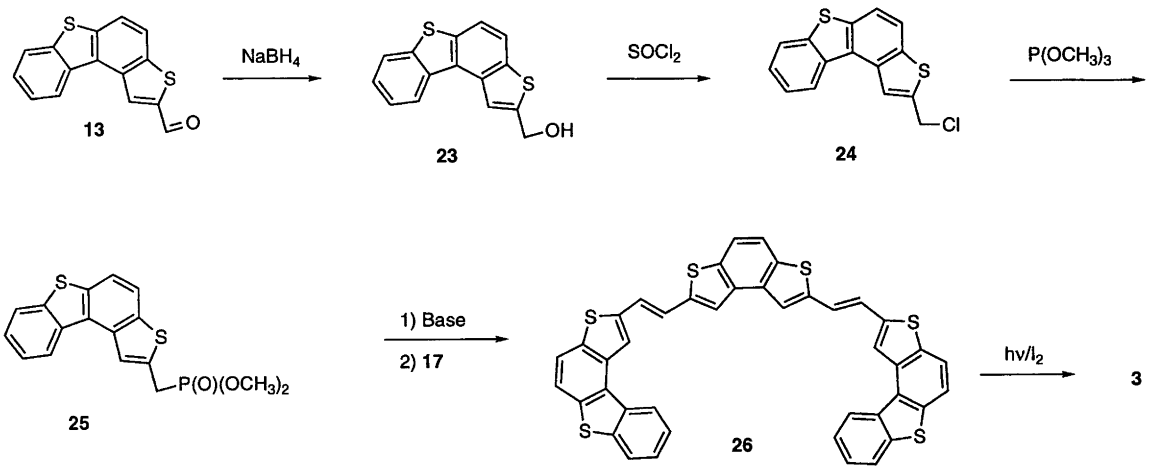
Photocyclization: general procedures. Two procedures for the photocyclizations[3] were followed, depending on the solubility of the starting materials.



Scheme 3.



Scheme 4.



Scheme 5.

1. Soluble compounds **11**, **15**, **19**. Approximately 6 g of the starting material were dissolved in 1.8 l of toluene and 0.5 equiv. of I_2 was added. The solution was irradiated with a Q-700 lamp at 20–30°C while air was bubbled through the solution. The irradiation was stopped when no more starting material was visible by TLC (aluminia; petroleum ether–toluene). The toluene solution was transferred to a conical flask containing sodium dithionite (5 g) and water (200 ml) and stirred for 1–2 h. The organic phase was dried with $MgSO_4$ and evaporated under vacuum to a volume of ca. 150 ml. The residue was filtered through a short column (5 × 10 cm) of alumina (Woelm, basic, super 1), evaporated to dryness and crystallized from heptane unless otherwise stated.

2. Insoluble compounds **9**, **14**, **18**, **22**, **26**. 0.5–1 g was suspended in 1.8 l of toluene and 0.5 equiv. of I_2 was added. The solution was irradiated with a Q-700 lamp at 50–60°C while air was bubbled through the solution. The irradiation was stopped 2 h after a homogeneous solution was formed. The reaction was worked up as described above, except that toluene was used for the final crystallization.

*5,8-Dithia[5]helicene (***1***).* 1,2-Bis(benzo[*b*]thiophen-2-yl)-ethene **9** was cyclised photochemically to 5,8-dithia[5]-helicene **1** in 52% yield, according to procedure 2. M.p. 180–180.5°C (Lit.[3] 183–185°C). MS: *m/z* 290 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.53 (m, 4 H, Ar), 7.92 (s, 2 H, Ar), 7.98 (m, 2 H, Ar), 9.03 (m, 2 H, Ar).

*5,8,11,14-Tetrathia[9]helicene (***2***).* 2,7-Bis[2-(benzo[*b*]-thiophen-2-yl)ethenyl]thieno[3,2-*e*]benzo[*b*]thiophene **18** or 1,2-bis(thieno[3-2-*a*]dibenzothiophen-2-yl)ethene **14** was cyclised photochemically to tetrathia[9]helicene **2** in 48% and 55% yield, respectively, using procedure 2. M.p. 320–322°C. MS: *m/z* 502 (M^+). ^{1}H NMR ($CDCl_3$): δ 6.04 (d, 1 H, Ar), 6.11 (t, 1 H, Ar), 6.97 (t, 1 H, Ar), 7.48 (d, 1 H, Ar), 7.76 (d, 1 H, Ar), 7.99 (d, 1 H, Ar), 8.25 (s, 1 H, Ar).

*5,8,11,14,17,20-Hexathia[13]helicene (***3***).* 2,7-Bis[2-(thieno[3,2-*a*]dibenzothiophen-2-yl)ethenyl]thieno[3,2-*e*] benzo[*b*]thiophene **26** or 1,2-bis(thieno[2,3-*j*]benzothieno-[3,2-*a*]dibenzothiophen-2-yl)ethene **22** was cyclised photochemically to 5,8,11,14,17,20-hexathia[13]helicene **3** in 45% yield, according to procedure 2. M.p. >330°C (from toluene). MS: *m/z* 714 (M^+). Analysis: helicene-:toluene (1:1): Found (Calc.), C: 72.88 (72.91), H: 3.38 (3.25). ^{1}H NMR ($CDCl_3$): δ 5.12 (d, 1 H, Ar), 5.87 (t, 1 H, Ar), 6.90 (t, 1 H, Ar), 7.52 (d, 1 H, Ar), 7.58 (d, 1 H, Ar), 7.69 (d, 1 H, Ar), 7.73 (d, 1 H, Ar), 7.80 (d, 1 H, Ar), 7.87 (s, 1 H, Ar).

*Benzo[*b*]thiophene-2-carbaldehyde (***5***).* To a solution of butyllithium (130 ml, 0.33 mol, 2.5 M in hexanes) in dry THF (150 ml) at −70°C was added a solution of benzo-[*b*]thiophene **4** (Aldrich) (40 g, 0.3 mol) in THF (100 ml) over a period of 20 min. The solution was heated to −10°C for 20 min, and recooled to −70°C and dry DMF (25 ml) in THF (50 ml) was added dropwise. After the addition, the solution was heated to −30°C and poured onto 1 l of ice containing 65 g of conc. HCl. The aqueous phase was extracted with ether (3 × 100 ml). The combined organic phases were washed with water (3 × 100 ml), dried with $MgSO_4$ and evaporated to yield **5** (45.8 g, 95%) as a yellow oil which crystallized upon standing. M.p. ca. 30°C (Lit.[10] m.p. 32.5–33.0°C). The product was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 2 H, Ar), 7.8 (m, 3 H, Ar), 10.0 (s, 11 H, CHO).

*2-(Hydroxymethyl)benzo[*b*]thiophene (***6***).* To a hot solution of compound **5** (23.5 g, 0.14 mol) in MeOH (150 ml) was added $NaBH_4$ (2.5 g) in small portions. When the addition was complete, the reaction was cooled and water (250 ml) was added. The mixture was extracted with ether (4 × 100 ml). The combined organic phases were washed with water (4 × 100 ml) dried over $MgSO_4$ and evaporated and the solid was crystallized from toluene to yield white **6** (23.4 g, 98%). M.p. 102–103°C (Lit.[11] m.p. 99–100°C). ^{1}H NMR ($CDCl_3$): δ 3.0 (t, 1 H, OH), 4.8 (d, 2 H, CH_2), 7.3 (m, 3 H, Ar), 7.8 (m, 2 H, Ar).

*2-Chloromethylbenzo[*b*]thiophene (***7***).* To a solution of compound **6** (23.4 g, 0.14 mol) in toluene (200 ml) warmed to ca. 50°C was added $SOCl_2$ (15 ml). After 2 h the solution was evaporated to yield **7** (26 g, 100%) as a slightly brown oil which crystallized upon standing (Lit.[11] m.p. 55–56°C). The solid was used in the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 4.8 (s, 2 H, CH_2), 7.3 (m, 3 H, Ar), 7.7 (m, 2 H, Ar).

*Diethyl(benzo[*b*]thiophen-2-ylmethyl)phosphonate (***8***).* Compound **7** (26 g, 0.14 mol) and freshly distilled triethyl phosphite (50 ml) were refluxed overnight and then distilled under vacuum, to yield **8**, b.p. 170–180°C, 11 mmHg (Lit.[12] 175–185°C, 11.5 mmHg), (26.3 g, 66.1%). ^{1}H NMR ($CDCl_3$): δ 1.2 (m, 6 H, CH_3), 3.4 (d, 2 H, CH_2), 4.1 (m, 2 H, CH_2), 7.3 (m, 3 H, Ar), 7.7 (m, 2 H, Ar).

*1,2-Bis(benzo[*b*]thiophen-2-yl)ethene (***9***).* To a solution of compound **5** (0.65 g, 4 mmol) and the phosphonate ester **8** (1.1 g, 0.004 mol) in THF (100 ml) was added potassium *tert*-butoxide (0.6 g, 0.005 mol). After 2 h water (100 ml) was added. The product was isolated by filtration, washed with water and MeOH and dried. Crystallization from toluene afforded yellow **9** (0.9, 77%). M.p. 305–306.5°C (Lit.[3] 300–301°C). MS: *m/z* 292 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 2 H, CH), 7.29–7.36 (m, 6 H, Ar), 7.69–7.80 (m, 4 H, Ar).

*1-(Benzo[*b*]thiophen-2-yl)-2-(thien-2-yl)ethene (***11***).* As for compound **15**. Compound **5** (0.12 mol) and compound **10** (0.12 mol) gave **11** in 93% yield. M.p. 176–176.5°C (from EtOH), (Lit.[3] m.p. 180–181°C). ^{1}H NMR

($CDCl_3$): δ 7.05 (m, 1 H, Ar), 7.11–7.18 (m, 3 H, Ar, CH), 7.25–7.30 (m, 2 H, Ar), 7.30–7.39 (m, 2 H, Ar), 7.70–7.82 (m, 2 H, Ar).

*Thieno[3,2-*a*]dibenzothiophene (***12***).* Compound **11** was cyclised photochemically to **12** in 73% yield, according to procedure 1. M.p. 142–143°C (Lit.[3] m.p. 149–150°C). MS: *m/z* 240 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.55 (m, 2 H, Ar), 7.74 (d, 1 H, Ar), 7.83 (d, 1 H, Ar), 7.96 (m, 2 H, Ar), 8.25 (d, 1 H, Ar), 8.55 (d, 1 H, Ar).

*Thieno[3,2-*a*]dibenzothiophene-2-carbaldehyde (***13***).* As for compound **5** except that the product was isolated by filtration, washed with water, dried and crystallized from toluene. Compound **12** (0.087 mol) gave **13** in 88% yield. M.p. 184–185°C, ^{1}H NMR ($CDCl_3$): δ 7.55 (m, 2 H, Ar), 7.92 (m, 3 H, Ar), 8.45 (m, 1 H, Ar), 8.72 (s, 1 H, Ar), 10.19 (s, 1 H, CHO).

*1,2-Bis(thieno[3,2-*a*]dibenzothiophen-2-yl)ethene (***14***).* To dry THF (100 ml) at 0°C under an atmosphere of argon was added dropwise $TiCl_4$ (2.4 ml, 0.022 mol). Zinc dust (2.8 g, 0.042 mol) was added and the solution was refluxed for 2 h. Dry pyridine (1.4 ml) was added and the solution was refluxed. After 30 min, compound **13** (5.4 g, 0.02 mol) in dry THF (30 ml) was added and the solution was refluxed overnight. The solvent was removed under reduced pressure and 50 g of ice and conc. HCl (75 ml) were added and the solution stirred for 30 min. The yellow precipitate was collected, washed with water and dried. Quantitative yield. M.p. >330°C. MS: *m/z* 504 (M^+).

*1,2-Bis(thien-2-yl)ethene (***15***).* To a solution of diethyl (thien-2-ylmethyl)phosphonate[4] **10** (23.4 g, 0.1 mol) and thiophene-2-carbaldehyde (11.2 g, 0.1 mol) in THF (100 ml) was added with cooling potassium *tert*-butoxide (13.0 g, 0.11 mol), after 0.5 h water (200 ml) was added and the product isolated by filtration and washed with water and dried. Crystallization from ethanol afforded yellow (**15**) (16.5 g, 87%). M.p. 131.5–132°C (Lit.[4] m.p. 133–134°C) ^{1}H NMR ($CDCl_3$): δ 6.99 (m, 2 H, Ar), 7.04 (m, 4 H, Ar, CH), 7.18 (m, 2 H, Ar).

*Thieno[3,2-*e*]benzo[*b*]thiophene (***16***).* Compound **15** was cyclized photochemically to thieno[3,2-*e*]benzothiophene **16** in 60% yield, according to procedure 1. M.p. 113–135°C (Lit.[4] 117–118°C). MS: *m/z* 190 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.60 (d, 2 H, Ar), 7.75 (d, 2 H, Ar), 7.86 (s, 2 H, Ar).

*Thieno[3,2-*e*]benzo[*b*]thiophene-2,7-dicarbaldehyde (***17***).* To a solution of butyllithium (21 ml, 0.053 mol, 2.5 M) in dry THF (40 ml) at −78°C was added a solution of thieno[3,2-*e*]benzothiophene **16** (4.0 g, 0.021 mol) in dry THF (40 ml) over a period of 15 min. After a further 10 min, the solution was allowed to warm to −10°C and thereafter recooled to −78°C. A solution of dry DMF (5 ml) in THF (20 ml) was added over a period of 15 min. The solution was allowed to warm to −30°C and poured onto ice (200 ml) containing 15 ml conc. HCl. The crude product was isolated by filtration, washed with water and MeOH and dried. Soxhlet extraction with CH_2Cl_2 afforded **17** as a yellow powder (4.2 g, 81%). M.p. >330°C (Lit.[3] 252°C charring), MS: *m/z* 246 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.99 (s, 1 H, Ar), 8.42 (s, 1 H, Ar), 10.20 (s, 1 H, CHO).

*2,7-Bis[2-(benzo[*b*]thiophen-2-yl)ethenyl]thieno[3,2-*e*]benzo[*b*]thiophene (***18***).* To a solution of thieno[3,2-*e*]benzothiophene-2,7-dicarboxaldehyde **17** (2.5 g, 0.01 mol) and diethyl 2-benzo[*b*]thiophen-2-ylmethylphosphonate **8** (6.0 g, 0.021 mol) in dry THF was added potassium *tert*-butoxide (2.5 g, 0.022 mol). The mixture was heated to reflux for 45 min, cooled and poured onto ice. The crude product was isolated by filtration, washed with water and MeOH and dried to afford the yellow **18** (5.0 g, 100%). M.p. >330°C. MS: *m/z* 506 (M^+).

*1-(Thieno[3,2-*a*]dibenzothiophen-2-yl)-2-(thien-2-yl)ethene (***19***).* As for compound **9**. Thieno[3,2-*a*]dibenzothiophene-2-carbaldehyde **13** (0.037 mol) and **10** (0.037 mol) gave an 88% yield of **19**. M.p. 193–196.5°C. ^{1}H NMR ($CDCl_3$): δ 7.07 (m, 1 H, Ar), 7.18 (d, 1 H, Ar), 7.29 (m, 3 H, Ar, CH), 7.55 (m, 2 H, Ar), 7.79 (d, 1 H, Ar), 7.85 (d, 1 H, Ar), 7.97 (d, 1 H, Ar), 8.12 (s, 1 H, Ar), 8.53 (d, 1 H, Ar).

*Thieno[2,3-*j*]benzothieno[3,2-*a*]dibenzothiophene (***20***).* Compound **19** was cyclised photochemically to **20** in 63% yield according to procedure 1 (recrystallization from toluene). M.p. 198–199°C (Lit.[3] m.p. 210–212°C). ^{1}H NMR ($CDCl_3$): δ 7.11–7.47 (m, 4 H, Ar), 7.86–8.06 (m, 6 H, Ar).

*Thieno[2,3-*j*]benzothieno[3,2-*a*]dibenzothiophene-2-carbaldehyde (***21***).* As for compound **5** except that the product was isolated by filtration, washed with water, dried and crystallized from toluene. Thieno[2,3-*j*]benzothieno[3,2-*a*]dibenzothiophene **20** (0.010 mol) gave a 90% yield of **21**. M.p. 224–225°C, ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 1 H, Ar), 7.50 (m, 1 H, Ar), 7.89–8.04 (m, 4 H, Ar), 8.07–8.12 (m, 3 H, Ar), 9.86 (s, 1 H, CHO).

*1,2-Bis(thieno[2,3-*j*]benzothieno[3,2-*a*]dibenzothiophen-2-yl)ethene (***22***).* To dry THF (80 ml) at 0°C under an atmosphere of argon was added dropwise $TiCl_4$ (1.2 ml, 0.011 mol). Zinc dust (1.4 g, 0.021 mol) was added and the solution was refluxed for 2 h. Dry pyridine (0.7 ml) was added and the solution was refluxed a further 30 min. Thieno[2,3-*j*]benzothieno[3,2-*a*]dibenzothiophene-2-carboxaldehyde **21** (3.6 g, 0.01 mol) in dry THF (30 ml) was then added and the solution was refluxed overnight. The solvent was removed under reduced pressure after which 40 g of ice and conc. HCl (40 ml) were added and the solution was stirred for 30 min. The yellow precipitate

was collected, washed with water and dried. Quantitative yield. M.p. >330°C. MS: *m/z* 716 (M^+).

*2-(Hydroxymethyl)thieno[3,2-*a*]dibenzothiophene (***23***).* As for compound **6** except that the product was isolated by filtration, washed with water, dried and crystallized from toluene. Thieno[3,2-*a*]dibenzothiophene-2-carboxaldehyde **13** (0.026 mol) gave a 98% yield of **23**. M.p. 134–135.5°C, ^{1}H NMR ($CDCl_3$): δ 5.04 (d, 2 H, CH_2), 5.95 (t, 1 H, OH), 8.02 (m, 3 H, Ar), 8.36 (s, 1 H, Ar), 8.72 (m, 1 H, Ar).

*2-Chloromethylthieno[3,2-*a*]dibenzothiophene (***24***).* As for compound **7**. Compound **23** 0.026 mol gave a quantitative yield of **24**. M.p. 119–121°C. ^{1}H NMR ($CDCl_3$): δ 4.85 (s, 2 H, CH_2), 7.40 (m, 2 H, Ar), 7.78 (m, 4 H, Ar), 8.23 (m, 1 H, Ar).

*Diethyl thieno[3,2-*a*]dibenzothiophen-2-ylmethylphosphonate (***25***).* As for compound **8** except that the product was isolated by removal of excess triethylphosphite under vacuum and then dissolution of the solid in toluene and filtration of the solution through silica gel. 2-Chloromethylthieno[3,2-*a*]dibenzothiophene **24** (0.024 mol) gave a 75% yield of **25**. ^{1}H NMR ($CDCl_3$): δ 1.25 (m, 6 H, CH_3), 3.46 (d, 2 H, CH_2), 4.07 (m, 4 H, CH_2), 7.42 (m, 2 H, Ar), 7.76 (m, 4 H, Ar), 8.32 (m, 1 H, Ar).

*2,7-Bis[2-(thieno[3,2-*a*]dibenzothiophen-2-yl)ethenyl]thieno-[3,2-*e*]benzo[*b*]thiophen (***26***).* As for compound **18**. Thieno[3,2-*e*]benzothiophene-2,7-dicarbaldehyde **17** (0.010 mol) and compound **25** (0.020 mol) gave a quantitative yield of **26**. M.p. >330°C. MS: *m/z* 718 (M^+).

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