

Synthesis of Electro-active Compounds Suitable for Adsorption on Metal Surfaces

R. Alan Aitken* and Siddharth J. Jethwa

EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, U. K.

Introduction

I. Thiol - Gold adsorption

II. Tetrathiafulvalenes

1. *Direct adsorption on metal surfaces*
2. *TTF sulfides*
3. *TTF bearing a single CH₂SH group*
4. *TTFs with a single longer chain thiol tether*
5. *TTF dithiolates*
6. *TTFs bearing two CH₂SH groups and TTF-fused dihydro-1,2-dithiins*
7. *TTFs with two or more longer chain thiol tethers*
8. *TTFs with long chain 1,2-dithiolane tethers*

III. Extended TTFs

IV. Other Electro-active Functions

1. *Terphenyl compounds*
2. *C₆₀ derivatives*
3. *Porphyrins*
4. *Ruthenium complexes*
5. *Ferrocene derivatives*

V. Molecular Junctions

1. *Simple dithiols*
2. *Viologens*
3. *Di(arylalkynyl)biaryls and azulenes*
4. *TTFs and extended TTFs*

VI. TTF-carboxylic acids for adsorption on metal oxides and sulfides

Conclusion

Introduction

The adsorption of electro-active compounds onto metal surfaces has recently emerged as an important way to impose order on the individual molecules and examine their properties. The metal may also serve as an electrical contact and, by placing electro-active molecules between two metal surfaces, the concept of single molecule conduction may be realized. In most cases binding of the electro-active compound to a metal relies on a "tether" specially installed for this purpose and it is the synthetic aspects of preparing such compounds that are the subject of this review. Depending on the functional groups involved, the adsorption may be classed as "physisorption" or "chemisorption" but, since the focus is on the organic preparative procedures involved, the compounds are classified according to the nature of the functionality present rather than the precise nature of the adsorption. The presence of the electro-active function often limits the methods available for such synthesis and many common procedures may be unsuitable. In addition, such studies are often carried out by multi-disciplinary research groups and appear in journals unfamiliar to the organic chemist. This review covers the most significant methods used since the birth of this relatively new field around 1990. A recent review on surface-attached sensors for ion recognition also contains some relevant electroactive examples.¹

I. Thiol - Gold adsorption

A previous review of self-assembled monolayers of thiols on metal surfaces includes a useful table listing examples of the formation of such monolayers by interaction of many of the common organic functional groups with different metals, metal oxides and semiconductors.² It is clear that the interaction of thiols or their derivatives with a gold surface is the most widely studied, due both to the high affinity of sulfur for gold and the fact that gold does not suffer from problems caused by formation of surface oxides. Although most studies have involved aliphatic thiols,² aromatic thiols can also be used and self-assembled monolayers of 1,2-benzenedimethanethiol on gold³ and benzene-1,2-dithiol on both gold and silver⁴ have been reported. The use of multidentate adsorbates, which bind by two or more thiol groups, may also be advantageous.⁵

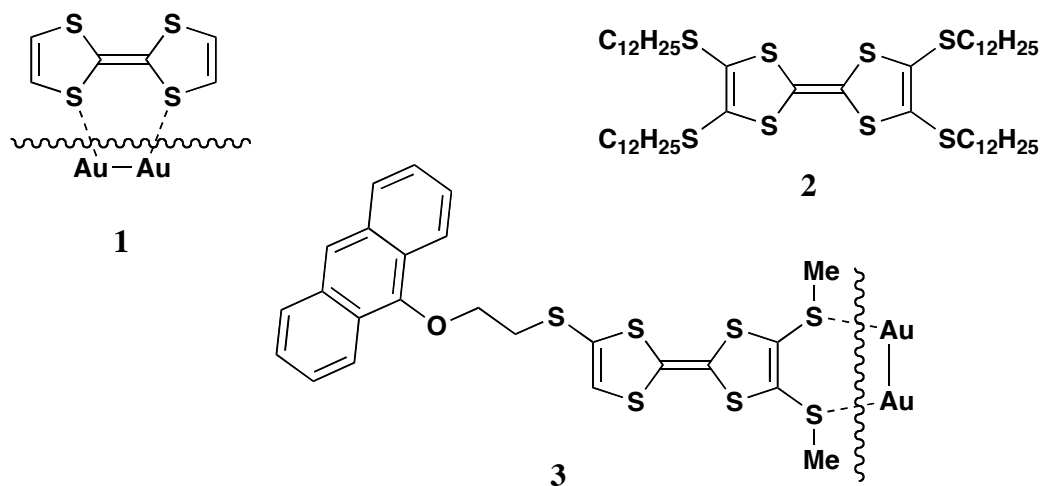
II. Tetrathiafulvalenes

1. Direct adsorption on metal surfaces

The adsorption of TTF itself on a gold surface as shown in **1** (*Scheme 1*) has been studied theoretically,^{6,7} and adsorption on silver⁷ and copper⁸ has also been reported. However this mode of adsorption is generally not useful for electronic applications and, for example, attempted formation of the classic TTF–TCNQ charge transfer complex on gold simply by co-adsorption of the two components leads to a mixed phase.⁹ The co-immobilization of TTF with 3-mercaptopropionic acid or 11-mercaptoundecanoic acid on gold illustrates another approach avoiding direct binding of the electro-active molecule to the metal surface.¹⁰

2. TTF sulfides

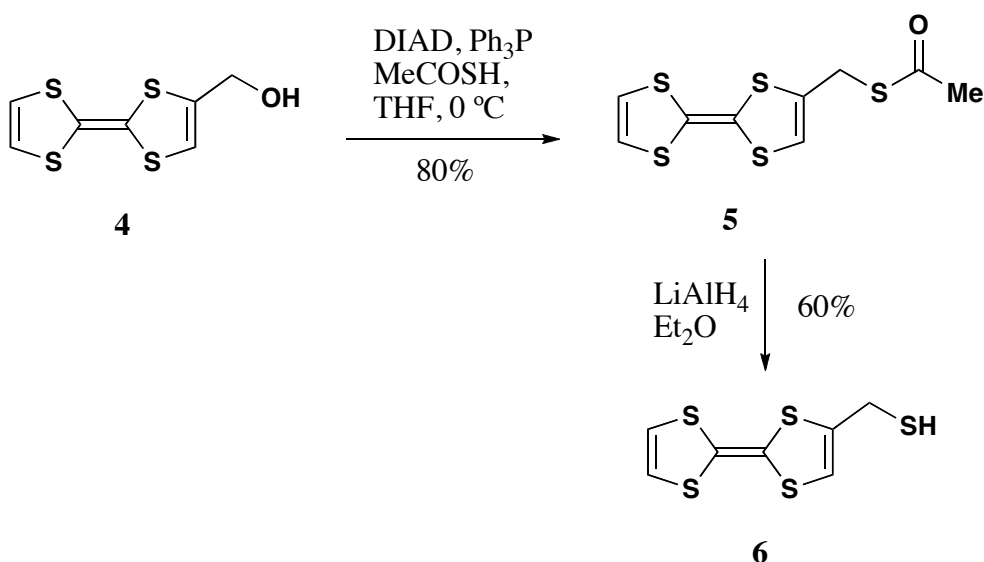
Self-assembly of tetradodecylthio-TTF **2** (*Scheme 1*) on a graphite surface has recently been described.¹¹ The anthracene-containing TTF derivative **3** was initially introduced as a chemiluminescent probe for singlet oxygen in homogeneous solution.¹² However it was later shown to assemble on the surface of gold nanoparticles, interacting as shown, but the weak nature of this interaction was emphasized by the rapid disassembly observed upon addition of hexane-1-thiol.¹³



Scheme 1

3. TTF bearing a single CH_2SH group

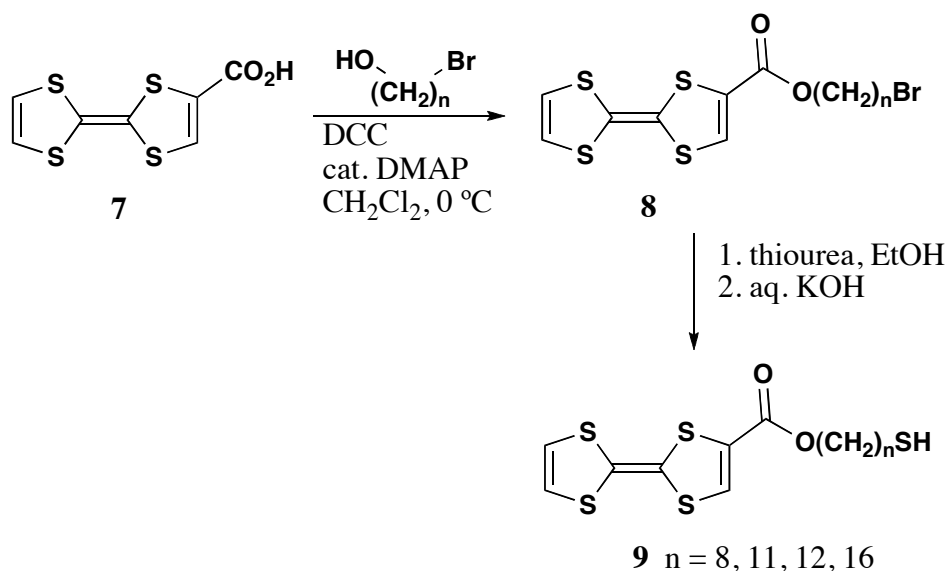
The simple mercaptomethyl-TTF **6** provides the first synthetic example.^{14,15} It forms self-assembled monolayers on gold and these have also been studied in the presence of added TCNQ. The synthesis (*Scheme 2*) involves condensation of the TTF alcohol **4** with thioacetic acid under Mitsunobu conditions to give the thioester **5**, which is then subjected to lithium aluminium hydride reduction. It should be noted that many of the alternative ways of activating the alcohol function towards nucleophilic displacement are incompatible with the presence of the TTF unit.



Scheme 2

4. TTFs with a single longer chain thiol tether

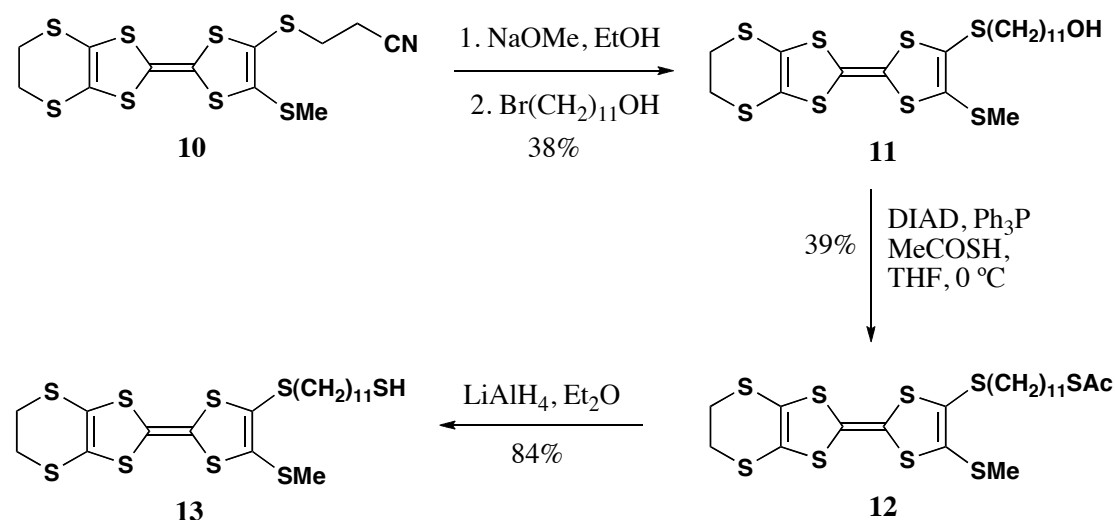
In pioneering work, Yip and Ward reported construction of a range of TTF esters **9** with a long alkyl chain terminated by a thiol (*Scheme 3*).¹⁶ TTF was deprotonated with LDA and treated with CO₂ to give the carboxylic acid **7** which was condensed with the appropriate ω-bromo alcohol using dicyclohexylcarbodiimide to give the bromoesters **8**. Reaction of these with thiourea followed by KOH hydrolysis then afforded the products **9**. These reactions were, however, rather inefficient with an overall yield in going from **7** to **9** of just 15% for n = 16.



Scheme 3

More recently the ethylenedithio-TTF derivative **13** was prepared and the electrochemical response of self-assembled monolayers was determined as well as its behaviour when embedded in a monolayer of decane-1-thiol on gold.^{17,18} In this case

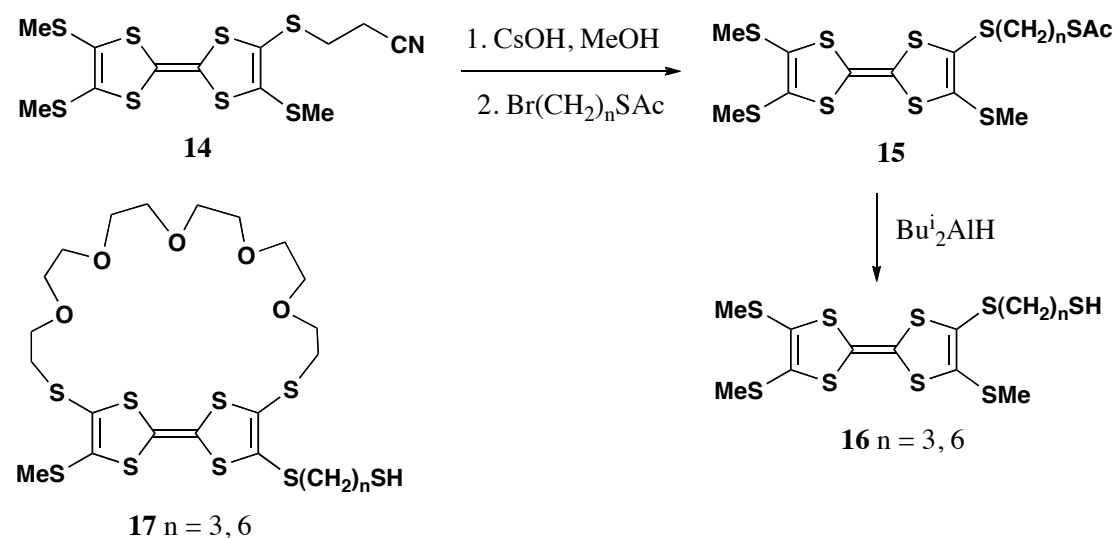
the synthesis (*Scheme 4*) starts by unmasking a thiolate function by base treatment of the 2-cyanoethyl sulfide in **10** followed by treatment with 11-bromoundecanol to give



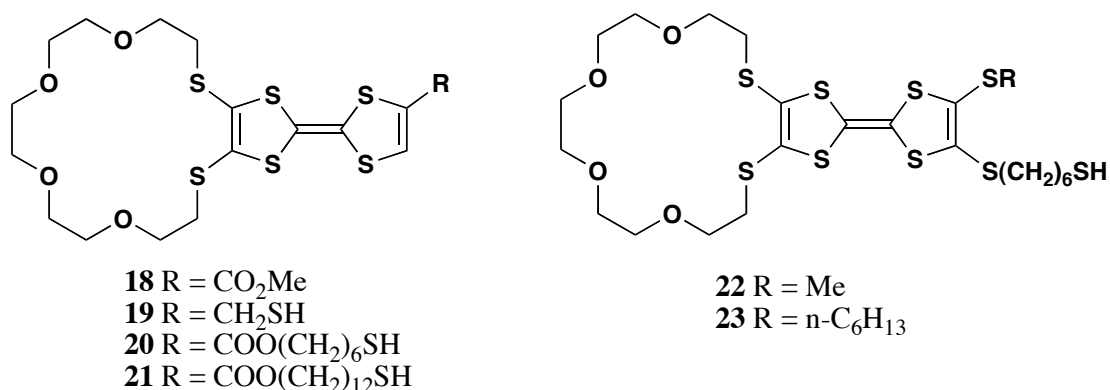
Scheme 4

11. Such use of the 2-cyanoethyl sulfide as a masked form of the thiolate and its deprotection with base involving a retro-Michael reaction with elimination of acrylonitrile was first introduced by Becher and coworkers,¹⁹ and has proved very useful in TTF chemistry. Condensation of **11** with thioacetic acid under Mitsunobu conditions gives **12** and this is subjected to lithium aluminium hydride reduction to give the product **13**.¹⁷

A slightly different approach is evident in preparation of the methylthio-TTFs **16** bearing thiol-terminated C₃ and C₆ chains (*Scheme 5*).²⁰ In this case a step is saved by reacting the cyanoethyl compound **14** with base then a bromide already containing the acetylthio group to give **15**. Diisobutylaluminium hydride is then used reduce off the acetyl group to generate the thiol **16**. Exactly the same approach was also applied to synthesis of the crown ether analogues **17**, which were studied as potential electrochemical sensors for Ba²⁺ at a gold electrode,²⁰ and similar metal-chelating acyclic polyether analogues.²¹

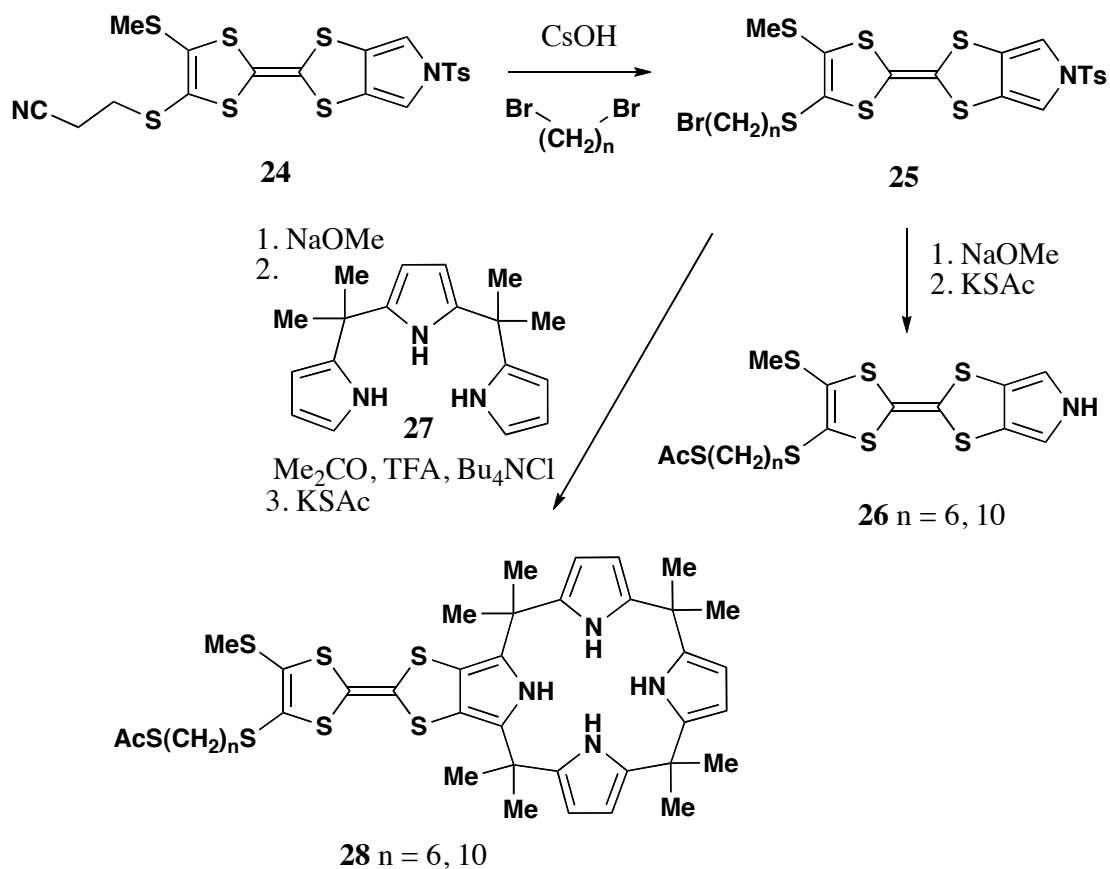


Scheme 5



Scheme 6

Crown ether-containing TTF derivatives have been of considerable interest for ion sensor applications and several other derivatives suitable for adsorption on gold have been prepared (*Scheme 6*).^{22,23} Reduction of the ester **18** using diisobutylaluminium hydride to give the corresponding alcohol was followed by Mitsunobu condensation with thioacetic acid and LiAlH₄ reduction, exactly as in Scheme 2, to give the thiol **19**. On the other hand hydrolysis of **18** to the corresponding acid with sodium hydroxide followed by application of the procedures of Scheme 3 using 6-bromohexanol and 12-bromododecanol afforded the derivatives



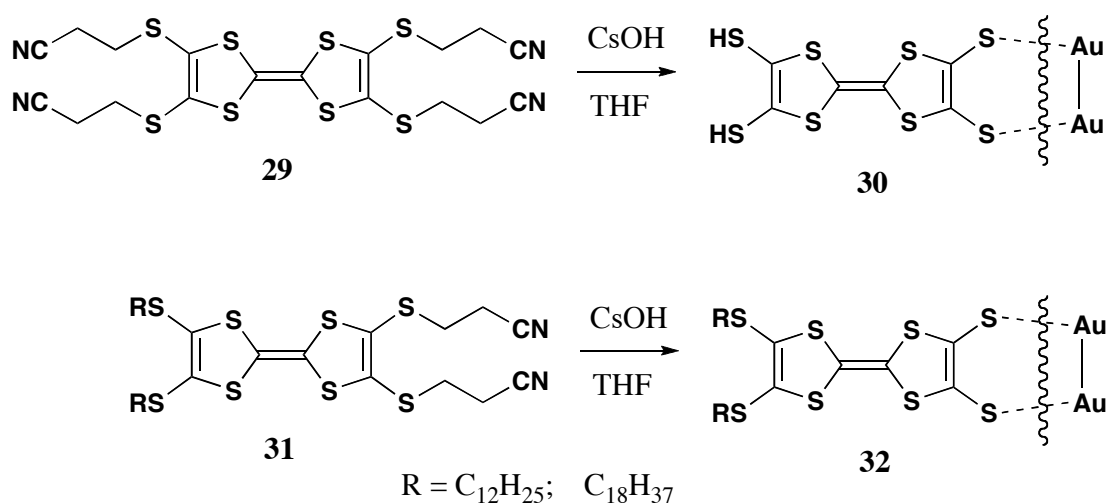
Scheme 7

20 and **21**, respectively.²² Installation of the terminal thiol function in compounds **22** and **23** was achieved, starting from the corresponding silyl-protected alcohols, by deprotection using tetrabutylammonium fluoride then treatment as in Scheme 2.²³

Installation of long-chain thiol functions to the pyrrole-fused TTF **24** was achieved by deprotection using CsOH in the presence of a dibromoalkane to give **25** (Scheme 7).²⁴ N-Deprotection followed by reaction with potassium thioacetate then gave the target compounds **26** while deprotection and reaction with a tripyrrole fragment **27** followed by potassium thioacetate gave the calix[4]pyrrole compounds **28**.

5. TTF dithiolates

As mentioned in section I, multidentate thiols have often been used and the influence of the number of anchoring sulfur groups on the properties has been examined theoretically for benzene- and anthracene-based molecular devices.²⁵

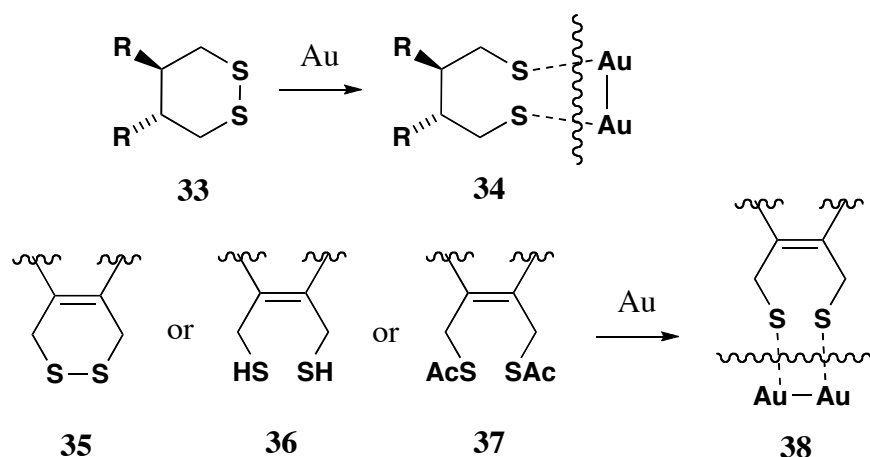


Scheme 8

Generation of TTF-tetrathiolate by treatment of the tetrakis(cyanoethyl) compound **29** with caesium hydroxide using Becher's method,¹⁹ has been used to form monolayers with structure **30** on gold (Scheme 8).²⁶ Application of the same procedure to the TTF derivatives **31** with long alkyl chains at the other side likewise gives self-assembled monolayers based on structure **32**.²⁷

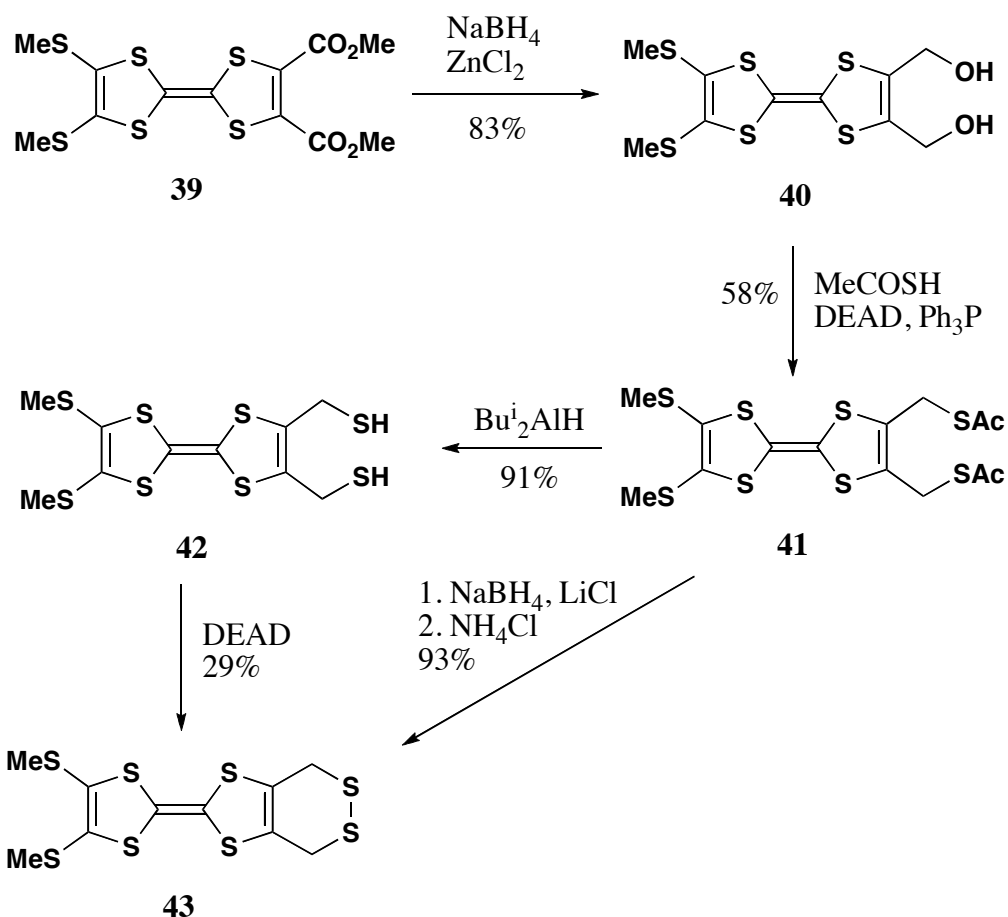
6. TTFs bearing two CH₂SH groups and TTF-fused dihydro-1,2-dithiins

In a pioneering report in 1983, a range of substituted 1,2-dithianes **33** were observed to adsorb readily to a gold surface with cleavage of the weak S–S bond to give the adsorbed structure **34** (Scheme 9).²⁸ Although electro-active groups were not used at that time, it was later realized that both the cyclic disulfide function **35** and the corresponding dithiol **36** are viable precursors for self-assembled monolayers **38** on gold. In fact the interaction is so favourable that spontaneous loss of acetyl groups can be observed making **37** a third suitable function for attachment to the metal surface.

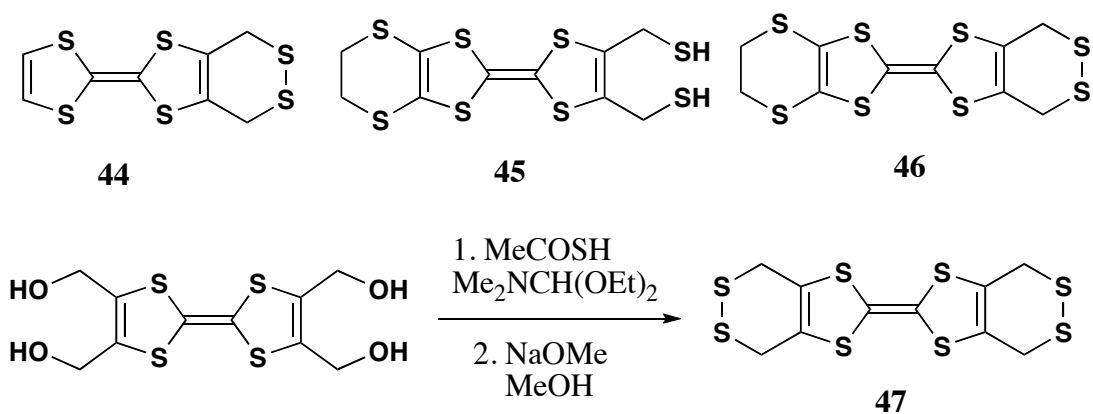


Scheme 9

A theoretical analysis of the binding of the unsubstituted TTF derivative of type **36**, 4,5-bis(mercaptomethyl)TTF has also appeared.⁶ The preparative methods used for TTF compounds of these types are illustrated by the conversion of **39**, by way of **40**, into **41**, **42** and **43** (*Scheme 10*).²⁹ Reduction of the diester with sodium borohydride and zinc chloride gives the diol **40** which is condensed with thioacetic acid under Mitsunobu conditions to afford **41**. This can be either reduced to the dithiol **42** using diisobutylaluminium hydride or converted directly into the dihydro-1,2-dithiin **43** by borohydride reduction followed by treatment with ammonium chloride. Oxidation of the dithiol **42** to **43** may also be achieved directly in low yield with diethyl azodicarboxylate. The same method was also used to prepare the unsubstituted analogue **44** (*Scheme 11*),³⁰ For the ethylenedithio-TTF compounds **45** and **46** the same procedures were also used with the important exception that the Mitsunobu step was replaced by condensation with thioacetic acid in the presence of dimethylformamide diethyl acetal.^{29,30} This method was also employed in the preparation of the symmetrical TTF-bis(dihydro-1,2-dithiin) **47** which is isomeric both with **46** and the more familiar bis(ethylenedithio)TTF or "ET".³¹ Despite their obvious potential for surface adsorption, such studies on these compounds do not appear to have been carried out.

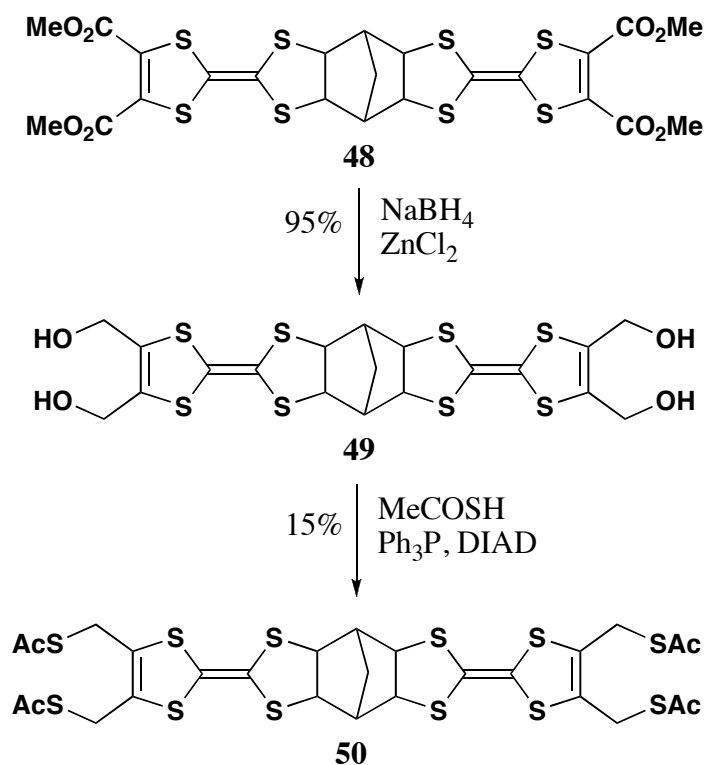


Scheme 10



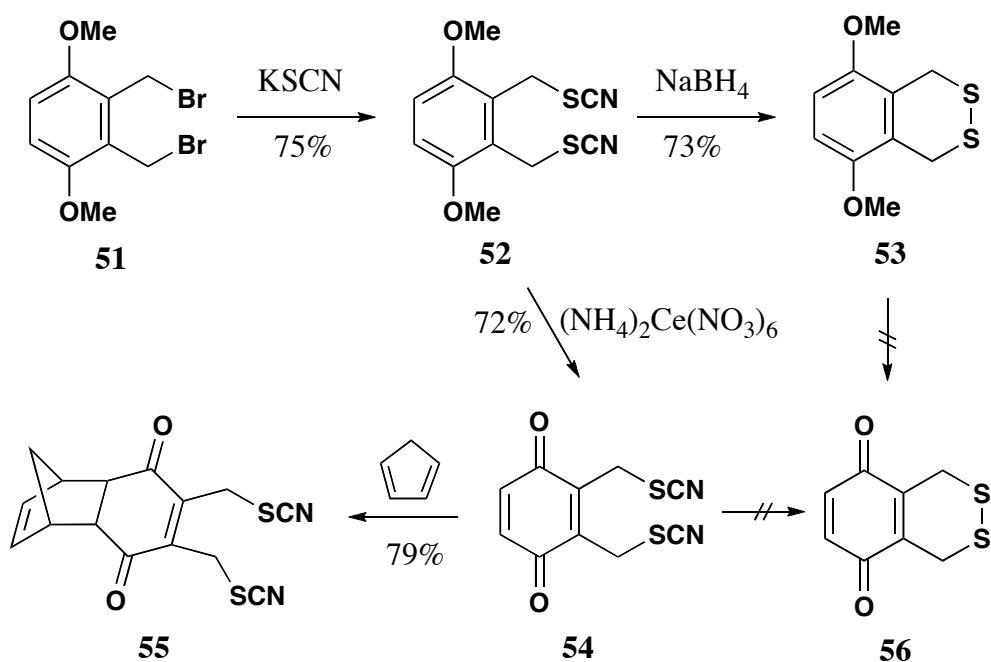
Scheme 11

A further recent illustration of the use of these methods is the synthesis of the tetrakis(acetylthio)bis(dihydro-TTF) **50** (Scheme 12).³² This uses the same methods as shown in Scheme 10 to reduce the tetraester **48** to the tetraol **49** and condense this with thioacetic acid to give the product which was adsorbed on gold with spontaneous loss of the *S*-acetyl groups.



Scheme 12

Finally in this section, it should be mentioned that the fused ring dihydro-1,2-dithiin has also been examined as a suitable way to adsorb other electro-active functions to a gold surface. An example of such work towards adsorbing a quinone (*Scheme 13*) shows a further method³³ of forming the dithiin ring by reduction of a bis(thiocyanate), but also emphasizes the pitfalls inherent in such an approach.³⁴ Thus

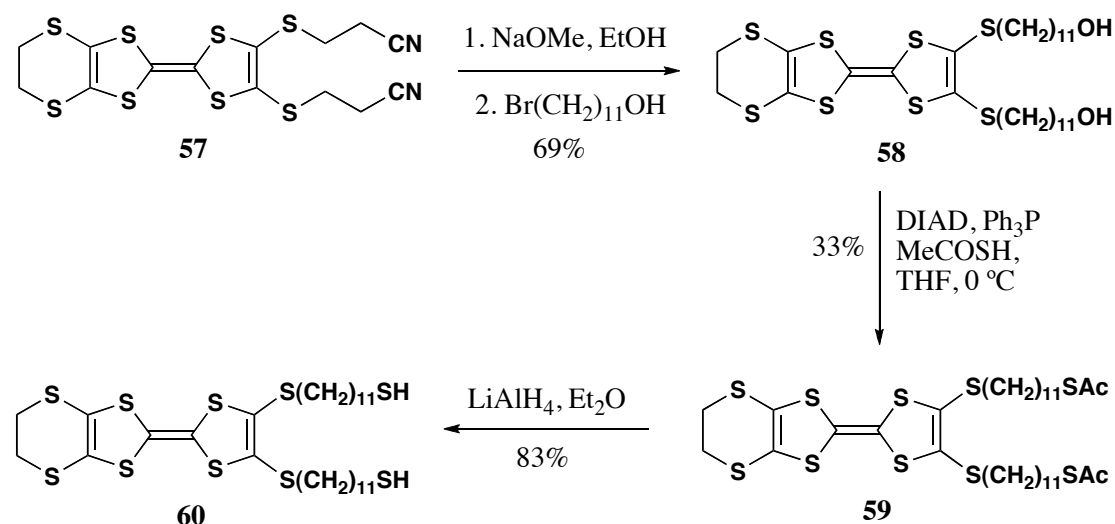


Scheme 13

the dibromide **51** is readily converted into the bis(thiocyanate) **52** and this reacts with sodium borohydride to generate the dihydrobenzo-1,2-dithiin **53**. However attempted deprotection of the dimethoxybenzene to give the corresponding quinone **56** using ceric ammonium nitrate failed, and instead resulted in formation of the monosulfoxide of **53**. On the other hand, deprotection at the bis(thiocyanate) stage readily gave **54**, but reductive cyclization of either this, or its Diels-Alder adduct **55** with cyclopentadiene, resulted in undesired reduction at the carbonyl groups and **56** remains elusive.³⁴

7. TTFs with two or more longer chain thiol tethers

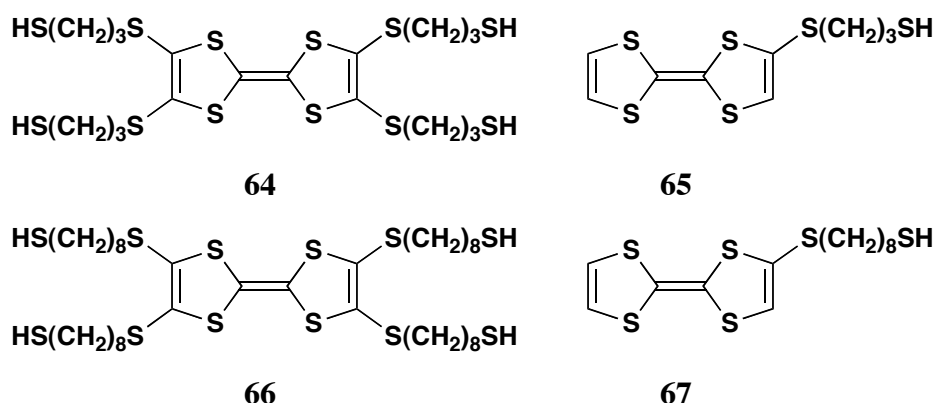
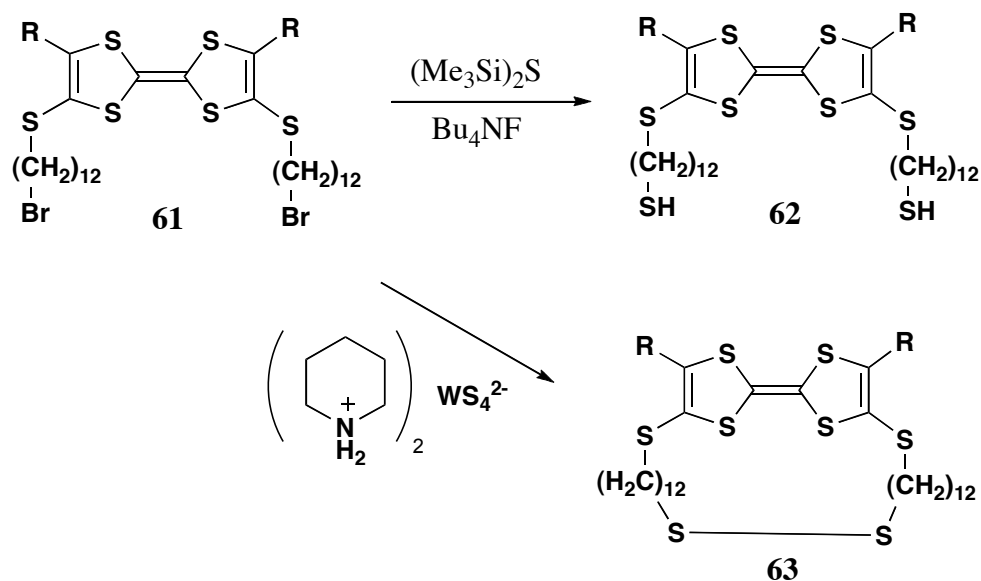
The ethylenedithio-TTF derivative **60** bearing two thiol-terminated C₁₁ chains (*Scheme 14*) is readily prepared by unmasking of **57** to the dithiolate and alkylation with 11-bromoundecanol to give **58** followed by Mitsunobu condensation with thioacetic acid to afford **59** and finally LiAlH₄ reduction.¹⁷



Scheme 14

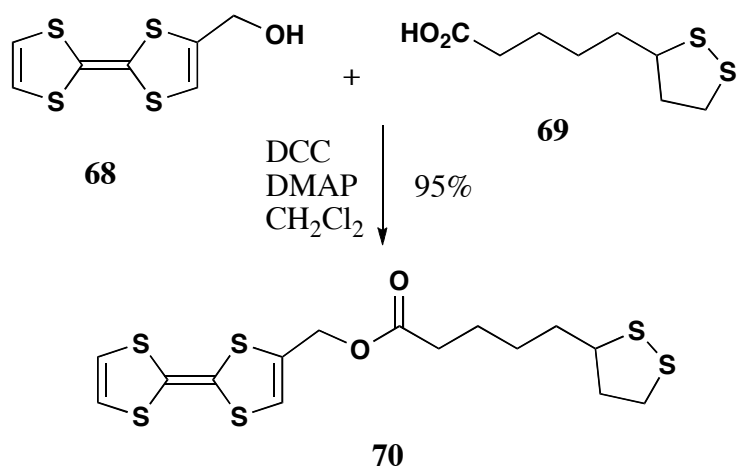
TTFs with two long thiol-terminated chains, one on each ring, have also been prepared (*Scheme 15*).³⁵ For this the TTFs **61** were prepared with bromoalkyl chains already in place and for shorter R groups, treatment with hexamethyldisilthiane and tetrabutylammonium fluoride gave the desired dithiols **62**. For longer R groups, a different method was used, namely reaction with the piperidinium tetrathiotungstate which gave the disulfides **63**. Both **62** (R = butyl) and **63** (R = dodecyl) formed good self-assembled monolayers on gold.³⁵

The TTF-tetrathiol **64** (*Scheme 16*) readily forms self-assembled monolayers on gold and these are much more electrochemically stable than those formed from the corresponding monothiol **65** used for comparison.³⁶ However details of the synthesis of **64** and **65** have not appeared. The same authors also later reported similar properties for the homologues **66** and **67** with C₈ chains, and in that case gave a brief indication that they were prepared by treatment of the corresponding thiolates with 8-iodooctyl thioacetate followed by LiAlH₄ reduction.³⁷

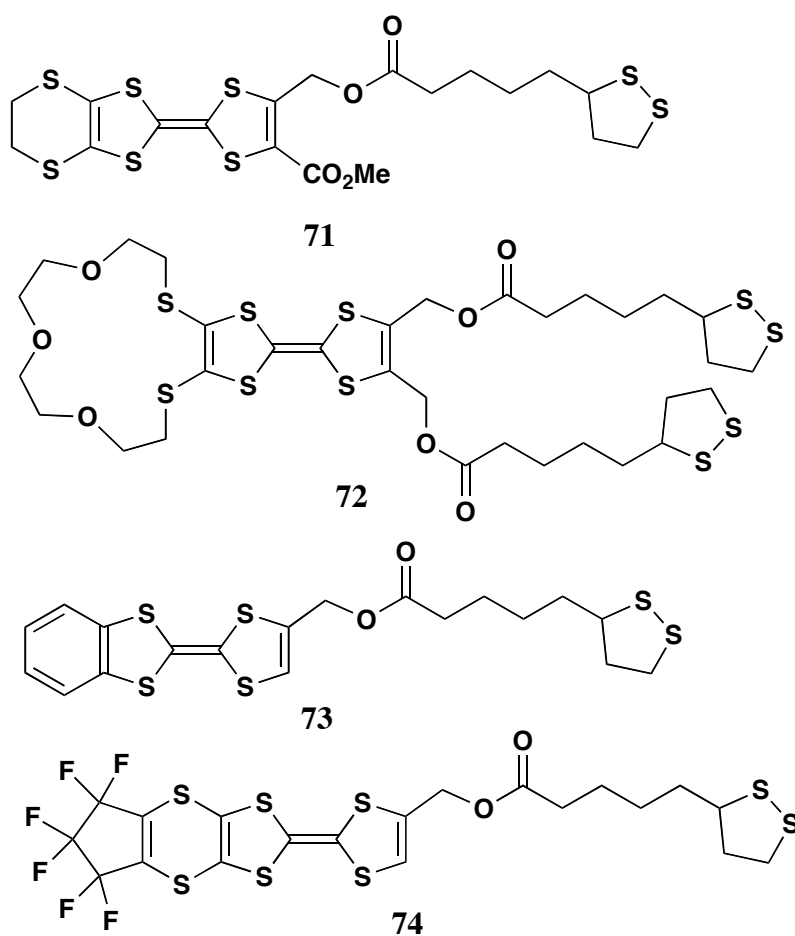


8. TTFs with long chain 1,2-dithiolane tethers

Esterification with the readily available thioctic acid **69** allows attachment of a chain terminating in the 1,2-dithiolane ring which is known to adsorb readily to gold much in the same way as the 1,2-dithianes **33** mentioned earlier. Typical reaction conditions are illustrated for hydroxymethyl-TTF **68** (*Scheme 17*) giving the product **70** in excellent yield.³⁸ In the same way, compound **71**, its analogue with two pendant dithiolane groups, and larger ring crown ether compounds such as **72** have also been prepared (*Scheme 18*).^{39,40} More recently, the new derivatives **73** and **74** have been reported, and the surface wettability of their monolayers on gold has been determined.⁴¹ In the case of **74** procedures for formation of the starting alcohol from the corresponding TTF dimethyl ester as well as the final esterification are described.



Scheme 17

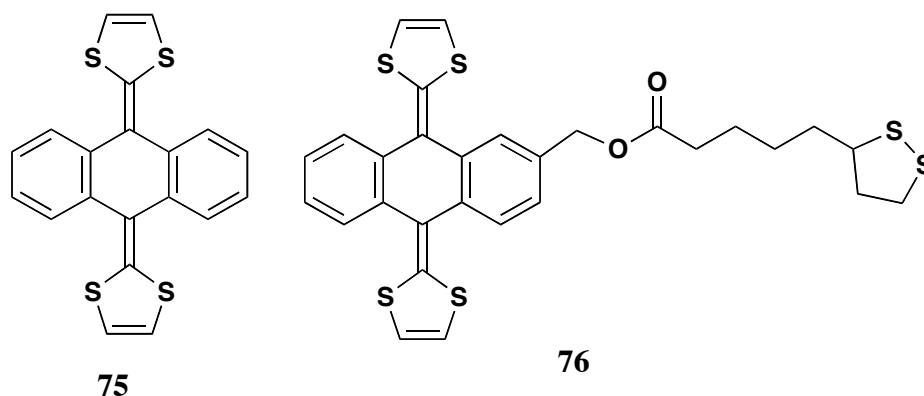


Scheme 18

III. Extended TTFs

The adsorption of extended analogues of TTF on metal surfaces is much less developed. The growth and structure of self-assembled monolayers of compound **75** on gold has been studied,⁴² and this same donor has also been co-adsorbed with a functionalized C₆₀ derivative on gold giving a donor-acceptor "superlattice".⁴³ A rare

example of an extended TTF analogue with a covalently attached group specifically for binding to a metal is the thioctic acid derivative **76** (*Scheme 19*) which was prepared using the same method as shown for the simple TTF derivative **70**.³⁸

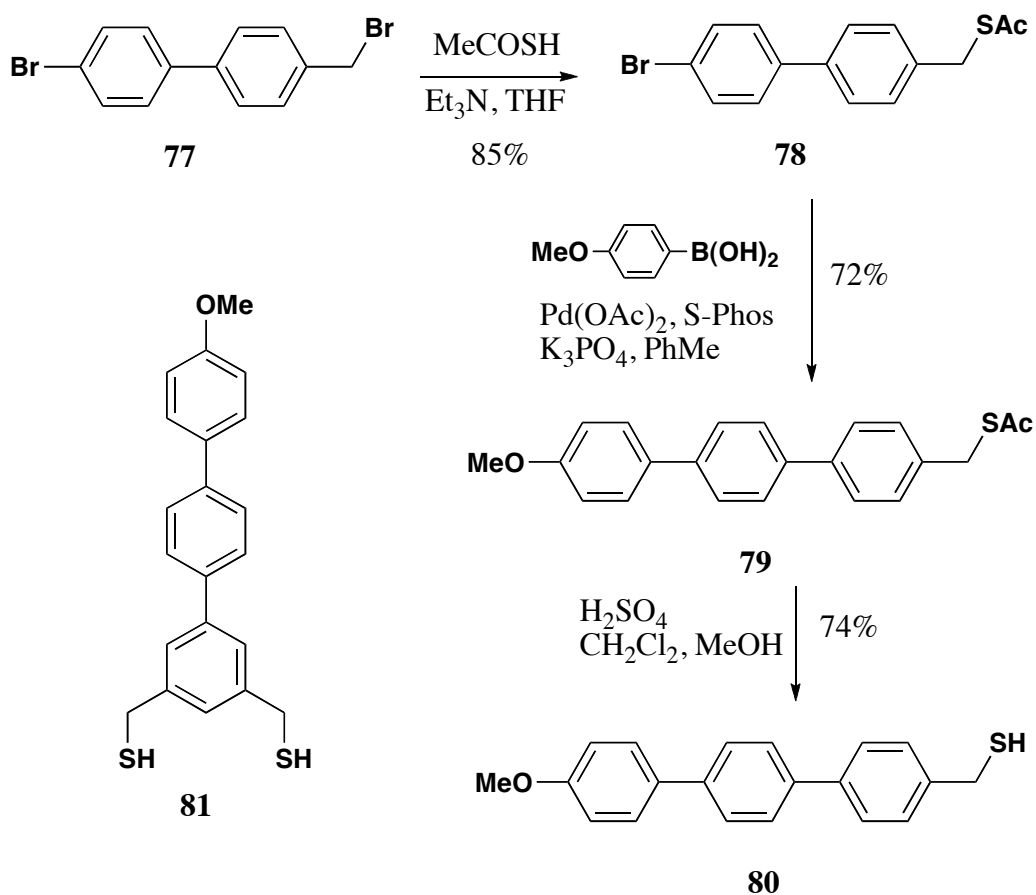


Scheme 19

IV. Other Electro-active Functions

1. Terphenyl compounds

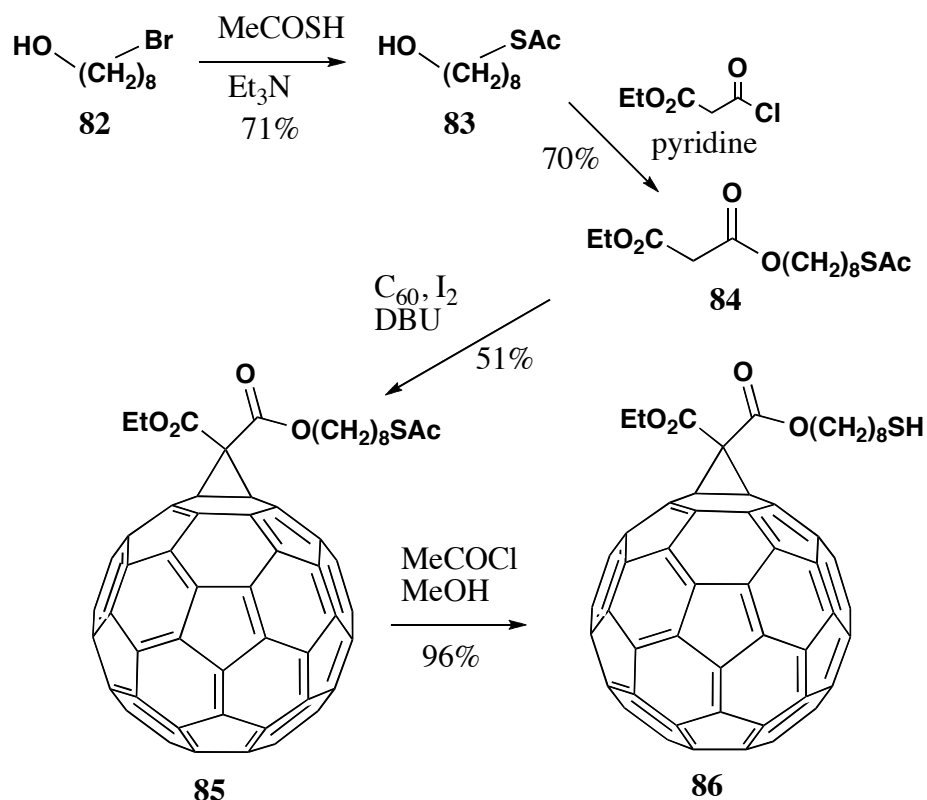
The structure and optical properties of self-assembled monolayers of the methoxyterphenyl **80** (*Scheme 20*) on gold have been reported.⁴⁴ The synthesis begins with reaction of the benzylic bromide **77** with thioacetic acid and triethylamine to give the thioacetate **78**. Suzuki coupling of this with the methoxyphenylboronic acid affords **79** and the acetyl group is removed by acid hydrolysis to give the thiol **80** in good overall yield. An exactly similar approach was used to prepare the analogue **81** with two anchoring thiol groups.⁴⁴



Scheme 20

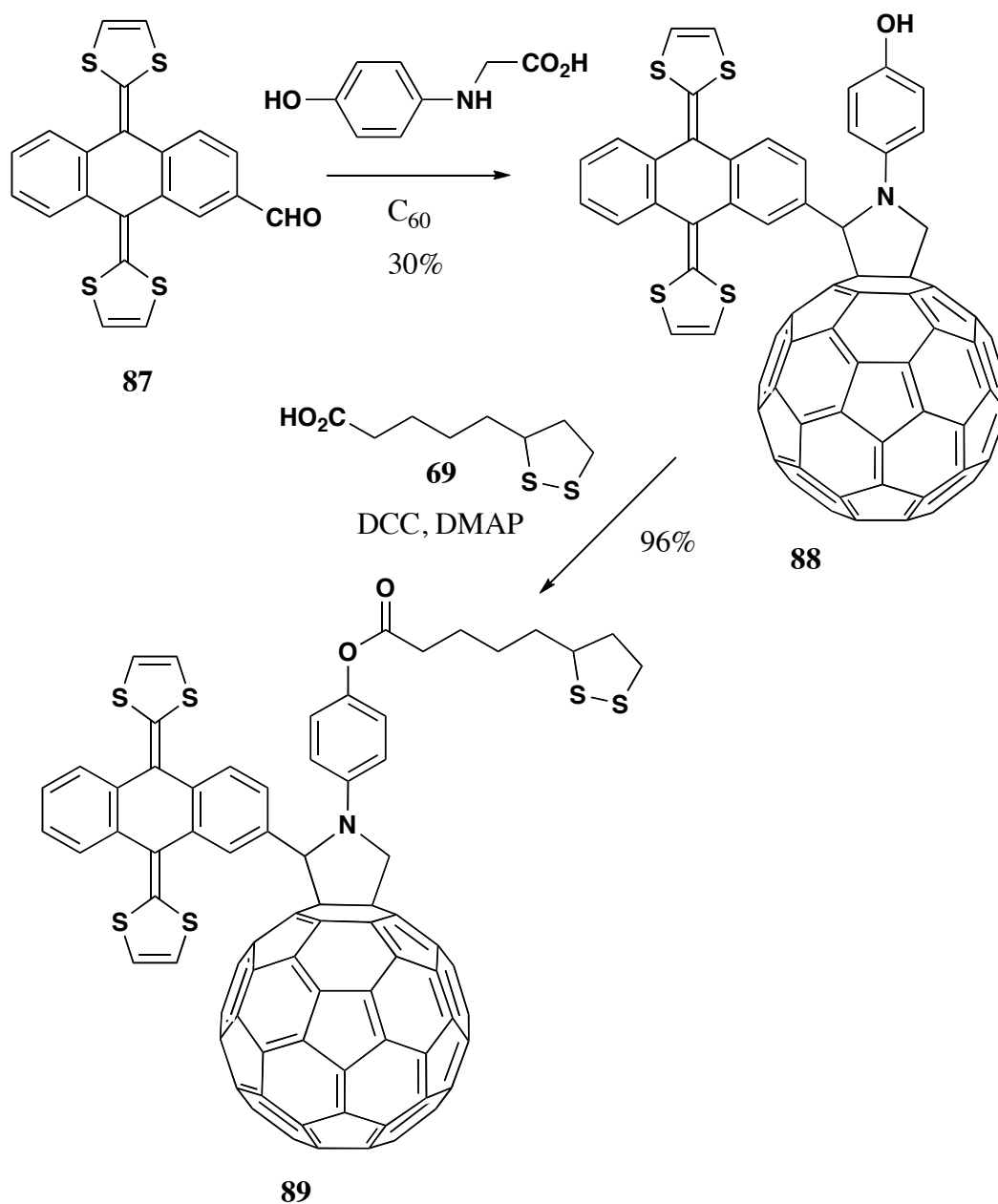
2. C_{60} derivatives

A rare example of this type is provided by compound **86** prepared starting from 8-bromooctanol **82** (Scheme 21).^{45,46} Reaction with thioacetic acid and triethylamine to give **83** is followed by reaction with ethyl oxalyl chloride to give **84** and this then undergoes a cyclopropanation reaction on C_{60} to give **85**. Final deprotection to give thiol **86** is achieved almost quantitatively using acid hydrolysis with acetyl chloride in methanol.



Scheme 21

The hybrid extended TTF / C_{60} compound **89** was prepared by initial functionalization of C_{60} by 1,3-dipolar cycloaddition with the azomethine ylide formed from extended TTF aldehyde **87** and *N*-4-hydroxyphenylglycine in boiling chlorobenzene (Scheme 22). DCC-mediated condensation with thioctic acid **69** using the method of Scheme 17 then proceeded in excellent yield to give **89** which formed self-assembled monolayers on a gold surface.⁴⁷



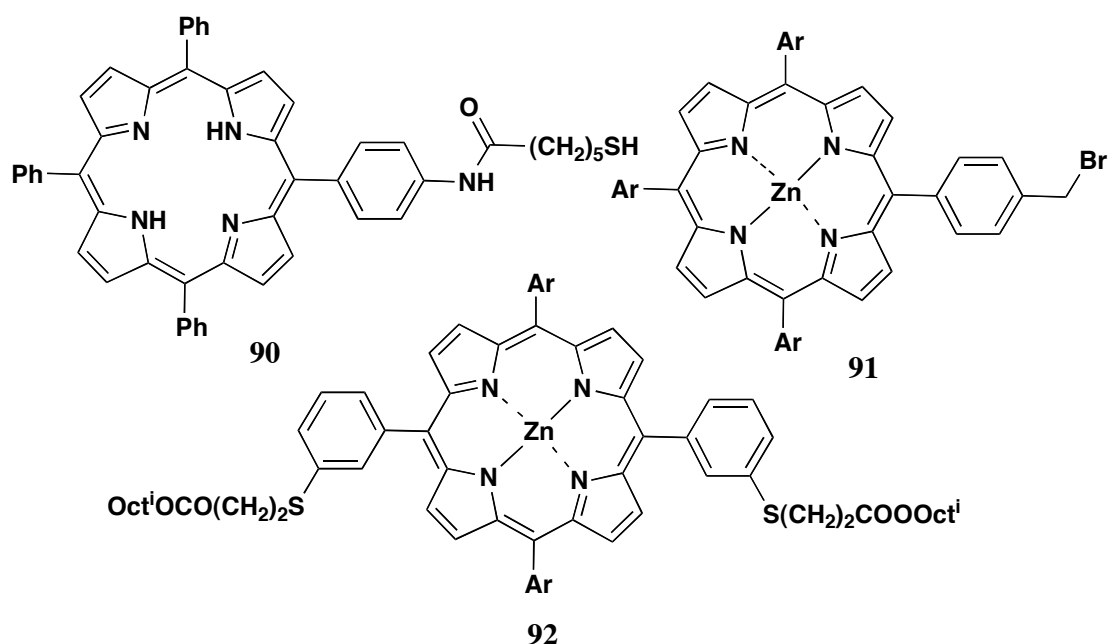
Scheme 22

3. Porphyrins

There has been a great deal of work in the area of sulfur-functionalized porphyrins and for reasons of space only representative examples are given. Two broad approaches may be identified: introduction of sulfur functionality to a preformed porphyrin or incorporation of a sulfur functionalized aldehyde into the porphyrin forming reaction, either mixed with a non-functional aldehyde or on its own.

As an example of the former approach, compound **90** (Scheme 23) was prepared from the corresponding 4-aminophenyl porphyrin by reaction with 6-tritylthiohexanoyl chloride followed by deprotection of the SH using mercuric acetate and hydrogen sulfide.⁴⁸ The same authors also described similar double functionalization of a (trans) di(2-aminophenyl) analogue and cobalt derivatives of both porphyrins were studied on a gold electrode. In another typical study, a range of zinc porphyrins **91** were converted into compounds suitable for surface adsorption by

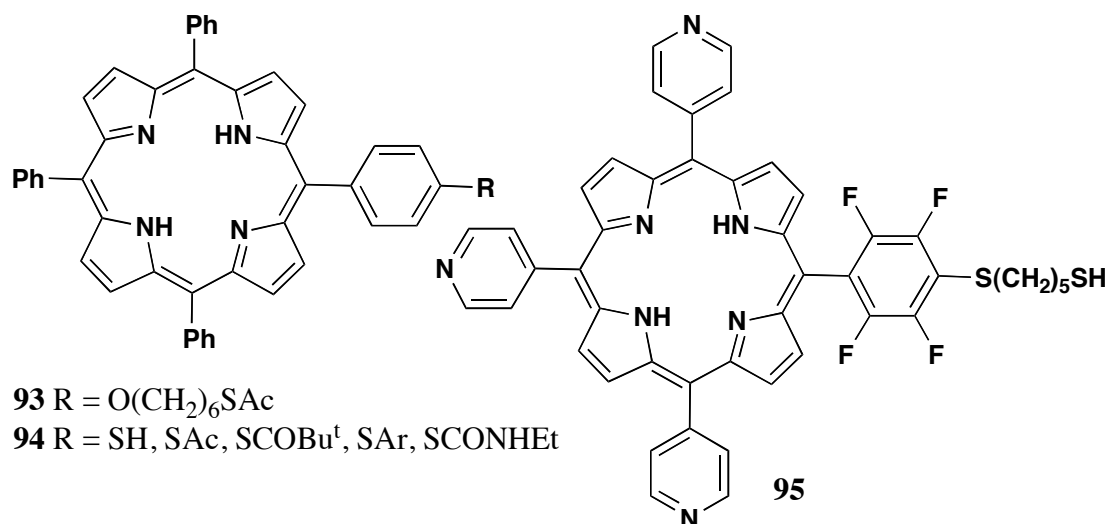
nucleophilic displacement of the bromine by potassium thioacetate and potassium selenoacetate, with subsequent hydrolysis using KOH in the former case giving the thiol.^{49,50} In these studies adsorption to a silicon surface with a view to molecular information storage was also studied. In a more recent study, it was found that attempts to carry out Suzuki coupling of a zinc dibromodiarlylporphyrin with 3-(acetylthio)phenylboronic acids failed due to incompatibility of the acetylthio group with the conditions, but the problem could be overcome using the protecting groups shown in product **92**, derived by addition of the thiol to isooctyl (2-ethylhexyl) acrylate.⁵¹



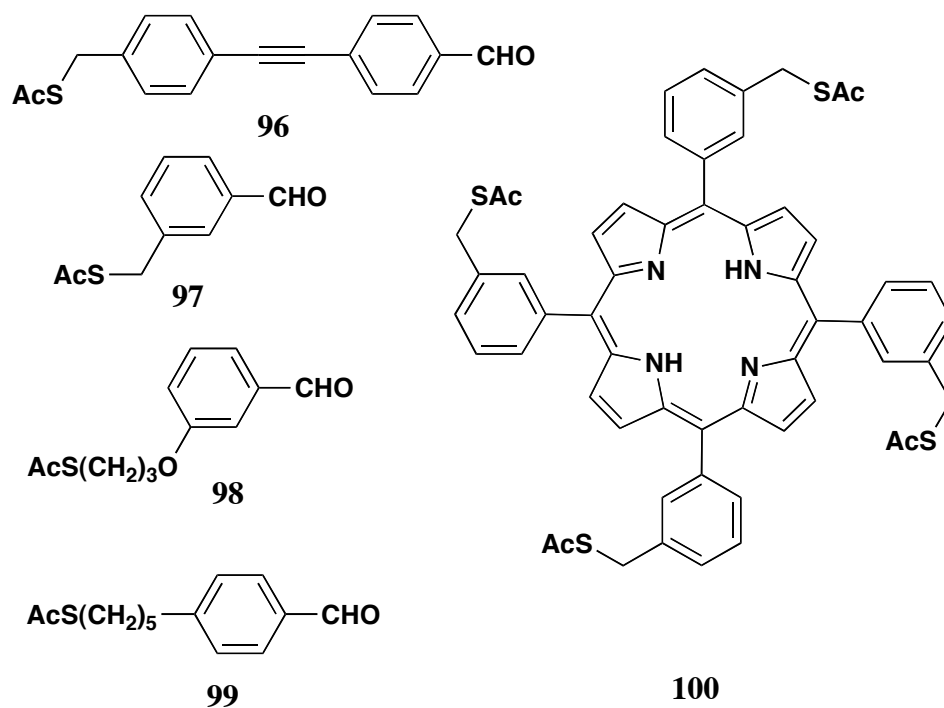
Scheme 23

A wide range of sulfur-substituted benzaldehydes have been combined with benzaldehyde or alkylated benzaldehydes in the reaction with pyrrole to form products such as **93**,⁵² and **94** (Scheme 24).^{53,54} In the latter study aldehydes bearing a *meta* sulfur substituent were also used. A particularly interesting example is compound **95** formed from a mixed coupling of pyridine-4-carboxaldehyde and pentafluorobenzaldehyde with pyrrole followed by treatment with pentane-1,5-dithiol and diethylamine which results in displacement of the 4-fluorine to give the product in 79% yield.⁵⁵

Incorporation of aldehydes such as **96**⁵⁴ into the porphyrin formation gives products with one, two, three or four such groups depending on the aldehyde ratios used (Scheme 25),⁵⁶ and porphyrins with four sulfur-containing groups are obtained from aldehydes such as **97**,⁵³ **98** and **99**.⁵⁷ In the case of the porphyrin derived from **97**, compound **100**, the direct observation of *S*-acetyl deprotection on a silver surface was later reported.⁵⁸



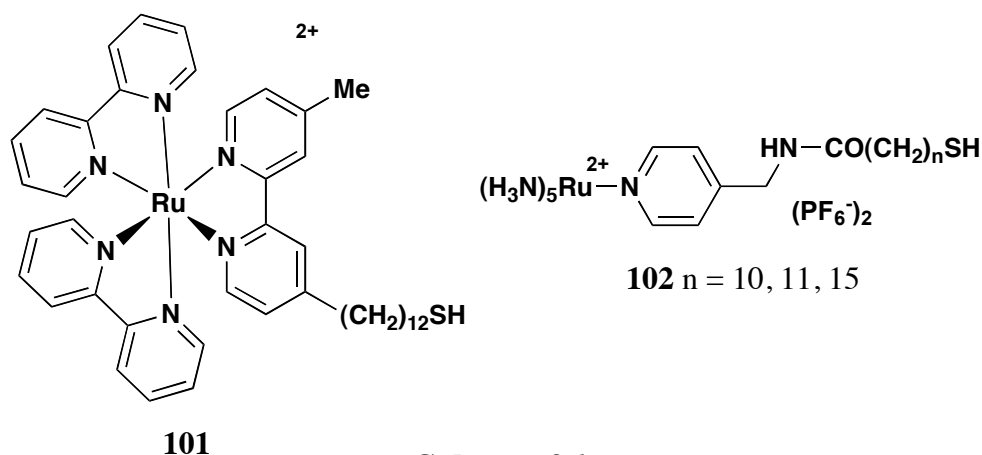
Scheme 24



Scheme 25

4. Ruthenium complexes

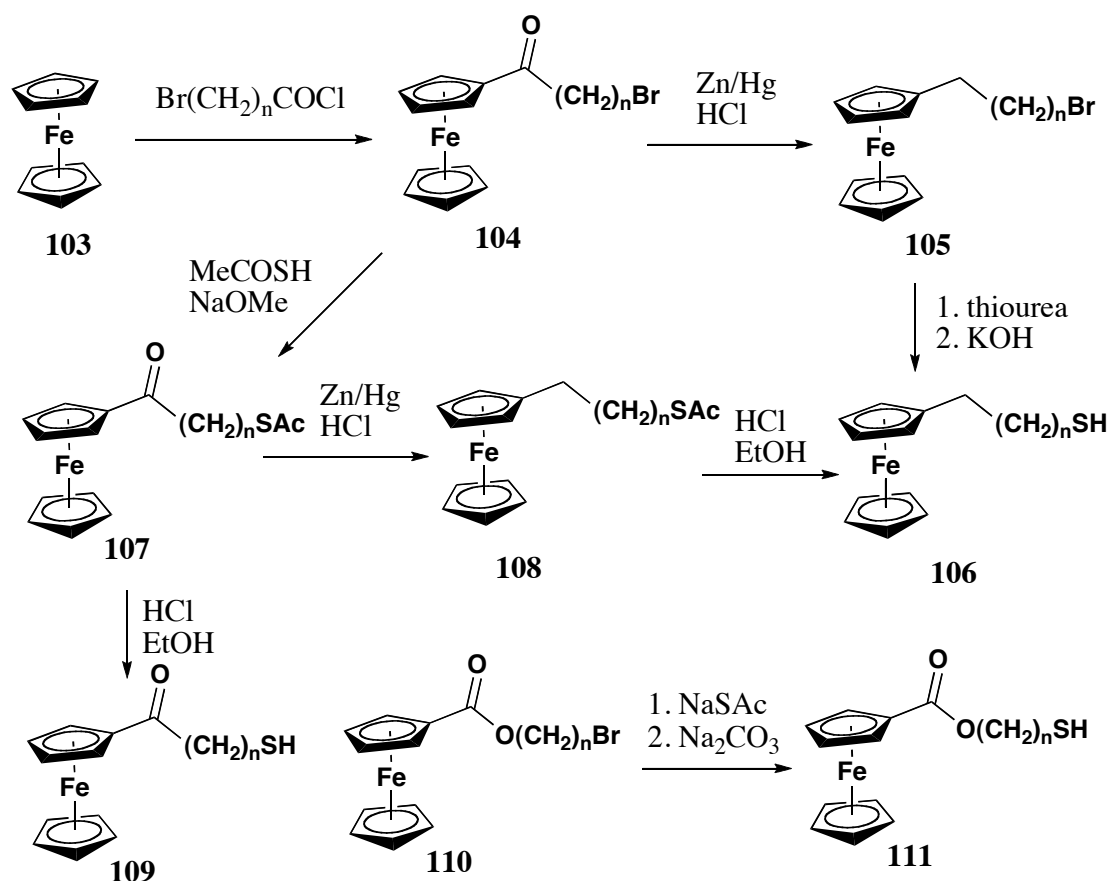
Again in this area there are two major approaches: complexation of a ligand already containing a thiol group and introduction of a thiol to an existing ligand. An example of the former approach is the formation of **101** (Scheme 26) simply by mixing the thiol-bearing ligand with unfunctionalized bipyridyl during complex formation.⁵⁹ The thiol group was introduced to the ligand by treating the bromododecyl bipyridyl with sodium hydrogen sulfide in dimethyl sulfoxide. An example of reaction at an already complexed ligand is the formation of complexes **102** by reaction of the appropriate ω-mercaptocarboxylic acid with the 4-(aminomethyl)pyridyl complex.⁶⁰



Scheme 26

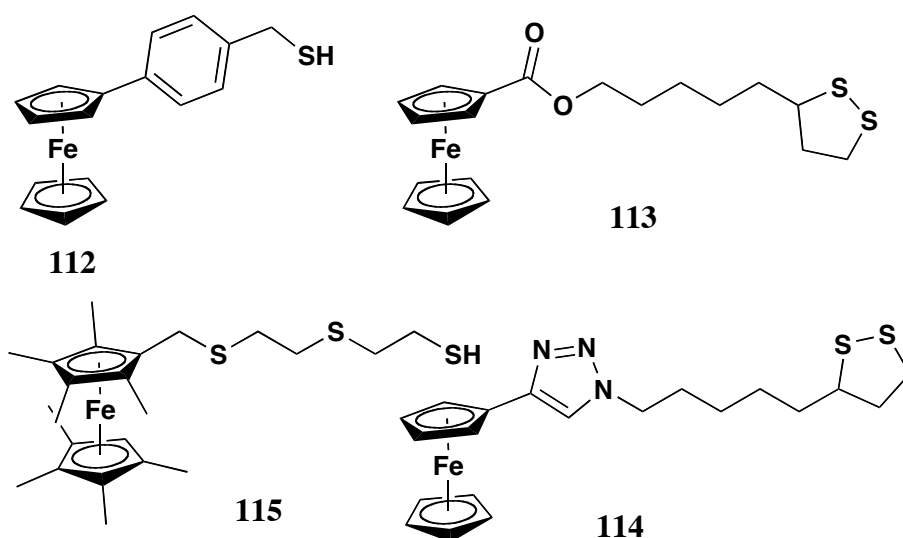
5. Ferrocene derivatives

Attaching long-chain thiol groups to ferrocene has been achieved in several different ways (*Scheme 27*). Friedel Crafts acylation with an ω -bromoacid chloride converts ferrocene **103** into **104** and Clemmensen reduction of this to **105** followed by treatment with thiourea followed by KOH gives **106** for $n = 5$ and 10 .^{61, 62} Alternatively **104** can be treated with thioacetic acid to give **107** which is then reduced to **108** and hydrolyzed to give **106** and this method has been used for $n = 10$ and 15 .⁶³ In addition, compound **98** can be hydrolyzed to give thiol **109** still retaining the carbonyl group for $n = 10$.⁶⁴ Starting from ferrocenecarboxylic acid, the bromo ester **110** is formed by condensation with the ω -bromo acid and subsequent treatment with sodium thioacetate followed by sodium carbonate gives the mercapto esters **111** for $n = 11$ and 16 .⁶³



Scheme 27

Various other ferrocene derivatives have been prepared for adsorption on surfaces (*Scheme 28*) including the benzyl compound **112** formed by sequential treatment of the benzylic alcohol with $\text{Ph}_3\text{P}/\text{CBr}_4$, potassium thioacetate and potassium hydroxide.⁴⁹ The two 1,2-dithiolane derivatives **113** and **114** are formed, respectively, by esterification of ferrocenecarboxylic acid and an azide 1,3-dipolar cycloaddition to ethynylferrocene.⁶⁵ The unusual octamethyl compound **115** is prepared by intercepting the corresponding ferrocenylmethyl cation with the anion of bis(2-mercaptoethyl) sulfide.⁶⁶

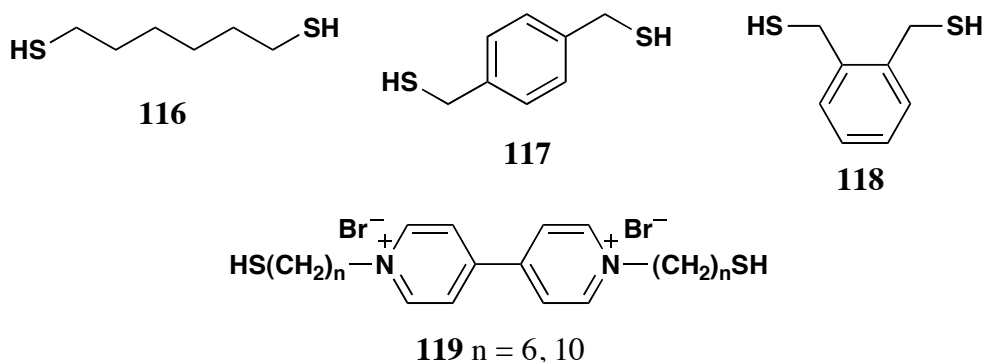


Scheme 28

V. Molecular Junctions

1. Simple dithiols

Although many of the compounds already considered have two or more groups for adsorption to a metal surface, the focus of most of these studies has been on the properties of self-assembled monolayers on a single metal surface. A newer area is the design of single molecule conductors or "molecular wires" that can act as connectors between two metal surfaces, often the substrate and tip in a scanning tunneling microscope. Attempts have been made to measure conductivity in molecular junctions of simple thiols such as **115**–**117** (*Scheme 29*) between gold contacts, although rather inconsistent results were produced.⁶⁷



Scheme 29

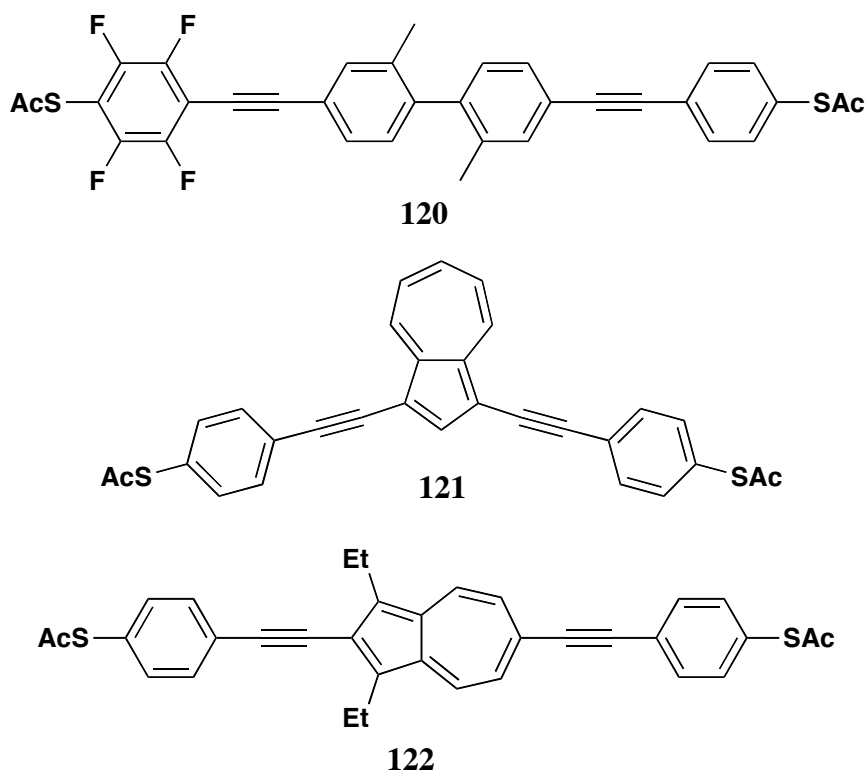
2. Viologens

A series of 4,4'-bi(pyridinium salts) or viologens **119** bearing thiol-terminated chains (*Scheme 29*) have been shown to adsorb to gold electrodes and gold nanoparticles for $n = 10$,⁶⁸ and later to behave as molecular wires in single molecule experiments with an STM tip for $n = 6$.⁶⁹ In both cases the compounds were readily prepared by treating

4,4'-bipyridyl with an ω -acetylthioalkyl bromide followed by removal of the *S*-acetyl groups with acetyl chloride in methanol.

3. Di(arylkynyl)biaryls and azulenes

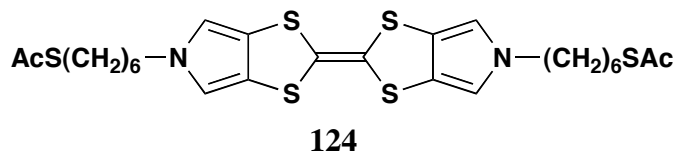
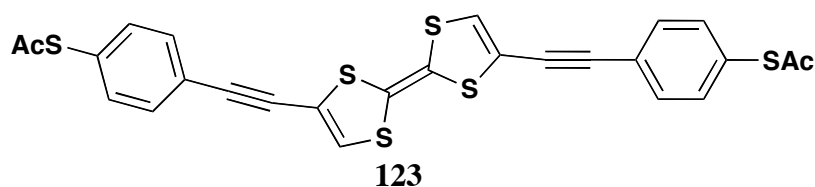
The unsymmetrical di(arylkynyl)biaryl **120** (Scheme 30) was shown to adsorb between two gold surfaces with loss of the *S*-acetyl groups and to behave as a molecular diode.⁷⁰ In a more recent study a range of bis(acetylthio) functionalized azulenes such as **121** and **122** were prepared and studied as single molecule junctions.⁷¹ In both cases palladium-catalyzed Sonogashira coupling using 4-(acetylthio)phenylacetylene and the appropriate aryl halides gives the products in excellent yield.



Scheme 30

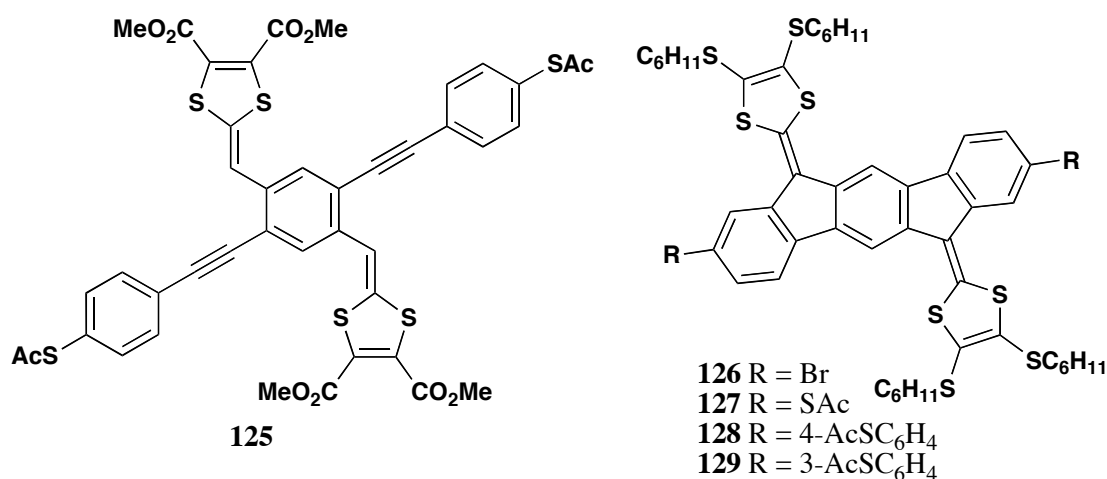
4. TTFs and extended TTFs

The acetylthio-terminated dialkynyl-TTF **123** (Scheme 31) may be prepared by Sonogashira coupling either between 4-(acetylthio)phenylacetylene and diiodo-TTF or the diethynyl-TTF and 4-(acetylthio)iodobenzene.⁷² The compound is observed to behave as a molecular nanowire between atomic sized gold electrodes. There has also been considerable interest in the acetylthio-terminated dipyrrolo-TTF **124** which has been investigated as a single molecule junction or molecular wire.^{73,74} The synthesis in this case involves treatment of the parent NH dipyrrolo-TTF with sodium hydride and 1,6-dibromohexane followed by potassium thioacetate.



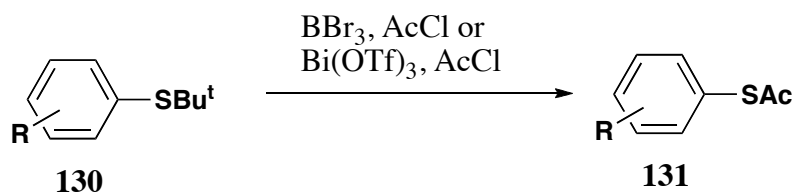
Scheme 31

The extended TTF derivative **125** (Scheme 32) is prepared by first constructing the bis(trimethylsilylethynyl) extended TTF, using a Wittig reaction to introduce the dithiole rings.⁷⁵ The terminal diyne is then liberated using potassium carbonate deprotection and coupled under Sonogashira conditions with 4-(*tert*-butylthio)bromobenzene. Finally the *S-tert*-butyl groups are replaced by *S*-acetyl by treatment with BBr₃ and acetyl chloride.



Scheme 32

Preparation of the bis(acetylthio) extended TTF compounds **127–129** starts from the dibromide **126**.⁷⁶ Treatment with potassium thioacetate gives **127** while Suzuki reaction with the 3- or 4-(*tert*-butylthio)phenylboronic acid, followed by treatment with BBr₃ and acetyl chloride gives **128** and **129**. The unsymmetrical hybrid compound with one *meta* and one *para*-substituted ring was also prepared.⁷⁶



Scheme 33

References

1. N. H. Evans, H. Rahman, J. J. Davis and P. D. Beer, *Anal. Bioanal. Chem.*, **402**, 1739 (2012).
2. J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, **105**, 1103 (2005).
3. C. H. Kim, S. W. Han, T. H. Ha and K. Kim, *Langmuir*, **15**, 8399 (1999).
4. Y. J. Lee, I. C. Jeon, W. Paik and K. Kim, *Langmuir*, **12**, 5830 (1996).
5. P. Chinwangso, A. C. Jamison and T. R. Lee, *Acc. Chem. Res.*, **44**, 511 (2011).
6. H. Fueno, M. Hayashi, K. Nin, A. Kubo, Y. Misaki and K. Tanaka, *Curr. Appl. Phys.*, **6**, 939 (2006).
7. B. Martorell, A. Clotet and J. Fraxedas, *J. Comput. Chem.*, **31**, 1842 (2010).
8. Y. Wang, C. Urban, J. Rodríguez-Fernández, J. M. Gallego, R. Otero, N. Martín, R. Miranda, M. Alcamí and F. Martín, *J. Phys. Chem. A*, **115**, 13080 (2011).
9. N. Gonzalez-Lakunza, I. Fernández-Torrente, K. J. Franke, N. Lorente, A. Arnau and J. I. Pascual, *Phys. Rev. Lett.*, **100**, 156805 (2008).
10. S. Campuzano, R. Gálvez, M. Pedrero, F. J. M. de Villena and J. M. Pingarrón, *J. Electroanal. Chem.*, **526**, 92 (2002).
11. M. N. Nair, C. Mattioli, M. Cranney, J.-P. Malval, F. Vonau, D. Aubel, J.-L. Bubendorff, A. Gourdon and L. Simon, *J. Phys. Chem. C*, **119**, 9334 (2015).
12. X. Li, G. Zhang, H. Ma, D. Zhang, J. Li and D. Zhu, *J. Am. Chem. Soc.*, **126**, 11543 (2004).
13. G. Zhang, D. Zhang, X. Zhao, X. Ai, J. Zhang and D. Zhu, *Chem. Eur. J.*, **12**, 1067 (2006).
14. R. Yuge, A. Miyazaki, T. Enoki, E. Ito, F. Nakamura and M. Hara, *Mol. Cryst. Liq. Cryst.*, **370**, 273 (2001).
15. R. Yuge, A. Miyazaki, T. Enoki, K. Tamada, F. Nakamura and M. Hara, *J. Phys. Chem. B*, **106**, 6894 (2002).
16. C. M. Yip and M. D. Ward, *Langmuir*, **10**, 549 (1994).
17. Y. Yokota, A. Miyazaki, K. Fukui, T. Enoki, K. Tamada and M. Hara, *J. Phys. Chem. B*, **110**, 20401 (2006).
18. Y. Yokota, K. Fukui, T. Enoki and M. Hara, *J. Am. Chem. Soc.*, **129**, 6571 (2007).
19. N. Svenstrup, K. M. Rasmussen, T. K. Hansen and J. Becher, *Synthesis*, 809 (1994).
20. G. Trippé, M. Oçafrain, M. Besbes, V. Monroche, J. Lyskawa, F. Le Derf, M. Sallé, J. Becher, B. Colonna and L. Echegoyen, *New J. Chem.*, **26**, 1320 (2002).
21. J. Lyskawa, M. Oçafrain, G. Trippé, F. Le Derf, M. Sallé, P. Viel and S. Palacin, *Tetrahedron*, **62**, 4419 (2006).
22. A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Marenco, J. Yarwood, M. J. Joyce and S. N. Port, *Adv. Mater.*, **10**, 395 (1998).
23. A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, J. Moloney, J. A. K. Howard, M. J. Joyce and S. N. Port, *J. Org. Chem.*, **65**, 8269 (2000).
24. L. G. Jensen, K. A. Nielsen, T. Breton, J. L. Sessler, J. O. Jeppesen, E. Levillain and L. Sanguinet, *Chem. Eur. J.*, **15**, 8128 (2009).
25. A. Martín-Lasanta, D. Miguel, T. García, J. A. López-Villanueva, S. Rodríguez-Bolívar, F. M. Gómez-Campos, E. Buñuel, D. J. Cárdenas, L. A. de Cienfuegos and J. M. Cuerva, *ChemPhysChem*, **13**, 860 (2012).
26. L. R. Ditzler, C. Karunatilaka, V. R. Donuru, H. Y. Liu and A. V. Tivanski, *J. Phys. Chem. C*, **114**, 4429 (2010).

27. E. Gomar-Nadal, G. K. Ramachandran, F. Chen, T. Burgin, C. Rovira, D. B. Amabilino and S. M. Lindsay, *J. Phys. Chem. B*, **108**, 7213 (2004).
28. R. G. Nuzzo and D. L. Allara, *J. Am. Chem. Soc.*, **105**, 4481 (1983).
29. P. Hudhomme, P. Blanchard, M. Sallé, S. Le Moustarder, A. Riou, M. Jubault, A. Gorgues and G. Duguay, *Angew. Chem. Int. Ed. Engl.*, **36**, 878 (1997).
30. P. Hudhomme, S. Le Moustarder, C. Durand, N. Gallego-Planas, N. Mercier, P. Blanchard, E. Levillain, M. Allain, A. Gorgues and A. Riou, *Chem. Eur. J.*, **7**, 5070 (2001).
31. C. Durand, P. Hudhomme, G. Duguay, M. Jubault and A. Gorgues, *Chem. Commun.*, 361 (1998).
32. S. J. Jethwa, F. Grillo, H. A. Früchtl, G. J. Simpson, M.-J. Treanor, R. Schaub, S. M. Francis, N. V. Richardson and R. A. Aitken, *Chem. Commun.*, **50**, 10140 (2014).
33. M. Oda, Y. Zhang, N. C. Thanh, S. Hayashi, S. Zuo and S. Kuroda, *Heterocycles*, **68**, 1031 (2006).
34. R. A. Aitken, S. J. Jethwa, N. V. Richardson and A. M. Z. Slawin, *Tetrahedron Lett.*, **57**, 1563 (2016).
35. E. Dahlstedt, J. Hellberg, R. M. Petoral Jr. and K. Uvdal, *J. Mater. Chem.*, **14**, 81 (2004).
36. H. Fujihara, H. Nakai, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 737 (1999).
37. H. Nakai, M. Yoshihara and H. Fujihara, *Langmuir*, **15**, 8574 (1999).
38. M. A. Herranz, L. Yu, N. Martín and L. Echegoyen, *J. Org. Chem.*, **68**, 8379 (2003).
39. H. Liu, S. Liu and L. Echegoyen, *Chem. Commun.*, 1493 (1999).
40. S.-G. Liu, H. Liu, K. Bandyopadhyay, Z. Gao and L. Echegoyen, *J. Org. Chem.*, **65**, 3292 (2000).
41. J. Casado-Montenegro, M. Mas-Torrent, F. Otón, N. Crivillers, J. Veciana and C. Rovira, *Chem. Commun.*, **49**, 8084 (2013).
42. C. Urban, D. Eciija, Y. Wang, M. Trelka, I. Preda, A. Vollmer, N. Lorente, A. Arnau, M. Alcamí, L. Soriano, N. Martín, F. Martín, R. Otero, J. M. Gallego and R. Miranda, *J. Phys. Chem. C*, **114**, 6503 (2010).
43. R. Otero, D. Eciija, G. Fernández, J. M. Gallego, L. Sánchez, N. Martín and R. Miranda, *Nano Lett.*, **7**, 2602 (2007).
44. G. Bruno, F. Babudri, A. Operamolla, G. V. Bianco, M. Losurdo, M. M. Giangregorio, O. H. Omar, F. Mavelli, G. M. Farinola, P. Capessuto and F. Naso, *Langmuir*, **26**, 8430 (2010).
45. M. Fibbioli, K. Bandyopadhyay, S.-G. Liu, L. Echegoyen, O. Enger, F. Diederich, P. Bühlmann and E. Pretsch, *Chem. Commun.*, 339 (2000).
46. M. Fibbioli, K. Bandyopadhyay, S.-G. Liu, L. Echegoyen, O. Enger, F. Diederich, D. Gingery, P. Bühlmann, H. Persson, U. W. Suter and E. Pretsch, *Chem. Mater.*, **14**, 1721 (2002).
47. M. Sierra, M. A. Herranz, S. Zhang, L. Sánchez, N. Martín and L. Echegoyen, *Langmuir*, **22**, 10619 (2006).
48. J. Zak, H. Yuan, M. Ho, K. Woo and M. D. Porter, *Langmuir*, **9**, 2772 (1993).
49. A. Balakumar, A. B. Lysenko, C. Carcel, V. L. Malinovskii, D. T. Gryko, K.-H. Schweikart, R. S. Loewe, A. A. Yasseri, Z. Liu, D. F. Bocian and J. S. Lindsey, *J. Org. Chem.*, **69**, 1435 (2004).
50. A. A. Yasseri, D. Syomin, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, *J. Am. Chem. Soc.*, **126**, 15603 (2004).

51. J. Wan, H. Sun and X. Huang, *Chin. J. Chem.*, **30**, 1841 (2012).
52. N. Nishimura, M. Ooi, K. Shimazu, H. Fujii and K. Uosaki, *J. Electroanal. Chem.*, **473**, 75 (1999).
53. D. T. Gryko, C. Clausen and J. S. Lindsey, *J. Org. Chem.*, **64**, 8635 (1999).
54. D. T. Gryko, C. Clausen, K. M. Roth, N. Dontha, D. F. Bocian, W. G. Kuhr and J. S. Lindsey, *J. Org. Chem.*, **65**, 7345 (2000).
55. Y.-H. Chan, A. E. Schuckman, L. M. Pérez, M. Vinodu, C. M. Drain and J. D. Batteas, *J. Phys. Chem. (C)*, **112**, 6110 (2008).
56. A. A. Yasserli, D. Syomin, V. L. Malinovskii, R. S. Loewe, J. S. Lindsey, F. Zaera and D. F. Bocian, *J. Am. Chem. Soc.*, **126**, 11944 (2004).
57. A. H. Ell, G. Csjernyik, V. F. Slagt, J.-E. Bäckvall, S. Berner, C. Puglia, G. Ledung and S. Oscarsson, *Eur. J. Org. Chem.*, 1193 (2006).
58. O. P. H. Vaughan, M. Turner, F. J. Williams, A. Hille, J. K. M. Sanders and R. M. Lambert, *J. Am. Chem. Soc.*, **128**, 9578 (2006).
59. Y. S. Obeng and A. J. Bard, *Langmuir*, **7**, 195 (1991).
60. H. O. Finklea and D. D. Hanshew, *J. Am. Chem. Soc.*, **114**, 3173 (1992).
61. K. Uosaki, Y. Sato and H. Kita, *Langmuir*, **7**, 1510 (1991).
62. G. K. Rowe and S. E. Creager, *Langmuir*, **7**, 2307 (1991).
63. C. E. D. Chidsey, C. R. Bertozzi, T. M. Putvinski and A. M. Mujisce, *J. Am. Chem. Soc.*, **112**, 4301 (1990).
64. J. J. Hickman, D. Ofer, C. Zou, M. S. Wrighton, P. E. Laibinis and G. M. Whitesides, *J. Am. Chem. Soc.*, **113**, 1128 (1991).
65. D. Captao, R. Sahli, N. Raouafi, B. Limoges, C. Fave and B. Schöllhorn, *ChemElectroChem*, **3**, 1422 (2016).
66. C. Zou and M. S. Wrighton, *J. Am. Chem. Soc.*, **112**, 7578 (1990).
67. J. Ulrich, D. Esrail, W. Pontius, L. Venkataraman, D. Millar and L. H. Doerrler, *J. Phys. Chem. B*, **110**, 2462 (2006).
68. D. L. Gittins, D. Bethell, R. J. Nichols and D. J. Schiffrin, *Adv. Mater.*, **11**, 737 (1999).
69. W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Höbenreich, D. J. Schiffrin and R. J. Nichols, *J. Am. Chem. Soc.*, **125**, 15294 (2003).
70. M. Ebling, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber and M. Mayor, *Proc. Natl. Acad. Sci. U. S. A.*, **102**, 8815 (2005).
71. F. Schwarz, M. Koch, G. Kastlunger, H. Berke, R. Stadler, K. Venkatesan and E. Lörtscher, *Angew. Chem. Int. Edn.*, **55**, 11781 (2016).
72. F. Giacalone, M. A. Herranz, L. Grüter, M. T. González, M. Calame, C. Schönenberger, C. R. Arroyo, G. Rubio-Bollinger, M. Vélez, N. Agrait and N. Martín, *Chem. Commun.*, 4854 (2007).
73. E. Leary, S. J. Higgins, H. van Zalinge, W. Haiss, R. J. Nichols, S. Nygaard, J. O. Jeppesen and J. Ulstrup, *J. Am. Chem. Soc.*, **130**, 12204 (2008).
74. N. J. Kay, S. J. Higgins, J. O. Jeppesen, E. Leary, J. Lycoops, J. Ulstrup and R. J. Nichols, *J. Am. Chem. Soc.*, **134**, 16817 (2012).
75. J. K. Sørensen, M. Vestergaard, A. Kadziola, K. Kilså and M. B. Nielsen, *Org. Lett.*, **8**, 1173 (2006).
76. M. Mansø, M. Koole, M. Mulder, I. J. Olavarria-Contreras, C. L. Andersen, M. Jevric, S. L. Broman, A. Kadziola, O. Hammerich, H. S. J. van der Zant and M. B. Nielsen, *J. Org. Chem.*, **81**, 8406 (2016).
77. M. Jevric, A. U. Petersen, M. Mansø, A. Ø. Madsen and M. B. Nielsen, *Eur. J. Org. Chem.*, 4675 (2015).

78. Z.-P. Lv, Z.-Z. Luan, H.-Y. Wang, S. Liu, C.-H. Li, D. Wu, J.-L. Zuo and S. Sun, *ACS Nano*, **9**, 12205 (2015).
79. Z.-P. Lv, Z.-Z. Luan, P.-Y. Cai, T. Wang, C.-H. Li, D. Wu, J.-L. Zuo and S. Sun, *Nanoscale*, **8**, 12128 (2016).
80. A. André, D. Zherebetsky, D. Hanifi, B. He, M. S. Khoshkhoo, M. Jankowski, T. Chassé, L.-W. Wang, F. Schreiber, A. Salleo, Y. Liu and M. Scheele, *Chem. Mater.*, **27**, 8105 (2015).