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Synthesis of Covalently Linked Oligo(phenyleneethynylene) Wires Incorporating Dithiafulvene Units – Redox-Active "H-Cruciforms"

Frederik Præstholm Jørgensen,[a] Johannes F. Petersen,[a] Cecilie Lindholm Andersen,[a] Anders B. Skov,[a] Martyn Jevric,[a] Ole Hammerich,[a] and Mogens Brøndsted Nielsen*[a]

Abstract: Controlled alignment and self-assembly of molecular wires is one of the challenges in the field of molecular electronics. Here we take an approach by which two oligo(phenyleneethynylene)s (OPEs) are linked together via one vinylogous linker. These molecules thus incorporate a central stilbene part from which the two OPE wires are propagating in a so-called "H-cruciform"-like motif. Each ring of the central stilbene unit also contains a redox-active dithiafulvene (DTF) unit and this part of the molecule can thus be considered as an extended tetrathiafulvalene (TTF). Here we present how such H-cruciforms based on OPE3 and OPE5 molecular wires are prepared by Sonogashira coupling reactions and how the OPEs are functionalized with thioester end-caps as potential electrode anchoring groups. The optical and redox properties of these molecules are also presented. Unsymmetrical systems are achieved by subjecting a differentially protected diethynyl-substituted derivative of terephthalaldehyde to a phosphite-mediated coupling reaction in the presence of a 1,3-dithiol-2-thione. This reaction forms the central stilbene-extended TTF with alkyne substituents and relies on an "umpolung" of the *para* substituents from electron-withdrawing CHO groups to electron-donating DTF groups in a conversion also promoted by the phosphite.

Introduction

π-Conjugated molecules such as oligo(phenyleneethynylene)s (OPEs) have been widely examined as molecular wires for electron transport in molecular electronics.[1] Functionalization of the OPE by donor and/or acceptor groups offers a way to tune its electronic properties, providing for example molecules exhibiting rectification[2] or zero-bias conductance behavior upon charging[3] (Kondo effect, resulting from unpaired spins) in molecular junctions. The electron donor tetrathiafulvalene (TTF, Figure 1) has also played a significant role in the field of molecular electronics since the proposal by Aviram and Ratner of the possibility for rectification in donor-acceptor systems with an aliphatic bridge between donor (TTF) and acceptor (tetracyanoquinodimethane) units.[4] Inspired by the molecular wire properties of OPEs and redox-active properties of TTF, we have developed a class of cruciform-like molecules, such as **1** (Figure 1),[5] incorporating an extended TTF unit orthogonally to an OPE wire with thioacetate electrode anchoring groups, and we have shown how this unit influenced molecular conductance in self-assembled monolayers,[6] break-junctions,[7] and gated three-terminal junctions.[3] For the OPE5 **1** interesting Kondo effect behavior was observed for three different charge/spin states.

By serendipity we found that a more advanced cruciform motif, with "H-cruciform" shape,[8] could conveniently be prepared in a phosphite-mediated coupling between a 1,3-dithiol-2-thione and a trimethylsilyl-protected diethynyl terephthalaldehyde.[9] Such molecules, **2** and **3** (Figure 1), can also be considered as stilbene-extended TTFs with alkynyl functionalities (or OPV2-extended TTFs; OPV = oligo(phenylenevinylene)). The alkyne units are potential sites for further coupling reactions after removal of the silyl protecting groups, and here we show that this is indeed the case. As such, the H-cruciform motif acts as a scaffold for the construction of molecules with either two parallel and covalently linked OPE3 or OPE5 molecular wires. Thus, via the central stilbene unit we can conveniently control the alignment of two molecular wires.

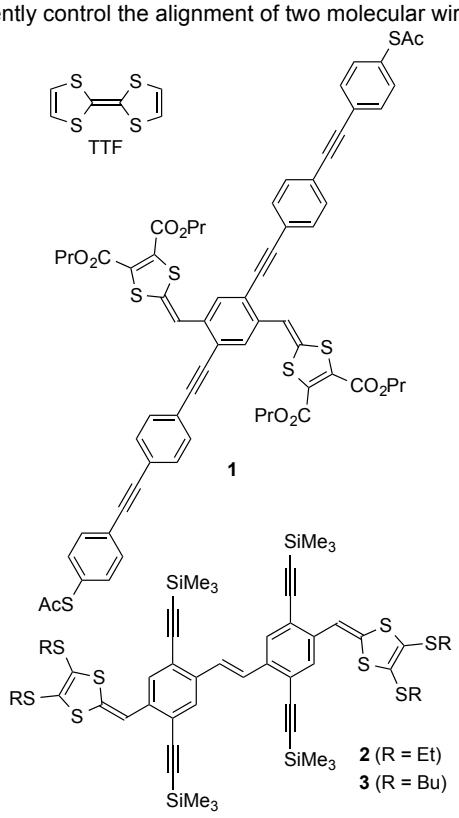

Figure 1. Cruciform and H-Cruciforms based on TTF.

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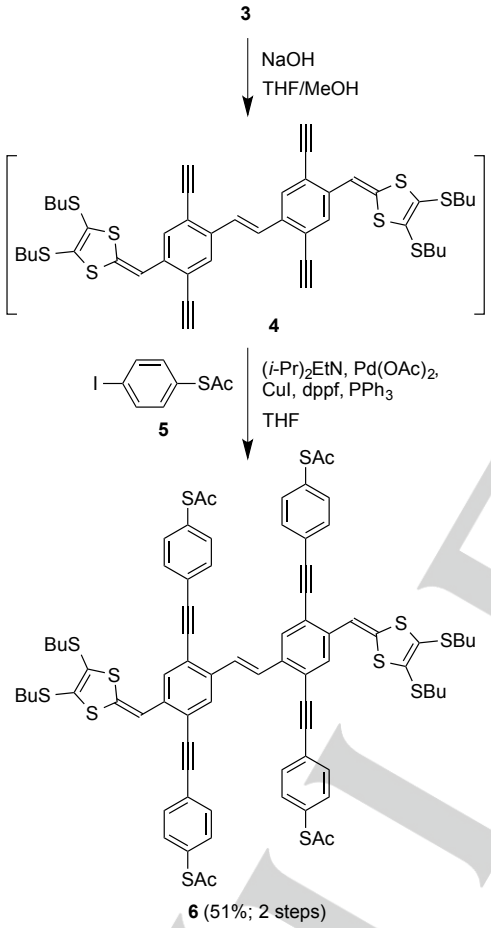
Results and Discussion

Synthesis. First, we decided to employ **3** as a precursor for an H-cruciform consisting of two OPE3 wires. The synthesis is shown in Scheme 1. Removal of the four trimethylsilyl groups was accomplished by NaOH in MeOH and THF, furnishing the intermediate **4**, which was then treated with the aryl iodide **5**[5a] under Sonogashira coupling conditions. Thereby the target molecule **6** was furnished in a good yield of 51% over two steps. The intermediate **4** was also isolated and fully characterized in a separate reaction (providing it in a yield of 66%). Its structure was confirmed by X-ray crystallographic analysis (Figure 2). While there is some disorder in the butyl chains, the structure shows that the π-system is almost entirely planar.



Scheme 1. Synthesis of OPE3 H-cruciform. dppf = 1,1'-bis(diphenylphosphino)ferrocene.

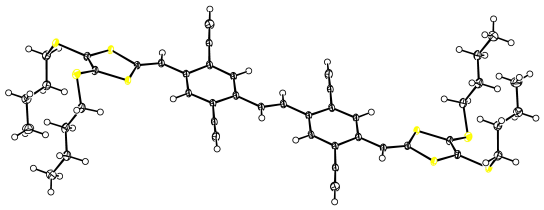
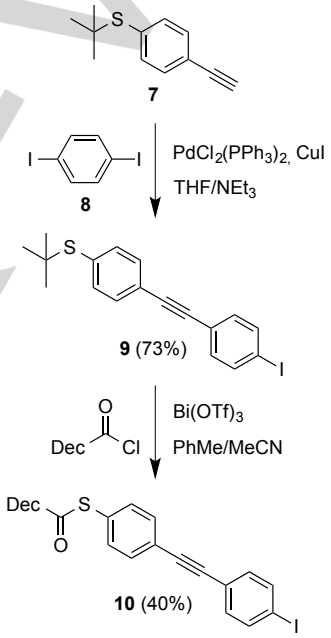
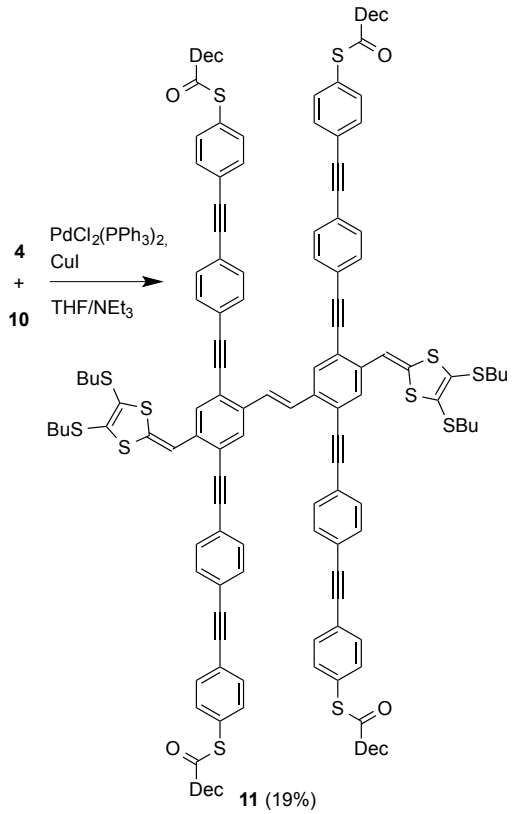


Figure 2. Molecular structure of **4** (Space group P $2_1/c$: CCDC 1512666; Space group P c: CCDC: 1512490).

The next objective was to expand the system into two OPE5 units. For this purpose an OPE2 (tolane derivative) was first prepared according to Scheme 2. The terminal alkyne **7**[10] was treated with an excess of 1,4-diiodobenzene (**8**) under Sonogashira conditions, providing OPE2 **9**. The *tert*-butylthio end-group was converted into the thioester **10** by treatment with undecanoyl chloride and bismuth(III) triflate; a method that was recently shown to work well for the synthesis of thioacetates.[11] We chose the long decyl group to ensure solubility of the final OPE5 H-cruciform target. Indeed, we assume that this thioester could in general be a convenient way of getting organic components of poor solubility into molecular electronics junctions by an *in situ* generation of the thiolate. Finally, compounds **4** and **10** were subjected to Sonogashira couplings, furnishing the OPE5 H-cruciform **11** in a yield of 19%, which corresponds to a "yield" of 66% per coupling reaction (Scheme 3).

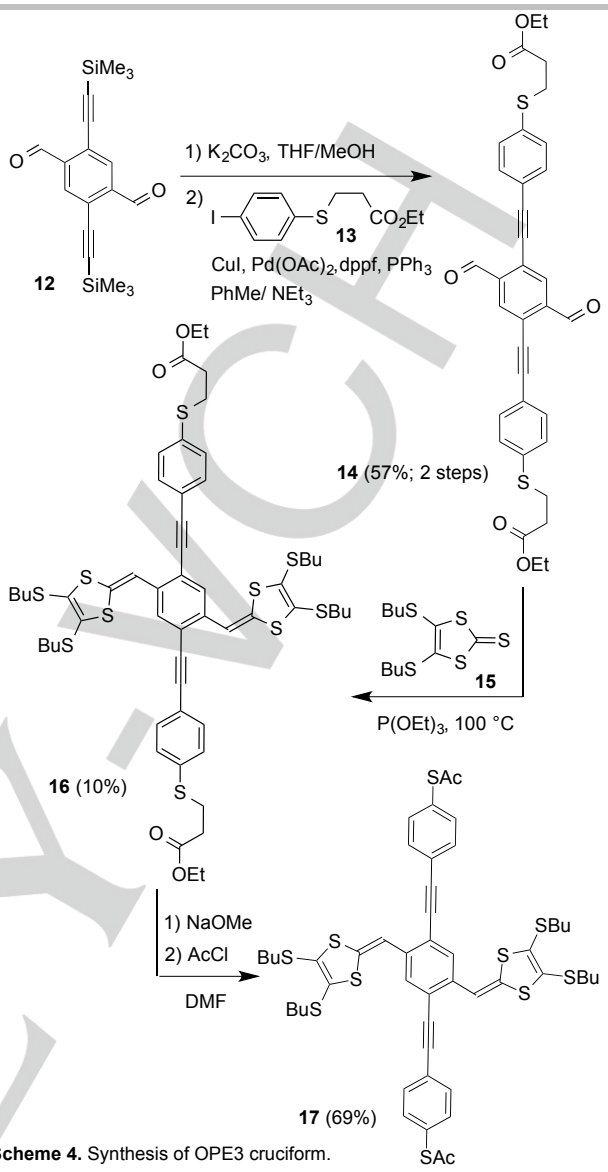


Scheme 2. Synthesis of OPE2 with thioundecanoate end-cap.



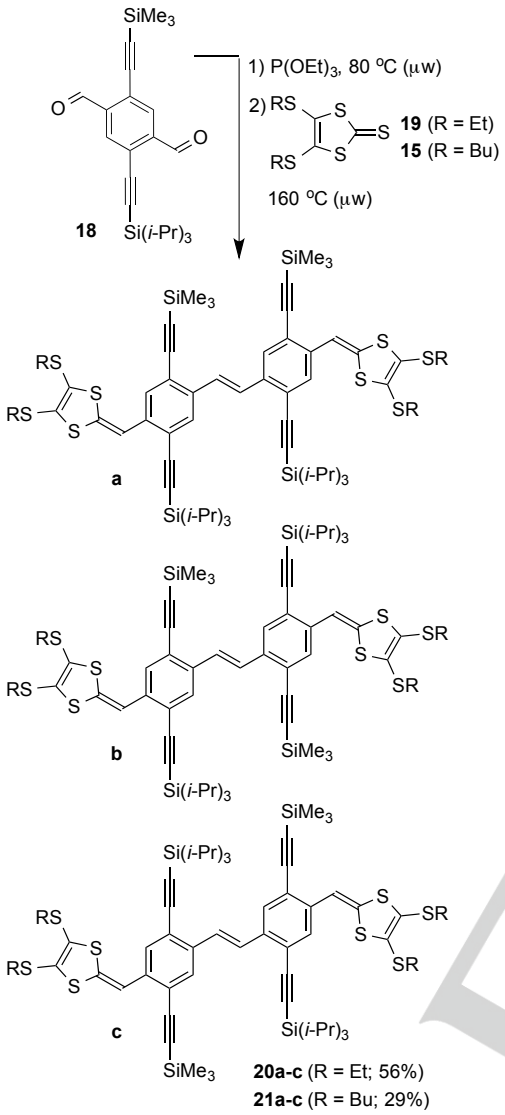
Scheme 3. Synthesis of OPE5 H-cruciform.

We also attempted an approach where the OPE part is constructed before the stilbene unit is made by phosphite-mediated coupling of two aldehyde groups. Thus, subjecting the known[12] compound **12** to desilylation followed by a cross-coupling with the aryl iodide **13** (prepared by reduction of iodobenzenesulfonyl chloride using triphenylphosphine followed by treatment with ethyl 3-bromopropionate as described in the Experimental Section) gave the OPE3 **14** with two $CH_2CH_2CO_2Et$-protected thiolate end-groups (Scheme 4). These protecting groups are less labile than the thioacetate groups for the subsequent coupling using triethylphosphite. This reaction was conducted in the presence of the easily prepared 1,3-dithiol-2-thione **15** [13]. Nevertheless, a complicated mixture of products resulted from which we were able to isolate the OPE3 cruciform **16**, albeit in rather poor yield (10%). We did not manage to isolate the corresponding H-cruciform, but cannot exclude that it could be present in the mixture. Compound **16** was treated with strong base, generating the thiolate groups, and acetyl chloride, which afforded the acetyl-protected compound **17** in good yield.



Scheme 4. Synthesis of OPE3 cruciform.

Finally, we focus on how to prepare unsymmetrical H-cruciforms. Compound **18** (known[14], but prepared according to a slightly modified route; see SI), containing differentially protected alkynes was heated using microwave irradiation together with either the 1,3-dithiol-2-thione **19**[15] or **15** in triethylphosphite to furnish a mixture of three isomeric compounds, **20a-c** and **21a-c**, respectively (Scheme 5). Importantly, first **18** was heated alone in the presence of phosphite to promote formation of a 1,3,2-dioxaphospholane intermediate *via* coupling of two aldehyde groups (Intermediate **I**; Figure 3), promoted by the electron-withdrawing aldehyde group in the *para* position according to our previous mechanistic suggestion.[9b] Addition of the 1,3-dithiol-2-thione and increasing the temperature then results in phosphite-mediated formation of the dithiafulvene units (intermediate **II**; Figure 3); these electron-donating units subsequently promote conversion of the central dioxaphospholane into an *E*-alkene.



Scheme 5. Synthesis of unsymmetrical H-cruciforms (μw = microwave heating).

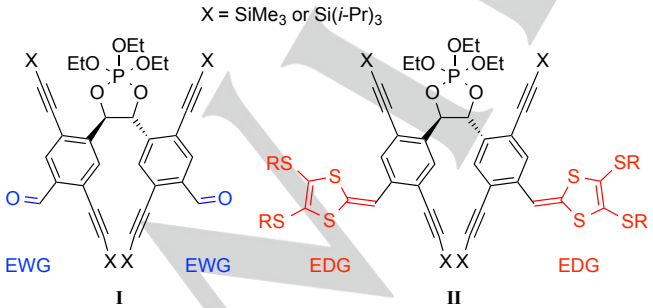


Figure 3. Intermediates in the synthesis of H-cruciforms. The "umpolung" from electron-withdrawing groups (EWG) to electron-donating groups (EDG) in the *para* positions to the central dioxaphospholane is crucial for the final conversion into a stilbene.

The isomeric products (**a-c**) could unfortunately not be separated, but we managed to obtain single crystals of one of the isomers (**20b**). Albeit of rather poor quality, the X-ray crystallographic data unambigously confirmed the substitution pattern (see SI). These compounds are potential building blocks for further acetylenic scaffolding. We employed microwave heating in the syntheses of **20a-c** and **21a-c** rather than conventional heating that was originally employed in our syntheses of the symmetrical H-cruciforms **2** and **3**[9b] where 2,5-bis((trimethylsilyl)ethynyl)terephthalaldehyde was first stirred in triethylphosphite at 60 °C for 30 min and then at 110 °C for 6 h after addition of the 1,3-dithiol-2-thione.[16] Depending on the scale of the synthesis, 1.2-1.7 equivalents of the 1,3-dithiol-2-thione were employed relative to the terephthalaldehyde starting material. We find that the syntheses of compounds **2** and **3** are also conveniently done using microwave heating (see SI), reducing the reaction times considerably and providing better reproducibility (as sometimes complicated reaction mixtures do result).

UV-Vis Absorption Spectroscopy. The UV-Vis absorption spectra of **4**, **6**, **11**, and **17** measured in CH_2Cl_2 are shown in Figure 4. The H-cruciform OPE structures **6** and **11** show longest-wavelength absorption maxima at 474 nm and 475 nm, respectively, which are redshifted relative to the longest-wavelength absorption of the simpler cruciform motifs **4** (459 nm) and **17** (455 nm). These absorptions are attributed in particular to the extended TTF part of the molecule. They are also redshifted relative to the absorptions of (*E*)-stilbene at 295 and 307 nm (in MeCN).[17] In addition, compound **11** shows an absorption at 368 nm, which is characteristic for the OPE5 scaffold,[18] while compounds **6** and **17** show absorptions at 338 and 346 nm, respectively, which are characteristic for the OPE3 scaffold.[18] This analysis is a very simplistic way of dissecting the large π-conjugated motifs into individual chromophoric parts, which are of course not decoupled from each other.

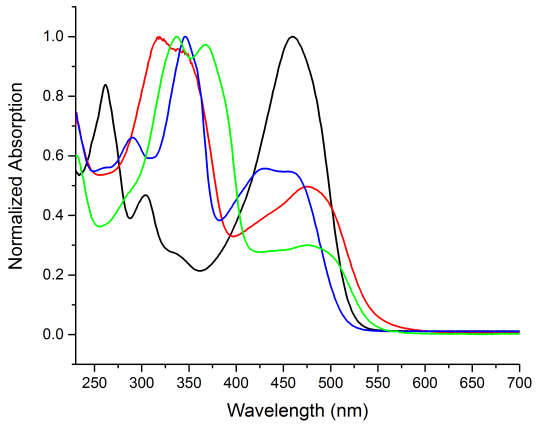


Figure 4. Normalized UV-Vis absorption spectra of compound **4** (black curve), **6** (red curve), **11** (green curve), and **17** (blue curve) in CH_2Cl_2.

Cyclic Voltammetry. The electrochemical oxidation of compounds **3**, **4**, **6**, and **11** was studied by cyclic voltammetry. A

typical voltammogram is shown in Figure 5. A chemically irreversible oxidation peak is observed for **4** at 0.38 V (*vs.* Fc/Fc^+) during the first forward scan at a scan rate of 0.2 Vs^{-1} with no sign of reverse current corresponding to the reduction of the initially formed radical cation, $\mathbf{4}^{\bullet+}$, being observed during the backward scan. Instead, two reduction peaks are observed at 0.17 V and -0.01 V with the corresponding oxidation peaks being observed at the second forward scan. This behavior is in agreement with a mechanism that during the first forward scan includes the dimerization of the initially formed radical cation to a dimer dication followed by deprotonation and further oxidation of the neutral dimer to the dication. The successive reduction of the dimer dication to the radical cation and the neutral dimer is then observed during the backward scan and the re-oxidation of the dimer to radical cation and the dication is observed at the second forward scan. The observed reactivity of $\mathbf{4}^{\bullet+}$ parallels that observed for structurally related 2-methylene-1,3-dithioles.[19] Owing to the fast follow-up reaction of $\mathbf{4}^{\bullet+}$, the oxidation peak observed at 0.38 V cannot be related to $E^{o'}$ for the reversible one-electron oxidation of **4**.[20] However, it was observed that the effect of the dimerization of $\mathbf{4}^{\bullet+}$ could be minimized by carrying out cyclic voltammetry at higher scan rates. The results obtained for **4** are shown in Figure 6 that summarizes the voltammograms observed at scan rates ranging from 20 to 1000 Vs^{-1}. A peak corresponding to the reduction of $\mathbf{4}^{\bullet+}$ is clearly seen at the higher scan rates, which allows for an estimate of the $E^{o'}$ value taken as the average of the peak potentials. The voltammograms for compounds **3**, **6**, and **11** are shown in the SI and the resulting values of $E^{o'}$ for all four compounds are summarized in Table 1. They all undergo an oxidation at ca. 0.4 V *vs.* Fc/Fc^+. Thus, the OPE3 units present in **6** seem to have no significant influence on the oxidation of the central stilbene-extended TTF unit. For comparison, the benzene-extended TTF **22**[9a],[21] shown in Figure 7 exhibits an irreversible oxidation peak at 0.16 V *vs.* Fc/Fc^+ in CH_2Cl_2/MeCN (1:1) (see the SI). Thus, it appears that the stilbene spacer of the H-cruciforms makes these molecules more difficult to oxidize than **22**. A similar effect is seen by comparison of the onset potentials (Table 1).

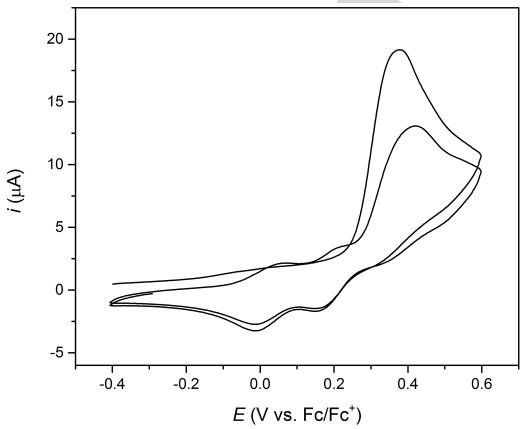


Figure 5. Cyclic voltammogram of **4** (0.5 mM) recorded at a glassy carbon disk electrode (d = 3 mm) in CH_2Cl_2/MeCN 1:1, 0.2 M Bu_4NPF_6. The voltage scan rate was 0.2 Vs^{-1}.

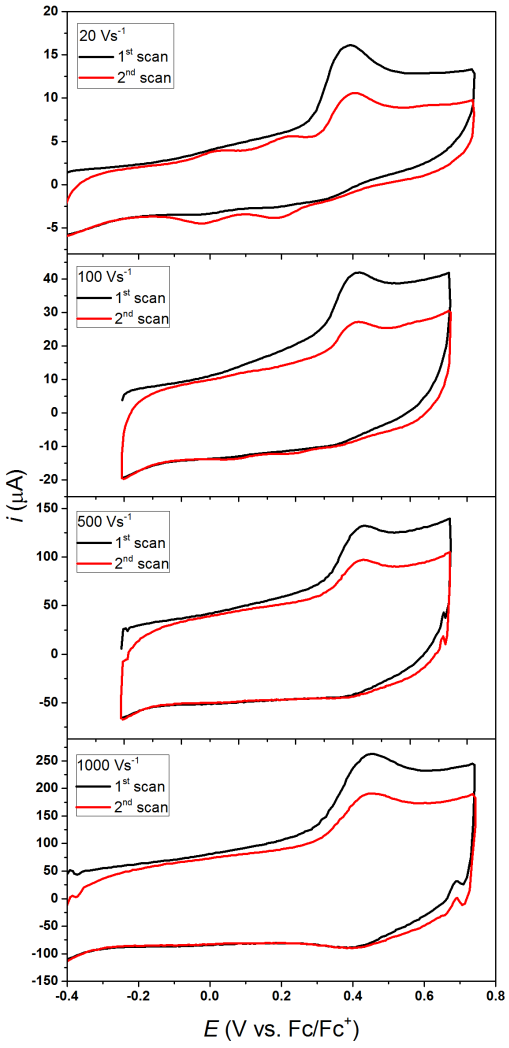


Figure 6. First and second scan of the cyclic voltammograms of **4** (0.5 mM) recorded at a platinum disk electrode (d = 0.6 mm) in CH_2Cl_2/MeCN 1:1, 0.2 M Bu_4NPF_6. The voltage scan rates are (from top to bottom): 20 Vs^{-1}, 100 Vs^{-1}, 500 Vs^{-1}, and 1000 Vs^{-1}.

Table 1. Oxidation potentials determined by cyclic voltammetry.[a]

Compound	E^0 [b] (V *vs.* Fc/Fc^+)	Onset potential [c] (V *vs.* Fc/Fc^+)
3	0.39	0.28
4	0.43	0.26
6	0.41	0.16
11	-[d]	0.27
22	-[d]	0.09

[a] In CH_2Cl_2/MeCN (1:1), 0.2 M Bu_4NPF_6. [b] Scan rate: 1000 Vs^{-1}; working electrode: Pt (0.6 mm). [c] Scan rate: 0.2 Vs^{-1}; working electrode: Glassy carbon (3 mm). [d] Could not be obtained.

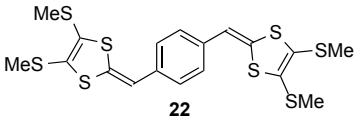


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Figure 7. Benzene-extended TTF.

Conclusions

In this work we have shown that H-cruciform motifs are readily prepared by phosphite-mediated coupling reactions using microwave heating. On account of the four ethynyl substituents, the H-cruciform is a convenient building block in Sonogashira coupling reactions for achieving 2-dimensional molecular wires incorporating two parallel OPE units, orthogonally situated relative to a redox-active stilbene/OPV2-extended TTF unit. This presents a covalent approach to parallel alignment of OPE3 and OPE5 molecular wires. Based on the optical and redox properties, the H-cruciforms can in a simplified view be considered as three separate units, one OPV2-TTF and two OPEs. Thus, characteristic absorptions can be identified for the OPEs and for the extended TTF. We imagine that the central OPV2 could in future work be further expanded to longer OPVs to allow for the alignment of additional OPE wires. The dithiafulvene units undergo irreversible oxidations at low scan rates due to intermolecular reactions, but using high scan rates these reactions could be suppressed, which allowed us to determine the oxidation potentials of the new H-cruciforms. Importantly, irreversible oxidations only present a problem in solution where radical cations can react intermolecularly and not necessarily in a molecular electronics junction. Thus, successful conductance measurements on several charge states of an OPE5-TTF cruciform motif (molecule **1**) were previously achieved,[3] where unpaired electrons provided Kondo effect behavior. Single-molecule conductance studies on the new series of H-cruciform molecules will be focus of future work.

Experimental Section

Cyclic Voltammetry. Cyclic voltammetry was carried out in MeCN/CH_2Cl_2 (1/1) containing Bu_4NPF_6 (0.2 M) as the supporting electrolyte with voltage scan rates in the range 0.1-1000 Vs^{-1}. The solvent mixture was chosen as a compromise between solubility and solution resistance as a low solution resistance is important for fast scan voltammetry. Voltammograms were recorded using an Autolab PGSTAT12 instrument driven by the Nova 1.11 software. *iR*-compensation was used in all experiments. For slow scan voltammetry the working electrode was either a circular glassy carbon disk (d = 3 mm) or a circular platinum disk electrode (d = 0.6 mm) and for fast scan voltammetry a circular platinum disk electrode (d = 0.6 mm) was used. The counter electrode was a platinum wire and the reference electrode was a silver wire immersed in the solvent-supporting electrolyte mixture and physically separated from the solution containing the substrate by a ceramic frit. The potential of the reference electrode was determined *vs.* the ferrocene/ferrocenium (Fc/Fc^+) redox couple in separate experiments. Solutions were purged with argon saturated with solvent for at least ten minutes before the measurements were made after which a stream of argon was maintained over the solutions. The temperature was ~297 K. The substrate concentrations were 0.5 mM (**4** and **6**) or 0.25 mM (**22**). In two cases (**3** and **11**) the solubility was only limited and the voltammograms were obtained from saturated solutions.

Synthesis and Standard Characterization – General Information. Air and water sensitive reactions were carried out under argon (balloon technique) or under nitrogen. Degassing was performed by flushing argon or nitrogen through the solvent for 20 min while subjecting the solution to ultrasound. All commercial available chemicals and solvents were used as received. ^{1}H NMR spectra was measured on a Bruker instrument with cryo-probe at 500 MHz. ^{13}C NMR was measured on the same instrument but at 126 MHz. NMR solvents used were $CDCl_3$ (referenced to δ_H = 7.26 ppm and δ_C = 77.16), C_6D_6 (referenced to δ_H = 7.16 ppm and δ_C = 128.06) and DMSO-d_6 (referenced to δ_H = 2.50 ppm and δ_C = 39.52). Coupling constants (J) was given in Hertz (Hz). $CDCl_3$ was passed through activated Al_2O_3 prior to use. THF was freshly distilled over the sodium/benzophenone couple. Other anhydrous solvents were collected from an IT (Innovative Technology) installation of the model PS-MD-05. Thin-layer chromatography (TLC) was performed on precoated (silica 60) aluminum plates with fluorescence indicator. Flash column chromatography was carried out on silica (SiO_2) with particle size of 40-63 µm from ROCC. All extended TTFs was purified on silica (SiO_2) from Geduran with a particle size of 40-63 µm. Dry column vacuum chromatography was performed using silica (SiO_2) with a particle size of 15-40 µm from ROCC. Gas chromatography – mass spectrometry (GC-MS) was performed on an Agilent apparatus with *tert*-butylmethyl ether as injection solvent. High resolution mass spectrometry (HR-MS) was carried out on a FT-ICR spectrometer using either matrix assisted laser desorption ionization (MALDI) with dithranol as matrix or electrospray ionization (ESI+) with methanol + 1% TFA. Elemental analyses were performed either at London Metropolitan University or at the Department of Chemistry, University of Copenhagen. Melting points are uncorrected.

(*E*)-1,2-Bis(4-((4,5-bis(butylthio)-1,3-dithiol-2-ylidene)methyl)-2,5-diethynylphenyl)ethene (4): To a solution of **3** (503 mg, 0.44 mmol) in a mixture of THF (40 mL) and MeOH (40 mL) was added sodium hydroxide (200 mg, 5.0 mmol). The reaction mixture was left stirring for 30 min, then partitioned between sat. aqueous NH_4Cl (300 mL) and Et_2O (300 mL). The phases were separated and the organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was further purified by flash column chromatography (30% CH_2Cl_2 in heptane) to yield **4** as an orange solid (250 mg, 66%). TLC (30% CH_2Cl_2 in heptane): R_f = 0.41. Mp 162 – 165 °C. ^{1}H NMR (500 MHz $CDCl_3$): δ 7.84 (s, 2H), 7.58 (s, 2H), 7.49 (s, 2H), 6.92 (s, 2H), 3.51 (s, 2H), 3.45 (s, 2H), 2.85 (t, J = 7.4 Hz, 4H), 2.84 (t, J = 7.4 Hz, 4H), 1.77 – 1.58 (m, 8H), 1.51 – 1.40 (m, 8H), 0.95 (t, J = 7.4 Hz, 6H), 0.94 (t, J = 7.4 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.16, 137.14, 135.93, 129.79, 129.56, 128.86, 127.22, 124.88, 121.97, 120.66, 110.74, 84.01, 83.83, 81.84, 81.81, 36.18, 35.97, 32.02, 31.87, 21.86, 21.84, 13.78, 13.75 ppm. Anal. Calcd. for $C_{46}H_{48}S_8$: C, 64.44; H, 5.64. Found: C, 64.23; H, 5.43. HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 856.1543 [$M^{+\bullet}$], calcd for ($C_{46}H_{48}S_8^{+\bullet}$): *m/z* 856.1516.

(*E*)-*S*,*S*',*S*'',*S*'''-(((Ethene-1,2-diylbis(5-((4,5-bis(butylthio)-1,3-dithiol-2-ylidene)methyl)benzene-2,1,4-triyl))tetrakis(ethyne-2,1-diyl))tetrakis(benzene-4,1-diyl)) tetraethanethioate (6): Sodium hydroxide (172 mg, 4.3 mmol) was added to a stirring solution of **3** (158 mg, 0.14 mmol) in a mixture of THF (40 mL) and MeOH (40 mL). Stirring was continued for 20 min, and then the mixture was partitioned between sat. aqueous NH_4Cl (300 mL) and Et_2O (300 mL). The phases were separated and the organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The orange solid was

transferred to a flask containing 1-acetylthio-4-iodobenzene (**5**) (275 mg, 0.99 mmol), $Pd(OAc)_2$ (14 mg, 62 µmol), CuI (4.5 mg, 24 µmol), dppf (17 mg, 31 µmol) and triphenylphosphine (27.5 mg, 105 µmol). An argon flushed solution of THF (25 mL) and diisopropylethylamine (1 mL, 5.7 mmol) was added via cannula and the reaction was subjected to ultrasonication for 18 hours at 40 °C. The crude reaction mixture was partitioned between sat. aqueous NH_4Cl (100 mL) and CH_2Cl_2 (100 mL). The phases were separated and the organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (1% EtOAc in toluene) to yield **6** as a red solid (103 mg, 51%). TLC (1% EtOAc in toluene): R_f = 0.26. Mp 162 – 165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.75 (s, 2H), 7.62 (d, *J* = 8.4 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 4H), 7.53 (s, 2H), 7.43 (d, *J* = 8.4 Hz, 4H), 7.35 (d, *J* = 8.4 Hz, 4H), 6.98 (s, 2H), 2.95 – 2.79 (m, 8H), 2.46 (s, 6H), 2.43 (s, 6H), 1.74 – 1.60 (m, 8H), 1.51 – 1.41 (m, 8H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 193.42, 193.37, 136.89, 136.75, 135.73, 134.48, 134.44, 132.34, 132.33, 129.39, 128.95, 128.95, 128.70, 128.65, 127.44, 124.84, 124.33, 122.44, 121.33, 111.09, 95.56, 95.27, 89.74, 89.53, 36.24, 35.97, 32.00, 31.87, 30.48, 30.44, 21.86, 21.84, 13.79, 13.77 ppm (1 masked peak). Anal. Calcd. for $C_{78}H_{72}O_4S_{12}$: C, 64.25; H, 4.98. Found: C, 64.13; H, 5.17. HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 1456.2077 [$M^{+\bullet}$], calcd for ($C_{78}H_{72}O_4S_{12}^{+\bullet}$): *m/z* 1456.2074.

***tert*-Butyl(4-((4-iodophenyl)ethynyl)phenyl)sulfane (9):** To an argon flushed solution of *tert*-butyl(4-ethynylphenyl)sulfane (**7**) (1.41 g, 7.41 mmol), 1,4-diiodobenzene (**8**) (7.52 g, 22.8 mmol) in THF (30 mL) and triethylamine (30 mL) was added $PdCl_2(PPh_3)_2$ (385 mg, 0.55 mmol) and CuI (147 mg, 0.77 mmol). The reaction mixture was left stirring 14 hours at ambient temperature, after which time the reaction mixture was partitioned between sat. aqueous NH_4Cl (100 mL) and CH_2Cl_2 (100 mL). The phases were separated and the organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (0-5% CH_2Cl_2 in heptane) to furnish **9** as a white solid (2.11 g, 73%). TLC (heptanes): R_f = 0.22. Mp 87 – 89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 1.30 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.72, 137.40, 133.77, 133.24, 131.62, 123.41, 122.73, 94.50, 90.39, 90.05, 46.69, 31.14 ppm. Anal. Calcd. for $C_{18}H_{17}IS$: C, 55.11; H, 4.37. Found: C, 55.22; H, 4.28. GC-MS (EI): *m/z* 392 [$M^{+\bullet}$].

***S*-(4-((4-Iodophenyl)ethynyl)phenyl) undecanethioate (10):** To a stirring solution of **9** (300 mg, 0.76 mmol) and undecanoyl chloride (1.2 mL, 5.4 mmol) in a mixture of MeCN (16 mL) and toluene (4 mL) was added bismuth(III) trifluoromethanesulfonate (180 mg, 0.27 mmol), and stirring was continued for 3 hours at ambient temperature. The reaction mixture was added to cold sat. aqueous $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (20 mL). The organic phase was filtered through cotton wool, then concentrated *in vacuo*, and the resulting oil was purified by flash column chromatography (20% CH_2Cl_2 in heptanes) to yield **10** as a white solid (153 mg, 40%). TLC (20% CH_2Cl_2 in heptanes): R_f = 0.19. Mp 114 – 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), ca. 7.25 ("doublet" – overlapping with the $CHCl_3$ signal, "2H"), 2.69 – 2.63 (m, 2H), 1.75 – 1.68 (m, 2H), 1.39 – 1.23 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm (one signal obscured by the solvent). ^{13}C NMR (126 MHz, $CDCl_3$): δ 197.09, 137.73, 134.40, 133.29, 132.23, 128.66, 124.10, 122.63, 94.60, 90.23, 90.11, 44.03, 32.04, 29.69, 29.56, 29.44, 29.39, 29.11, 25.73, 22.83, 14.27. ppm. Anal. Calcd. for $C_{25}H_{29}IOS$: C, 59.52; H, 5.79. Found: C, 59.45; H, 5.70. HR-MS (ESI+, FT-ICR, MeOH + 0.1% TFA): *m/z* 505.1067 [M+H$^+$], calcd for ($C_{25}H_{30}IOS^+$): *m/z* 505.1057.

(*E*)-*S*,*S*',*S*'',*S*'''-(((((Ethene-1,2-diylbis(5-((4,5-bis(butylthio)-1,3-dithiol-2-ylidene)methyl)benzene-2,1,4-triyl))tetrakis(ethyne-2,1-diyl))tetrakis(benzene-4,1-diyl))tetrakis(ethyne-2,1-diyl))tetrakis(benzene-4,1-diyl)) tetraundecanethioate (11): To an argon purged flask containing **4** (42 mg, 49 µmol), **10** (130 mg, 258 µmol), $PdCl_2(PPh_3)_2$ (12 mg, 17 µmol) and CuI (3 mg, 16 µmol) was added an argon flushed solution of triethylamine (40 mL) and THF (40 mL) via cannula, and the resulting solution was subjected to ultrasonication at 35 °C for 24 hours. The mixture was concentrated *in vacuo* and the crude residue was purified by flash column chromatography (20% CH_2Cl_2 in CS_2) to afford **11** as a red solid (22 mg, 19%). TLC (25% CH_2Cl_2 in CS_2): R_f = 0.52. Mp >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (s, 2H), 7.72 (s, 2H), 7.56 (d, *J* = 8.3 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 4H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.46 (d, *J* = 8.3 Hz, 4H), 7.45 (d, *J* = 8.3 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 4H), 7.40 (s, 2H), 7.33 (d, *J* = 8.3 Hz, 4H), 7.21 (d, *J* = 8.3 Hz, 4H), 6.99 (s, 2H), 2.93 – 2.87 (m, 8H), 2.70 – 2.62 (m, 8H), 1.78 – 1.65 (m, 16H), 1.54 – 1.44 (m, 8H), 1.42 – 1.24 (m, 56H), 0.97 (t, *J* = 7.4 Hz, 6H), 0.95 (t, *J* = 7.3 Hz, 6H), 0.89 (t, *J* = 6.9 Hz, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 196.85, 196.78, 136.48, 136.43, 135.53, 134.34, 134.33, 132.35, 132.28, 131.95, 131.92, 131.74, 131.70, 129.05, 128.85, 128.52, 128.45, 127.65, 125.00, 124.08, 124.02, 123.29, 123.21, 123.20, 123.18, 122.54, 121.31, 111.39, 96.17, 95.69, 91.12, 90.98, 90.87, 90.80, 90.26, 90.20, 44.06, 44.00, 36.30, 36.01, 32.08, 32.06, 32.03, 31.92, 29.77, 29.74, 29.67, 29.63, 29.50, 29.49, 29.48, 29.47, 29.24, 29.21, 25.77, 25.71, 22.85, 22.85, 21.92, 21.90, 14.28, 13.84, 13.81 ppm (2 masked peaks). HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 2361.8940 [$M^{+\bullet}$], calcd for ($C_{146}H_{160}O_4S_{12}^{+\bullet}$): *m/z* 2361.8993.

Ethyl 3-([4-iodophenyl]thio)propanoate (13): Triphenylphosphine (18.0 g, 68.6 mmol) was slowly added to a stirring solution of 4-iodobenzenesulfonyl chloride (7.02 g, 23.21 mmol) in argon flushed anhydrous acetonitrile (125 mL) under argon. The reaction mixture was heated to 60 °C for 20 min, whereafter water (0.82 mL, 45.5 mmol) was added, followed by addition of potassium carbonate (9.3 g, 67.3 mmol). Ethyl 3-bromopropionate (4.6 mL, 35.9 mmol) was added and the contents of the vessel were heated to reflux point for 20 hours. The reaction mixture was poured into Et_2O and passed through a short plug of silica and subsequently purified using flash column chromatography (50% CH_2Cl_2 in heptanes) to yield **13** as an off-white solid (7.67 g, 98%). Mp 39.0 – 40.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H) 7.09 (d, *J* = 8.4 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.15 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.66, 138.11, 135.64, 131.65, 91.52, 60.96, 34.39, 28.98, 14.33 ppm. Anal. Calcd. for $C_{11}H_{13}IO_2S$: C, 39.30; H, 3.90. Found: C, 39.33; H, 3.52. GC-MS (EI): *m/z* 336 [$M^{+\bullet}$].

Diethyl 3,3'-((((2,5-diformyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(sulfanediyl))dipropionate (14): To a solution of **12** (1.01 g, 3.08 mmol) in a mixture of THF (35 mL) and MeOH (80 mL) was added potassium carbonate (2.11 g, 15.2 mmol) and the contents of the vessel were stirred for 10 min, whereafter the mixture was poured into Et_2O (300 mL), washed with water (3 x 300 mL) followed by brine (300 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The white residue was transferred to a flask with CuI (59 mg, 0.31 mmol), $Pd(OAc)_2$ (139 mg, 0.62 mmol), triphenylphosphine (324 mg, 1.24 mmol), dppf (342 mg, 0.62 mmol) and ethyl 3-([4-iodophenyl]thio)propanoate (**13**) (3.62 g, 10.8 mmol) and placed under an atmosphere of argon. Argon flushed toluene (50 mL) and triethylamine (5 mL, 35.9 mmol) were added via cannula and the reaction mixture was left stirring for 15 hours at ambient temperature. The crude reaction mixture was partitioned between sat. aqueous NH_4Cl (200 mL) and CH_2Cl_2 (200 mL) and the phases separated. The organic phase was washed with brine (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column

chromatography (1% EtOAc in CH_2Cl_2) to yield compound **14** as a yellow solid (1.05 g, 57%). TLC (CH_2Cl_2): R_f = 0.61. Mp 157 – 159 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 2H), 8.17 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 4H), 7.34 (d, *J* = 8.3 Hz, 4H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.24 (t, *J* = 7.4 Hz, 4H), 2.67 (t, *J* = 7.4 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 190.46, 171.62, 138.71, 138.32, 132.63, 132.39, 128.51, 126.09, 119.19, 98.81, 84.71, 61.06, 34.27, 28.12, 14.35 ppm. Anal. Calcd. for $C_{34}H_{30}O_6S_2$: C, 68.21; H, 5.05. Found: C, 68.22; H, 4.73. HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 599.1584 [M+H$^+$], calcd for ($C_{34}H_{31}O_6S_2^+$): *m/z* 599.1557.

Diethyl 3,3'-((((2,5-bis((4,5-bis(butylthio)-1,3-dithiol-2-ylidene)methyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(sulfanediyl))dipropionate (16): An argon flushed solution of **14** (99.5 mg, 0.17 mmol), **15** (211 mg, 0.68 mmol) and triethylphosphite (5 mL) was heated to 100 °C for 4.5 hours, whereafter triethylphosphite was removed using high vacuum. The residue was subjected to flash column chromatography (70% CH_2Cl_2 in heptanes) to yield **16** as an orange solid (18 mg, 10%). TLC (70% CH_2Cl_2 in heptane): R_f = 0.40. Mp 82 – 85 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 4H), 7.49 (s, 2H), 7.34 (d, *J* = 8.3 Hz, 4H), 6.94 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.22 (t, *J* = 7.4 Hz, 4H), 2.86 (t, *J* = 7.4 Hz, 4H), 2.84 (t, *J* = 7.4 Hz, 4H), 2.66 (t, *J* = 7.4 Hz, 4H), 1.69 – 1.60 (m, 8H), 1.50 – 1.41 (m, 8H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.71, 136.90, 135.56, 134.74, 132.22, 128.98, 128.83, 128.64, 124.81, 121.13, 120.89, 111.48, 95.69, 88.68, 60.99, 36.18, 35.93, 34.38, 31.99, 31.87, 28.53, 21.85, 21.83, 14.35, 13.77, 13.76 ppm. Anal. Calcd. for $C_{56}H_{66}O_4S_{10}$: C, 59.86; H, 5.92. Found: C, 59.99; H, 5.74. HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 1122.2182 [M$^{+\bullet}$], calcd for ($C_{56}H_{66}O_4S_{10}^{+\bullet}$): *m/z* 1122.2163.

***S,S'*-(((2,5-Bis((4,5-bis(butylthio)-1,3-dithiol-2-ylidene)methyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate (17):** To a solution of **16** (35 mg, 31.2 µmol) in argon flushed DMF (2 mL) was added sodium methoxide (1 mL, 0.124 M, 124 µmol). The color of the solution changed from yellow/brown to an intense red. After 10 min, acetyl chloride (11 µL, 155 µmol) was added and the red color faded. The reaction mixture was left stirring for a further 20 min, whereafter the volatiles were removed under a stream of nitrogen. The residue was purified by flash column chromatography (50% CH_2Cl_2 in heptane) to yield **17** as a yellow solid (21.7 mg, 69%). TLC (50% CH_2Cl_2 in heptane): R_f = 0.52. Mp 142 – 145 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 8.03 (s, 2H), 7.35 (s, 2H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 2.56 (t, *J* = 7.3 Hz, 4H), 2.49 (t, *J* = 7.3 Hz, 4H), 1.82 (s, 6H), 1.49 – 1.33 (m, 8H), 1.23 – 1.08 (m, 8H), 0.71 (t, *J* = 7.4 Hz, 6H), 0.69 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 191.55, 136.66, 135.75, 134.55, 132.53, 129.65, 129.23, 129.08, 125.35, 124.33, 121.96, 112.11, 96.24, 90.06, 36.09, 35.88, 32.04, 31.87, 29.71, 21.84, 21.80, 13.68, 13.65 ppm. Anal. Calcd. for $C_{50}H_{54}O_2S_{10}$: C, 59.60; H, 5.40. Found: C, 59.49; H, 5.43. HR-MS (MALDI+, FT-ICR, dithranol): *m/z* 1006.1347 [M$^{+\bullet}$], calcd for ($C_{50}H_{54}O_2S_{10}^{\bullet+}$): *m/z* 1006.1325.

Unsymmetrical H-Cruciforms (20a-c): In a microwave vial, compound **18** (172 mg, 0.42 mmol) was dissolved in triethylphosphite (2.5 mL), and the solution was flushed for 5 min with nitrogen. The vial was then sealed and heated to 80 °C for 10 min by microwave irradiation. Upon cooling, **19** (128 mg, 0.50 mmol; 1.2 equiv.) was added through the seal, followed by heating to 160 °C for 10 min by microwave irradiation. The resulting red solution was then poured into stirred MeOH. Upon completed addition, the MeOH turned cloudy orange. Stirring was stopped and precipitation was allowed at 5 °C for 2 hours. The resulting orange precipitate was then isolated by filtration. Drying afforded the isomeric product mixture **20a-c** as an orange powder (141 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.68 – 7.58 (m, 2H), 7.48 (s, 1H), 7.40 (s, 1H), 7.03 (s, 1H), 6.91 (s, 1H), 2.97 – 2.78 (m, 8H), 1.40 – 1.28 (m, 12H), 1.26 – 1.07 (m, 42H), 0.39 – 0.22 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.21, 137.08, 136.84, 136.68, 136.06, 135.93, 135.80, 135.76, 135.71, 129.56, 129.42, 128.72, 128.67, 128.64, 128.47, 128.34, 128.18, 127.95, 127.42, 126.90, 126.50, 125.88, 125.19, 125.17, 123.03, 122.90, 122.72, 122.57, 121.98, 121.95, 121.33, 121.29, 112.07, 111.99, 111.49, 111.42, 105.16, 105.10, 104.93, 103.21, 103.07, 101.84, 101.71, 101.20, 101.09, 98.22, 98.08, 97.96, 30.72, 30.50, 30.44, 18.95, 15.32, 15.17, 15.12, 11.54, 11.47, 0.25, 0.11. HR-MS (MALDI+, FT-ICR; dithranol): *m/z* 1200.3730 [M$^{+\bullet}$], calcd for ($C_{62}H_{88}S_8Si_4^+$): *m/z* 1200.3723.

Unsymmetrical H-Cruciforms (21a-c): In a microwave vial, compound **18** (720 mg, 1.75 mmol) was dissolved in triethylphosphite (10 mL), and the solution was flushed for 15 min with nitrogen. The vial was then sealed and heated to 80 °C for 10 min by microwave irradiation. Upon cooling, **15** (653 mg, 2.10 mmol; 1.2 equiv.) was added through the seal, followed by heating to 160 °C for 10 min by microwave irradiation. The resulting red solution was then poured into vigorously stirred MeOH. Upon completed addition, the MeOH turned cloudy orange. Stirring was stopped and precipitation was allowed at 5 °C overnight. The resulting orange precipitate was then isolated by filtration. Drying afforded the isomeric product mixture **21a-c** as an orange powder (334 mg, 29%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 – 7.79 (m, 2H), 7.71 – 7.61 (m, 2H), 7.46 (s, 1H), 7.41 (s, 1H), 7.03 (s, 1H), 6.91 (s, 1H), 2.88 – 2.83 (m, 8H), 1.69 – 1.63 (m, 8H), 1.48 – 1.44 (m, 8H), 1.21 – 1.14 (m, 42H), 0.97 – 0.92 (m 12H), 0.35–0.24 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.24, 137.11 136.85, 136.68, 136.18,136.00, 135.94, 135.93, 135.90, 135.87, 129.51, 129.37, 128.71, 128.64, 128.47, 128.41, 128.37, 128.33, 128.16, 127.93, 127.41, 127.14, 126.86, 126.48, 125.85, 125.82, 125.17, 125.14, 122.90, 122.71, 122.56, 121.94, 121.91, 121.30, 121.26, 111.93, 111.86, 111.45, 111.37, 105.16, 104.94, 103.21, 103.10, 101.78, 101.64, 101.20, 101.08, 98.19, 98.05, 97.92, 95.99, 36.19, 35.95, 35.90, 32.05, 31.98, 31.90, 21.87, 21.84, 21.79, 18.95, 13.78, 13.75, 11.57, 11.53, 11.47, 0.25, 0.24, 0.11. HR-MS (MALDI+, FT-ICR; dithranol): *m/z* 1312.4944 [M$^{+\bullet}$], calcd for ($C_{70}H_{104}S_8Si_4^+$): *m/z* 1312.4975.

Supporting Information

Additional synthetic protocols, electrochemical data, NMR and mass spectra, and X-ray crystallographic data.

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[21] For studies on related benzene-extended TTFs, see Ref. 19a.

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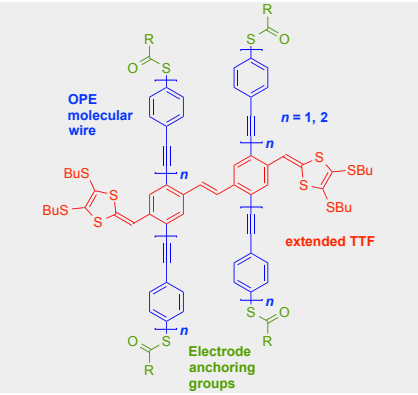
FULL PAPER

The synthesis of large π-conjugated motifs based on two parallel oligo(phenyleneethynylene)s (OPEs) and an orthogonally situated redox-active stilbene-extended tetrathiafulvalene (TTF) is presented. The OPEs, either OPE3 or OPE5, are end-capped with thioester groups as potential electrode anchoring groups.



2-Dimensional Molecular wires*

*F. P. Jørgensen, J. F. Petersen, C. L. Andersen, A. B. Skov, M. Jevric, O. Hammerich, M. B. Nielsen**

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Synthesis of Covalently Linked Oligo(phenyleneethynylene) Wires Incorporating Dithiafulvene Units – Redox-Active "H-Cruciforms"