A New Class of Extended Tetrathiafulvalene Cruciform Molecules for Molecular Electronics with Dithiafulvene-4,5-Dithiolate Anchoring Groups

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Development of functional organic molecules as components for molecular electronics has attracted wide interest in recent years.[1] In particular, oligo(phenyleneethynylene)s (OPEs, **Figure 1**) constitute a class of π-conjugated molecules that has been used extensively as molecular wires for transmitting a current between two electrodes.[2] The electron donor tetrathiafulvalene (TTF, Figure 1) is another attractive molecule, undergoing two reversible one-electron oxidations at potentials that can be tuned by either peripheral substitution or by insertion of a π-conjugated spacer between the two rings.[3] In fact, the suggestion by Aviram and Ratner[4] in 1974 that a donor-σ-acceptor dyad consisting of TTF and tetracyanoquinodimethane could be employed as a molecular rectifier can be considered to be the birth of molecular electronics. Several intramolecular charge-transfer compounds have been synthesized with this objective[5] in mind and some have been studied in junction devices.[5c] In addition, TTF derivatives with thiol end-groups have been inserted between electrodes and the switching of molecular junction conductance by successive oxidation/reduction cycles has been demonstrated.[6] With the objective of combining the properties of OPEs and TTF, we have, in recent years,

developed synthetic protocols for so-called OPE-TTF cruciform molecules in which a π-extended TTF is placed orthogonally to an OPE wire.[7] Conducting-probe (CP) AFM measurements on self-assembled monolayers (SAMs) of the **OPE5-TTF**, shown in Figure 1, revealed a 9-fold increase in conductivity relative to a simple OPE5.[8] Moreover, this molecule has been contacted in a three-terminal geometry in which it was reversibly switched between three redox states by a gate electrode.[9] In the quest for more advanced molecules, we decided to include redox-active dithiafulvene (DTF) units containing protected thiol groups in each end of the wire as in molecules **1-4** (Figure 1). These molecules can be seen as a new class of TTF-based cruciform molecules where both the horizontal and vertical backbones are extended TTFs. Alternatively, the molecules can be seen as OPE3-TTF cruciforms end-capped with protected DTF-4,5-dithiolate anchoring groups. As thiolate protection groups, the molecules contain different combinations of cyanoethyl, acetyl, and methyl. Here we describe synthetic protocols for obtaining these molecular wires and their electronic properties, including CP-AFM studies of SAMs and mechanically controllable break-junction (MCBJ) experiments.

The cruciform molecules were prepared according to **Scheme 1**. The known extended TTF **5**[7a] with two ethynyl groups was subjected to Pd-catalyzed cross-coupling reactions with the aryliodides **6** and **7**, respectively, to furnish the OPE3-TTFs **8** and **9**. Next, the dialdehyde **9** was subjected to a phosphite-mediated coupling with the readily obtainable 1,3-dithiol-2-thione **10**[10] to provide cruciform **1**. One cyanoethyl protecting group at each end of the molecule was selectively removed by treatment with 2.1 molar equivalents of cesium hydroxide in 1-propanol; this alcohol was used as solvent to prevent transesterification reactions of the ester groups on the central DTF units. The resulting dithiolate was treated with acetyl chloride to give cruciform **2**, while treatment with methyliodide gave cruciform **3**. Both these compounds were isolated as *Z/E* mixtures (at least two isomers according to ¹H-NMR spectroscopy). Removal of the two remaining cyanoethyl groups of **3** followed by treatment with acetyl chloride gave cruciform **4**. We also attempted to remove all four cyanoethyl groups by different bases and subjected the suspected tetrathiolate to acetylation, but could not isolate the compound with four SAc groups as it seemed to decompose quite readily.

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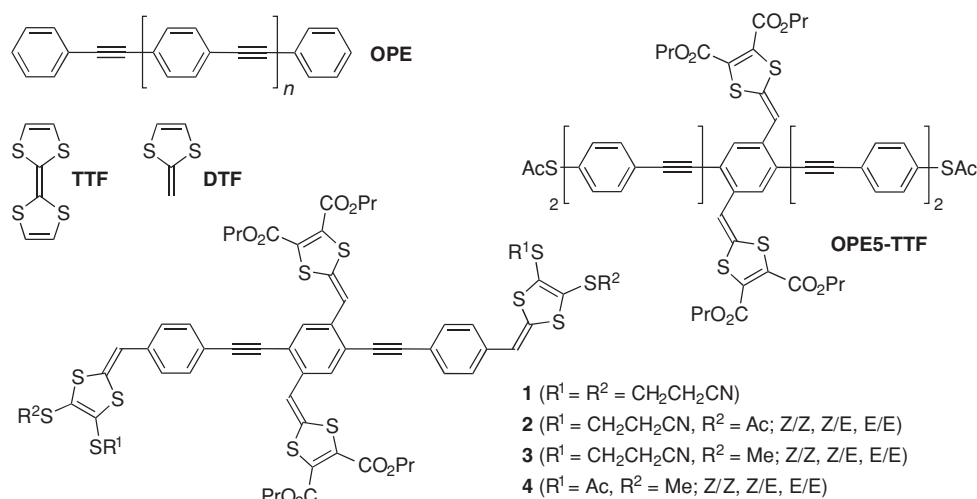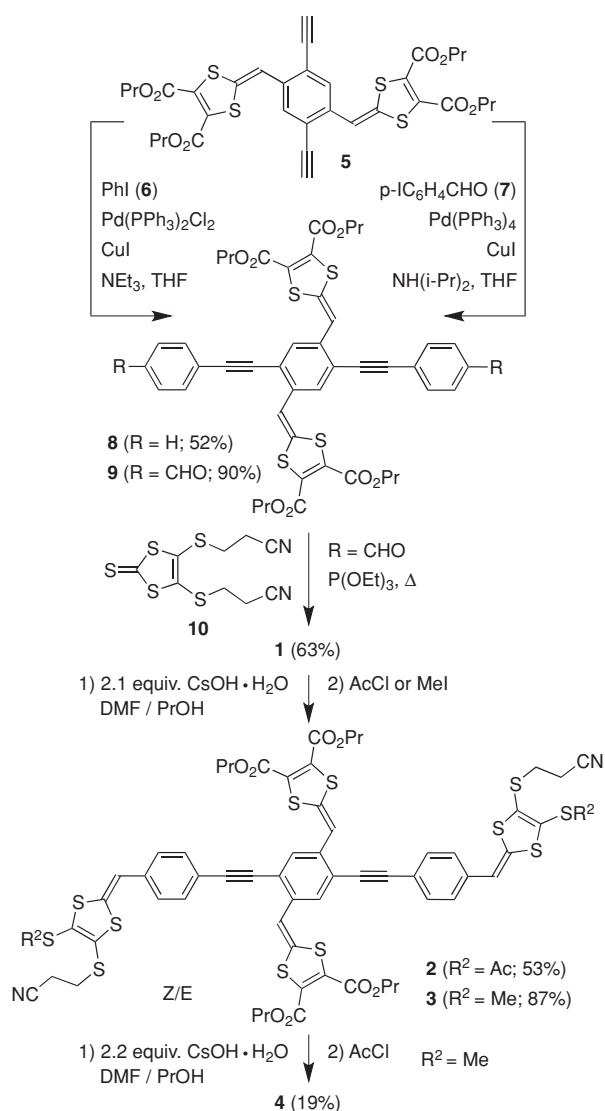Delft University of Technology
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Figure 1. Molecular structures.

1 (R¹ = R² = CH₂CH₂CN)
2 (R¹ = CH₂CH₂CN, R² = Ac; Z/Z, Z/E, E/E)
3 (R¹ = CH₂CH₂CN, R² = Me; Z/Z, Z/E, E/E)
4 (R¹ = Ac, R² = Me; Z/Z, Z/E, E/E)

Scheme 1. Synthesis of cruciforms composed of two extended TTFs.

The longest wavelength absorption maxima of **1** and **8** (spectra are shown in SI, together with electrochemical data) were similar but the molar absorptivities were significantly stronger for **1** because it has twice as many DTF units, λ_{max} (**1**): 402 (1.1 × 10⁵ M⁻¹ cm⁻¹), 437 (sh); λ_{max} (**8**): 417 (4.9 × 10⁴ M⁻¹ cm⁻¹), 425 (sh).

Formation of SAMs from cyanoethyl-protected TTF thiolates has previously been reported using hydroxide as base[11] and includes studies on a bis(dodecylthio)-TTF tethered through two thiolate groups.[11a] We were, however, unable to form stable and homogenous monolayers from either **1**, using KOH/1-propanol, or **2**, using either NEt₃ (for removal of acetyl group only) or KOH/1-propanol. Further, the simple OPE3-TTF **8** could not form a SAM on a gold substrate. Gratifyingly, however, high quality SAMs of **4** on gold surfaces were achieved using 15% NEt₃ in THF (conditions developed by Valkenier *et al.*[12]). A cyclic voltammogram (CV) of an aqueous solution of K₃Fe(CN)₆/K₄Fe(CN)₆ recorded with SAM-covered Au electrodes shows that the waves for the Fe²⁺/Fe³⁺ redox couple are decreased and shifted relative to a CV using bare Au electrodes (see SI), which implies that the SAM partly blocks access to the Au surface. As judged from the CV, it seems that the SAM is somewhat less dense (contains pinholes) than that obtained previously for **OPE5-TTF**,[8] and the methyl group might hinder the S from reaching the Au surface as efficiently. The transport properties of the SAM were measured by CP-AFM using a Au coated conductive tip as the top electrode. **Figure 2** shows a typical *I–V* curve for the molecular junction and the resistance histogram generated from about 160 measurements. All the resistances were determined over a small voltage range (± 0.3 V). The main peak of the Gauss fitting curve was on the order of 10⁸ Ω, and the average resistance value was calculated to be 1.18 × 10⁹ Ω.

In order to further investigate the molecular conductance of the new cruciform motif, we turned to MCBJ experiments. Cruciform **2** was found to form stable molecular junctions. Measurements were performed at room temperature using gold electrodes, and the molecules were deposited onto the sample in a freshly prepared solution (0.1 × 10⁻³ M in CH₂Cl₂). The

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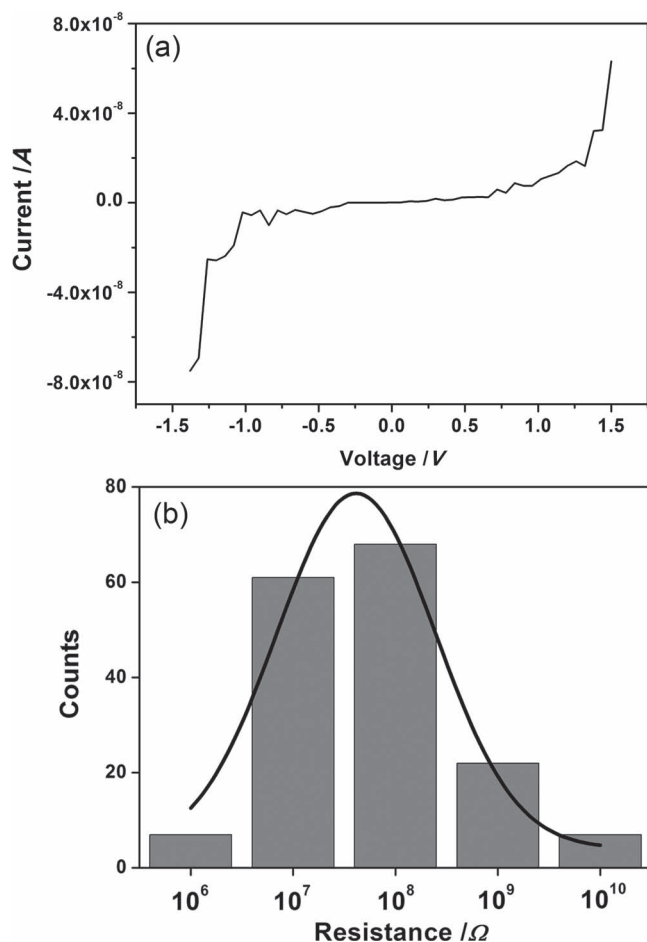
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Figure 2. Top: A typical *I–V* curve of the SAM molecular junction based on cruciform **4**. Bottom: Histogram of the SAM molecular junction resistance.
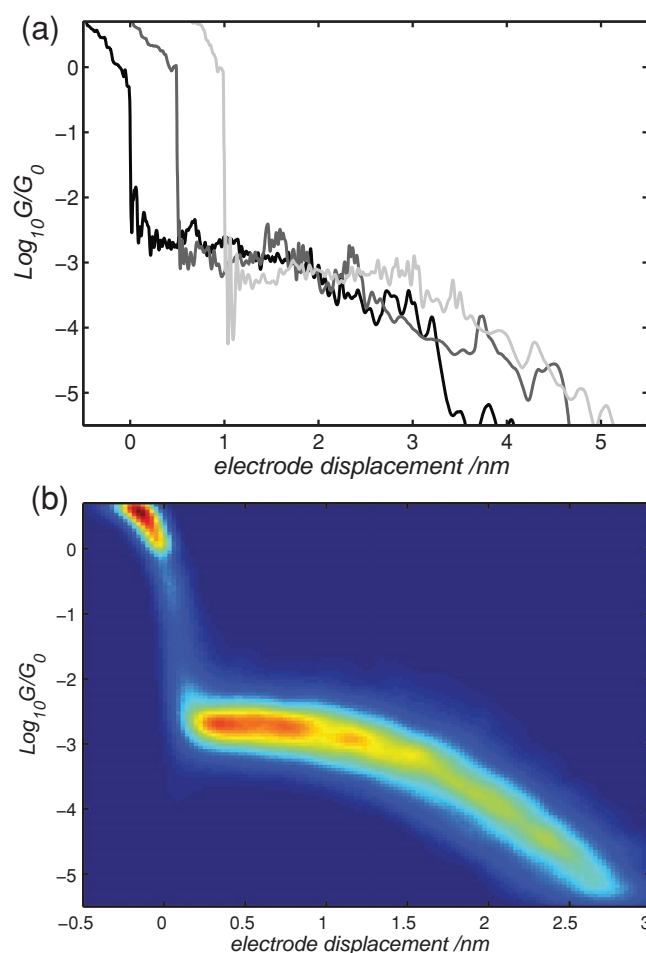

Figure 3. MCBJ experiments on cruciform **2** (0.1×10^{-3} M in CH_2Cl_2). Top: Individual breaking traces of gold. Bottom: Trace histogram built from 500 breaking traces of gold.

solvent did not show any additional features compared with empty gold junctions (the breaking traces of these are shown in SI). Cruciform **2** showed a clear conductance plateau around 10^{-3} G_0 (corresponding to a resistance of 1.3×10^7 Ω) with a length of roughly 2 nm (**Figure 3**). It is possible that the gradual drop in the conductivity between 2–2.5 nm is due to the presence of two or more π–π-stacked molecules in the junction, which may slide relative to each other as the electrodes are displaced. As noted above, the molecule exists as different *E/Z* isomers, but it has previously been shown that *cis/trans* isomerization about a double bond does not effect transport.[13] To ascertain whether this is also the case here, we performed transport calculations on different *E/Z* isomers and conformations, anchoring the molecule to a gold atom at an external sulfur in each end (see SI). The calculations revealed that the transmission at the Fermi level was almost the same for different *E/Z* isomers, although the through-space length differed by 3.4 Å. Yet, the through-bond length of the tunneling path is the same for the two configurations and the two tunneling paths have the same electronic coupling through the π-system, resulting in the same transport properties. Different conformers, i.e.,

rotations about single bonds, also had similar transmission around the Fermi level, although it may be that one conformation is more accessible for binding with the electrodes and dominates for purely steric reasons.

The much higher conductivity of **2** measured in the break junction in comparison with that measured of **4** by CP-AFM could possibly be explained by a more efficient anchoring configuration in the break junction, which may involve not only one of the end-sulfur atoms, but also direct binding to a DTF ring-sulfur atom in each end. The accessibility of all of the sulfur atoms in the end groups will depend on the degree of deprotection and the orientation of the molecules in the junction. Transport calculations (SI) suggest that for most binding configurations, the additional DTF units are likely to result in high levels of transport, as was seen in the comparison of **OPE5** with **OPE5-TTF** by CP-AFM,[8] as they introduce transport resonances close to the Fermi energy. In our calculations, the transport is sensitive to the degree of deprotection. Where end-sulfur atoms are protected, we see narrower transmission resonances and decreased transmission. Thus, the state of the end-sulfur atoms in an experiment may have both a steric impact on the

accessibility of these atoms for binding and also an electronic impact on the interaction with the electrodes.

An anchoring configuration in the break junction involving one of the central DTF rings could also be imagined, as long as an inefficient cross-conjugated current pathway[14] via the *meta*-configuration is avoided, as this would contradict the high conductance obtained. However, when subjecting OPE3 **8** to MCBJ studies (see SI), no binding was observed, in agreement with the failure to grow SAM of this molecule, suggesting that anchoring in **2** does indeed occur with via the DTF end-groups and not the central ones. Cruciform **1** was also measured in two different MCBJ samples, but it was difficult to obtain stable molecular junctions and only few (5–10%) breaking traces showed conductance plateaus (see SI) characterized by a high resistance of $1.3 \times 10^9\ \Omega$. Thus, presence of the cleavable acetyl group[15] seems important to enforce the anchoring of **2**. It is worth noting that the resistance of **1**, containing four protected thiolates, in the break junction is of the same order of magnitude as that of **4** in the monolayer, which supports inefficient anchoring of **4** in the SAM to the AFM tip electrode.

The OPE3-TTF **8** is structurally identical to the central part of cruciforms **1-4**. We managed to obtain single crystals of **8** (grown from CH_2Cl_2/ heptane), which were subjected to X-ray crystallography (**Figure 4**). Importantly, the central extended TTF part has an almost planar structure, while the two phenyl end-groups are slightly twisted out of this plane. Both single-crystal and thin-film devices were fabricated from **8**, but none

of these showed any field effect transistor performance (for details, see SI).

In conclusion, a series of new OPE-TTF cruciforms, containing two orthogonally oriented π-extended TTFs, has been developed with different protection groups for the four thiolate end-groups. The synthesis takes advantage of selective cyanoethyl deprotection–alkylation/acetylation reactions. While attempts at forming homogenous SAMs of cruciform **2** using different bases to remove the cyanoethyl and/or acetyl protecting groups failed, this molecule did form stable molecular junctions in break-junction experiments. A cleavable acetyl protecting group was required to obtain a stable junction, signalling that anchoring via an end-sulfur atom (thiolate) is in play. A remarkably low spread in bias conductance shows the great potential of the DTF-thiolate anchoring group for such studies. CP-AFM measurements on a SAM of the related cruciform **4** showed a resistance that was two orders of magnitude higher, suggesting that the conductivity depends on subtle changes in the ability to contact the molecule, i.e., less efficient contact seems to be achieved between the AFM tip and the DTF anchoring group. Anchoring via the DTF group presented in this paper is particularly important for the future development of gate-controlled devices based on the new cruciform motif, in which its four redox-active DTF groups are used for controlling conductivity changes, or for development of donor-acceptor dyads as molecular rectifiers.

[CCDC 875277 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
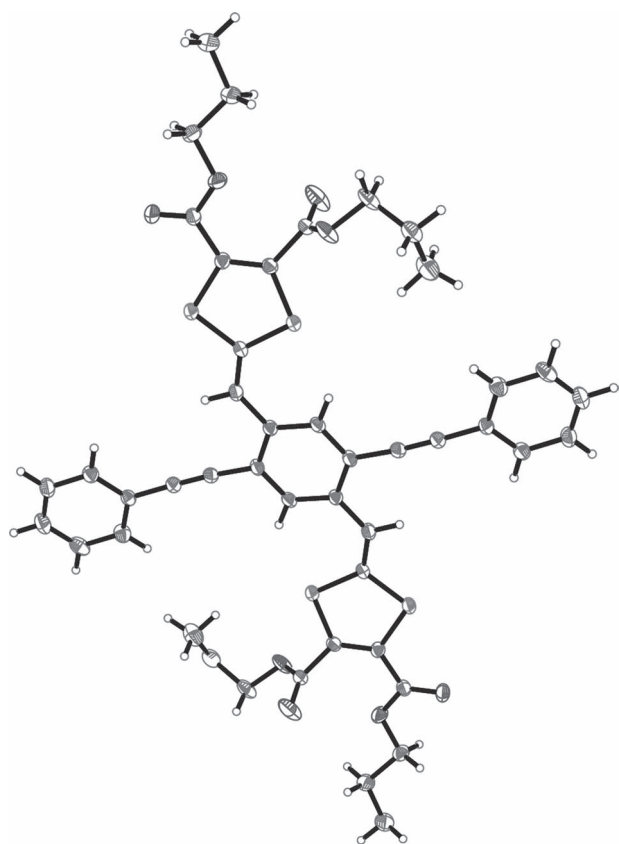
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Figure 4. Crystal structure of OPE3-TTF **8**.

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