Synthesis and (spectro)electrochemistry of mixed-valent diferrocenyl–dihydrothiopyran derivatives†

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Three novel diferrocenyl complexes were prepared and characterised. 2,2-Diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran (1, sulphide) was accessible by the hetero-Diels–Alder reaction of diferrocenyl thiketone with 2,3-dimethyl-1,3-butadiene. Stepwise oxidation of 1 gave the respective oxides 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1-one (2, sulfoxide) and 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3, sulfone), respectively. The molecular structures of 1 and 3 in the solid state were determined by single crystal X-ray crystallography. The oxidation of sulphide 1 to sulfone 3, plays only a minor role on the overall structure of the two compounds. Electrochemical (cyclic voltammetry (= CV), square wave voltammetry (= SWV)) and spectrotroelectrochemical (in situ UV-Vis/NIR spectroscopy) studies were carried out. The CV and SWV measurements showed that an increase of the sulphur atom oxidation from −2 in 1 to +2 in 3 causes an anodic shift of the ferrocenyl-based oxidation potentials of about 100 mV. The electrochemical oxidation of 1–3 generates mixed-valent cations 1+–3+. These monooxidised species display low-energy electronic absorption bands between 1000 and 3000 nm assigned to IVCT (= Inter-Valence Charge Transfer) electronic transitions. Accordingly, the mixed-valent cations 1+–3+ are classiﬁed as weakly coupled class II systems according to Robin and Day.

Introduction

Recently, mixed-valent (= MV) species have attracted considerable attention in particular in the ﬁeld of molecular electronics as they offer the possibility to act as model compounds for molecular wires, switches and other electronic building blocks.1–15 Besides these foreseen technological applications MV compounds are used in electron transfer studies and are of key importance in biological systems.16–20

Ferrocenyl groups are often used in organometallic chemistry as redox-active terminal units, because ferrocene is thermally stable in its neutral and oxidised form.21 In addition, ferrocenyl/ferrocenium groups in mixed-valent species show an excellent electrochemical reversibility of the Fe(II)/Fe(III) redox couple, i.e. 2,5-diferrocenyl ﬁve-membered heterocycles,8,22–32 the electron transfer between the Fe(II)/Fe(III) centres, i.e. from the donor (Fe(II)) to the acceptor (Fe(III)) ion, manifests itself by the appearance of characteristic absorptions, i.e. IVCT (= Inter-Valence Charge Transfer) bands in the near infrared (NIR) spectral range.8,33

Two distinct modes of the electronic communication between the donor and acceptor metal centres in the MV state exist: “through bond” and “through space”.5,6,34 The “through bond” mechanism is characteristic for molecules in which π-conjugated connectivities are linking the two redox-active metal termini,5,6 while the “through space” mechanism requires a close proximity of the interacting centres.34 Depending on the degree of the electronic communication, three classes of MV complexes are distinguished according to the Robin and Day classiﬁcation: non-coupled (class I), weakly-coupled (class II) and fully delocalized (class III) systems.35 Based on the linking group constitution, ﬁve structural types of dinuclear transition-metal compounds are known (types A–E), as schematically shown in Fig. 1.

Among the type A and type B molecules (Fig. 1), the respective diferrocenyl-functionalized systems have been extensively studied,5,6,36,40–42 whereas compounds of structural type D...
CMe2, SiMe2 or GeMe2 bridges, depend on the distance between the metal centres.37 It was found that the extent of the increased bulkiness of the linker unit due to the presence of sterically demanding groups in the latter compounds as compared to the Fe2CH2+ cation. In addition, the strength of the metal–metal interactions in type D compounds featuring CMe2, SiMe2 or GeMe2 bridges, depend on the effective distance between the metal centres.37 It was found that the extent of the electronic coupling in the MV species decreases with an increase of the atomic radius of the bridging atom (e.g. in the order CMe2 > SiMe2 > GeMe2).

In continuation of our works in the area of electron-transfer studies in (multi)ferrocenyl-functionalised organic and organometallic compounds,8,11,22–32,45–49 we herein present the synthesis and characterisation of 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran (1, sulphide), 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1-oxide (2, sulfoxide) and 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3, sulfone) are shown in Scheme 1.

Synthesis

The synthetic methodologies for the preparation of 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran (1, sulphide), 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1-oxide (2, sulfoxide) and 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3, sulfone) are shown in Scheme 1.

Sulphide 1 was prepared via the hetero-Diels–Alder cycloaddition of diferrocenythioketone50,51 with 2,3-dimethyl-1,3-butadiene in a sealed glass-tube at 75 °C (Experimental section).52 After appropriate work-up, compound 1 was obtained as a red solid in 65% yield. Treatment of sulphide 1 with hydrogen peroxide (30%) and selenium dioxide as oxidising reagents53 in methanol gave the respective sulfoxide 2, which was purified by column chromatography in 87% yield (Experimental section). Further oxidation of 2 with m-chloroperoxybenzoic acid (= MCPBA) in dichloromethane produced bridge was chosen, due to its bulkiness and the presence of the oxidisable sulphur atom in a position adjacent to the redox-active ferrocenyl groups. This S-atom reactivity allows us to synthesise three closely related derivatives 1–3 and investigate the influence of the different electron-withdrawing character of the aliphatic bridge on the IVCT properties of the mixed valence species 1–3.

Results and discussion

Synthesis

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\[
\text{(Fc)}_2C=\text{S} + \text{Fc} \rightarrow \text{Fc}^+ \xrightarrow{(i)} \text{S}^+ \xrightarrow{(ii)} \text{O} \xrightarrow{(iii)} \text{S}^+ \xrightarrow{(iv)} \text{O}
\]

Scheme 1 Synthesis of 1–3 (MCPBA = m-chloroperoxybenzoic acid, Fc = ferrocenyl group). (i) 75 °C, 50 h; (ii) 30% H2O2, SeO2, CH3OH, 0 °C to r.t., 10 min; (iii) MCPBA, CH2Cl2, –20 °C, 2 h, then r.t. 24 h and 2nd portion MCPBA at r.t. 24 h.
sulfone 3 at ambient temperature in 21% yield (Scheme 1, Experimental section).54

Compounds 1–3 are red solids soluble in common organic solvents. All three compounds are stable towards air and moisture in the solid state and in solution.

Compounds 1–3 were characterised by IR and NMR (1H, 13C[1H]; for more details see Fig. S1–S3, ESI†) spectroscopy and high-resolution mass spectrometry. The molecular structures of 1 and 3 in the solid state were determined by single crystal X-ray diffraction analysis. Electrochemical investigations were carried out by using cyclic voltammetry (= CV), square wave voltammetry (= SWV) and in situ UV-Vis/NIR spectroelectrochemistry.

X-ray structure determination

Single-crystals of 1 and 3 suitable for a single crystal X-ray diffraction analysis were obtained by slow diffusion of hexane into a dichloromethane solution of 1 and by slow diffusion of hexane into a diethyl ether solution of 3. ORTEP diagrams of 1 and 3 are shown in Fig. 2, while selected bond distances (Å) and angles (°) are listed in Table 1. Crystal and structure refinement data are presented in the ESI (Table S1).

Compound 1 crystallizes in the orthorhombic space group Pcab, while complex 3 crystallizes in the triclinic space group P1. In the crystal packing of 3, two independent molecules (A and B) are observed. The structure analysis of both molecules confirmed the expected structures in which the two ferrocenyl groups are bonded to a sulphide (1) or a sulfone (3) moiety (Fig. 2). All ferrocenyl units show an eclipsed conformation with nearly equivalent distances between Fe and the centroid of the cyclopentadienyl rings (Table 1).

The oxidation of sulphide 1 to sulfone 3, however, plays only a minor role on the overall structure of the two compounds. A similar behaviour was found for a series of sulphur-containing heterocycles in which the oxidation of the sulphur atom has almost no impact on the geometrical parameters of the heterocycles.54,55 The only bond distances which are somewhat influenced by oxidation are S–CFe and S–CH3 (Table 1), whereby the corresponding bonds in 3, as compared to 1, are shortened by 0.02 Å, as previously observed by Petrov.54,55 In both compounds, the thiopyran ring adopts a half-chair conformation to limit the steric repulsion between the different substituents (Fig. 2). In these carbon-bridged diferrocenyl complexes, the Fe···Fe distances are 5.6377(6) (1), 5.6824(9) (3A) and 5.6785(9) Å (3B), respectively. These values are comparable to those found in analogous carbon-bridged diferrocenyl compounds.56 Interestingly, the dihedral angles between the two planes of the covalently bonded cyclopentadienyl rings are quite acute in 1 (61.4°) and molecule 3A (63.1°), while in 3B this dihedral angle is normal at 76.6°.56

UV-Vis spectroscopy, electrochemistry and spectroelectrochemistry

The electronic properties of the ferrocenyl-functionalised compounds 1–3 were studied by using UV-Vis, cyclic (= CV) and square wave voltammetry (= SWV) and in situ UV-Vis/NIR spectroelectrochemistry.

Compounds 1–3 show relatively weak absorptions in the visible region and stronger absorptions at higher energies (Fig. 3) as it is characteristic for ferrocene derivatives.57,58

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**Table 1** Selected bond distances (Å) and angles (°) of 1 and 3 (Cp–Cfe = Cp ring connected to the bridging carbon atom (Cfe) of the diferrocenyl unit)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>3A</th>
<th>3B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond distances</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe···Fe</td>
<td>5.6377(6)</td>
<td>5.6824(9)</td>
<td>5.6785(9)</td>
</tr>
<tr>
<td>S–CFe</td>
<td>1.850(2)</td>
<td>1.834(3)</td>
<td>1.832(3)</td>
</tr>
<tr>
<td>S–CH3</td>
<td>1.799(2)</td>
<td>1.767(3)</td>
<td>1.771(3)</td>
</tr>
<tr>
<td>C=C</td>
<td>1.339(3)</td>
<td>1.344(5)</td>
<td>1.331(5)</td>
</tr>
<tr>
<td>C=C–CFe</td>
<td>1.515(3)</td>
<td>1.527(4)</td>
<td>1.518(5)</td>
</tr>
<tr>
<td>C=C–Cp</td>
<td>1.517(3)</td>
<td>1.527(4)</td>
<td>1.526(4)</td>
</tr>
<tr>
<td>Fe-centroid (Cp–Cfe)</td>
<td>1.657</td>
<td>1.656</td>
<td>1.653</td>
</tr>
<tr>
<td>Fe-centroid (Cp–Cfe′)</td>
<td>1.658</td>
<td>1.656</td>
<td>1.643</td>
</tr>
<tr>
<td>Fe-centroid (Cp)</td>
<td>1.660</td>
<td>1.659</td>
<td>1.646</td>
</tr>
<tr>
<td>Fe-centroid (Cp′)</td>
<td>1.658</td>
<td>1.658</td>
<td>1.650</td>
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<tr>
<td>Bond angles</td>
<td></td>
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</tr>
<tr>
<td>S–CFe–CFe</td>
<td>107.91(13)</td>
<td>104.9(2)</td>
<td>105.3(2)</td>
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<tr>
<td>CFe–S–CH3</td>
<td>97.30(10)</td>
<td>100.65(16)</td>
<td>101.20(16)</td>
</tr>
<tr>
<td>CFe–CFe–Cp</td>
<td>111.20(16)</td>
<td>112.1(2)</td>
<td>110.0(3)</td>
</tr>
<tr>
<td>O=S−O</td>
<td>117.81(15)</td>
<td>117.57(16)</td>
<td></td>
</tr>
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</table>

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**Fig. 2** ORTEP diagrams of 1 and 3 (two independent molecules in the crystal, 3A and 3B) at 50% probability level.
processes, the electrode potentials between the oxidation and the reduction of the studied compounds is about 60 mV smaller than that in non-oxidised 1 (Fig. 4).

The redox separation between the 1st and the 2nd oxidation processes, however, is not affected by the different degree of the sulfur oxidation and is ca. 370 mV throughout the series. Due to the use of [Bu4N][B(C6F5)4]25,63 as weakly coordinating counter-ion within the electrolyte, the ion-pairing effects are minimised70–72 and thus, the electrostatic stabilization forces between the ferrocenyl groups are increased, when compared with diferrocenylmethane measured in [Bu4N][ClO4]2 (ΔE° = 120 mV).73

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The UV-Vis/NIR spectroelectrochemical measurements were performed in an OTTLE (= Optically Transparent Thin-Layer Electrochemistry) cell74 using an analyte concentration of 2.0 mmol L–1 and [Bu4N][B(C6F5)4] (0.1 mol L–1) as supporting electrolyte in dichloromethane (1–3) or acetonitrile (2). The UV-Vis/NIR spectra are depicted in Fig. 6 (1), 7 (2), and 8 (3). The spectrum measured in acetonitrile (2) is shown in Fig. S5.

The appropriate compounds were oxidised by stepwise increasing the potentials (step width 25, 50 and 100 mV). Thus, the studied compounds 1–3 underwent oxidation to the mono-cationic 1+–3+ and di-cationic 1++–3++ species, respectively. After complete oxidation, each sample was reduced at –200 mV to prove the reversibility of the redox processes. The resulting UV-Vis/NIR spectra were identical to those of the starting molecules. During the oxidation of 1–3 a broad band with a very low intensity (€max = 100 L mol–1 cm–1) between 1000 and 3000 nm appeared (Fig. 6–8). A further increase of the potential resulted in the decrease of this band. Such a behaviour is typically observed for intervalence charge transfer (= ICT) absorptions.2,11 The experimental spectra can be deconvoluted into three Gaussian-shape bands assigned to an

Table 2 Cyclic voltammetry data of 1–3a

<table>
<thead>
<tr>
<th>Compd.</th>
<th>E° [mV] (ΔE°) [mV]</th>
<th>Eox [mV] (ΔE°) [mV]</th>
<th>ΔE° [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–90 (73)</td>
<td>275 (75)</td>
<td>365</td>
</tr>
<tr>
<td>2</td>
<td>–15 (75)</td>
<td>355 (76)</td>
<td>370</td>
</tr>
<tr>
<td>3</td>
<td>5 (73)</td>
<td>375 (83)</td>
<td>370</td>
</tr>
</tbody>
</table>

a Potentials vs. FeH/FeH+, scan rate 100 mV s–1 at glassy carbon electrode of a 1.0 mmol L–1 solution in dry dichloromethane; 0.1 mol L–1 [N′Bu4][B(C6F5)4] as supporting electrolyte at 25 °C. b E° = Formal potential. c ΔE° = Difference between the oxidation and the reduction potential. d ΔE° = Potential difference between the two ferrocenyl-related redox processes (Eox – E1).
IVCT, a ligand field transition, and a band representing the edge to the higher energy absorptions. The sum of these three Gaussian-shaped bands fits almost exactly with the experimental spectra. The deconvolution reveals the intensity $\varepsilon_{\text{max}}$, the full width-at-half-height $\Delta \nu_{1/2}$ and the $\nu_{\text{max}}$ values for the IVCT component. The solvent polarity change from $P = 3.1$ (dichloromethane) to $P = 5.8$ (acetonitrile),\textsuperscript{75} resulting in a shift of the $\nu_{\text{max}}$ value from 5250 cm$^{-1}$ to 7525 cm$^{-1}$. It is remarked that strong solvatochromic shifts are expected for IVCT absorption bands being of distinct charge transfer character. Thus, the IVCT assignment of the observed NIR absorption features (Fig. 6–8 and Table 3) is further substantiated. The appearance of low energy ligand field transitions is characteristic for ferrocenyl containing compounds as for example demonstrated by UV/Vis-NIR measurements of mono ferrocenyl thiophenes.\textsuperscript{27} The numerical data derived from the deconvolution procedure is summarised in Table 3. However, the data should be of the $\nu_{\text{max}}$ value from 5250 cm$^{-1}$ to 7525 cm$^{-1}$. It is remarked that strong solvatochromic shifts are expected for IVCT absorption bands being of distinct charge transfer character. Thus, the IVCT assignment of the observed NIR absorption features (Fig. 6–8 and Table 3) is further substantiated. The appearance of low energy ligand field transitions is characteristic for ferrocenyl containing compounds as for example demonstrated by UV/Vis-NIR measurements of mono ferrocenyl thiophenes.\textsuperscript{27} The numerical data derived from the deconvolution procedure is summarised in Table 3. However, the data should be

**Table 3** NIR absorption data of the IVCT band of 1$^+–$3$^+$.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compd.</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\varepsilon_{\text{max}}$ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\Delta \nu_{1/2}$ (cm$^{-1}$)</th>
<th>$\Delta \nu_{1/2}$\textsubscript{Hush} \textsuperscript{b} (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^+$ (DCM)</td>
<td>5200 (100)</td>
<td>4950</td>
<td>3468</td>
<td></td>
</tr>
<tr>
<td>2$^+$ (DCM)</td>
<td>5250 (100)</td>
<td>4900</td>
<td>3478</td>
<td></td>
</tr>
<tr>
<td>2$^+$ (ACN)</td>
<td>7525 (60)</td>
<td>7850</td>
<td>4169</td>
<td></td>
</tr>
<tr>
<td>3$^+$ (DCM)</td>
<td>5300 (95)</td>
<td>4900</td>
<td>3512</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured in dry dichloromethane (DCM) or acetonitrile (ACN) using [Bu$_4$N][B(C$_6$F$_5$)$_4$] (0.1 mol dm$^{-3}$) as supporting electrolyte at 25 °C.\n
\textsuperscript{b} Values calculated as $(\Delta \nu_{1/2})_{\text{Hush}} = (2310 \varepsilon_{\text{max}})^{1/2}$ according to the Hush relationships for weakly coupled systems.\textsuperscript{76}
Conclusions

Within this study it was shown that 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran (1) is readily available through a hetero-Diels–Alder cyclo-addition reaction of diferrocenylthioketone with 2,3-dimethyl-1,3-butadiene. Stepwise oxidation of the sulphur atom in 1 afforded the corresponding S-oxides: 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1-oxide (2, sulfide) and 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3, sulfone). Electrochemical measurements on 1–3 revealed well separated redox events related to the two ferroceny1 groups. The corresponding $E'_1$ and $E'_2$ potentials are shifted anodically in the order of $1 < 2 < 3$. This is accounted for the increasing electron-withdrawing effect of the adjacent S, SO, and SO$_2$ fragments on the ferroceny1 groups. Thus, the Fe-centred orbitals in 2 and 3 are more stabilised than in 1. A single crystal X-ray diffraction study of 1 and 3 revealed that the chemical oxidation of the sulphur atom has only a negligible influence on the overall molecule's geometry (bond lengths and angles). Nevertheless, the X-ray analyses have also shown that the Fe–Fe distances in 1 and 3 are shorter than that in Fe$_2$CH$_2$ (5.765 Å). This effect is ascribed to the steric hindrance exerted by the 4,5-dimethyl-3,6-dihydro-2H-thiopyran ring. It has also been demonstrated that the cyclic 4,5-dimethyl-3,6-dihydro-2H-thiopyran group enables weak metal–metal electronic interactions in the mono-oxidised species 1–3$^+$, as confirmed by the appearance of weak IVCT absorptions characteristic for mixed-valent systems (=$ MV$). This allows to categorise cations 1–3$^+$ as weakly coupled class II MV systems according to Robin and Day. Moreover, the extent of metal–metal electronic interactions in 1–3$^+$ does not change significantly with the oxidation state of the sulphur atom (sulphide (1) → sulfoxide (2) → sulfone (3)). In summary, our results demonstrate that stericly demanding 2H-thiopyran-derived bridges enable metal–metal electronic interactions between redox centres in mixed-valent molecular systems. In the studied MV species, most probably, the “through space” mechanism is dominantly operative.

Experimental section

General data and reagents

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM). Dichloromethane was purified by distillation from CaH$_2$ prior to use and methanol was purified by distillation over magnesium. 2,3-Dimethyl-1,3-butanediene, $m$-chloroperbenzoic acid, 30% hydrogen peroxide and selenium dioxide were purchased from commercial suppliers and were used without further purification.

Instruments

$^1$H NMR (600 MHz) and $^{13}$C{H} NMR (150 MHz) spectra were recorded with a Bruker Avance III 600 spectrometer operating at 298 K in the Fourier transform mode. Chemical shifts are reported in $\delta$ units (ppm) as residual CDCl$_3$ ($^1$H $\delta$ 7.26 ppm, $^{13}$C $\delta$ 77.00 ppm) as the reference. Infrared spectra were recorded with a FTIR Nexus Nicolet apparatus. Mass spectra were recorded with a Varian 500-MS IT mass spectrometer (ESI) or with a Finnigan Mat95 mass spectrometer (EI). Microanalyses were determined by Analytical Services of the Polish Academy of the Sciences, Łódź. UV-Vis absorption spectra were recorded with a Varian Cary 300 double beam spectrometer.

DFT computations and spectroelectrochemical measurements

The geometry optimisations and electronic transition calculations were performed using density-functional theory (= DFT) and time dependent density-functional theory (= TD DFT) with Becke’s three parameter functional$^{78}$ with the non-local Lee–Yang–Parr correlation functional (B3LYP)$^{79}$ and the standard 6-31G(d,p) basis set as implemented in the Gaussian 09 program package.$^{80}$

Electrochemical measurements of 1.0 mmol L$^{-1}$ dichloromethane solutions of 1–3 were performed in a dried, argon purged cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. Dichloromethane solutions (0.1 mol L$^{-1}$) containing [Bu$_4$N]−[B(C$_6$F$_5$)$_4$]$_2$ were used as supporting electrolyte. For the measurements a three electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm$^2$) and an Ag/Ag$^{+}$ (0.01 mmol L$^{-1}$ [AgNO$_3$]) reference electrode fixed on a Luggin capillary was applied. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 micron and then with a 1/4 micron diamond paste. The reference electrode was constructed from a silver wire inserted into a 0.01 mmol L$^{-1}$ [AgNO$_3$] and 0.1 mol L$^{-1}$ [Bu$_4$N][B(C$_6$F$_5$)$_4$] acetonitrile solution in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted into a second Luggin capillary containing a 0.1 mol L$^{-1}$ [Bu$_4$N][B(C$_6$F$_5$)$_4$]
dichloromethane solution and a Vycor tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within 5 mV. Experimental potentials were referenced against an Ag/Ag+ reference electrode but the presented results are referenced against ferrocene as an internal standard as required by IUPAC. To achieve this, each experiment was repeated in the presence of 1 mmol L⁻¹ decamethylferrocene (= Fe∗). Data were processed on a Microsoft Excel spreadsheet to set the formal reduction potentials of the FeH/FeH⁺ couple to 0.0 V. Under our conditions the Fe∗/Fe⁺ couple was at −619 mV vs. FcH/FcH⁺ (ΔEREF = 60 mV), while the FcH/FcH⁺ couple itself was at 220 mV vs. Ag/Ag⁺ (ΔEREF = 61 mV). Spectroelectrochemical UV-Vis/NIR measurements of 2.0 mmol L⁻¹ solutions of 1–3 in dichloromethane (1–3) or acetonitrile (2) containing 0.1 mol L⁻¹ of [Bu₄N][BF₄] as the supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemistry) cell with a Varian Cary 5000 spectrophotometer at 25 °C. The values obtained by deconvolution could be reproduced within εmax, 100 L mol⁻¹ cm⁻¹; εmax, 50 cm⁻¹ and Δν1/2, 50 cm⁻¹.

Synthesis of 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3)

A mixture of diferrocenyl thioketone (399 mg, 0.96 mmol) and selenium dioxide (4.26 mg, 0.03 mmol) were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH⁺ couple to 0.0 V. Under our conditions the Fc*/Fc*+ couple was at −669 mV vs. Ag/Ag+ (p = 61 mV). Spectroelectrochemical UV-Vis/NIR measurements of 2.0 mmol L⁻¹ solutions of 1–3 in dichloromethane (1–3) or acetonitrile (2) containing 0.1 mol L⁻¹ of [Bu₄N][BF₄] as the supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemistry) cell with a Varian Cary 5000 spectrophotometer at 25 °C. The values obtained by deconvolution could be reproduced within εmax, 100 L mol⁻¹ cm⁻¹; εmax, 50 cm⁻¹ and Δν1/2, 50 cm⁻¹.

Synthesis of 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1-oxide (2)

Hydrogen peroxide (30%, 71 mg) and selenium dioxide (72 mg, 0.65 mmol) in water (1 mL) were subsequently added to a stirred solution of 1 (312 mg, 0.63 mmol) in methanol (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min and then for an additional 5 min at ambient temperature. The reaction was quenched with water (~7 mL) and extracted with dichloromethane. The organic layer was washed with brine, separated and dried over anhydrous MgSO₄ and then all volatile materials were evaporated. The residue was subjected to chromatography on SiO₂ (diethyl ether–hexane, ratio 3/1 (v/v)) to give pure sulfoxide 2 as red crystals in 87% yield (281 mg).

1H NMR (600 MHz, CDCl₃): δ = 4.90–4.89 (m, 1H, C₂H₄), 4.36–4.35 (m, 1H, C₂H₄), 4.32–4.31 (m, 1H, C₂H₄), 4.30–4.29 (m, 1H, C₂H₄), 4.28 (s, 5H, C₂H₅), 4.27–4.26 (m, 1H, C₂H₄), 4.22–4.21 (m, 1H, C₂H₄), 4.05–4.04 (m, 1H, C₂H₄), 4.00–3.99 (m, 1H, C₂H₄), 3.88 (s, 5H, C₂H₅), 3.18 (d, JₐH,H₁ = 18.6 Hz, 1H, C₂H₅), 3.01 (d, JₐH,H₂ = 18.0 Hz, 1H, CH₂), 2.97 (d, JₐH,H₂ = 15.6 Hz, 1H, CH₂), 2.50 (d, JₐH,H₂ = 15.6 Hz, 1H, CH₂), 1.84 (s, 3H, CH₃), 1.68 (s, 3H, CH₃). 

Synthesis of 2,2-diferrocenyl-4,5-dimethyl-3,6-dihydro-2H-thiopyran-1,1-dioxide (3)

m-Chloroperbenzoic acid (45 mg, 0.26 mmol) was added to a stirred solution of sulphoxide 2 (100 mg, 0.19 mmol) in dichloromethane (20 mL) at ~20 °C. The resulting reaction mixture was stirred at ~20 °C for 2 h and then for an additional 24 h at ambient temperature. Afterwards, the 2nd portion of MCPBA (45 mg, 0.26 mmol) was added and the mixture was stirred at ambient temperature for another 24 h. Subsequently, a saturated NaHCO₃ solution was added in a single portion and the resulting mixture was extracted with dichloromethane. The organic layer was washed with brine, separated and dried over anhydrous MgSO₄. Then all volatile materials were evaporated. The residue was subjected to preparative TLC on SiO₂ (diethyl ether–hexane, ratio 1/1 (v/v) as eluent). Sulfone 3 was obtained as a red solid in 21% (21 mg) yield.

1H NMR (600 MHz, CDCl₃): δ = 4.47 (bs, 2H, C₂H₄), 4.21–4.20 (pq, JₐH,H₁ = 1.98 Hz, 1.74 Hz, 2H, C₂H₄), 4.13 (s, 10H, C₂H₄), 3.32 (s, 2H, CH₃), 3.06 (s, 2H, CH₃), 1.91 (s, 3H, CH₃), 1.69 (s, 3H, CH₃). 

Single-crystal X-ray structure analysis of 1 and 3

Red crystals of 1 were obtained by slow evaporation of a chloroform–hexane solution containing 1, while red crystals of 3 were grown by the slow evaporation of a diethyl ether–hexane solution containing 3 at ambient temperature. Data were collected with a Stoe Image Plate Diffraction system equipped with a φ circle goniometer using Mo Kα graphite monochromatic radiation (λ = 0.71073 Å) with φ range 0–200°. The structures were solved by direct methods applying the program SHELXS-97, while the refinement and all further calculations were carried out with SHELXL-97. The hydrogen atoms
were included in calculated positions and treated as riding atoms using the SHELXL default parameters, except for the N–H hydrogen atoms which were located on the Fourier difference map and refined. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-square on $F^2$. Crystallographic details for 1 and 3 are summarized in Table S1 (see ES†).

CCDC 1031233 (1) and 1031234 (3) contain the supplementary crystallographic data for this paper.

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Notes and references