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Journal of Materials Chemistry
www.rsc.org/materials

Synthesis of tetrathiafulvalenes suitable for self-assembly applications†

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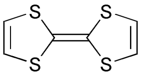
Received 26th August 2003, Accepted 24th October 2003
First published as an Advance Article on the web 13th November 2003

A series of new tetrathiafulvalenes, with double alkylthiol or alkyldisulfide substitution, have been prepared with a synthetic procedure that allows variation of different substituents. The target compounds **6a–e** and **15e–i** are sparsely soluble in organic solvents, but TTFs **6d** and **15g** gave a relatively dense packed monolayer upon exposure to gold surfaces.

Introduction

Tetrathiafulvalenes (TTFs) (**1**) are the most successful class of heterocycles in terms of creating highly conducting[1] and superconducting organic crystalline materials.



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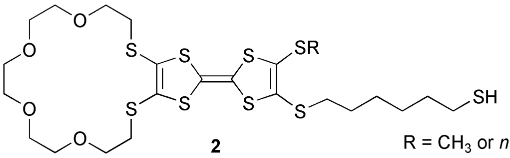
Good intermolecular overlap between TTF π-stacks gives high charge carrier mobilities, especially when sulfur substituents can create a two-dimensional network of contacts, thereby suppressing Peierls-distortion.[2] Many systems have been studied in detail and valuable insights in the solid state physics of organic materials have been achieved.[3] These valuable properties have rarely been possible to transfer to more tractable systems, as in the case of oligothiophenes.[4] Langmuir–Blodgett films of tetrathiafulvalenes have been studied and thin films have been prepared with interesting results,[5] but few electronic devices such as field-effect transistors have been realized.

The self-assembly methodology, where alkylthiols self-assembles on an active metal surface, offers an alternative way of preparing ordered thin films of organic materials.[6]

If successful this would then open up the possibility of transferring the unique properties of tetrathiafulvalene charge transfer salts to thin film devices.[7]

Self-assembly monolayer (SAM) systems with tetrathiafulvalenes have previously been studied by several groups. TTF-SAMs were first reported by Yip and Ward[8] but these systems were not particularly electrochemically stable. Bryce and co-workers studied a TTF with one alkylthiol attached to TTF substituted with a crown ether *i.e.* (**2**),[9] which proved to yield more stable SAMs. A structural variation of **2** has been presented by Sallé and co-workers (**3**),[10] as well as by Eschegoyen and co-workers (**4**).[11]



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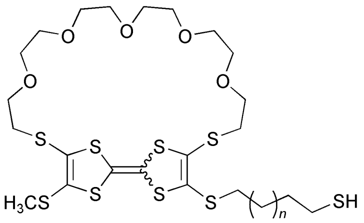
R = CH_3 or n-C_6H_{13}



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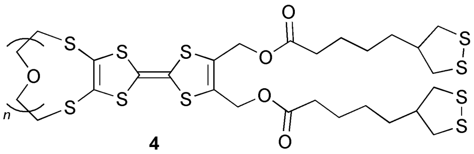
n = 0 or 3



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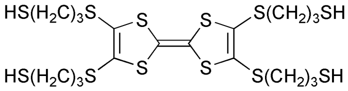
n = 0, 3, 4 or 5



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All three variations have been evaluated as electrochemical probes for different anions. Fujihara *et al.* have demonstrated that multiple short chain alkylthiol substituents can create highly stable SAMs (**5**).[12]

Other applications proposed for SAMs are for instance in tunneling devices.[13]

In order to be able to create a SAM that could work as an organic thin film field-effect transistor (OTF-FET) with

DOI: 10.1039/b310260b

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† Electronic supplementary information (ESI) available: Characterization data for the new compounds. See http://www.rsc.org/suppdata/jm/b3/b310260b/

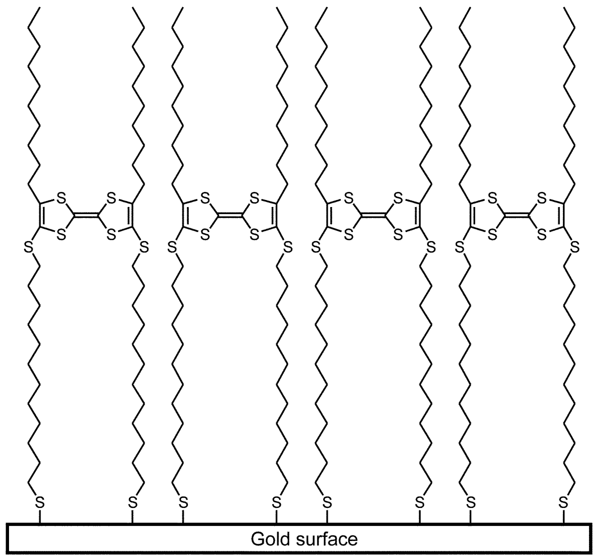


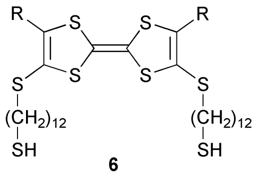
Fig. 1 Attempted idealised TTF-SAM structure.

appreciable charge carrier mobility, we should design a system that is able to form a stable SAM where a defined vertical region (layer) consists of a relatively densely packed electroactive π-system, *e.g.* TTF (Fig. 1).

The distances, both between the π-system and the surface, as well as "above" the electroactive region, should be possible to vary by the chosen synthesis. These regions should consist of alkyl- (sp^3) chains, in order to isolate the conducting layer from the surface.

We envisaged that a tetrathiafulvalene system that could form a stable SAM should have at least two alkylthiol "legs" as well as considerable alkyl substitution "above" the TTF-layer. It was also found desirable to avoid statistic phosphite couplings in the synthesis of unsymmetrical tetrathiafulvalenes.

We therefore decided to synthesize tetrathiafulvalenes of type **6**, which we anticipated to show several advantages but also a few drawbacks:



6

(i) The synthesis of **6** should allow relatively straightforward strategies for satisfying the demand for easy variation of the two different alkyl chains, as well as being a robust and reliable synthesis scheme.

(ii) The double alkyl thiols will render SAM stability, probably enhanced by a long upper alkyl chain, which also may self-assemble and form a stabilizing layer "above" the TTF π-stacking layer.

(iii) The two lower sulfur substituents should facilitate a more extended overlap between adjacent tetrathiafulvalenes, leading to higher charge carrier mobility.

(iv) The alkyl thiol chains are rather separated by the TTF-units, which can create a void in the SAM. This "space" perhaps has to be filled with additional free alkylthiols to develop a more uniform layer but in turn leading to more complicated SAM-studies.

The SAM-candidates of type **6** exist in equilibrium between a *cis* and *trans* diastereomer in the presence of acids.[14] This can also make the kinetics of monolayer formation more difficult to study, but it might be possible to overcome this by performing the self-assembly under equilibrium conditions (low pH and elevated temperatures).

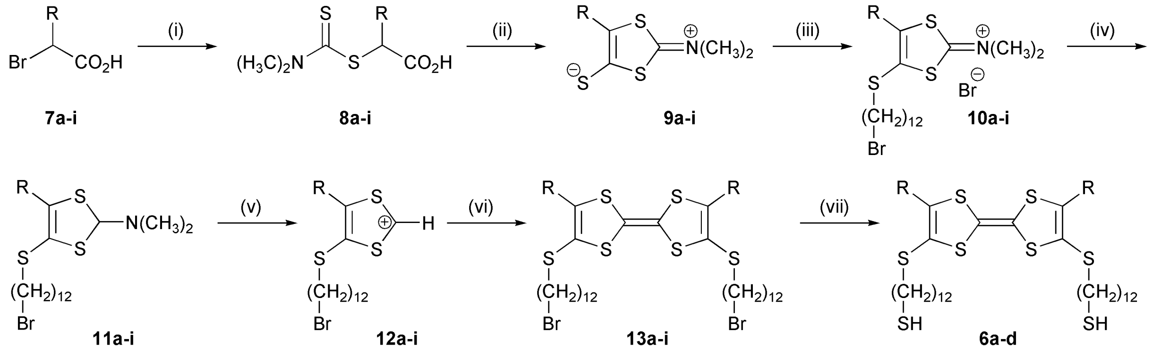
We present here the synthesis and full characterization of the self-assembly candidates, as well as some preliminary results on film formation.

Results and discussion

To create structures that would self-assemble, our first consideration was to choose a rather long alkylthiol chain that would attach to the substrate and preferably form an electronically insulating layer between the TTF units and the surface. In turn we could vary the R-group in **6** freely, with different alkyl chain lengths, to see if we could achieve more densely packed structures.

The synthetic sequence, which is described in Scheme 1, is a modification of a previously published procedure.[15]

The α-brominated carboxylic acid underwent a substitution reaction when treated with the sodium salt of *N*,*N*-dimethyldithiocarbamic acid, to give **8a–i** in 60–93% yield. The crystallinity varies with the chain length of the R-substituent. Compounds **8a–i** were, without further purification, dissolved in acetone and treated with acetic anhydride and triethylamine. The presumed intermediate is a 4-oxyl mesoion, which underwent a [1,3]-dipolar cycloaddition with simultaneous release of carbonyl sulfide when carbon disulfide was added to the solution. The products **9a–i** were obtained as yellow mesoionic precipitates in 40–96% yield. These products are stable at room temperature and can be stored at ambient temperature and atmosphere for several years without significant decomposition. Alkylation of **9a–i** at the thiolate functionality was carried out in acetone with 1,12-dibromododecane in excess. The reaction proceeded smoothly at reflux in less than 6 h to yield 4-dodecylthio-1,3-dithiolium salts **10a–i** in 72–99% yield. Reduction of **10a–i** with sodium borohydride in ethanol[16] to the corresponding amines **11a–i** (61–91% yield) followed by deamination by treatment with concentrated



Scheme 1 **a**: R = CH_3, **b**: R = C_2H_5, **c**: R = C_3H_7, **d**: R = C_4H_9, **e**: R = C_6H_{13}, **f**: R = $C_{10}H_{21}$, **g**: R = $C_{12}H_{25}$, **h**: R = 1-naphthyl, **i**: R = 2-naphthyl. *Reagents and conditions*: (i) Me_2NCS_2Na, EtOH, 0 °C; (ii) Ac_2O, Et_3N, CS_2, rt, acetone; (iii) $Br(CH_2)_{12}Br$, acetone, reflux; (iv) $NaBH_4$, EtOH, rt; (v) HPF_6, H_2SO_4, 0 °C; (vi) Et_3N, CH_3CN, rt, N_2; (vii) $(Me_3Si)_2S$, (n-Bu)$_4$NF, THF, −10° C.

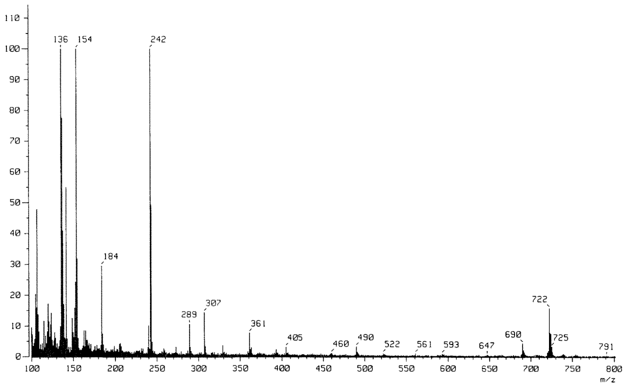
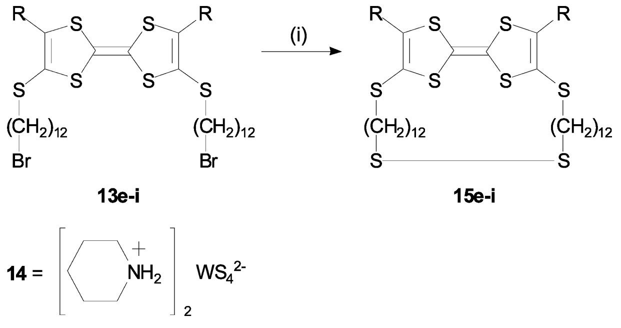


Fig. 2 FAB-MS of **6b**.

sulfuric acid and hexafluorophosphoric acid, yielded 1,3-dithiolium hexafluorophosphates **12a–i**. These compounds are highly hygroscopic and decompose quickly in air and were therefore reacted without further purification with triethylamine in dry acetonitrile, which gave TTFs **13a–i** in fair yields after purification. On treating **13** with hexamethyldisilathiane and $(n\text{-Bu})_4NF$, according to a recent procedure,[17] target compounds **6a–e** were obtained. Due to the low solubility of these sticky products, they could not be purified by column chromatography and analyses of these compounds were not trivial. The structures were not suitable for NMR-characterization due to the low solubility in most organic solvents. The issue was further complicated by FAB-MS and MALDI-TOF spectra of products **6b–e**, since they showed predominantly the $(M - 2)^+$ ion (Fig. 2 shows the FAB-spectrum of **6b**), which would suggest the presence of a disulfide (inter- or intramolecular) or other insaturations. However, treatment of **6b** with DTT (dithiothreitol) which would have reduced all disulfide groups, left the mass spectrum unaffected.

The IR spectra showed a weak absorption at 2522 cm^{-1}, indicating the presence of an S–H bond. Our speculation of the FAB-MS behavior is that the compounds interact (self-assembles) with a metal surface in the mass spectrometer, which can cause an oxidation to the dehydrogenated form. Moreover, elemental analysis confirmed that bromine had been substituted with sulfur. For TTFs **13e–i** we used another approach to achieve our "target" molecules.[18] Compounds **13e–i** were converted to the corresponding disulfides by the reaction with a nucleophilic sulfur transfer agent **14**[19] according to Scheme 2, yielding target TTFs **15e–i** as cyclic disulfides. The products, which precipitated from DMF, were filtered off and washed with diethyl ether to give products with a sticky apperance.

The electrochemical behavior of TTFs **13a–i** has been investigated by cyclic voltammetry (CV) in dichloromethane and the data are collected in Table 1.



Scheme 2 *Reagents and conditions*: (i) **14**, DMF, 70 °C.

Table 1 Electrochemical data for TTFs **13a–i**[a]

	E^1/V	E^2/V	$\Delta E = (E^2 - E^1)$/V
13a	0.43	0.78	0.36
13b	0.42	0.78	0.36
13c	0.41	0.77	0.36
13d	0.42	0.78	0.36
13e	0.42	0.77	0.36
13f	0.42	0.78	0.36
13g	0.42	0.77	0.36
13h	0.49	0.78	0.29
13i	0.50	0.81	0.30

[a] 1 mM $(n\text{-Bu})_4NClO_4$ (0.1 M) in CH_2Cl_2, scan rate 500 mV s^{-1}, *E vs.* SCE.

Due to the low solubility of TTFs **6a–d** and **15e–i** in dichloromethane at room temperature no cyclic voltammograms could be taken from solution but this will be further investigated together with film forming properties. All measured cyclic voltammograms for compounds **13** exhibit two reversible one electron transfer processes corresponding to the successive formation of the cation radical (E^1) and dication (E^2) as expected for TTFs. The 1-naphthyl-substituted TTF **13h** even showed a third oxidation as illustrated in Fig. 3. This may be due to oxidation of the naphthalene ring system, no corresponding reduction was however observed, indicating a more reactive, unstable oxidized species. As was expected, the values of the oxidation potentials and the difference $\Delta E = E^2 - E^1$ were comparable with previously reported results for TTF (**1**), $E^1_{1/2} = 0.33$ and $E^2_{1/2} = 0.71$.[20] What could be noted was that the naphthyl-substituted TTFs showed a slight positive shift of E^1, compared to the alkyl-substituted TTFs, but similar potential of E^2, that gave a 60–70 mV decrease of ΔE.

The film forming ability of TTF-thiols **6d** and **15g** were tested. The *n*-butyl-substituted TTF **6d** were immersed in toluene solution for a month, at room temperature and 70 °C, in the absence and presence of methanesulfonic acid. The corresponding dodecyl derivative **15g** were also immersed for one month. The results from ellipsometry and advancing contact angles are shown in Table 2. Both TTFs gave monolayers of good and reproducible quality. It is clear from Table 2 that

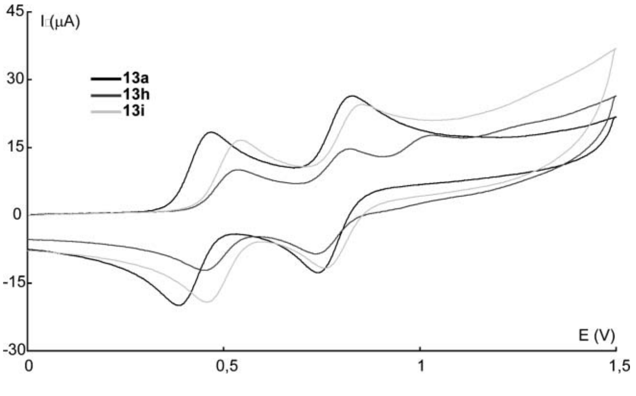


Fig. 3 Cyclic voltammograms of TTFs **13a**, **13h** and **13i**.

Table 2 Ellipsometric thickness (*d*), advancing (θ_a) and receding (θ_r) contact angles of water of TTF-thiol molecules on gold

TTF Sample	*D*/Å	θ_a/°	θ_r/°
6d[b]	19.6 ± 0.3	75	63
6d[a,b]	19.2 ± 0.2	69	55
15g[b]	15.0 ± 0.3	76	67
6d[c]	16.0 ± 0.4	77	65
6d[d]	15.9 ± 0.4	74	49
6d[a,e]	18.0 ± 0.3	63	53

[a] In the presence of 0.5 μmol of (10 mol%) $MeSO_3H$. [b] Incubated for 4 weeks (3 weeks at 70 °C + 1 week at rt). [c] Incubated for 1 week at rt. [d] Incubated for 48 h at 70 °C. [e] Incubated for 24 h at 70 °C.

longer times and more acidic conditions do not alter the thickness of the film to any substantial degree. It is also clear that the film thickness is less than would be anticipated from a stretched molecular arrangement as in Fig. 1. Interestingly enough the longer alkyl chain on TTF **15g**, does not result in a higher monolayer thickness.

The advancing contact angle of water on both type of monolayers indicates a more hydrophobic than hydrophilic surface due to the alkyl chains present on the topmost part of the organic film. These values do not indicate a high surface hydrophobicity, suggesting that the ring structure may somehow be on top of the film and partially influences the hydrophilicity of the surface. The advancing contact angle value is comparable to that of the $HS(CH_2)_{11}OCH_3$ monolayer ($\theta_a = 74°$) when adsorbed on gold.[21] For comparison, the advancing contact angle value of $HS(CH_2)_{16}CH_3$ is known to be 115°.[21] The high hysteresis value (difference between advancing and receding contact angle) also indicates a more heterogenous outermost layer at the micron scale.

The thickness and contact angle measurement results suggest a film formation of **6d** and **15g** incubated for a month having densely packed alkylthiol chains on the surface, and with ring structures and alkyl tails exposed on the topmost part of the layer. The surface region is not well ordered, with the alkyl chains to some degree penetrating down into the alkylthiol region. A more definitive description and characterization of these monolayers will be possible after IR and XPS-studies which are now in progress.

Conclusions

The synthesis of a new series of tetrathiafulvalenes with either double alkylthiol (**6a–e**) or alkyldisulfide (**15e–i**) substitution has been accomplished. A versatile synthetic procedure is presented which allows a variety of substituents to be present. TTFs **6d** and **15g** gave relatively dense packed monolayers on gold, with inner alkyl chains more organized and outer alkyl-chains randomly organized with *gauche* defects.

Experimental

Electrochemical measurments

Cyclic voltammetry was carried out at ambient temperature in CH_2Cl_2 at 500 mV s^{-1} with $(n\text{-Bu})_4NClO_4$ (0.1 M) as electrolyte and measured *vs.* a SCE reference electrode. The half-wave potential for the ferrocene–ferrocenium couple was found to be 0.49 V in our system.

Sample preparation for self-assembly

The substrate used is a 2000 Å thick electron beam evaporated-polycrystalline gold layer on Si(100) with 20–25 Å thick Ti as adhesion promoter. Prior to incubation, the gold samples were carefully cleaned to remove organic contamination. The substrates were incubated in the following toluene-based solutions (200 μM): **6d**, **6d**–10 mol% $MeSO_3H$ and **15g**. The immersion periods were: 24 h, 48 h, 1 week and 1 month. The samples were kept in the dark and at either room temperature or heated at 70 °C during the incubation period. Ultrasonic rinsing with toluene for 5 min and N_2 blow-drying of samples were carried out directly before mounting in measurement apparatus.

Ellipsometry

Single-wavelength ellipsometry was performed using an automatic Rudolph Research AutoEL ellipsometer with He–Ne laser light source, $\lambda = 632.8$ nm, at an angle of incidence of 70°. The freshly cleaned gold sample substrates were measured prior to their incubation, and the collected average value of the refractive index was later used in a model "ambient/organic film/gold", assuming an isotropic, transparent organic layer with a refractive index of $n = 1.5$. The film thickness is calculated as an average of measurements at five different spots on the sample of each compound.

Contact angle goniometry

Contact angles were measured with Ramé-Hart NRL 100 goniometer, in air, *i.e.* without control on the humidity, using fresh MilliQ water. At least five measurements of advancing and receding contact angle were done per sample.

Syntheses

NMR spectra were recorded on a Bruker AM 400 (400 MHz) or Bruker DMX 500 (500 MHz) spectrometer, *J* values are given in Hz. Assignment of ^1H NMR spectra could not be performed for the TTFs **6** and **15** due to isomeric mixtures. Mass spectra were recorded on a Finnigan SSQ 7000 or a Bruker Reflex III MALDI-MS instrument. The starting materials are commercially available except for **7h** and **7i**, which were obtained *via* bromination of the corresponding 1- and 2-naphthylacetic acids. Piperidinium tetrathiotungstate (**14**) was synthesized according to a literature procedure.[20] Where stated, the silica gel was deactivated with a 2 M HCl solution with subsequent drying at rt before use. THF was distilled from sodium/benzophenone, all other solvents were either distilled or were HPLC grade.

8: General procedure. 0.10 mol of α-bromocarboxylic acid was dissolved in 150 ml EtOH and 0.15 mmol of the sodium salt of *N*,*N*-dimethyldithiocarbamic acid was added in portions while cooling the mixture in an ice-bath. After stirring over night, the mixture was poured on 200 ml ice–water and acidified with 25 ml conc. HCl. The product was filtered off and dissolved in CH_2Cl_2, washed with water, and dried over $MgSO_4$. The solvent was evaporated, yielding **8**.

9: General procedure. 20 mmol of **8** was dissolved in 30 ml dry acetone and treated with 6 ml Ac_2O, 6 ml Et_3N and 6 ml CS_2, successively, separated by a couple of minutes. At first a yellow color developed and as the CS_2 was added, the color darkened while carbonyl sulfide escaped (**CAUTION**: toxic!) and after a few minutes orange yellow crystals of the product precipitated. After 6 h the product was filtered off and washed with cold acetone, yielding **9**.

10: General procedure. 49 mmol of **9** was refluxed in acetone with 245 mmol of 1,12-dibromododecane until the yellow color faded. After cooling to room temperature 500 ml hexane was added and the flask put in a freezer over night. The white precipitate formed was filtered off and washed with acetone and Et_2O to remove traces of starting materials, affording **10**.

11: General procedure. 3 mmol of **10** was dissolved in 30 ml 99% EtOH and cooled in an ice-bath to 0 °C. $NaBH_4$ was added over a period of 5 min. After 1 h 30 ml a 10% solution of NH_4Cl and 60 ml Et_2O were added and the layers were separated. The organic phase was then washed with water, dried over $MgSO_4$, filtered, and evaporated to dryness, yielding **11**.

12: General procedure. **11** was added to 7.5 ml ice-cold conc. H_2SO_4. After 30 min of stirring the mixture was poured over 25 ml ice containing 1.5 ml 60% HPF_6. The product was filtered off and dissolved in 10 ml CH_2Cl_2. The filtrate was extracted once with CH_2Cl_2 and the two organic phases were combined, dried over $MgSO_4$, filtered, and evaporated in vacuum to yield **12**.

13: General procedure. 1 equiv. of **12** was dissolved in dry CH_3CN and Et_3N (1.2 equiv.) was added dropwise to the stirred solution. At first a red brown color was observed which rapidly faded as oily droplets of the red product, **13** appeared. After 15 min the solvent was decanted and the product was washed with EtOH and dried in vacuum. The product was purified by chromatography on a deactivated silica gel column, where **13** was obtained after evaporation of solvent.

6: General procedure. To a stirred solution of **13** (1 equiv.) in freshly distilled THF (0.5 M) cooled in an ice-bath to −10 °C, hexamethyldisilathiane (2.4 equiv.) was added dropwise, followed by a 1.1 M solution of $(n\text{-Bu})_4NF$ in THF (2.2 equiv.). The reaction was monitored by TLC as the mixture was allowed to warm to room temperature and the color darkened. Once all starting **13** had reacted, the reaction mixture was diluted with Et_2O and washed with saturated aqueous ammonium chloride. The organic phase was dried over $MgSO_4$ and the solvent evaporated, yielding **6** as a sticky orange product. An analytically pure sample could be obtained by washing the product with Et_2O. Attempts to purify the product by column chromatography have not been successful.

15: General procedure. **13** (1 equiv.) was dissolved in dry DMF (0.2 M) and treated with 1.25 equiv. of piperidinium tetrathiotungstate (**14**). The yellow reaction mixture darkened during the addition and turned orange during heating (70 °C) over night. The solvent was decanted and the sticky red precipitate was washed with Et_2O, followed by THF. The residual solvent was evaporated, yielding **15** as a sticky red material that was characterized by either HRMS or elemental analysis.

Acknowledgements

Financial support from the Swedish Research Council as well as the Foundation for Strategic Research is gratefully acknowledged. The assistance of Anna Herland and Andreas Woldegiorgis is also gratefully acknowledged.

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