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Monopyrrolotetrathiafulvalenium dication and its complexation with 1,5-dinaphtho[38]crown-10

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The synthesis and characterisation of a monopyrrolotetrathiafulvalene dication $\mathbf{1}^{2+}$, isolated both as its perchlorate (ClO_4^-) and hexachloroantimonate ($SbCl_6^-$) salt, is described. The complexation between the π-electron acceptor $\mathbf{1}^{2+}$ and the π-electron donating macrocyclic polyether 1,5-dinaphtho[38]crown-10 (1/5DN38C10) has been investigated using ^{1}H NMR spectroscopy and a binding constant (K_a) of $3.7 \pm 0.3 \times 10^2\,M^{-1}$ was obtained for the $\mathbf{1}^{2+} \subset$ 1/5DN38C10 complex (as its perchlorate salt) in acetonitrile at 298 K. The results reveal that the strength of the binding between $\mathbf{1}^{2+}$ and 1/5DN38C10 is one order of magnitude smaller than that for the binding between the parent tetrathiafulvalene (TTF) dication (i.e. TTF^{2+}) and 1/5DN38C10.

Keywords: crown ether; host–guest chemistry; oxidation; supramolecular chemistry; tetrathiafulvalenes

Introduction

The redox-active tetrathiafulvalene (TTF) unit and its derivatives have been intensively studied in the past three decades (*1*), because they can exist in three stable forms, specifically TTF(0), $TTF^{\cdot+}$ and TTF^{2+}, and for this reason TTF derivatives have found widespread use in materials chemistry (*2*). In recent years, however, the growing utility of TTF derivatives as building blocks in macrocyclic and supramolecular chemistry has revealed that the TTF unit is useful beyond the field of materials chemistry and the unique π-electron donor properties of TTF and its derivatives have been used to prepare a number of intriguing molecular and supramolecular systems, including chemical sensors (*3*), charge separating ligands (*4*), porphyrins (*5*), artificial muscles (*6*), molecular shuttles (*7*), chemical springs (*8*) and synthetic switches (*9*). Previous studies (*10*) have shown that TTF and its derivatives are excellent recognition sites for the π-electron accepting tetracationic cyclophane (*11*), cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$). Although a considerable range of catenanes (*12*, *13*) and rotaxanes (*7*, *13*, *14*), incorporating a TTF unit in conjunction with $CBPQT^{4+}$, have been reported, the use of the TTF dication (i.e. TTF^{2+}) as an π-electron acceptor in supramolecular chemistry has only been rarely described in the literature. In fact, to the best of our knowledge, only one example has been reported in the literature (*15*), namely the use of the parent TTF dication as a guest for the π-electron donating macrocyclic polyether 1,5-dinaphtho[38]crown-10 (1/5DN38C10). The binding constant (K_a) for the $TTF^{2+} \subset$ 1/5DN38C10 complex was determined to be $4.1 \times 10^3\,M^{-1}$ in acetonitrile at 298 K, indicating a rather strong association between 1/5DN38C10 and the TTF dication. Therefore, we decided to elaborate on this fundamental finding. In this paper, we describe the synthesis and characterisation of a monopyrrolotetrathiafulvalene (MPTTF) dication isolated both as its perchlorate (ClO_4^-) and hexachloroantimonate ($SbCl_6^-$) salt followed by our complexation studies between the MPTTF dication and 1/5DN38C10.

Results and discussions

The MPTTF derivative investigated in this work, namely 5-methyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1,3-dithiolo[4,5-*c*]pyrrole (**1**) was prepared according to a slightly modified (cf. Experimental) literature procedure (*16*). The corresponding MPTTF dication $\mathbf{1}^{2+}$ was subsequently synthesised as outlined in Scheme 1. Addition of excess of iron(III)perchlorate ($Fe(ClO_4)_3$) dissolved in 1,2-dimethoxyethane to a solution of **1** in 1,2-dimethoxyethane produced a blue precipitate, which was filtered affording $\mathbf{1}\cdot(ClO_4)_2$ as an analytically dark blue powder in 75% yield. The bis(hexachloroantimonate) salt of $\mathbf{1}^{2+}$ (i.e. $\mathbf{1}\cdot(SbCl_6)_2$) was synthesised by addition of 2.3 equivalents of the chemical oxidant tris(4-bromophenyl)ammoniumyl hexachloroantimonate to a solution of **1** in dichloromethane providing $\mathbf{1}\cdot(SbCl_6)_2$ as a dark solid in 97% yield after precipitation using petroleum ether and filtration.

The absorption spectra (Figure 1) of $\mathbf{1}\cdot(ClO_4)_2$ and $\mathbf{1}\cdot(SbCl_6)_2$ recorded in acetonitrile at room temperature

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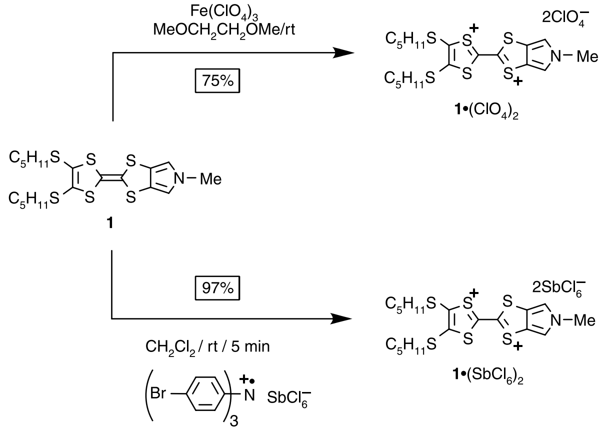


Scheme 1. Synthesis of **1**·$(ClO_4)_2$ and **1**·$(SbCl_6)_2$.

both shows a strong absorption band centred around 630 nm, which is characteristic of structures containing the doubly oxidised $MPTTF^{2+}$ unit (*9c*). A comparison (Figure 2) of the ^{1}H NMR spectra of the neutral **1** and the dicationic **1**·$(SbCl_6)_2$ revealed significant changes in the chemical shift of the signals associated with the protons located close to the MPTTF unit, by virtue of the deshielding arising from the two sets of cationic 6π-electron aromatic rings. Consequently, the signals for the NMe, SCH_2 and pyrrolo protons are shifted downfield with 0.55, 0.67 and 1.60 ppm, respectively, whereas the remaining protons on the pentyl chains only show small changes in their chemical shift values upon oxidation of the MPTTF unit to $MPTTF^{2+}$.

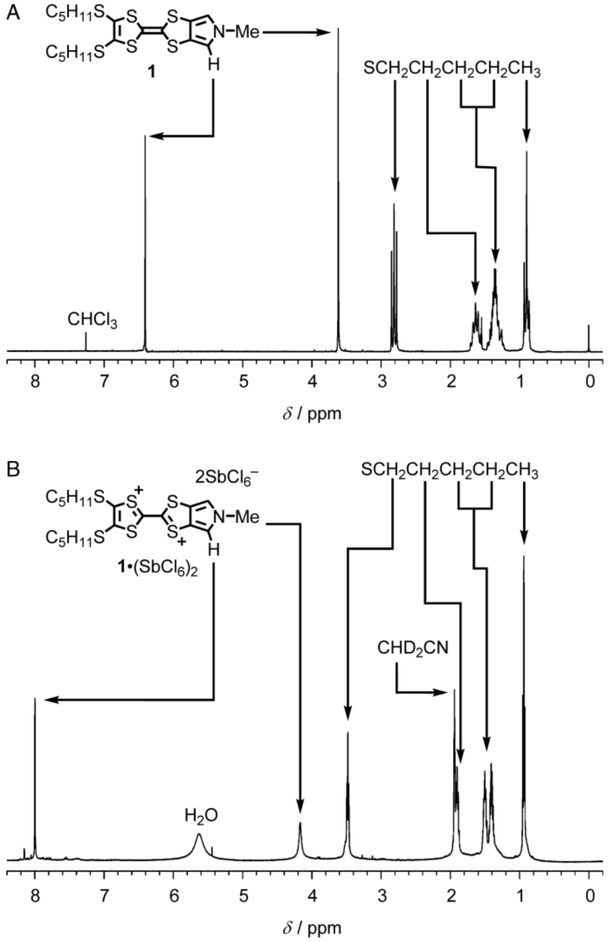


Figure 2. (A) ^{1}H NMR spectrum (300 MHz, 298 K) of the neutral MPTTF **1** recorded in $CDCl_3$ and (B) ^{1}H NMR spectrum (500 MHz, 298 K) of the MPTTF dication $\mathbf{1}^{2+}$ (as its $SbCl_6^-$ salt) recorded in CD_3CN.

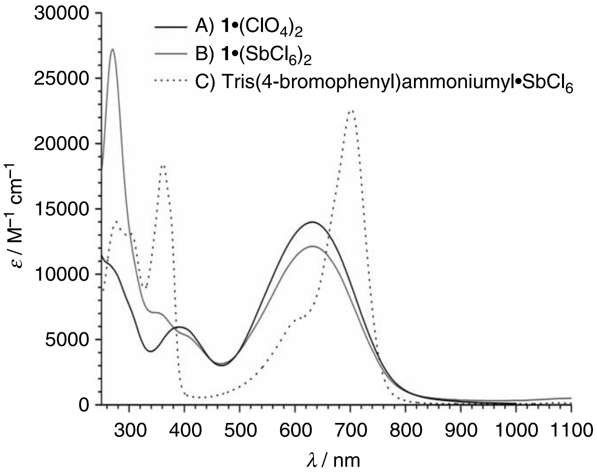


Figure 1. Absorption spectra recorded in MeCN at 293 K of (A) **1**·$(ClO_4)_2$, (B) **1**·$(SbCl_6)_2$ and (C) the oxidant tris(4-bromophenyl)ammoniumyl·$SbCl_6$.

Formation of the MPTTF dication $\mathbf{1}^{2+}$ (as its perchlorate salt) was also followed *in situ* using absorption spectroscopy in the region from 350 to 1000 nm. The titrational addition of 1 equivalent of iron(III)perchlorate to the yellow MPTTF compound **1** in acetonitrile at room temperature leads to the formation of the MPTTF radical cation $\mathbf{1}^{\cdot+}$ as evidenced by the production of an intense green-coloured solution and the appearance (Figure 3(A)) of two absorption bands centred on 432 and 761 nm, respectively, in the absorption spectra. The titration of the green-coloured acetonitrile solution containing the MPTTF radical cation $\mathbf{1}^{\cdot+}$ with an additional 1 equivalent of iron(III)perchlorate produce an intense blue-coloured solution and results in the disappearance (Figure 3(B)) of the 432 and 761 nm band, respectively, and the appearance of a more narrow absorption band at 637 nm consistent with the formation of the MPTTF dication $\mathbf{1}^{2+}$ (*vide supra*). Consequently, the doubly oxidised MPTTF unit $\mathbf{1}^{2+}$ can be readily distinguished from the neutral MPTTF unit **1** (pale yellow) and the mono-oxidised MPTTF unit $\mathbf{1}^{\cdot+}$ (green) by its intense blue colour.

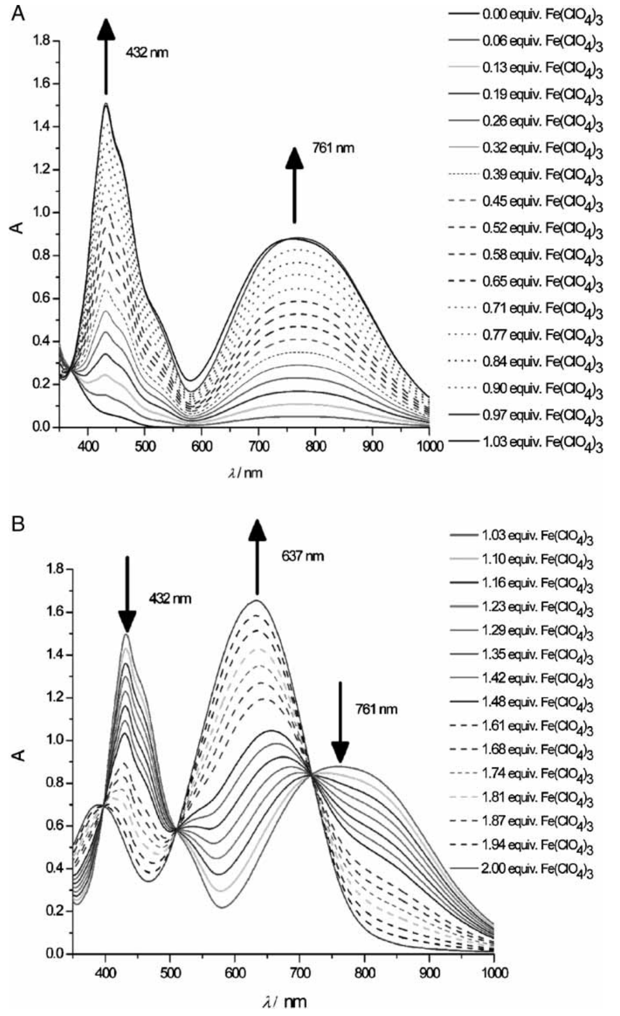
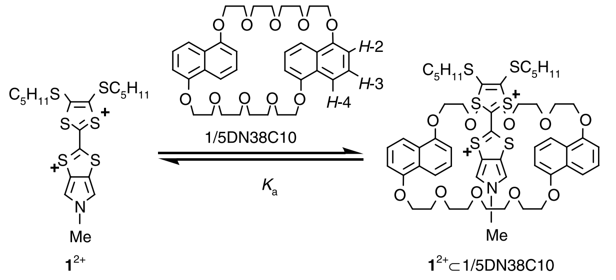


Figure 3. Absorption spectra of MPTTF **1** recorded in MeCN at 293 K upon addition of increasing amounts of iron(III)perchlorate. (A) 0–1 equivalent and (B) 1–2 equivalent.



Scheme 2. Complexation of $\mathbf{1}^{2+}$ by 1/5DN38C10.

The π-electron donating macrocyclic polyether 1/5DN38C10 was envisioned as a suitable host for the MPTTF dication $\mathbf{1}^{2+}$. By employing ^{1}H NMR spectroscopy $\mathbf{1}^{2+}$ was shown to form a complex with 1/5DN38C10. A comparison of the ^{1}H NMR spectra (CD_3CN, 298 K) of the non-complexed $\mathbf{1}^{2+}$ and $\mathbf{1}^{2+}$ in the presence of 1/5DN38C10 reveals significant chemical shift differences for the resonances associated with the aromatic *H*-2, *H*-3 and *H*-4 protons (Scheme 2) located on the 1/5DN38C10 macrocycle (upfield shifts, $\Delta\delta = -0.07$ to -0.23 ppm) indicating that $\mathbf{1}^{2+}$ is complexed by 1/5DN38C10. A continuous variation ^{1}H NMR experiment was carried out to determine the stoichiometry of the binding between $\mathbf{1}^{2+}$ and 1/5DN38C10. The job plot obtained (Figure 4) exhibit a maximum at a mole ratio of approximately 0.5, thus indicating that the 1/5DN38C10 receptor forms a 1:1 complex with $\mathbf{1}^{2+}$. To determine the binding constant (K_a) for the 1:1 complex between $\mathbf{1}^{2+}$ and the 1/5DN38C10 receptor, ^{1}H NMR titration experiments (Figure 5) were carried out in CD_3CN at 298 K. By following the changes (Figure 5) in the chemical shift for the resonances associated with the three non-equivalent aromatic protons (i.e. *H*-2–*H*-4) in the 1/5DN38C10 macrocycle, upon addition of an increasing amount of $\mathbf{1}^{2+}$ to the receptor 1/5DN38C10, the binding constant for this 1:1 interaction could be determined using non-linear curve fitting (*17*); this yielded an average K_a value of $3.7 \pm 0.3 \times 10^2\ M^{-1}$ for the interaction between the $\mathbf{1}^{2+}$ dication and 1/5DN38C10. A comparison of the K_a values for the $\mathbf{1}^{2+} \subset$ 1/5DN38C10 and $TTF^{2+} \subset$ 1/5DN38C10 ($K_a = 4.1 \times 10^3\,M^{-1}$, *vide supra*) complexes reveal that the strength of the binding between $\mathbf{1}^{2+}$ and 1/5DN38C10 is one order of magnitude smaller than that for the binding between TTF^{2+} and 1/5DN38C10. This observation can most likely be accounted for by the fact that the MPTTF unit is more steric hindered as compared to the TTF unit which leads to the formation of a less stable complex in the former case.

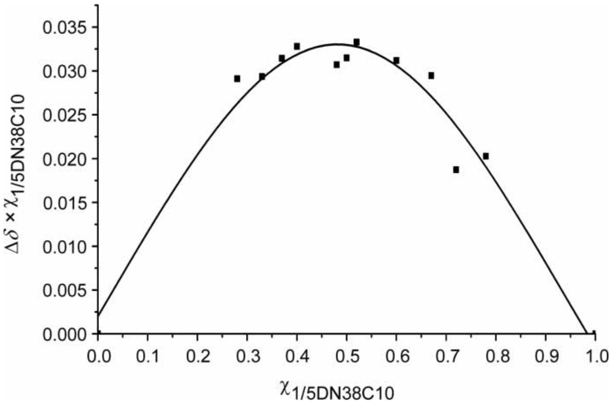


Figure 4. Job plot (CD_3CN, 298 K) corresponding to the interaction between the receptor 1/5DN38C10 and the substrate $\mathbf{1}^{2+}$ (as its hexachloroantimonate salt); these results are consistent with a 1:1 receptor-to-substrate binding. The *H*-4 proton in the naphthalene unit was used as the probe as this proton experience the largest changes in the chemical shift values upon mixing 1/5DN38C10 and $\mathbf{1}^{2+}$.

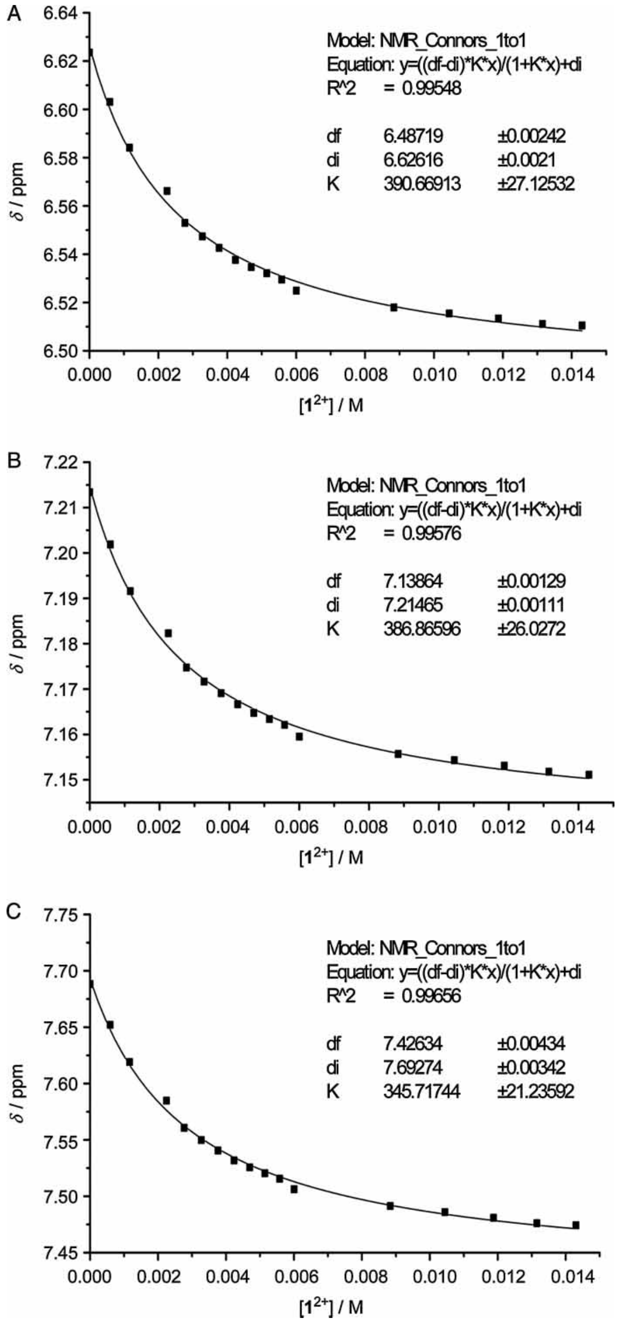


Figure 5. ^{1}H NMR (CD_3CN, 298 K) titration curves of the perturbation in the chemical shift of the three non-equivalent aromatic protons in the 1/5DN38C10 receptor upon addition of increasing amounts of $\mathbf{1}^{2+}$ (as its perchlorate salt). (A) *H*-2, (B) *H*-3 and (C) *H*-4. The data were analysed using standard curve-fitting methods (i.e. Connors 1:1 model) (*17*); this gave the values shown in the insets from which an average K_a value of $3.7 \pm 0.3 \times 10^2\,M^{-1}$ for the interaction between the $\mathbf{1}^{2+}$ dication and 1/5DN38C10 was obtained.

Conclusions

In conclusion, we have shown that it is possible to oxidise the MPTTF compound **1** to its corresponding dication $\mathbf{1}^{2+}$ using either iron(III)perchlorate or tris(4-bromophenyl) ammoniumyl hexachloroantimonate. The resulting salts $\mathbf{1}{\cdot}(ClO_4)_2$ and $\mathbf{1}{\cdot}(SbCl_6)_2$ were isolated and characterised. It was shown that $\mathbf{1}^{2+}$ forms a 1:1 complex with the π-electron donating macrocyclic polyether 1/5DN38C10 and a K_a value of $3.7 \pm 0.3 \times 10^2\,M^{-1}$ was obtained for the $\mathbf{1}^{2+} \subset$ 1/5DN38C10 complex (as its perchlorate salt) in acetonitrile at 298 K. These findings are undoubtedly not unimportant when it comes to future design and construction of supramolecular systems based on MPTTF dications.

Experimental

Chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA) and were used as received, except 2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (*18*) and 1,5-dinaphtho[38]crown-10 (1/5DN38C10) (*19*) which were synthesised according to literature procedures. All reactions were carried out under an anhydrous nitrogen atmosphere. Thin layer chromatography was carried out using aluminium sheets precoated with silica gel 60F (Merck 5554). The plates were inspected under UV light and, if required, developed in I_2 vapour. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Varian Gemini-300BB (300 MHz) or on Varian Unity (500 MHz) instrument using tetramethylsilane or the residual solvent as the internal standard. All chemical shifts are quoted on a δ scale in ppm, and all coupling constants (*J*) are expressed in Hertz (Hz). Samples were prepared using $CDCl_3$ or CD_3CN purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Absorption spectra were recorded on a Shimadazu 1601 spectrophotometer, while elemental analyses were performed by the Atlantic Microlab, Inc., Atlanta, Georgia.

*5-Methyl-2-[4,5-bis(pentylthio)-1,3-dithiole-2-ylidene]-1,3-dithiolo[4,5-*c*]pyrrole (1)*

2-(4,5-Bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (0.84 g, 1.88 mmol) was dissolved in anhydrous DMF (15 ml) and degassed (N_2, 15 min). NaH (60% suspension in mineral oil, 0.75 g, 18.8 mmol) was added in one portion, resulting in an immediate colour change from yellow to brown. The reaction mixture was stirred for 12 min at room temperature before iodomethane (2.6 ml, 41.8 mmol) was added. Stirring was continued for another hour before the reaction mixture was poured into brine (150 ml) and extracted with CH_2Cl_2 (2 × 100 ml). The combined organic phases were carefully washed with brine (2 × 100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting red-brown oil was purified by column chromatography (300 ml SiO_2, Ø = 5 cm, CH_2Cl_2/cyclohexane 1:1 v/v). The yellow band was collected and concentrated to give the title compound **1** as a yellow oil which solidified upon standing. Yield: 0.89 g (quant.); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.2$ Hz, 6H, $CH_2\mathit{CH_3}$), 1.23–1.46 (m, 8H, $\mathit{CH_2CH_2}CH_3$), 1.63 (pentet, $J = 7.2$ Hz, 4H, $SCH_2\mathit{CH_2}CH_2$), 2.81 (t, $J = 7.2$ Hz, 4H, $S\mathit{CH_2}CH_2$), 3.62 (s, 3H, $N\mathit{CH_3}$), 6.40 ppm (s, 2H, pyrrole-*H*); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$ ($CH_2\mathit{C}H_3$), 23.3 ($CH_2\mathit{C}H_2CH_3$), 29.6 ($\mathit{C}H_2CH_2CH_3$), 30.8 ($SCH_2\mathit{C}H_2$), 36.4 ($S\mathit{C}H_2CH_2$), 37.3 ($N\mathit{C}H_3$), 110.7 (fulvalene C=C), 113.6 (pyrrole-α), 119.1 (pyrrole-β), 120.1 (fulvalene C=C), 127.6 ppm (dithiole C=C).

5-Methyl-2-(4,5-bis(penylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-c]pyrrolium bis(perchlorate) (1·(ClO$_4$)$_2$)

***CAUTION!** The dry product is explosive. It will explode when heated to approximately 160°C. Explosion can also occur when scrapping the compound of a glass surface with a metal spatula.*

A solution of $Fe(ClO_4)_3 \cdot \times H_2O$ (1.92 g) in anhydrous 1,2-dimethoxyethane (20 ml) was added dropwise to a solution of 5-methyl-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (**1**) (0.097 g, 210 μmol) in anhydrous 1,2-dimethoxyethane (3 ml) resulting in a colour change from yellow to green followed by a colour change from green to blue and the formation of a dark blue precipitate. The precipitate was collected by filtration and washed with a small amount of anhydrous 1,2-dimethoxyethane to give a blue solid, which was dissolved in a minimum of anhydrous MeCN. Evaporation of the solvent *in vacuo* gave the title compound **1**·$(ClO_4)_2$ as a dark blue powder. Yield: 0.104 g (75%); UV–vis (MeCN, 293 K): λ_{max} (ε) = 404 nm ($7.2 \times 10^{3} M^{-1} cm^{-1}$), 633 nm ($1.4 \times 10^{4} M^{-1} cm^{-1}$); elemental analysis calculated (%) for $C_{19}H_{27}Cl_2NO_8S_6$: C 34.54, H 4.12, N 2.12, S 29.12; found: C 34.26, H 4.15, N 2.29, S 28.90.

5-Methyl-2-(4,5-bis(penylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-c]pyrrolium bis(hexachloroantimonate) (1·(SbCl$_6$)$_2$)

5-Methyl-2-(4,5-bis(pentylthio)-1,3-dithiole-2-ylidene)-1,3-dithiolo[4,5-*c*]pyrrole (**1**) (0.075 g, 162 μmol) was dissolved in CH_2Cl_2 (50 ml) and the resulting yellow solution was degassed (N_2) by placing the solution in an ultrasound bath for 15 min. Tris(4-bromophenyl)ammoniumyl hexachloroantimonate (0.301 g, 369 μmol) was added in one portion causing an immediate colour change from yellow to dark green. The mixture was stirred for 5 min under N_2 before being poured into petroleum ether (500 ml). Stirring was continued for another 30 min before the dark precipitate was collected by filtration and dried *in vacuo* providing the title compound **1**·$(SbCl_6)_2$ as a dark solid. Yield: 0.178 g (97%); ^{1}H NMR (500 MHz, CD_3CN): $\delta = 0.94$ (t, $J = 7.2$ Hz, 6H, $CH_2\mathit{CH_3}$), 1.40 (sextet, $J = 7.2$ Hz, 4H, $\mathit{CH_2}CH_3$), 1.47–1.53 (m, 4H, $\mathit{CH_2}CH_2CH_3$), 1.89 (pentet, $J = 7.2$ Hz, 4H, $SCH_2\mathit{CH_2}$), 3.48 (t, $J = 7.2$ Hz, 4H, $S\mathit{CH_2}CH_2$), 4.17 (s, 3H, $N\mathit{CH_3}$), 8 ppm (s, 2H, pyrrole-*H*); UV–vis (MeCN, 293 K): λ_{max} (ε) = 270 nm ($2.8 \times 10^{4} M^{-1} cm^{-1}$), 633 nm ($1.2 \times 10^{4} M^{-1} cm^{-1}$).

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