

Rearrangement of Diferrocenyl 3,4-thiophene dicarboxylate

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Experimental Part

General Procedures. Reaction was carried out under an atmosphere of argon using standard Schlenk techniques. Diethyl ether was purified by distillation from sodium/benzophenone ketyl. Hexane and chloroform were purified with a MBRAUN SPS-800 purification system.

Reagents. Thiophene-3,4-dicarbonyl dichloride (**1**), [1] 1-Hydroxymethylferrocene (**2**), [2] were synthesized according to literature procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Instruments. Infrared spectra were measured with a Thermo Nicolet 200 FT-IR spectrometer. NMR spectra were recorded using an BrukerAvance III 500 FT-NMR spectrometer (^1H NMR at 500.303 MHz, ^{13}C NMR at 125.813 MHz) at ambient temperature, unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the solvent as internal reference (CDCl_3 : ^1H NMR $\delta = 7.26$ ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR $\delta = 77.16$ ppm). [3] Coupling constants (J) are reported in Hertz (Hz) and integrations are reported in number of protons. The following abbreviations are used to describe peak patterns: s = singlet, pt = pseudo-triplet, dd = doublet-of-doublets, m = multiplet. The melting points (sealed off in argon flushed capillaries) were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Microanalysis was performed by using a Thermo FLASH EA 1112 Series instrument. High resolution mass spectra were recorded with a Bruker micrOTOF-QII spectrometer with an Apollo II ESI source.

Electrochemistry

The electrochemical measurements were carried out under an atmosphere of argon on $1.0 \text{ mmol} \cdot \text{L}^{-1}$ dichloromethane solutions containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ of $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as supporting electrolyte utilizing a Voltalab 10 electrochemical laboratory from Radiometer Analytical. [4,5] For cyclic voltammetry studies, a three electrode cell with a platinum auxiliary electrode, a glassy carbon working electrode (3.0 mm) and

a Ag/Ag⁺ reference electrode were used. The working electrode was prepared by polishing it with a Buehler microcloth using Buehler diamond pastes with decreasing sizes (1 to 0.25 μm). The Ag/Ag⁺ reference electrode was constructed from a silver wire inserted into a Luggin capillary with a Vycor tip containing a solution of 0.01 mol·L⁻¹ [AgNO₃] and 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄] in acetonitrile. This Luggin capillary was inserted into a second Luggin capillary with Vycor tip filled with a 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄] solution in dichloromethane. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within ± 5 mV. Experimentally potentials were referenced against a Ag/Ag⁺ reference electrode but the results are presented referenced against the FcH/FcH⁺ couple ($E^{0'} = 0.0$ V) as required by IUPAC. [6] When decamethylferrocene was used as an internal standard, the experimentally measured potential was converted into E vs Cp₂Fe/Cp₂Fe⁺ by addition of -0.61 V. [7] The cyclic voltammograms were taken after typical two scans and are considered to be steady state cyclic voltammograms in which the signal pattern differs not from the initial sweep. Finally, the experimental data were processed on Microsoft Excel worksheets.

Computational Details

Ab-initio calculations were performed using the GAUSSIAN 09 program package. [8] Full geometry optimization for compound **3** and **5** were performed using the B3LYP density functional method [9] with the 6-31+G(d,p) basis set for C, H, O, and S atoms and the effective core potential LANL2DZ basis set with for iron. The solvent effects were taken into account by using conductor-like polarizable continuum model (CPCM) method with dichloromethane as solvent. Frequency calculations were performed on the optimized geometries at the same level of theory; all computed vibrational transitions have no imaginary frequency implying that each optimized geometry is located at the global minimum point on the potential energy surface. Projected density of states (PDOS) has been evaluated through the calculated orbital populations for all compounds at the same level of theory, using GAUSSSUM 3.0 program. [10]

Preparation of 3,4-((FcCH₂OC(O))₂-^cC₄H₂S (**3**)

To [Fe(η^5 -C₅H₅)(η^5 -C₅H₄CH₂OH)] (250 mg, 1.16 mmol) dissolved in 15 mL of diethyl ether, 0.72 mL MeLi (1.60 M, 1.16 mmol) was added in single portion at 0 °C. The resulting yellow suspension was stirred at this temperature for 15 min. The resulting reaction solution was cooled to -78 °C and treated with a solution of diacid chlorides 3,4-(ClC(O))₂-^cC₄H₂S (**1**) (121 mg, 0.58 mmol) in 10 mL diethyl ether dropwise over 10 min. The reaction mixture was slowly warmed to ambient temperature, and stirred overnight. After filtration through a pad of Celite, the solvent was removed under reduced pressure to give a yellow solid. The solid was washed with n-hexane twice and dried under vacuum. Precipitation the solid with CHCl₃/n-hexane (3:1) afforded yellow solid of the title compound.

Yield: 309 mg (0.54 mmol, 94 % based on **1**). Anal. calcd. for C₂₈H₂₄Fe₂O₄S (568.24 g/mol): C, 59.18; H, 4.26. Found C, 58.85; H, 4.28 %. Mp: 165 °C (decomp.). IR (NaCl, $\tilde{\nu}$ in cm⁻¹): ν_{CO} 1706 (s). ¹H NMR (CDCl₃): δ 7.79 (s, 2 H, C₄H₂S), 5.04 (s, 4 H, CH₂), 4.32 (pt, $J_{\text{HH}} = 1.7$ Hz, 4 H, C₅H₄), 4.20 (pt, $J_{\text{HH}} = 1.7$ Hz, 4 H, C₅H₄), 4.18 (s, 10 H, C₅H₅). ¹³C{¹H} NMR (CDCl₃): δ 163.02 (CO), 133.53 (C_i-C₄H₂S), 131.76 (C₄H₂S), 80.97 (C_i-C₅H₄), 70.00 (C₅H₄), 69.02 (C₅H₄), 68.72 (C₅H₅), 63.89 (CH₂). HR-ESI-MS (positive ion mode) m/z: Calcd. for C₂₈H₂₄Fe₂O₄S (M⁺) 568.0094 found 568.0096.

Preparation of Thieno[3,4-*c*]furan-1,3-dione (**4**)

In attempts to grow single crystals from **3**, 50 mg of **3** (0.0880 mmol) was dissolved in chloroform: hexane (1 mL : 4 mL) solvent mixtures under air at -18 °C, it was found that **3** further reacts with moisture and forms hydroxymethyl ferrocene (**2**) and 3,4-thiophenedicarboxylic anhydride (**4**). Hydroxymethyl ferrocene (**2**) was soluble in the crystallization solvent while the 3,4-thiophenedicarboxylic anhydride (**4**) was obtained as light yellow crystals.

Compound 2 [11]:

Yield: 11.4 mg (0.053 mmol, 60 % based on **3**). ^1H NMR (CDCl_3): δ 4.32 (d, 2 H; CH_2); 4.31 (bs, 2 H; C_5H_4), 4.24 (bs, 2 H; C_5H_4), 4.19 (s, 5 H; C_5H_5). ^{13}C NMR (CDCl_3): δ 88.13 ($\text{C}_i\text{-C}_5\text{H}_4$), 68.38 (C_5H_4), 68.24 (C_5H_4), 67.80 (C_5H_5), 60.50 (CH_2).

Compound 4 [12]:

Yield: 8.14 mg (0.053 mmol, 60 % based on **3**). ^1H NMR (CDCl_3): δ 8.03 (s, 2 H, $\text{C}_4\text{H}_2\text{S}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 156.02 (CO), 139.13 ($\text{C}_i\text{-C}_4\text{H}_2\text{S}$), 129.06 ($\text{C}_4\text{H}_2\text{S}$).

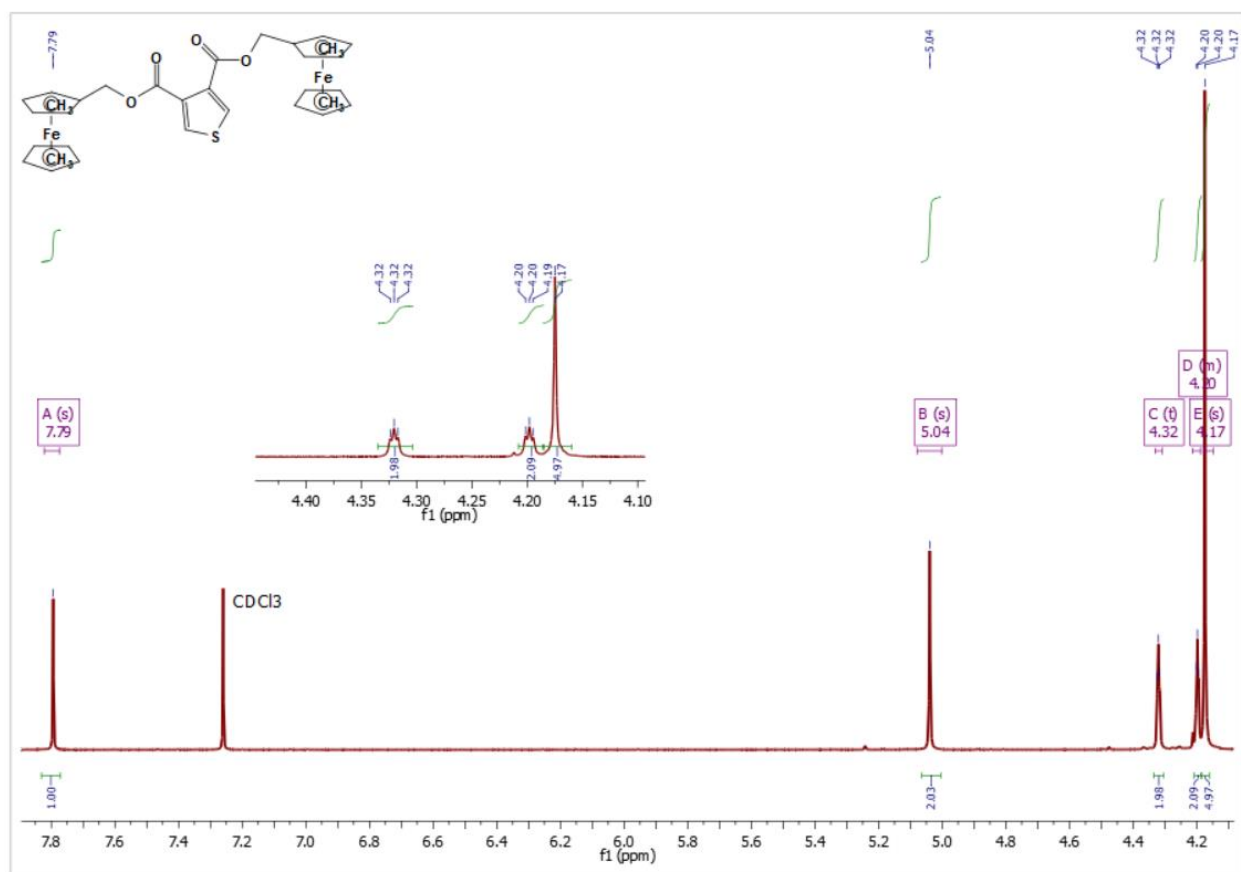


Figure S1. ^1H NMR spectrum of **3**.

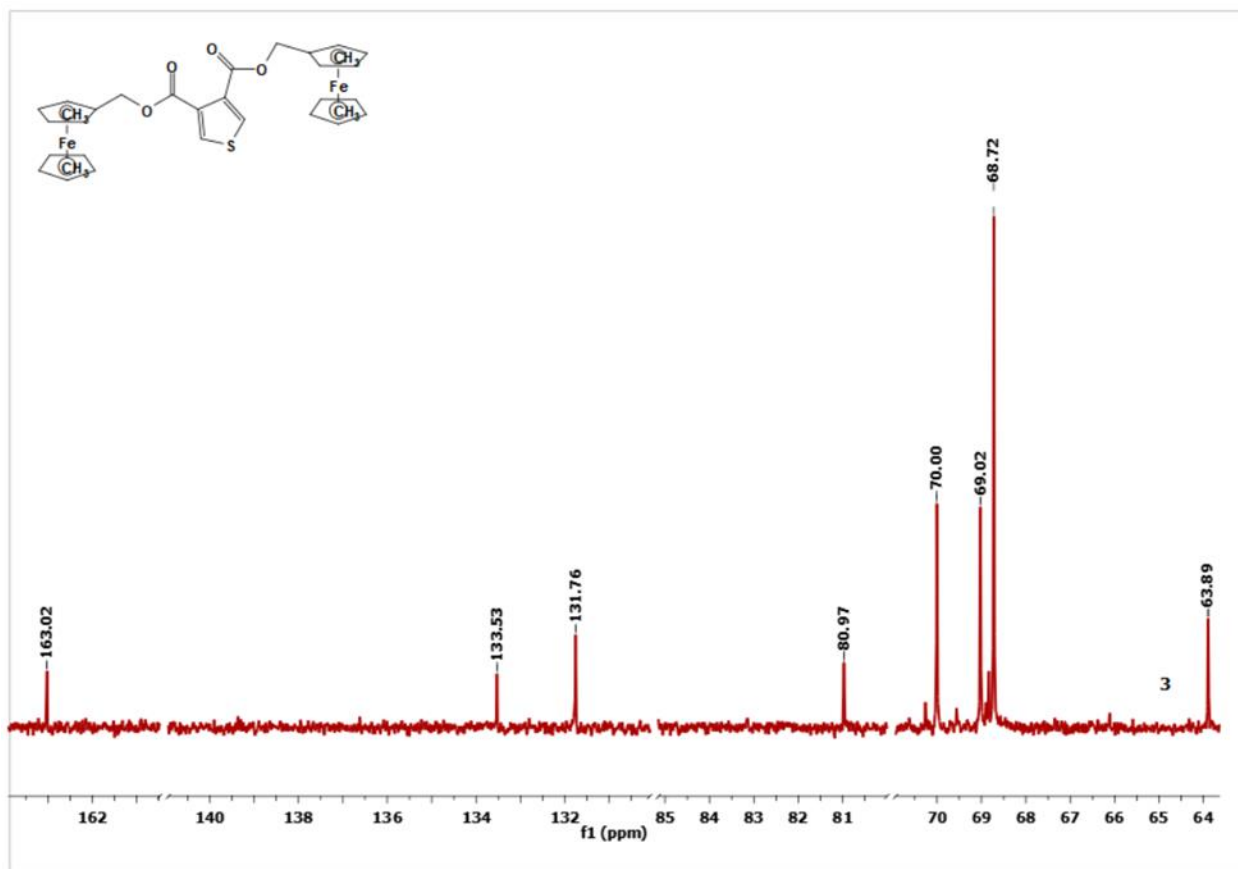


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3**.

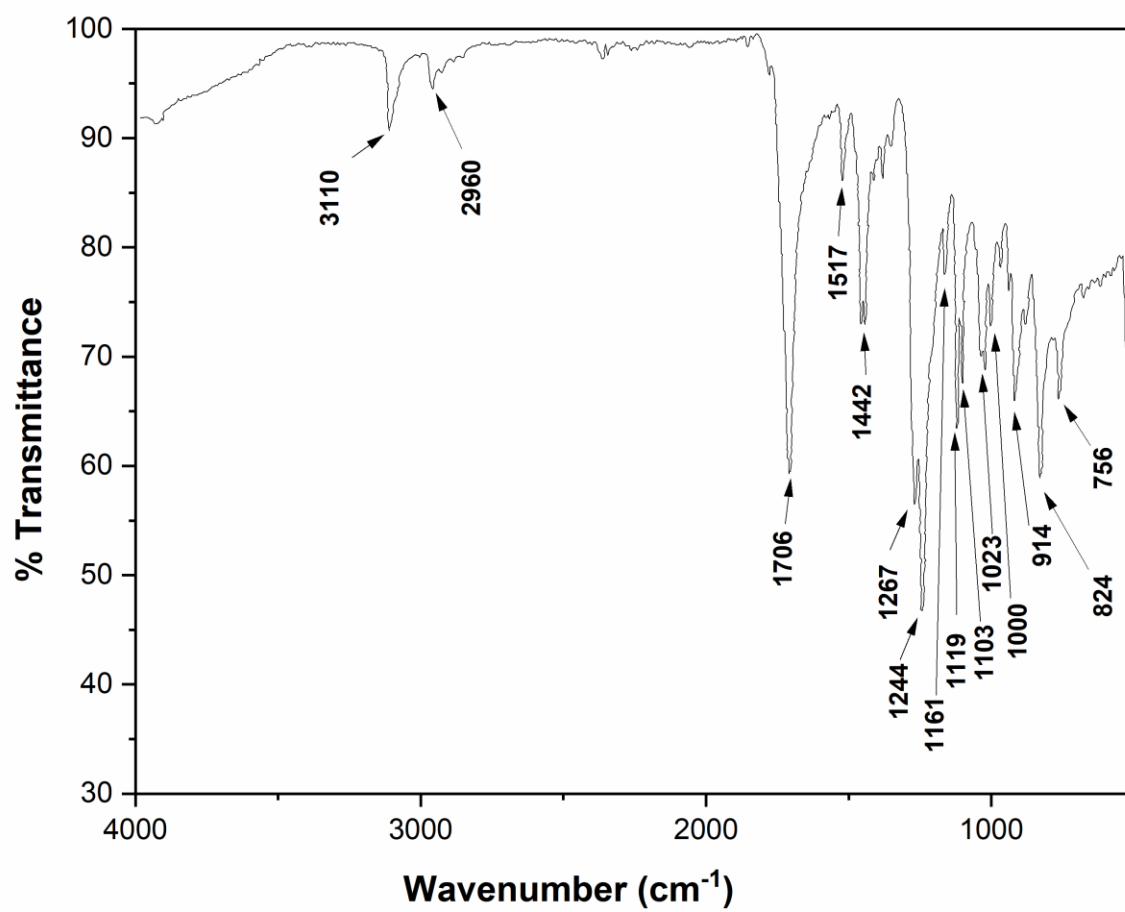


Figure S3. Infrared spectrum (KBr) of **3**.

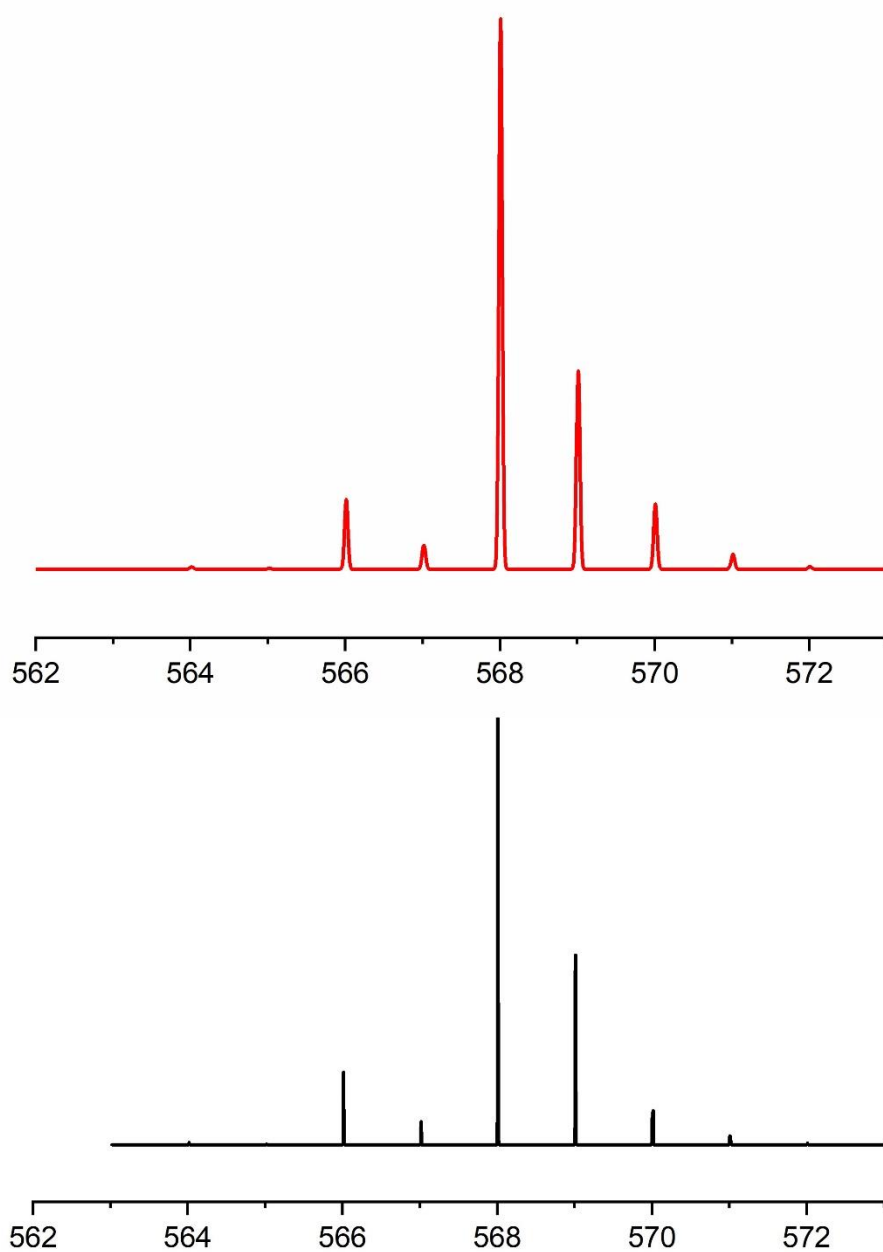


Figure S4. HR-ESI-MS spectrum of $\text{C}_{28}\text{H}_{24}\text{Fe}_2\text{O}_4\text{S}$ (**3**, top, red) obtained in an anthracene matrix and the predicted isotopic pattern (bottom, black). Monoisotopic mass for $\text{C}_{28}\text{H}_{24}\text{Fe}_2\text{O}_4\text{S}$ (M^+): Calc. Calc. 568.0094; Found 568.0096.

Table S1. Crystallographic data and refinement details for **4**.

Empirical formula	C ₆ H ₂ O ₅ S
Formula weight	154.14
Temperature (K)	120 K
Wavelength (Å)	1.54184
Crystal system	Tetragonal
space group	<i>P</i> 4 ₂ / <i>n</i>
Unit cell dimensions	
<i>a</i> (Å)	10.3099(8)
<i>b</i> (Å)	10.3099(8)
<i>c</i> (Å)	11.4790(15)
Volume (Å ³)	1220.1(2)
<i>Z</i>	8
Density (calculated) g/cm ³	1.678
Absorption coefficient mm ⁻¹	4.211
<i>F</i> (000)	624
Crystal size mm ³	0.18 x 0.1 x 0.1
θ range (°)	5.768 to 64.958
Index ranges	-8 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 11, -7 ≤ <i>l</i> ≤ 13
Reflections collected	1744
Independent reflections	1027 [<i>R</i> (int) = 0.0163]
Data Completeness	98.8 %
Data / restraints / parameters	1027 / 0 / 91
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0344, <i>wR</i> 2 = 0.0922
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0374, <i>wR</i> 2 = 0.0953
Largest diff. peak and hole (e.Å ⁻³)	0.286 and -0.277

Table S2. Calculated absolute HOMO and LUMO energies of compounds **3** and **5**, and the HOMO-LUMO gap. All units in eV.

Compound	HOMO	LUMO	LUMO-HOMO gap
3	-5.54	-1.20	4.34
5	-5.56	-2.24	3.32

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