Synthesis and (Spectro)Electrochemistry of Mixed-Valent Diferrocenyldihydrothiopyran Derivatives

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Synthesis and (Spectro)Electrochemistry of Mixed-Valent Diferrocenyl-dihydrothiopyran Derivatives

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Supplementary Information

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Figure S1 ^{1}H-NMR spectrum of **1**

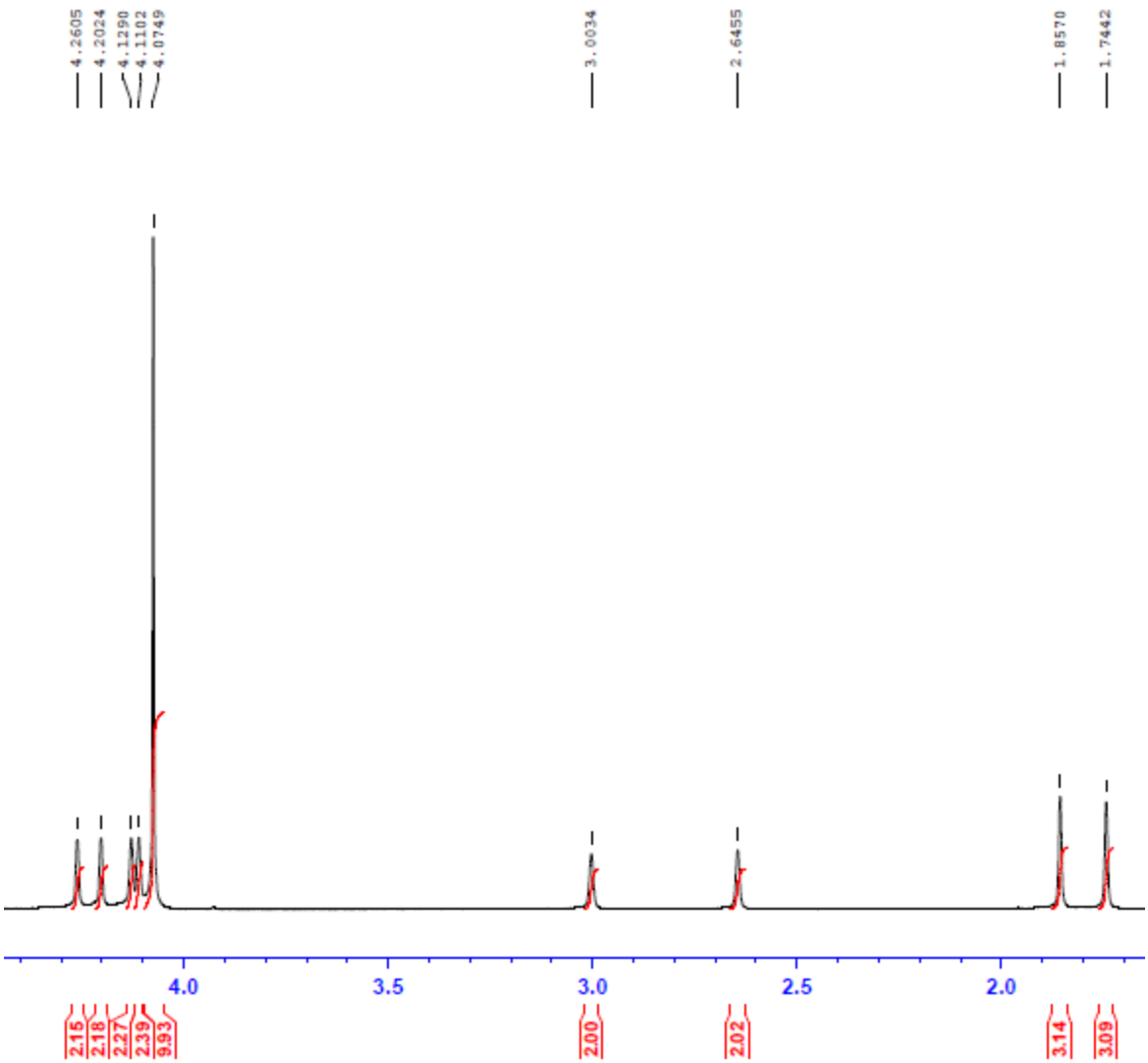
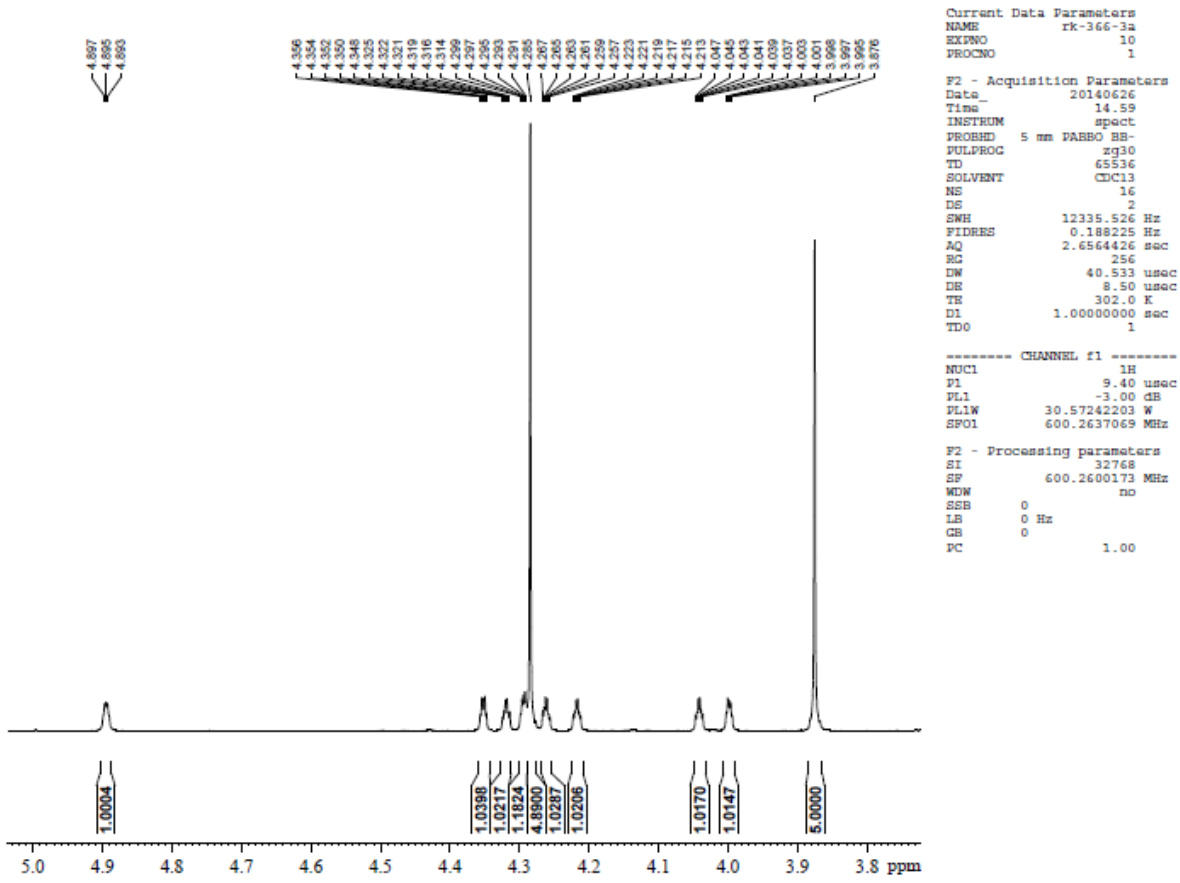


Figure S2 ^{1}H-NMR spectrum of **2**

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PROCNO                        1

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TD                       65536
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DE                       8.50 usec
TE                      302.0 K
D1                    1.00000000 sec
TD0                          1

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Figure S3 ^{1}H-NMR spectrum of **2**

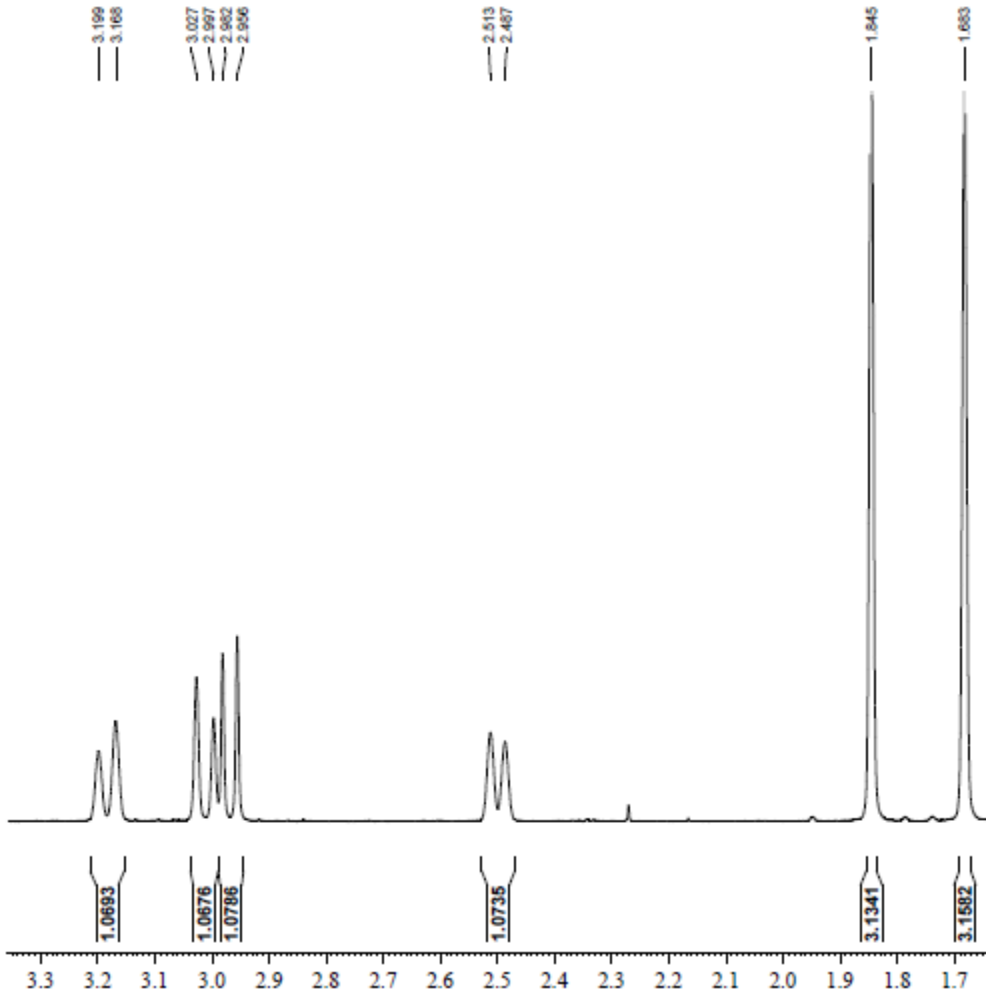

Figure S4 [1]H-NMR spectrum of **3**

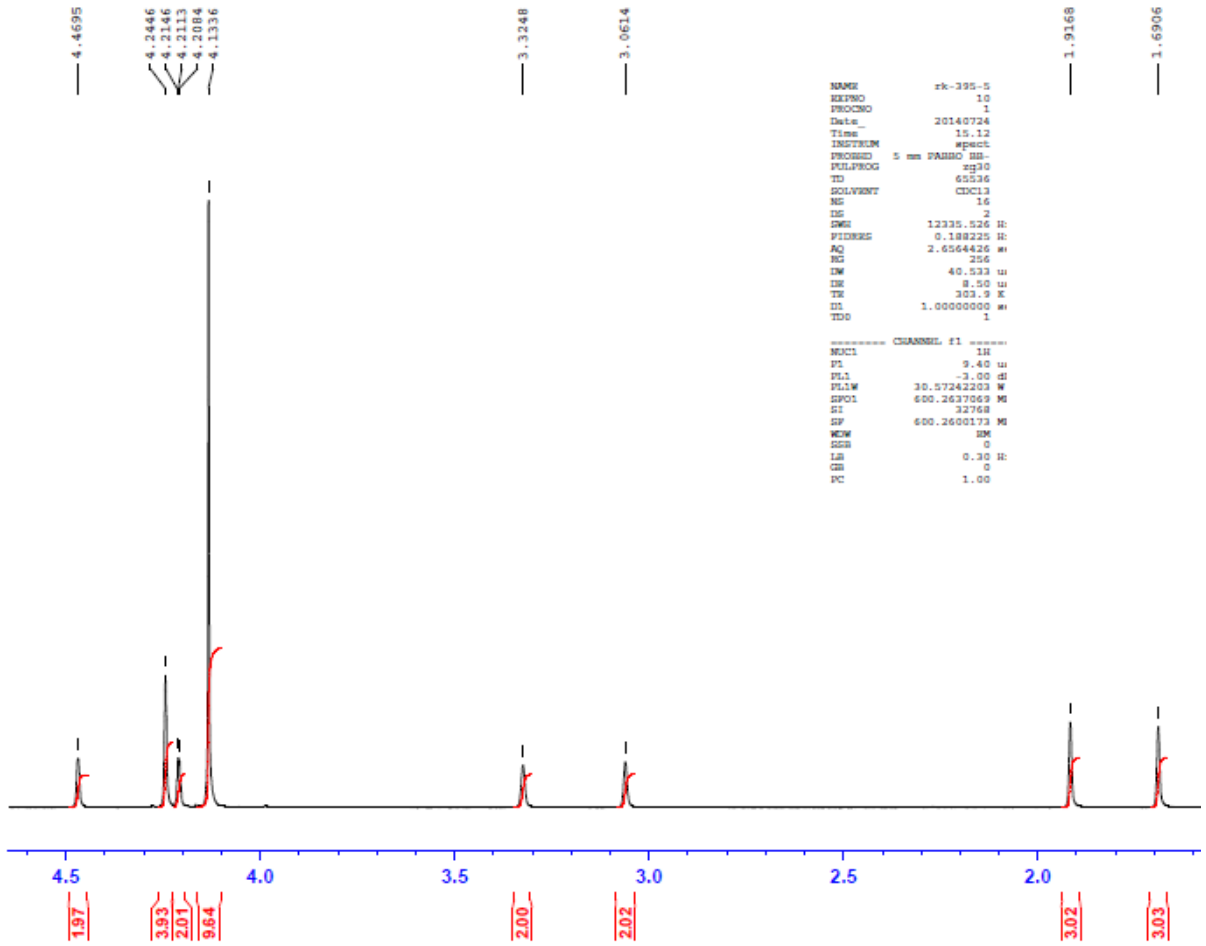

Figure S5. Left: UV-Vis/NIR spectra of **2** at 25 °C in acetonitrile (2.0 mmol·L^{-1}) at rising potentials (bottom: -200 to 525 mV; top: 525 to 1200 mV vs Ag/AgCl); supporting electrolyte $[Bu_4N][B(C_6F_5)_4]$. Right: Deconvolution of the NIR absorptions of $\mathbf{2}^{+}$ using three Gaussian shaped bands determined by spectroelectrochemistry in an OTTLE cell.

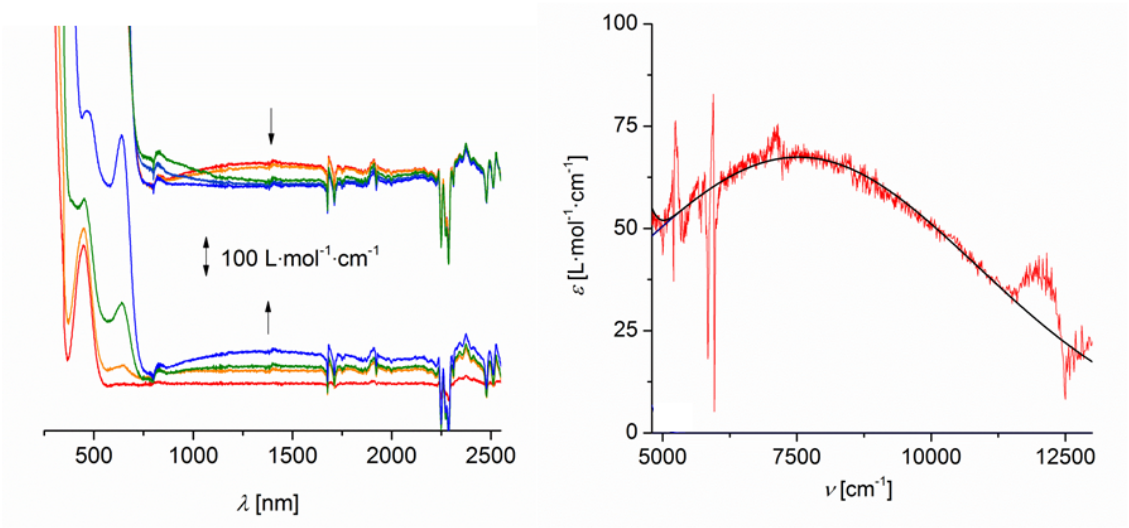

Table S1. Crystallographic and structure refinement parameters for **1** and **3**.

	1	**3**
Chemical formula	$C_{27}H_{28}Fe_2S$	$C_{27}H_{28}Fe_2O_2S$
Formula weight	496.25	528.25
Crystal system	Orthorhombic	Triclinic
Space group	*P cab* (no. 61)	*P* -1 (no. 2)
Crystal color and shape	red block	red block
Crystal size	0.18 x 0.18 x 0.16	0.21 x 0.20 x 0.16
a (Å)	9.7243(7)	12.7358(10)
b (Å)	13.7133(10)	14.2608(12)
c (Å)	32.524(2)	14.4554(11)
α (°)		103.754(6)
β (°)		115.357(6)
γ (°)		92.709(6)
V (Å^3)	4337.1(5)	2271.0(3)
Z	8	4
T (K)	173(2)	173(2)
D_c (g·cm^{-3})	1.520	1.545
μ (mm^{-1})	1.446	1.392
Scan range (°)	1.94 < θ < 29.23	1.63 < θ < 29.28
Unique reflections	5881	12288
Observed refls [I>2σ(I)]	2950	5481
R_{int}	0.0908	0.1299
Final *R* indices [I>2σ(I)]*	0.0288, wR_2 0.0389	0.0430, wR_2 0.0814
R indices (all data)	0.0835, wR_2 0.0431	0.1122, wR_2 0.0919
Goodness-of-fit	0.599	0.676
Max, Min Δρ/e (Å^{-3})	0.319, -0.299	0.397, -0.415

* Structures were refined on F_0^2: $wR_2 = [\Sigma[w (F_0^2 - F_c^2)^2] / \Sigma w (F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$