RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2020, **10**, 15030

Dimers of pyrrolo-annelated indenofluorene-extended tetrathiafulvalenes – large multiredox systems†

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Received 3rd March 2020
Accepted 31st March 2020

DOI: 10.1039/d0ra02787a

rsc.li/rsc-advances

Novel scaffolds of indenofluorene (IF)-extended tetrathiafulvalenes (TTF) were synthesized starting from a new pyrrolo-annelated **IF-TTF** monomer. Rigid *para*- and *meta*-phenylene linked dimers were obtained *via* *N*-arylation reactions of the monomer, and their optical and redox properties were elucidated by UV-Vis absorption spectroscopy and cyclic and differential pulse voltammetries.

Tetrathiafulvalene (**TTF**) is a redox-active unit that reversibly undergoes two sequential one-electron oxidations, forming first a radical cation (**TTF**$^{+}$) and subsequently a dication (**TTF**$^{2+}$) containing two aromatic 1,3-dithiolium rings, and it is due to these redox properties that it is an attractive unit for materials and supramolecular chemistries.[1]

Extension of the conjugated system, leading to so-called extended **TTF**s, has successfully been used as a tool to finely tune the redox properties and geometries of the various redox states.[2] For example, introduction of an indeno[1,2-*b*]fluorene (**IF**) core[3] has provided indenofluorene-extended **TTF**s of the general structure **IF-TTF** shown in Fig. 1. X-Ray crystallographic and computational studies reveal that all three redox states (0, +1, +2), generated in sequential and reversible steps, take a fully planar structure, and spectroelectrochemical studies have shown that the individual redox states exhibit significantly redshifted absorptions relative to those of **TTF**, **TTF**$^{+}$, and **TTF**$^{2+}$, respectively.[2]

Recently, we developed synthetic protocols for linking together two **IF-TTF** units *via* anchoring at a peripheral position of each dithiafulvene unit.[4] Such dimers unfortunately exist as unseparable mixtures of *cis* and *trans* isomers (*cf.*, the disubstituted **TTF**s shown in Fig. 1), and to avoid this problem of isomerism we decided to develop a synthetic protocol for fusing a pyrrole unit to one of the dithiole rings of **IF-TTF** as in target molecule **1** shown in Fig. 2. Indeed, the related mono-pyrrolo-annelated **TTF** (**MP-TTF**, Fig. 1) and bis-pyrrolo-annelated **TTF** have proven important as versatile π-donor building blocks in macromolecular and supramolecular chemistry.[5]

Dimerization of two units **1** *via* its nitrogen atom and a suitable linker would prevent formation of isomers. As linkers we decided to explore rigid phenylene units as in target molecules **2** (*para*-phenylene bridge) and **3** (*meta*-phenylene bridge) shown in Fig. 2. Previously prepared *cis*/*trans* isomeric **IF-TTF** dimers had flexible linkers and showed intramolecular associations upon oxidation,[4] which would be prevented by these rigid linkers. Moreover, intermolecular interactions are to a large extent prevented by the peripheral *tert*-butyl substituents that were chosen as substituent groups to enhance solubility of the dimers.

Synthesis of **1** proceeds according to Scheme 1, employing the known diketone **4**,[4] the *N*-tosyl-protected pyrrolo-annelated 1,3-dithiole-2-thione **I**[5a] and the phosphonate ester **II**[3b] as precursors. A phosphite-mediated coupling between **4** and **I** was carried out to give mono-olefinated product **5** in a yield of 61%. This compound was next subjected to a Horner–Wadsworth–Emmons olefination with compound **II**, deprotonated by sodium hexamethyldisilazide (NaHMDS), providing the tosyl-protected mono-pyrrolo **IF-TTF** **6** in good yield (76%). This compound was subsequently deprotected using NaOMe to give in almost quantitative yield the monopyrrolo **IF-TTF** **1** with a pyrrole N–H unit available for further reactions.

With monomer **1** in hand, *N*-arylation reactions with 1,4- and 1,3-diiodobenzene, catalyzed by an excess of CuI and (±)-1,2-*trans*-diaminocyclohexane, were conducted in THF at reflux

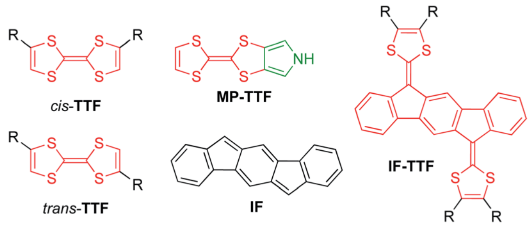

Fig. 1 Structures of *cis*/*trans*-isomeric TTFs, mono-pyrrolo-TTF (MP-TTF), indenofluorene (IF) and an indenofluorene-extended TTF (IF-TTF).

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† Electronic supplementary information (ESI) available: Synthetic protocols, NMR and UV-Vis absorption spectra. See DOI: 10.1039/d0ra02787a

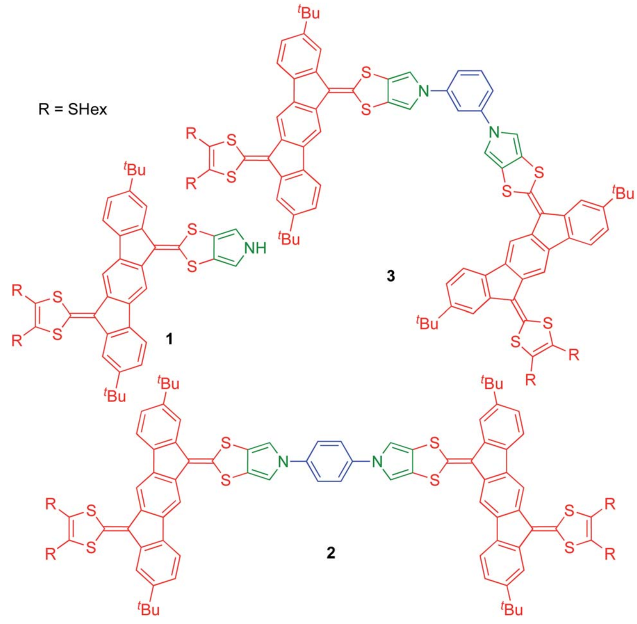
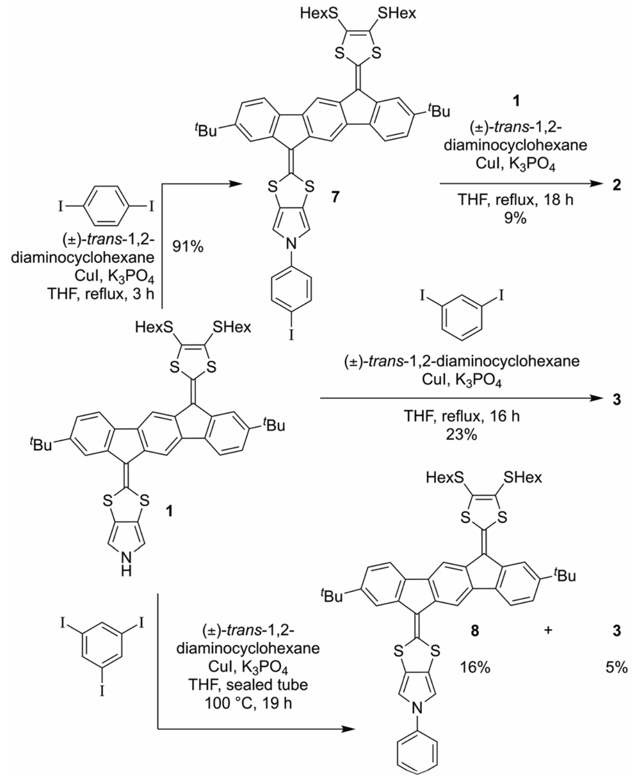
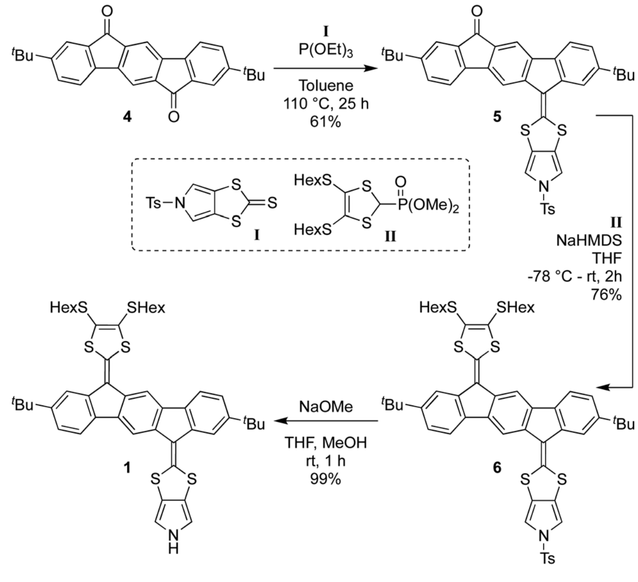


Fig. 2 New pyrrolo-annelated **IF-TTF** mono- and dimers.



Scheme 2 Synthesis of dimers **2** and **3**, and of mono-arylated species **7** and **8**.

(Scheme 2). This procedure, previously applied for *N*-arylation of pyrrolo-annelated **TTF**s,[6] yielded dimers **2** and **3**, respectively. The procedure worked best for 1,3-diiodobenzene. For the arylation reaction with 1,4-diiodobenzene it was observed that the first arylation progressed rather willingly, as the mono-arylated product **7** could be isolated in 91% yield after only 3 hours. Only when compound **7** was subjected to significantly longer reaction time, however, formation of dimer **2** was observed, and the compound was isolated in 9% yield after 18 hours of reaction time. This result indicates that the substitution of an iodide on the benzene ring with one **IF-TTF** unit, in the *para* position, decreases the reactivity of the second iodide significantly, possibly due to the strongly electron-donating character of the pyrrolo-**TTF**. Albeit inconvenient in the current work, it could be a potential advantage for stepwise construction of unsymmetrical scaffolds. For the corresponding reaction with 1,3-diiodobenzene smooth formation of the dimer **3** was observed, and this product was isolated in 23% after 16 hours, while no mono-arylated intermediate could be isolated.



Scheme 1 Synthesis of monomer **1** by stepwise olefination reactions. NaHMDS = sodium hexamethyldisilazide.

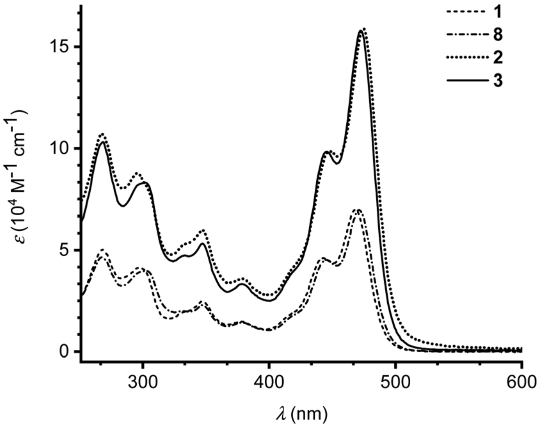


Fig. 3 UV-Vis absorption spectra of monomer **1** (dashed line), monomer **8** (dot dash dot) and dimers **2** (dotted line) and **3** (full line) in CH_2Cl_2 at 25 °C.

Table 1 Absorption maxima (λ_{max}) and extinction coefficients (ε) in CH_2Cl_2 at 25 °C, and oxidation potentials (from DPV) E_{ox} *vs.* Fc/Fc^+ in 1 : 1 CH_2Cl_2/C_6H_5Cl, for compounds **1**, **2**, **3** and **8**

Compound	λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1})	E_{ox} (V *vs.* Fc/Fc^+)
1	468 (6.99), 443 (4.61), 378 (1.47), 348 (2.46), 298 (4.13), 267 (5.00)	+0.18 (1e), +0.36 (1e)
2	475 (15.9), 448 (9.88), 379 (3.59), 347 (5.98), 295 (8.78), 267 (10.7)	+0.11 (1e), +0.44 (2e)
3	472 (15.8), 445 (9.84), 379 (3.32), 347 (5.32), 302 (8.31), 269 (10.3)	+0.14 (1e), +0.20 (1e), +0.41 (2e)
8	471 (6.97), 444 (4.52), 381 (1.41), 347 (2.29), 302 (3.98), 268 (4.65)	+0.22 (1e), +0.33 (1e)

Synthesis of a trimer consisting of three **IF-TTF** units around one central benzene ring was also attempted by coupling of monomer **1** and 1,3,5-triiodobenzene. However, when employing the conditions proven successful for synthesis of the dimers, no reaction was observed; instead, 86% of the starting material was re-isolated. Nevertheless, when conducting the reaction in a sealed vial and heating to 100 °C, full conversion of monomer **1** was observed. However, the isolated products were mono-arylated monomer **8** and previously isolated dimer **3**, and not the desired trimer. This result signals again that the reactivity of the iodides in the arylation reaction decreases upon introduction of **IF-TTF** units. Upon elevated pressure, as applied in the attempt to achieve the desired trimer, a competing reaction by which the iodides are substituted for hydrogen atoms is observed to exceed the arylation reaction. The mono-arylated compound **8** was used as a reference compound in subsequent studies of the synthesized dimers.

The photophysical properties of monomers **1** and **8** as well as dimers **2** and **3** were investigated by UV-Vis absorption spectroscopy in CH_2Cl_2 at 25 °C (Fig. 3). Absorption maxima and extinction coefficients are listed in Table 1. The longest-wavelength absorption maximum of **1** (468 nm) is close to that of the related **IF-TTF** with four peripheral SEt substituents (473 nm; R = SEt in Scheme 1).[3a] Expansion of the π-system with a benzene ring (compound **8**) had little effect on the longest-wavelength absorption maximum (471 nm). Linking the monomeric units by phenylene linkers, dimers **2** and **3**, did not change the longest-wavelength absorption maxima significantly either, but the intensity of the absorption was expectedly doubled (or slightly more than doubled).

Electrochemical studies of the synthesized compounds were conducted in 1 : 1 mixture of CH_2Cl_2/C_6H_5Cl containing 0.1 M NBu_4PF_6 as supporting electrolyte, and the cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) are shown in Fig. 4. Chlorobenzene was needed as co-solvent due to limited solubility of the dimers in neat CH_2Cl_2. Oxidation potentials are listed in Table 1 (taken from the DPVs), referenced against the ferrocene/ferrocenium (Fc/Fc^+) redox couple (recorded in a separate experiment). For monomer **1** two reversible, one-electron oxidations were observed, at +0.18 and +0.36 V *vs.* Fc/Fc^+, forming the radical cation and the dication, respectively. Similarly, monomer **8** was found to undergo two reversible one-electron oxidations at +0.22 and +0.33 V *vs.* Fc/Fc^+. For dimer **3** two reversible, one-electron oxidations were observed, at +0.14 and +0.20 V *vs.* Fc/Fc^+, forming the radical cation and the dication, respectively, followed by a reversible two-electron oxidation, at 0.41 V *vs.* Fc/Fc^+, forming the tetracation. The electrochemistry of dimer **2** is, however, more complicated. It exhibits a reversible one-electron oxidation at +0.11 V *vs.* Fc/Fc^+, hence at lower potential than for dimer **3** in accordance to the large linearly conjugated system provided by a *para*-phenylene bridge. The second oxidation seemed, however, to occur over a very broad potential range. As known from literature,[7] the isolated 1,4-di(*N*-pyrrolyl)benzene unit itself undergoes an irreversible oxidation, and in the case of dimer **2** it seems that the redox properties are affected significantly by this structural unit of the molecule; dimer **2** thereby acts less like a 'classical' extended **TTF**. The CV may as well be complicated by intermolecular interactions despite the bulky *tert*-butyl groups present on the **IF** cores. A reversible two-electron oxidation, possibly due to formation of the tetracation or higher oxidation states, is observed at +0.44 V *vs.* Fc/Fc^+, indicating that while the second oxidation wave is significantly broadened the reversibility is intact.

In conclusion, we have developed a convenient synthetic procedure to obtain the first pyrrolo-annelated **IF**-extended **TTF** that was successfully dimerized by *N*-arylation reactions. The resulting rigid dimers present new interesting multiredox systems to be explored further in future work. The possibility to perform functionalization at the α-carbon atoms of the pyrrole

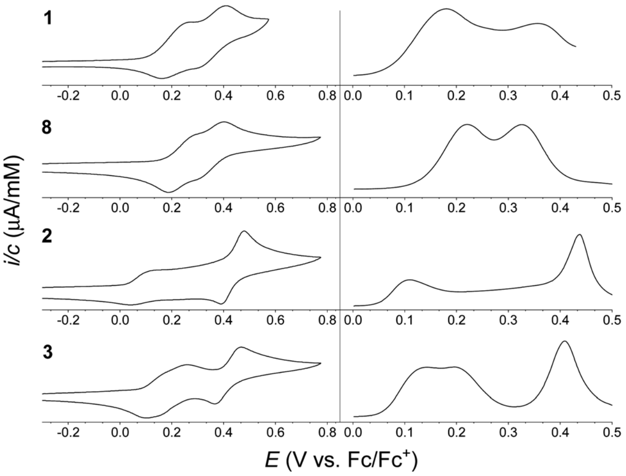


Fig. 4 Cyclic voltammograms (CVs) (left) and differential pulse voltammograms (DPVs) (right) of (from the top) **1** (0.38 mM), **8** (0.38 mM), **2** (0.37 mM) and **3** (0.43 mM); potentials *vs.* Fc/Fc^+ (solvent: 1 : 1 CH_2Cl_2/C_6H_5Cl; supporting electrolyte: 0.1 M NBu_4PF_6; scan rate: 0.1 V s^{-1}). Oxidation potentials listed in Table 1 are based on DPVs.

unit of these new scaffolds will also be interesting to pursue, taking advantage of the elaborate chemistry that has been developed for the parent mono- and bis-pyrrolo-annelated **TTF**s.[5]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Prof. Emeritus Ole Hammerich for fruitful discussions regarding the electrochemical studies.

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