# Synthesis of Oligo(phenyleneethynylene)s with Vertically Disposed Tetrathiafulvalene Units

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**Abstract:** Functionalized oligo(phenyleneethynylene)s (OPEs) show potential as molecular wires for molecular electronics. A selection of OPEs with vertically disposed extended tetrathiafulvalene (TTF) units has been synthesized by a combination of metal-cata-lyzed cross-coupling and Wittig reactions. Two general synthetic routes were developed. In one route, the OPE scaffold was first constructed and finally the extended TTF units were incorporated by Wittig reactions. In the second route, the extended TTF module was first prepared and subsequently incorporated into an OPE backbone by palladium-catalyzed cross-coupling reactions. The latter route was employed for functionalization with protected thiol end-groups. Owing to the shape of these redox-active molecules, they are termed 'OPE-TTF cruciforms'. The electronic properties were investigated by UV-Vis spectroscopy and by cyclic voltammetry.

Key words: alkynes, conjugation, cross-coupling, sulfur, Wittig reaction

Cruciform molecules based on two perpendicularly disposed  $\pi$ -systems are attractive as molecular wires and switches for molecular electronics and advanced materials<sup>1</sup> owing to their multiple linear and cross-conjugated pathways for  $\pi$ -electron delocalization. Calculations have revealed that cross-conjugated molecules exhibit distinctly different conductance characteristics to both linearly conjugated and saturated molecules.<sup>2</sup> By incorporation of redox-active units as vertical units in cruciform molecules, it may be possible to swap between linearly and cross-conjugated pathways along the wire via the redox state of these units. Oligo(phenyleneethynylene)s (OPEs) are an important class of molecules that have been employed as wires for molecular electronics.<sup>3</sup> We aim to develop synthetic protocols for functionalizing OPEs with vertically disposed tetrathiafulvalene (TTF) units, hereby generating cruciform-like OPE-TTFs.<sup>1a,f</sup> TTF is a good electron donor that can be oxidized reversibly in two one-electron oxidation steps, and it has, for this reason, been widely explored in molecular sensors, switches, and devices.4

The construction of OPE-TTF scaffolds requires suitable molecular building blocks. Benzene-extended TTFs were reported previously in 1991 by Sallé and co-workers.<sup>5</sup> Recently we developed efficient synthetic protocols to obtain extended TTFs **1** and **2** (Figure 1) based on a central

SYNTHESIS 2011, No. 4, pp 0539–0548 Advanced online publication: 23.12.2010 DOI: 10.1055/s-0030-1258385; Art ID: E28610SS © Georg Thieme Verlag Stuttgart · New York benzene core that also incorporates acetylenic units to allow for further scaffolding.<sup>1a,f</sup> Selective removal of the trimethylsilyl group in **2** followed by oxidative dimerization of the terminal alkyne provided access to the cruciform dimer **3**.<sup>1f</sup> It is worth noting that the intermediate terminal alkyne showed good stability. In previous attempts to construct oligomers functionalized with dithiafulvene (DTF) groups, we had employed di- or tetraethynylethenes as central cores. However, acetylenic scaffolding with these acetylenic compounds turned out troublesome on account of the limited stability of the terminal alkyne intermediates.<sup>6</sup>



Figure 1

In an alternative strategy, the dimer **3** was prepared by a fourfold Wittig reaction from the corresponding tetraaldehyde.<sup>1f</sup> In this protocol the central wire is first constructed with suitable functional groups, and in the final step these

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**Karsten Jennum** completed his M.Sc. supervision of Prof. Mogens Brøndstin 2009 in organic synthesis under the ed Nielsen. He is currently pursuing a

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groups are converted into dithiafulvene (DTF) units. We have now employed these two synthetic approaches for the preparation of different OPE3- and OPE5-TTFs, which may be used as redox-controlled wires for molecular electronics. Scheme 1 depicts the two general routes (A and B) for building the OPE-TTFs that were pursued. The optical and electrochemical properties of the compounds were also investigated.





Scheme 1 Retrosynthetic analysis of OPE-TTFs

Firstly, we synthesized an OPE3 with two vertically disposed TTFs according to the general route A described above (Scheme 2). The differentially protected diethynylbenzene derivative 4<sup>1f</sup> was selectively desilylated using potassium carbonate in methanol-tetrahydrofuran to provide the terminal alkyne 5. The conditions also led to transesterification of both ethyl ester groups into methyl esters. A twofold Sonogashira cross-coupling reaction<sup>7</sup> between this alkyne and 1,4-diiodobenzene furnished OPE3 6. The four ester groups were then reduced with diisobutylaluminium hydride, affording the tetraol 7 that was subsequently oxidized with pyridinium chlorochromate to afford the tetraaldehyde 8. Finally, fourfold Wittig reaction provided OPE3-TTF 9, employing the phosphorus ylide generated from the readily obtainable phosphonium salt 10<sup>8</sup> (Figure 2).

Scheme 2 Reagents and conditions: (i)  $K_2CO_3$ , MeOH, THF, 80%; (ii) 4-IC<sub>6</sub>H<sub>4</sub>I, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF, 73%; (iii) DIBAL-H, THF, 96%; (iv) PCC, CH<sub>2</sub>Cl<sub>2</sub>, 62%; (v) **10**, Et<sub>3</sub>N, MeCN, THF, 63%.



# Figure 2

The next objective was to synthesize an OPE5 with two vertically disposed TTF units. Here we chose the general route B (vide supra), starting from the extended TTF building block 2 (Scheme 3). Selective desilylation followed by Sonogashira cross-coupling reaction with excess 1,4-diiodobenzene afforded OPE2 11. A twofold

Sonogashira cross-coupling reaction between this iodide and 1,4-diethynylbenzene<sup>9</sup> gave OPE5-TTF **12**. This compound showed good solubility in chlorinated solvents. It was not stable, however, for a prolonged time in solution, which limited its detailed characterization.



Scheme 3 Reagents and conditions: (i)  $K_2CO_3$ , MeOH, THF; (ii) 4-IC<sub>6</sub>H<sub>4</sub>I, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF, 30% (two steps); (iii) 4-HC=C-C<sub>6</sub>H<sub>4</sub>-C=CH, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF, 26%.

For application of OPE-TTF cruciforms as redox-controlled wires for molecular electronics, protected thiol end-groups were incorporated. First, we subjected **1** to desilylation followed by cross-coupling reaction with an *S*-acetyl-protected 4-bromobenzenethiol, which gave the cruciform wire **13** incorporating two protected thiol groups (Scheme 4). This compound was previously synthesized in a slightly different manner,<sup>1a</sup> namely by treating the related cruciform containing *tert*-butyl-protected thiol groups with boron tribromide and acetyl chloride.

To increase the solubility of the product obtained from desilylation of compound **1**, we developed a small series of extended TTFs for which the methyl ester groups were



Scheme 4 Reagents and conditions: (i) K<sub>2</sub>CO<sub>3</sub>, MeOH, THF; (ii) 4-BrC<sub>6</sub>H<sub>4</sub>SAc, Pd(Pt-Bu<sub>3</sub>)<sub>2</sub>, CuI, *i*-Pr<sub>2</sub>NH, THF, toluene, 32% (2 steps).

extended to longer alkyl esters (Table 1). These molecules were made under standard conditions for desilylation ( $K_2CO_3$ , alcohol, THF), but the scope of the reaction depended strongly on the size of the alcohol. By using small, non-bulky alcohols, we were able to desilylate compound **1** within two hours at room temperature (entries 1 and 2). Treatment with propan-1-ol resulted additionally in transesterification to provide the final product **14** (Figure 3). When using longer alcohols (entries 3 and 4), the desilylation reaction was retarded significantly or even ceased. Thus, using decan-1-ol the transesterified, but non-desilylated, product **15** (Figure 3) was obtained. Yet, desilylation of this compound was conveniently accomplished simply by adding tetrabutylammonium fluoride to the reaction mixture.





Compound **14** was subjected to a twofold cross-coupling reaction with a large excess of 1,4-diiodobenzene (Scheme 5), providing the OPE3 **16** with two iodophenyl functionalities for further scaffolding.

In addition, compound **14** was treated with excess 1-iodo-4-[(trimethylsilyl)ethynyl]benzene in a Sonogashira reaction (Scheme 6) to provide OPE3 **17** incorporating two

 Table 1
 Desilylation and Transesterification of Compound 1 with Different Alcohols (K<sub>2</sub>CO<sub>3</sub>, THF)

Alcohol	Desilylation	Transesterification	Temp, time	Yield (%)
МеОН	yes	-	r.t., 45 min	98 <sup>a</sup>
PrOH	yes	yes	r.t., 2 h	90 (14)
BuOH	yes (slow)	yes	40 °C, 5 h	56 <sup>b</sup>
Me(CH <sub>2</sub> ) <sub>9</sub> OH	no	yes (slow)	40 °C, 18 h	47 (15)

<sup>a</sup> Ref. 1a.

<sup>b</sup> The yield was estimated from NMR data and corresponds to both transesterification and desilylation.



Scheme 5 Reagents and conditions: (i)  $K_2CO_3$ , PrOH, THF, 90%; (ii)  $4-IC_6H_4I$ , PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF, 53%.

protected alkyne units. Compounds 16 and 17 are useful building blocks for further scaffolding. Thus, desilylation of 17 followed by cross-coupling reaction with excess 1-(acetylthio)-4-iodobenzene (18) provided OPE5 cruciform 19 with two acetyl-protected thiol end-groups (Scheme 7). Thereby we succeeded in developing two OPE wires (13 and 19) with a single vertically disposed TTF unit and with different lengths between the two sulfur anchoring groups.

Finally, we became interested in developing an improved synthesis of the known compound **18**, which is extensively employed for incorporating molecular 'alligator clips' into molecular wires. We found that its synthesis could be carried out in two steps under mild conditions starting



Scheme 6 Reagents and conditions: (i)  $4-IC_6H_4CCSiMe_3$ , PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF, 62%.



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from the commercially available 4-iodobenzenesulfonyl chloride (20) (Scheme 8). Reduction of 20 with triphenylphosphine in toluene<sup>10</sup> provided 4-iodobenzenethiol (21) in moderate yield. This method is a convenient alternative to monolithiation of 1,4-diiodobenzene with *tert*butyllithium followed by addition of elementary sulfur.<sup>11</sup> Compound 21 was then converted quantitatively into the

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more stable acetylthio compound **18**. In addition the synthesis of **18** is shortened by two steps compared to the latest synthetic improvement involving a Newman–Kwart thiocarbamate rearrangement at high temperature.<sup>12</sup>



Scheme 8 *Reagents and conditions*: (i) Ph<sub>3</sub>P, toluene, 60 °C, 48%; (ii) AcCl, py, 99%.

We subjected the cruciform 9 to detailed NMR spectroscopic analysis employing Heteronuclear Single Quantum Coherence (HSQC), Heteronuclear Multiple Quantum Coherence (HMQC), and Attached Proton Test (APT) methods. All chemically inequivalent nuclei in the cruciform 9 gave rise to separate signals in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The result of the analysis is listed in Table 2 and Figure 4. The signals for the two different carbon nuclei of the central phenylene ring were readily assigned. While the signals originating from the six different carbon nuclei of the outer C<sub>6</sub>H<sub>2</sub> rings were unequivocally identified, they could only be partly assigned to the individual nuclei. The six different carbon nuclei of the two DTF rings were assigned to the resonances at  $\delta = 129.7, 129.8,$ 131.5, 131.7, 133.5, and 133.8. The two latter signals presumably correspond to the C2 of the 1,3-dithiole rings, even though no HMQC cross-peaks to the fulvene protons were observed.

The absorption spectra of OPE-TTF cruciforms **9**, **14**, and **19** dissolved in CH<sub>2</sub>Cl<sub>2</sub> are revealed in Figure 5. OPE3 **9** shows a broad absorption in the range 350–500 nm with maxima at 354, 382 ( $\varepsilon = 60,300 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 416 nm (broad). By comparison with the extended TTF **14** ( $\lambda_{\text{max}} = 424 \text{ nm}, \varepsilon = 67,400 \text{ M}^{-1} \text{ cm}^{-1}$ ), the broad absorption at 416 nm is attributed to the extended TTF units. OPE5 **19** shows a very strong absorption at 365 nm with a molar absorptivity of 145,000 M<sup>-1</sup> cm<sup>-1</sup> ascribed to the OPE scaffold which is in accordance to previously reported data for the OPE5 system.<sup>13</sup> In addition, compound **19** 





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<sup>13</sup> C NMR ( $\delta$ )	Assignment <sup>a</sup>	
11.5	<i>C</i> H(CH <sub>3</sub> ) <sub>3</sub>	
18.9	$CH(CH_3)_3$	
53.5, 53.6 <sup>b</sup>	$CO_2CH_3$	
89.7	$C \equiv C 2 \text{ or } 9$	
96.3	<i>C</i> ≡C 10	
99.4	<i>C</i> ≡C 1	
104.7	$C \equiv C 2 \text{ or } 9$	
112.7	C= <i>C</i> H 13 or 14	
121.3	Ar 5 or 8	
122.2	Ar 5 or 8	
123.2	Ar 11	
128.5	Ar 4 or 7	
129.5	Ar 4 or 7	
129.7, 129.8, 131.5, 131.7	DTF ring-C	
131.8	Ar 12	
133.5, 133.8	DTF ring-C	
134.8	Ar 3, 6	
159.8, 160.2	$CO_2CH_3$	

<sup>a</sup> For labelling, see Figure 4.

<sup>b</sup> Four different carbon nuclei (i.e., overlapping signals).

exhibits a broad shoulder absorption at 426 nm which is assigned to the TTF moiety.



Figure 5 UV-Vis absorption spectra  $(CH_2Cl_2)$  of compound 9, 14, and 19

The electrochemistry of compound **9** in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The compound underwent irreversible oxidations at 0.48 and 0.86 V vs Fc<sup>+</sup>/Fc (Figure 6, curves A). Electrolysis at 1.2 V followed by electrolysis at 0 V vs Fc<sup>+</sup>/Fc provided a new species exhibiting quasi-reversible electrochemistry (Figure 6, curves B). According to DPV the new species is oxidized at 0.23 V. The UV-Vis absorption spectrum of the product (Figure 6, inset) showed a redshifted absorption maximum relative to that of **9** and an increase in the molar absorptivity, which suggests the formation of a more conjugated system. Compound **13** showed similarly irreversible oxidations (at ca. 0.50 and 0.85 V vs Fc<sup>+</sup>/Fc). Electrolysis at 0.9 V followed by electrolysis at 0 V vs Fc<sup>+</sup>/Fc provided again a new species with a more reversible electrochemical nature. This product of electrolysis had a similar first oxidation potential (0.20 V) as that formed from **9**. In all, the electrochemistry of the cruciform molecules is rather complicated and an interpretation of the results requires further experiments, which are outside the scope of this paper.



**Figure 6** Cyclic voltammetry (top) and differential pulse voltammetry (bottom) of **9** (labeled A). Electrolysis at 1.2 V followed by electrolysis at 0 vs Fc<sup>+</sup>/Fc provided the voltammograms labeled B. The inset shows the absorption spectra of **9** before and after electrolysis. Counter electrode: Pt wire; Working electrode Pt disk; Reference electrode: Ag/Ag<sup>+</sup> (10mM). Scan rate for cyclic voltammetry: 0.1 V/s. Solvent: CH<sub>2</sub>Cl<sub>2</sub>. Counter electrolyte: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

In conclusion, stepwise protocols for the synthesis of several novel OPE-TTFs have been developed. In one route, the OPE is first constructed with aldehyde groups along the wire, which in a final step are subjected to Wittig reactions to furnish the dithiafulvene functionalities. In another route, extended TTFs incorporating acetylenic units are linked together via palladium-catalyzed cross-coupling reactions. While an OPE3 scaffold with two vertically disposed TTFs displayed good stability, the related OPE5 decomposed after prolonged time in solution. In contrast, OPE3 and OPE5 scaffolds with one central TTF unit and protected thiol end-groups exhibited good stability and are currently subject to single-molecule conductivity studies.

All palladium-catalyzed reactions were performed in degassed solvents, by sonicating the solvent with argon bubbling. TLC was carried out on commercially available pre-coated plates (Merck 60  $F_{254}$ ). Melting points were measured on a microscope hot stage

melting point apparatus or a silicone oil bath apparatus and are uncorrected. 1H, 13C, APT, HMQC, HMBC NMR spectra were recorded on 300 or 500 MHz instruments using an internal deuterium lock. UV-Vis spectra were obtained using a Varian CARY50 spectrophotometer, and cuvette path lengths of 1 cm. Spectra are corrected for solvent absorption (background). Calculated extinction coefficients have uncertainties estimated to 10% due to limited sample quantities. Cyclic voltammograms and differential pulse voltammograms were measured in a 3-electrode setup using a CHI-potentiostat, with platinum as the working electrode, a Pt wire as the counter electrode, and Ag/Ag<sup>+</sup> was used as reference electrode. However, all potentials are reported against ferrocene (II/III) measured under the same conditions. All voltammograms are measured in CH2Cl2 with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. Spectra of oxidized species (spectroelectrochemistry) were measured using a Varian CARY50 spectrophotometer, and cuvette path lengths of 1 mm. The working electrode was here a platinum grid immersed in the cuvette, and the potential was kept fixed during the measurement, again using a platinum wire as the counter electrode, and Ag/Ag<sup>+</sup> as the reference electrode.

## **Compound 5**

To a soln of **4** (0.563 g, 1.13 mmol) in THF (20 mL) and MeOH (10 mL) was added  $K_2CO_3$  (0.138 g, 1.00 mmol). The mixture was stirred under argon at r.t. for 8 h and then poured into  $CH_2Cl_2$  (150 mL). The mixture was washed with  $H_2O$  (3 × 100 mL) and sat. aq NaCl (75 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to furnish the product (0.360 g, 80%) as a yellow solid; mp 78–79 °C.

 $^1\text{H}$  NMR (300 MHz, CDCl\_3):  $\delta$  = 8.10 (s, 1 H), 8.08 (s, 1 H), 3.96 (s, 3 H), 3.92 (s, 3 H), 3.50 (s, 1 H), 1.15 (m, 21 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 165.7, 165.4, 136.7, 136.6, 135.3, 134.8, 123.5, 122.0, 103.6, 100.3, 84.7, 81.0, 52.8, 18.8, 11.4.

MS (FAB):  $m/z = 399 [M + H^+]$ .

Anal. Calcd for  $C_{23}H_{30}O_4Si: C, 69.31; H, 7.59$ . Found: C, 69.34; H, 7.66.

# **OPE3** Tetraester 6

Compound **5** (0.447 g, 1.120 mmol), 1,4-diiodobenzene (0.123 g, 0.374 mmol),  $PdCl_2(PPh_3)_2$ , and CuI (0.046 g, 0.241 mmol) were dissolved in degassed THF (20 mL), whereafter degassed Et<sub>3</sub>N (10 mL) was added under argon. The mixture was stirred under argon for 4 h and then poured into CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The mixture was washed with sat. aq NH<sub>4</sub>Cl (2 × 150 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The residue was subjected to column chromatography (silica gel, 10% EtOAc–heptane) to provide the product (0.237 g, 73%) as a yellow solid; mp 175–176 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.13 (s, 4 H), 7.57 (s, 4 H), 4.00 (s, 6 H), 3.94 (s, 6 H), 1.16 (s, 42 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 165.9, 165.5, 136.9, 135.8, 135.3, 134.0, 132.0, 123.5, 123.0, 122.9, 103.9, 100.1, 96.5, 89.7, 52.8 (two overlapping signals), 18.8, 11.2.

MS (FAB):  $m/z = 872 [M + H^+]$ .

Anal. Calcd for  $C_{52}H_{62}O_8Si_2$ : C, 71.69; H, 7.17. Found: C, 71.25; H, 7.34.

#### **OPE3** Tetraol 7

A soln of **6** (0.210 g, 0.241 mmol) in THF was cooled to 0 °C. 1 M DIBAL-H in hexane (2.41 mL) was added dropwise over 5 min, and the mixture was then allowed to reach r.t. After stirring for 2 h, the mixture was poured into  $CH_2Cl_2$  (200 mL). The mixture was washed with sat. aq NH<sub>4</sub>Cl (2 × 100 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to provide the product (0.175 g, 96%) as a white solid; mp 191–195 °C.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 7.65 (s, 4 H), 7.64 (s, 2 H), 7.56 (s, 2 H), 5.44 (t, *J* = 5.6 Hz, 2 H), 5.43 (t, *J* = 5.9 Hz, 2 H), 4.71 (d, *J* = 5.9 Hz, 4 H), 4.66 (t, *J* = 5.6 Hz, 4 H), 1.12 (s, 42 H).

<sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ): δ = 142.9, 142.5, 131.8, 129.7, 129.0, 122.6, 119.7, 119.6, 104.1, 96.9, 94.9, 89.0, 60.7 (two overlapping signals), 18.5, 10.7.

MS (FAB):  $m/z = 759 [M + H^+]$ .

Anal. Calcd for  $C_{48}H_{62}O_4Si_2$ : C, 75.94; H, 8.23. Found: C, 75.58; H, 8.55.

## **OPE3 Tetraaldehyde 8**

To a mixture of **7** (0.160 g, 0.211 mmol) in anhyd  $CH_2Cl_2$  (40 mL) were added PCC (0.318 g, 1.46 mmol), 4 Å molecular sieves (ca. 30 spheric pieces), and Celite (2 g). The mixture was stirred at r.t. for 3 h under argon and then filtered through a short plug of silica gel (under suction). The silica gel was washed with  $CH_2Cl_2$  (120 mL), and the combined organic filtrates were concentrated in vacuo to provide the product (0.098 g, 62%) as a yellow solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.63 (s, 2 H), 10.62 (s, 2 H), 8.18 (s, 2 H), 8.13 (s, 2 H), 7.61 (s, 4 H), 1.16 (s, 42 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 190.5, 190.3, 138.9, 138.3, 133.4, 132.3, 132.2, 126.7, 125.7, 123.0, 103.3, 100.7, 98.1, 86.5, 18.8, 11.3.

MS (FAB):  $m/z = 752 [M + H^+]$ .

Anal. Calcd for  $C_{48}H_{54}O_4Si_2$ : C, 76.40; H, 7.25. Found: C, 76.38; H, 7.79.

#### **OPE3-TTF 9**

Compound **8** (0.090 g, 0.120 mmol) and the phosphonium salt **10** (0.304 g, 0.600 mmol) were dissolved in anhyd THF (10 mL) and anhyd MeCN (3 mL). Then Et<sub>3</sub>N (0.117 mL, 0.725 mmol) was added, and the mixture was stirred at r.t. for 3 h, whereafter it was poured into CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The mixture was then washed with H<sub>2</sub>O (2 × 100 mL) and sat. aq NaCl (100 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The residue was subjected to column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> to 5% EtOAc–CH<sub>2</sub>Cl<sub>2</sub>) to furnish the product (117 mg, 63%) as a red solid; mp 130–132 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57 (s, 4 H), 7.48 (d, *J* = 0.6 Hz, 2 H), 7.47 (d, *J* = 0.6 Hz, 2 H), 6.98 (s, 2 H), 6.92 (s, 2 H), 3.88 (s, 3 H), 3.87 (2 s, 6 H), 3.85 (s, 3 H).

 $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.2, 159.8, 134.8, 133.8, 133.5, 131.8, 131.7, 131.5, 129.8, 129.7, 129.5, 128.5, 123.2, 122.2, 121.3, 112.7, 104.7, 99.4, 96.3, 89.7, 53.6, 53.5, 53.5 (two overlapping signals), 18.9, 11.5.

MS (FAB):  $m/z = 1559 [M + H^+]$ .

Anal. Calcd for  $C_{76}H_{78}O_{16}S_8Si_2$ : C, 58.51; H, 5.04. Found: C, 58.16; H, 5.06.

#### OPE2-TTF 11

To a mixture of **2** (0.271 g, 0.333 mmol) in THF (10 mL) and MeOH (10 mL) was added  $K_2CO_3$  (0.10 g). After stirring at r.t. for 20 min, Et<sub>2</sub>O (200 mL) was added, and the mixture was washed with H<sub>2</sub>O (100 mL) and sat. aq NaCl soln (100 mL). The organic phase was dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The red residue was mixed with 1,4-diiodobenzene (0.44 g, 1.33 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.012 g, 0.0167 mmol, 5 mol%), and CuI (0.003 g, 0.0167 mmol, 5 mol%). Then degassed THF (12 mL) and degassed Et<sub>3</sub>N (4 mL) were added under argon. After stirring at r.t. for 20 h, the mixture was poured into CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with sat. aq NH<sub>4</sub>Cl (50 mL), and sat. aq NaCl. The organic phase was dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo. The red-brown residue was subjected to column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>)

to provide the product (0.093 g, 30%) as a red solid; mp 142–144  $^{\circ}\mathrm{C}.$ 

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.59 (d, *J* = 8.3 Hz, 2 H), 7.54 (2 s, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 6.95 (s, 1 H), 6.85 (s, 1 H), 3.95–3.81 (m, 12 H), 1.21–1.01 (m, 21 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 160.1 (three overlapping signals), 159.9, 137.8, 135.2, 134.8, 133.8, 133.5, 133.2, 131.7, 131.5, 129.7 (two overlapping signals), 129.4, 128.4, 122.4, 122.1, 121.2, 112.7 (two overlapping signals), 104.7, 99.4, 95.6, 94.9, 88.9, 53.6 (two overlapping signals), 53.5, 53.5, 18.9, 11.5.

MS (MALDI-TOF): m/z = 944 (M<sup>+</sup>).

Anal. Calcd for  $C_{41}H_{41}IO_8S_4Si: C, 52.11; H, 4.37.$  Found: C, 52.30; H, 4.45.

# OPE5-TTF 12

Compound **11** (0.043 g, 0.045 mmol) was mixed with 1,4-diethynylbenzene (2.5 mg, 0.022 mmol),  $PdCl_2(PPh_3)_2$  (5 mg, 0.0011 mmol, 5 mol%), and CuI (1 mg, 0.005 mmol, 20 mol%) under argon. Then argon-degassed THF (4 mL) and argon-degassed Et<sub>3</sub>N (1 mL) were added. After stirring at r.t. for 20 h, the mixture was poured into CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The mixture was passed through a short plug of silica gel and then subjected to repeated column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> to 5% EtOAc-CH<sub>2</sub>Cl<sub>2</sub>) to provide the product (10 mg, 26%) as a red solid; mp 184–186 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.67–7.51 (m, 12 H), 7.49 (d, J = 2.7 Hz, 4 H), 7.02 (s, 2 H), 6.95 (s, 2 H), 3.97–3.68 (4 s, 24 H), 1.21 (2 s, 42 H).

MS (MALDI-TOF): *m*/*z* = 1758/1759/1760/1761/1762/1763/1764/ 1765 [M<sup>+</sup>/M + H<sup>+</sup>/isotopologues].

# **OPE3-TTF 13**

Desilylated **1** (20.6 mg, 0.035 mmol), 1-(acetylthio)-4-bromobenzene (40 mg, 0.17 mmol), CuI (1.3 mg, 0.007 mmol), and Pd(PtBu<sub>3</sub>)<sub>2</sub> (1.9 mg, 0.004 mmol) were dissolved in degassed *i*-Pr<sub>2</sub>NH (0.6 mL), toluene (1 mL), and THF (1 mL) under argon. Then the mixture was subjected to ultrasonication at 50 °C for 90 min. The mixture was evaporated onto Celite and purified by anhyd column chromatography (1. 0 to 100% CH<sub>2</sub>Cl<sub>2</sub>-heptane; 2. 0 to 10% MeOH–CH<sub>2</sub>Cl<sub>2</sub>), providing the product (10 mg, 32%) as a red solid. The analytical data were in accordance to those previously reported.<sup>1a</sup>

#### Extended TTF 14

To a soln of 1 (0.290 g, 0.397 mmol) in PrOH (60 mL) and THF (15 mL) was added  $K_2CO_3$  (1.01 g). After stirring at r.t. for 90 min, the mixture was poured into  $CH_2Cl_2$  (150 mL). The organic soln was passed through a short plug of silica gel. After concentration in vacuo, the product (0.251 g, 90%) was obtained as a dark red solid; mp 166–168 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40 (s, 2 H), 6.85 (s, 2 H), 4.29 (t, *J* = 6.8 Hz, 8 H), 3.45 (s, 2 H), 1.72 (m, 8 H), 1.06 (t, *J* = 7.4 Hz, 12 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 159.7, 159.6, 135.2, 134.3, 131.4, 129.9, 129.4, 120.9, 111.9, 84.5, 81.4, 68.5, 68.5, 21.9 (two overlapping signals), 10.4 (two overlapping signals).

MS (FAB):  $m/z = 698 [M + H^+]$ .

Anal. Calcd for  $C_{34}H_{34}O_8S_4$ : C, 58.43; H, 4.90. Found: C, 58.33; H, 4.99.

#### **Extended TTF 15**

To a soln of compound 1 (0.52 g, 0.71 mmol) in decan-1-ol (8 mL) and THF (10 mL) was added  $K_2CO_3$  (0.70 g). After stirring at 40 °C for 18 h under argon, the mixture was poured into Et<sub>2</sub>O (100 mL)

and washed with  $H_2O$  (4 × 50 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo to a red residue. The residue was purified (silica gel, CH<sub>2</sub>Cl<sub>2</sub>). After concentration in vacuo, the product (0.41 g, 47%) was obtained as dark red solid; mp 52–55 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.39 (s, 2 H), 6.84 (s, 2 H), 4.28–4.19 (m, 8 H), 1.75–1.63 (m, 8 H), 1.42–1.20 (m, 56 H), 0.92–0.83 (m, 12 H), 0.29 (s, 18 H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 159.8, 159.7, 135.1, 133.6, 131.3, 130.1, 128.7, 121.6, 112.6, 102.9, 102.5, 67.1, 67.1, 32.0, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.3, 29.3, 28.5, 28.5, 26.0, 25.9, 22.8, 14.3, 0.1.

MS (FAB):  $m/z = 1235 [M + H^+]$ .

Anal. Calcd for  $C_{68}H_{106}O_8S_4Si_2$ : C, 66.08; H, 8.64. Found: C, 65.65; H, 8.94.

# **OPE3-TTF 16**

To a soln of **14** (0.110 g, 0.157 mmol) in degassed THF (25 mL) and degassed  $Et_3N$  (5 mL) were added 1,4-diiodobenzene (1.23 g, 3.73 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (6.0 mg, 0.0086 mmol, 5 mol%), and CuI (1.8 mg, 0.0086 mmol, 5 mol%) under argon. After stirring for 19 h under argon, the mixture was poured into  $CH_2Cl_2$  (150 mL). The mixture was washed with sat. aq NH<sub>4</sub>Cl (100 mL) and sat. aq NaCl (100 mL), dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to a red residue. Column chromatography (silica gel, heptane–CH<sub>2</sub>Cl<sub>2</sub>, 100:0 to 0:100) gave the product (0.092 g, 53%) as orange crystals; mp 192.5–194.0 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, *J* = 8.4 Hz, 4 H), 7.48 (s, 2 H), 7.36 (d, *J* = 5.5 Hz, 4 H), 6.92 (s, 2 H), 4.21 (t, *J* = 6.7 Hz, 8 H), 2.02–1.53 (m, 8 H), 0.98 (t, *J* = 7.4 Hz, 12 H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 159.7 (two overlapping signals), 137.8, 134.9, 134.0, 133.3, 131.2, 130.2, 128.8, 122.4, 121.5, 112.3, 95.8, 94.9, 88.9, 68.5, 68.5, 21.9 (two overlapping signals), 10.5 (two overlapping signals).

MS (MALDI-TOF):  $m/z = 1104 [M + H^+]$ .

Anal. Calcd for  $C_{46}H_{40}I_2O_8S_4{:}$  C, 50.10; H, 3.66. Found: C, 50.36; H, 3.67.

# **OPE3-TTF 17**

To a soln of the dialkyne **14** (0.200 g, 0.29 mmol) in anhyd THF (12 mL) and Et<sub>3</sub>N (5 mL) were added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (12 mg, 0.017 mmol, 6 mol%) and CuI (10 mg, 0.044 mmol, 15 mol%). After stirring for 2 min, 1-iodo-4-[(trimethylsilyl)ethynyl]benzene (0.515 g, 1.72 mmol) was added. The mixture was allowed to stir at r.t. for 6 h under an inert atmosphere (argon). The mixture was then diluted with  $CH_2Cl_2$  (50 mL) and washed with sat. aq  $NH_4Cl$  (25 mL). The organic layer was dried ( $Na_2SO_4$ ) and concentrated in vacuo to a red-brown solid. The red-brown residue was subjected to column chromatography (silica gel,  $CH_2Cl_2$ ) to provide the product (0.188 g, 62%) as a red solid; mp 208–209 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53–7.46 (m, 10 H), 6.92 (s, 2 H), 4.25–4.18 (m, 8 H), 1.76–1.70 (m, 8 H), 1.02–0.94 (m, 12 H), 0.29–0.22 (m, 18 H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 159.7, 159.7, 134.9, 134.0, 132.1, 131.6, 131.3, 130.2, 128.9, 123.6, 122.9, 121.5, 112.4, 104.7, 96.8, 96.4, 89.4, 68.5, 68.5, 21.9 (two overlapping signals), 10.5 (two overlapping signals), 0.06.

MS (ESP+):  $m/z = 1043.4 [M + H^+]$ .

Anal. Calcd for  $C_{56}H_{58}O_8S_4Si_2$ : C, 64.64; H, 5.60; S, 12.29. Found: C, 64.38; H, 5.65; S, 12.12.

#### **OPE5-TTF 19**

The OPE3 17 (0.120 g, 0.115 mmol) was desilylated with TBAF-3 H<sub>2</sub>O (0.110 g, 0.35 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at r.t. for 5 min. The mixture was then diluted by CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the organic layer was washed with sat. aq NH<sub>4</sub>Cl. The organic layer was poured through a short column of silica gel using additional CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and concentrated in vacuo to a red solid. The red crude product was redissolved in anhyd THF (10 mL), then Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (6 mg, 0.017 mmol, 6 mol%) and CuI (5 mg, 0.044 mmol, 15 mol%) were added. i-Pr<sub>2</sub>NH (1 mL) was then added to the mixture and it was allowed to stand for 5 min before 1-(acetylthio)-4-iodobenzene (18, 0.192 g, 0.69 mmol) was added. The mixture was stirred under argon at r.t. for 2 h. The mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with sat. aq NH<sub>4</sub>Cl (25 mL) followed by brine (25 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo to a red-brown solid. Column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) gave the product (0.050 g, 36%) as a red solid; mp 204-206 °C.

IR (neat): 3062, 2970, 1755, 1628, 1553, 1272, 1115, 1038, 849, 627, 546 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.57–7.47 (m, 14 H), 7.35 (d, *J* = 8.5 Hz, 4 H), 6.92 (s, 2 H), 4.16–4.09 (m, 8 H), 2.35 (s, 6 H), 1.67–1.61 (m, 8 H), 0.93–0.86 (m, 12 H).

<sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 193.8, 160.1, 159.9, 135.4, 135.0, 134.8, 132.7, 132.3, 132.3, 131.9, 130.3, 129.4, 129.3, 124.6, 123.8, 123.4, 122.0, 112.6, 96.7, 91.2, 91.1, 89.8, 69.0, 68.9, 30.7, 22.4, 22.3, 10.7 (two overlapping signals).

MS (MALDI-TOF): m/z = 1197 (M<sup>+</sup>).

Anal. Calcd for  $C_{66}H_{54}O_{10}S_6$ : C, 66.09; H, 4.54; S,16.04. Found: C, 66.28; H, 4.56; S, 16.05.

## 4-Iodobenzenethiol (21)

4-Iodobenzenesulfonyl chloride 20 (4.00 g, 13.2 mmol) was dissolved in anhyd toluene (60 mL) in a 3-neck round-bottom flask with an N<sub>2</sub> inlet, reflux condenser, and CaCl<sub>2</sub> guard tube. Ph<sub>3</sub>P (10.4 g, 39.7 mmol) was added in portions and the mixture was stirred for 10 min (if the temperature had not reached 60 °C after addition of Ph<sub>3</sub>P, then the mixture should be heated for an additional 10 min at 60 °C). The mixture was then cooled below 50 °C and H<sub>2</sub>O (15 mL) was added. The mixture was allowed to stand for an additional 10 min. The aqueous layer was discarded, and the organic layer was extracted with aq 10% NaOH (2×40 mL). The alkaline aqueous extract was washed with toluene (2  $\times$  30 mL), acidified with aq 4 M HCl and extracted with  $CH_2Cl_2$  (2 × 40 mL). The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed under reduced pressure to obtain nearly pure 4-iodobenzenethiol. Column chromatography (silica gel, heptane-EtOAc, 9:1) gave the product (1.50 g, 48%) as white crystals. The analytical data were in accordance to those previously reported.<sup>11</sup>

## 1-(Acetylthio)-4-iodobenzene (18)

4-Iodobenzenethiol (**21**, 1.50 g, 6.35 mmol) was dissolved in pyridine (20 mL, dried over NaOH pellets) and under argon. AcCl (0.99 g, 0.90 mL, 12.7 mmol) was slowly added via syringe with vigorous stirring. The mixture was then stirred for 25 min and poured into H<sub>2</sub>O with crushed ice (approx. 100 mL). The cold H<sub>2</sub>O was extracted with heptane ( $2 \times 50$  mL) and the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed under reduced pressure to yield a colorless oil that slowly solidified to white crystals (1.76 g, 99%). The analytical data were in accordance to those previously reported.<sup>11,12</sup>

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