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Tetrathiafulvalene-functionalized triptycenes: synthetic protocols and elucidation of intramolecular Coulomb repulsions in the oxidized species

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Abstract—A large selection of triptycenes functionalized with tetrathiafulvalene (TTF) units as well as triptycenes containing extended TTFs as a part of the triptycene core have been synthesized utilizing new triptycene di- and tetraaldehydes as well as bis-, tetrakis- and hexakis(bromomethyl) derivatives. The largest scaffold contains a total of 12 TTFs around the central triptycene core. From spectroelectrochemical and chemical oxidation studies, we have elucidated the extent to which an increasing number of electrostatic interactions among oxidized TTF units exert an influence on the absorption characteristics.

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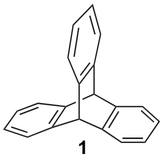
1. Introduction

The geometric features of the triptycene (**1**) skeleton make it appealing for exploitation in supramolecular chemistry.[1] The good electron donor tetrathiafulvalene (TTF) is another attractive molecule for both materials and supramolecular chemistry as it is oxidized reversibly in two one-electron steps.[2] In order to enhance the interactions between individual TTF units and the formation of mixed-valence radical cation salts, several macrocyclic,[3] ladder-like[4] and dendritic[5] TTF oligomers have been prepared during the past 10 years. Some of these molecules are also interesting as host molecules for electron deficient guest molecules. Moreover, oxidation of the TTFs to dications yields species that have a potential to form donor–acceptor complexes with electron rich molecules.[5g,6] We identified the triptycene core as a new and convenient scaffold for TTF oligomers and became interested in elucidating in a systematic manner the relationship between electrostatic interactions between oxidized TTF units and the absorption characteristics.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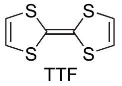
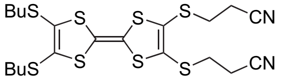


Synthetically, we benefit from readily available TTF building blocks **2**–**4**. The cyanoethyl group is an efficient protecting group for TTF thiolates as demonstrated by Becher and co-workers.[7] The two cyanoethyl groups of **2** can be removed stepwise by the action of a base such as CsOH or NaOMe, which allows two subsequent thiolate alkylations. In a theoretical study, this stepwise deprotection protocol was explained by an unfavourable Coulombic repulsion between two negatively charged thiolates on the same dithiole ring.[8] Phosphonate esters **3**[9] and phosphonium salt **4**[10] can be subjected to Wittig–Horner reactions.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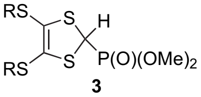
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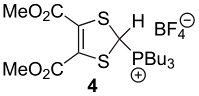
R = Bu: **3a**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Some of us[11] have recently devised a simple synthesis of triptycene di- and tetracarboxylic acids by oxidation of appropriate methyl precursors. Here, we wish to present the utilization of these compounds in efficient syntheses of

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Keywords: Redox systems; Spectroelectrochemistry; Supramolecular chemistry; Tetrathiafulvalenes; Triptycenes.

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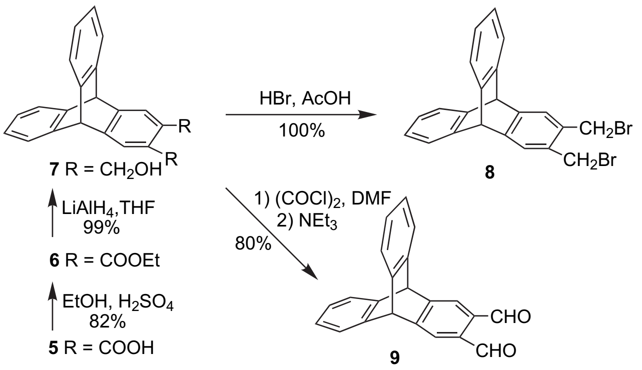
triptycene di- and tetraaldehydes as well as bis-, tetrakis- and hexakis(bromomethyl)triptycenes. The aldehydes are good substrates for the Wittig–Horner reaction with **3** or **4**, whereas the benzylic bromides represent reactive alkylation reagents towards thiolate anions generated from **2**. Hereby, a large selection of triptycenes functionalized with TTF as well as triptycenes containing extended TTFs as a part of the triptycene core have been obtained. Moreover, we have employed the triptycene unit as a core for a 12-TTF macromolecule.

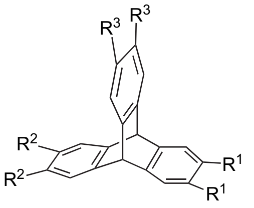
2. Results and discussion

Fischer esterification of the dicarboxylic acid **5** with EtOH gave the diethyl ester **6** (Scheme 1). The two ester groups were reduced with lithium aluminium hydride to provide the diol **7**. Treatment of compound **7** with HBr in acetic acid gave the dibromide **8**. Oxidation of **7** by pyridinium chlorochromate (PPC) gave the phthalide lactone rather than the desired dialdehyde. An analogous lactone formation has been observed in oxidation of 1,2-bis(hydroxymethyl)benzene.[12] Nevertheless, Swern oxidation of **7** successfully gave the dialdehyde **9**.



Scheme 1.

By similar reactions, the esters **10** and **11**, the alcohol **12** and the bromides **14** and **15** were prepared. The alcohol **13** proved difficult to isolate and was, therefore, used in the ensuing bromination step without purification.

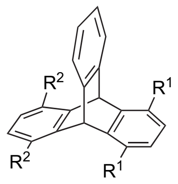


$R^1 = R^2 = CO_2Et, R^3 = H$: **10**
$R^1 = R^2 = R^3 = CO_2Et$: **11**

$R^1 = R^2 = CH_2OH, R^3 = H$: **12**
$R^1 = R^2 = R^3 = CH_2OH$ **13**

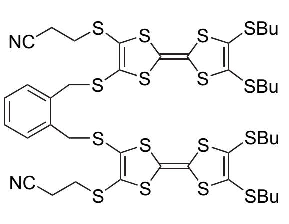
$R^1 = R^2 = CH_2Br, R^3 = H$: **14**
$R^1 = R^2 = R^3 = CH_2Br$: **15**

By a sequence of Fischer esterification, lithium aluminium hydride reduction and PCC oxidation, the new *para*-substituted derivatives **16**–**20** were prepared. The known dibromide **21** was obtained by NBS bromination according to a literature protocol.[13a] The tetrabromide **22** was obtained by analogous NBS bromination of the tetramethyl precursor **23**.[13,14] It should be mentioned that, in general, we experienced problems in obtaining the benzylic bromides analytically pure owing to their limited stabilities.



$R^1 = CO_2Et, R^2 = H$: **16**
$R^1 = CH_2OH, R^2 = H$: **17**
$R^1 = R^2 = CH_2OH$: **18**
$R^1 = CHO, R^2 = H$: **19**
$R^1 = R^2 = CHO$: **20**
$R^1 = CH_2Br, R^2 = H$: **21**
$R^1 = R^2 = CH_2Br$: **22**
$R^1 = R^2 = CH_3$: **23**

Triptycenes containing two TTF units were prepared from the dibromides **8** and **21** according to Scheme 2. Compound **2** was selectively deprotected with 1 equiv of caesium hydroxide and the resulting monothiolate was then alkylated in situ with the bromides to afford compounds **24** and **25**. Similarly, we prepared bis-TTFs **26** and **27** based on *o*- and *p*-xylene cores. The tetrabromides **14** and **22** served as precursors for triptycenes **28** and **29** containing four TTF units, while the hexabromide **22** was converted to the triptycene **30**.



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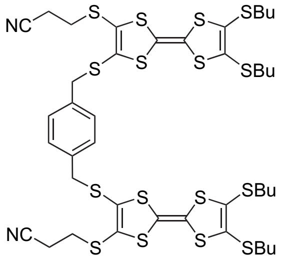

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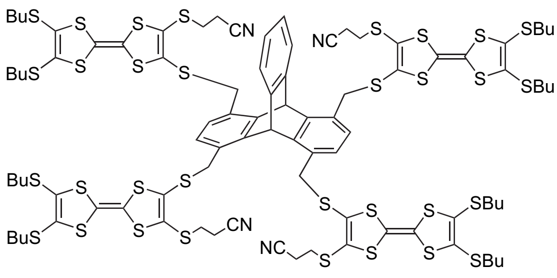

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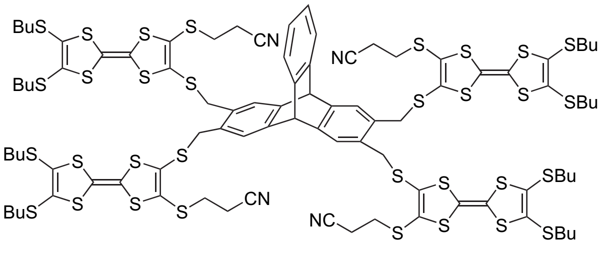

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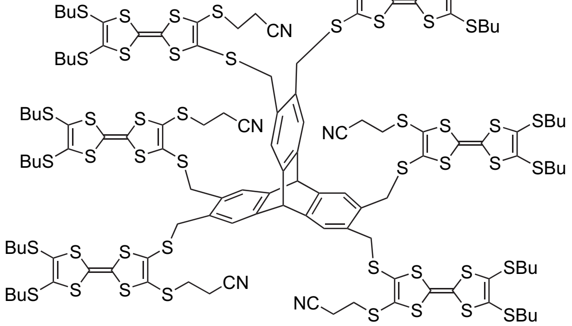

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