Electronic Supplementary Information (ESI)

for

The unusual ring scission of a quinoxaline-pyran-fused dithiolene system related to molybdopterin

Thibault Fogeron,[a] Pascal Retailleau,[b] Lise-Marie Chamoreau,[c] Marc Fontecave*[a] and Yun Li*[a]

[a] Laboratoire de Chimie des Processus Biologiques, UMR 8229 CNRS, Collège de France, UPMC Université Paris 6, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France.

E-mails: marc.fontecave@college-de-france.fr; yun.xu-li@college-de-france.fr

[b] Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Saclay, 1, av.de la Terrasse, 91198 Gif-sur-Yvette, France

[c] Sorbonne Universités, UPMC Université Paris 6, Institut Parisien de Chimie Moléculaire, UMR 8232 CNRS, 4 place Jussieu, 75252 Paris Cedex 5, France

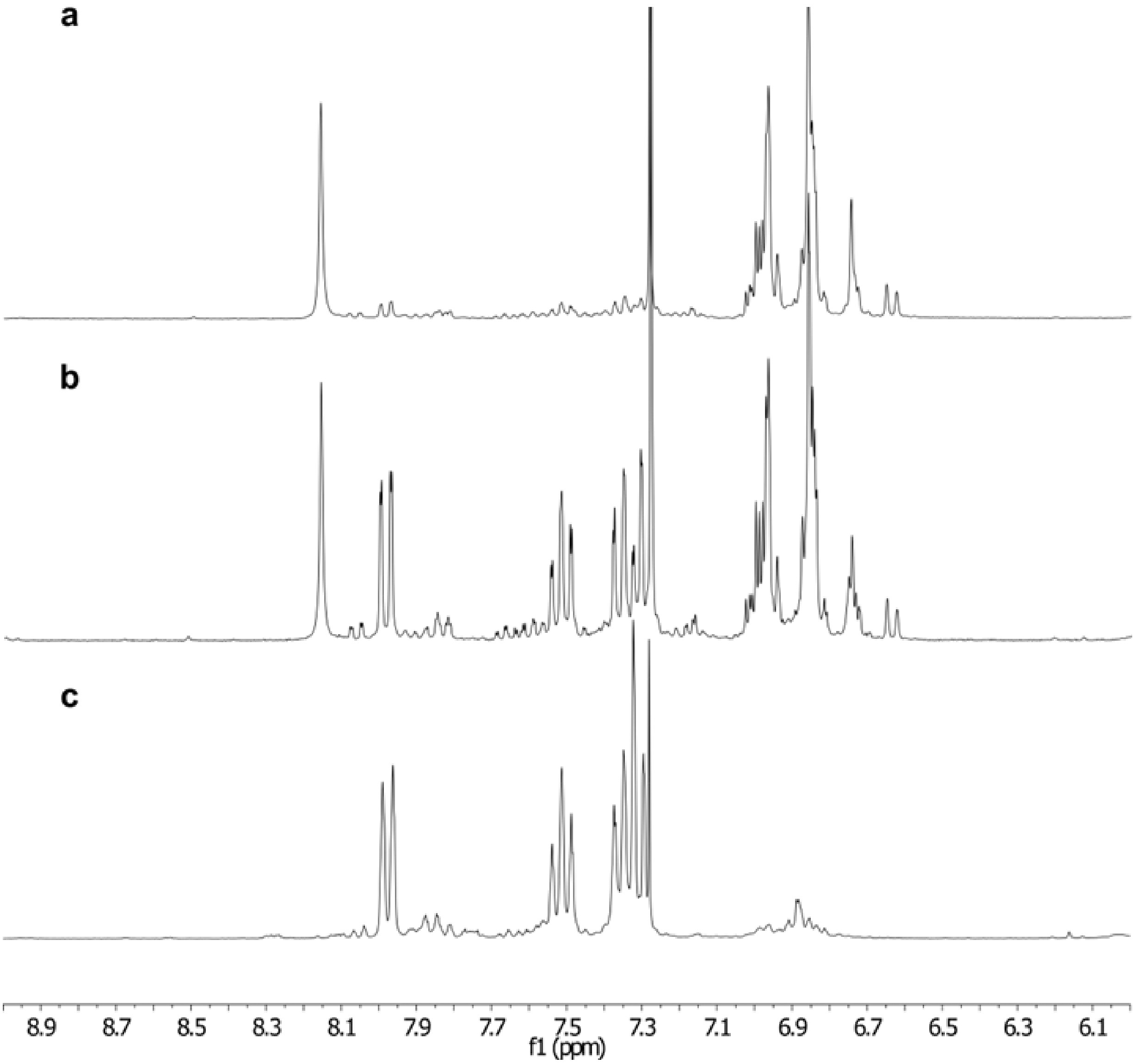

Figure S1. Partial ^{1}H NMR spectra in $CDCl_3$ of dithionite reduction of **1** (a): at 0 °C giving 3, (b): at rt giving **3** and **4**, (c): **3** after 3 days in a fridge giving **4**.

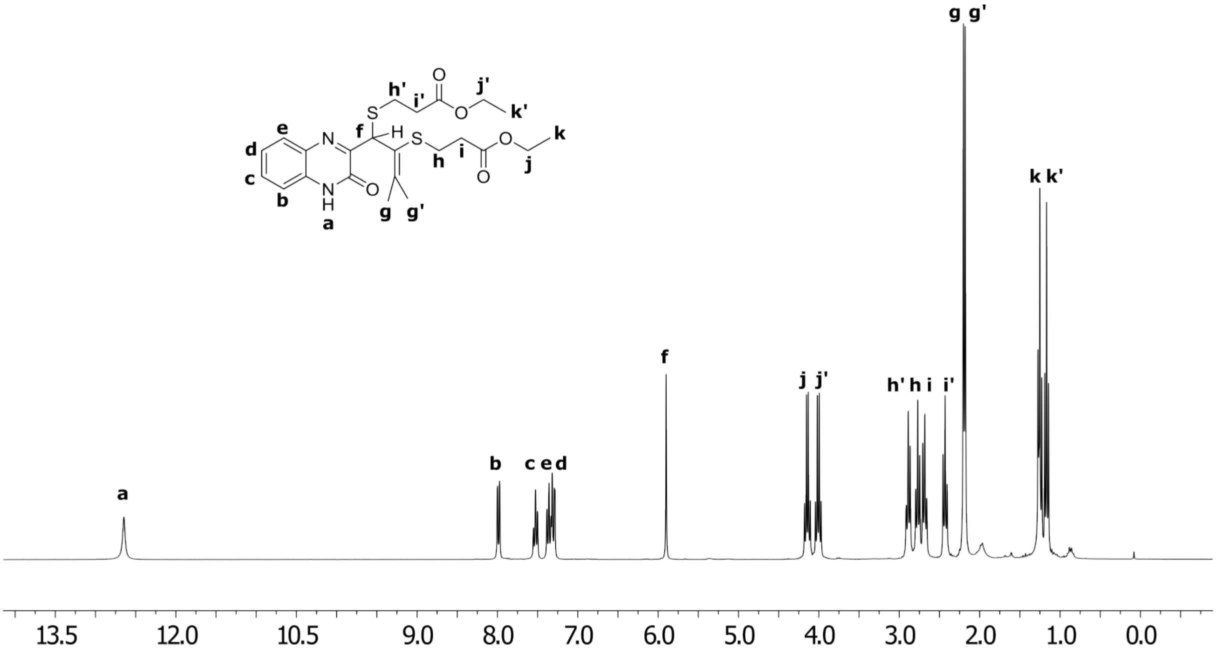

Figure S2. ^1H NMR spectrum ($CDCl_3$) and assignment of **4**.

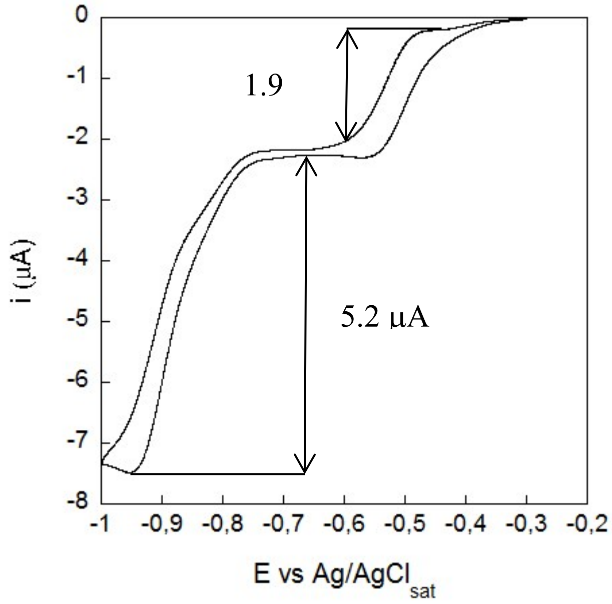

Figure S3. Cyclic voltammograms of complex **2** (0.5 mM) in CH_3CN with Bu_4NClO_4 (0.1 M) as the electrolyte, in the presence of 25 mM of HOAc Scan rate 1 mV s^{-1}; glassy carbon electrode (ϕ = 3 mm).

The number of electrons in the irreversible wave was determined using the following equation:[1]

$$I_p^{Rev} = \pm\, 0.446 n^{3/2} FAC(FD\nu/RT)^{1/2}$$

$I_p^{Irrev} = \pm\ 0.496n'FAC(FD\nu/RT)^{1/2}(\alpha n_a)^{1/2}$

where A is the geometric area of the electrode, F is the faraday's constant, R is the gas constant, T is the temperature, ν the scan rate of the experiment, D and C are respectively the diffusion coefficient and the concentration of the molecule, a is the transfer coefficient (usually assumed to be close to 0.5), n and n' are the total number of electrons transferred per molecule in the electrochemical processes and n_a is the number of electrons transferred per mole before the rate determining step, that in our case we assumed to be 1.

So we have $I_p^{Irrev}/\ I_p^{Rev} = n' * 0.496*0.5^{1/2}/0.446 \sim 0.78 * n'$

With $I_p^{Irrev} = 5.2$ µA and $I_p^{Rev} = 1.9$ µA we find n' = 3.51.

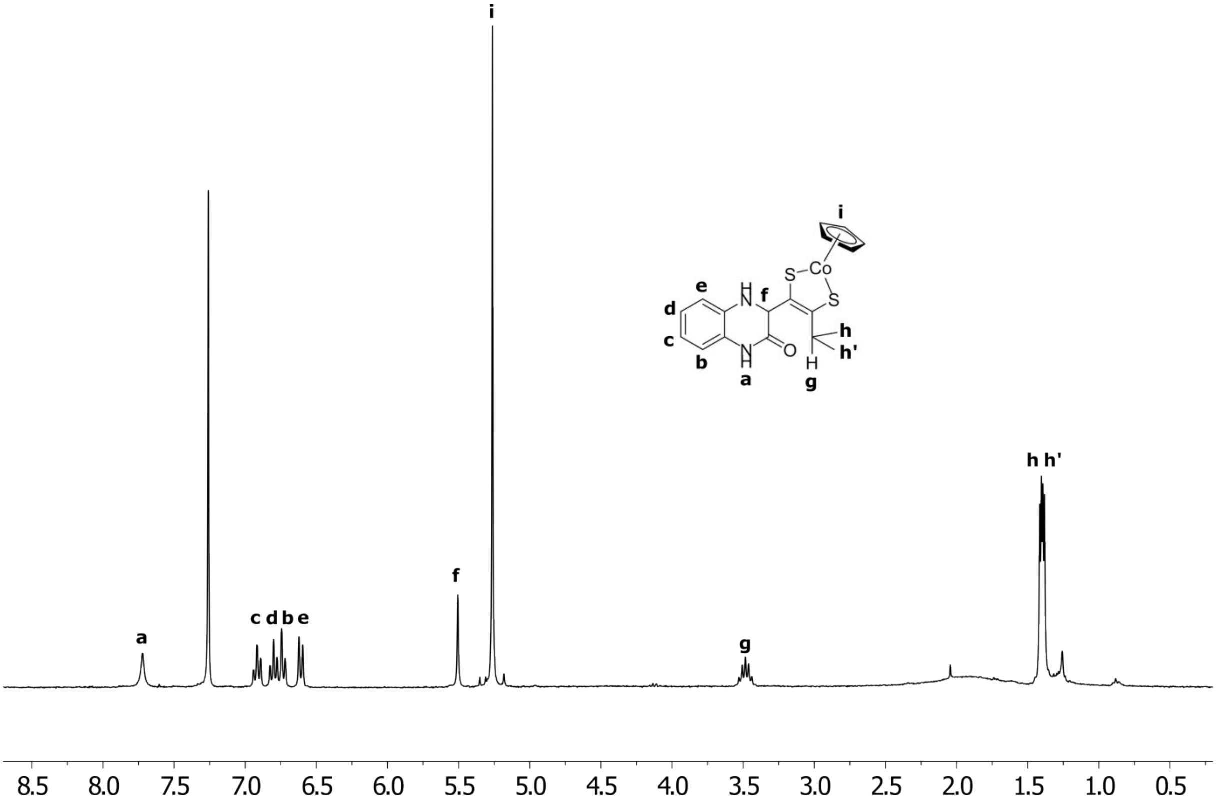

Figure S4. ^{1}H NMR spectrum ($CDCl_3$) and assignment of **7**.

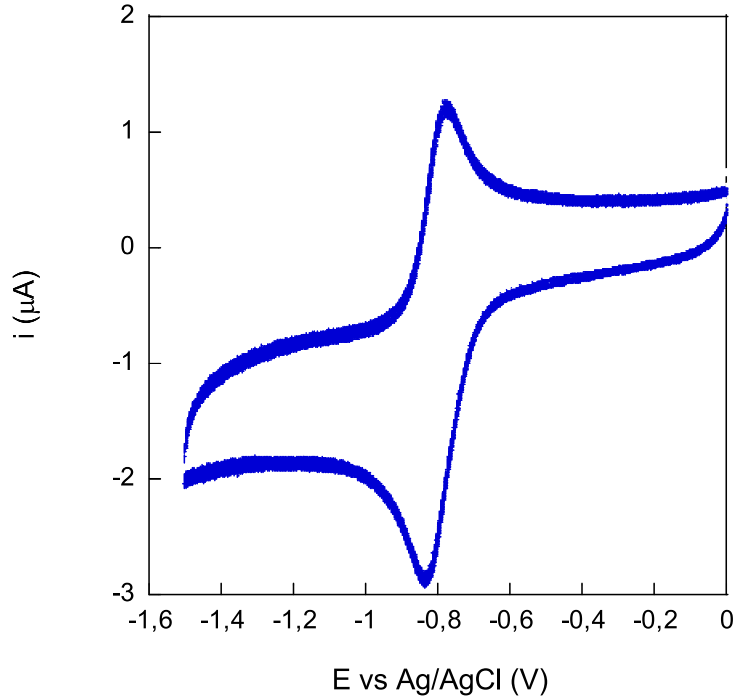

Figure S5. Cyclic voltammogram of complex **11** (0.2 mM) in CH_3CN with Bu_4NClO_4 (0.1 M) as the electrolyte. The third scan is represented. Scan rate 50 mV s^{-1}; glassy carbon electrode (ϕ = 3 mm).

Experimental Section

General methods

All starting materials were commercially available and were used without further purification. Solvents were purified by an MBRAUN SPS-800 Solvent Purification System. All reactions were carried out under air atmosphere unless specified. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-III 300 NMR spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C) at room temperature. High-resolution mass spectra (HRMS) were recorded on a LCT Premier XE mass spectrometer using ESI (electrospray ionization) at Institut de Chimie des Substances Naturelles in Gif-sur-Yvette. Mass spectra (MS) were recorded on an Applied Biosystems QSTAR pulsar I mass spectrometer using ESI (electrospray ionization) at Muséum National d'Histoire Naturelle (Paris). Flash chromatography was performed on Grace Reverlis® x2 with corresponding cartridges. UV-Vis spectra were recorded using a Cary 100 UV-Vis spectrophotometer instrument (Agilent).

All cyclic voltammetry (CVs) experiments were performed in a conventional three-electrode single-compartment cell. The potentiostat used in this study was SP 300 Bio-Logic (Bio-Logic Science Instruments SAS). A Pt wire was used as auxiliary electrode, saturated Ag/AgCl/KCl electrode separated from the solution by a salt bridge as reference electrode. Glassy carbon electrode GCE (1 or 3 mm diameter) was used as working electrode and was polished on wet polishing cloth using a 1 μm diamond suspension and a 0.05 μm alumina slurry. Solutions of acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP, Sigma-Aldrich) as the supporting electrolyte were deaerated with Ar for at least 15 min before CVs.

Controlled-potential electrolysis experiments were carried out at room temperature in a custom-built, gastight two-compartment electrochemical cell. The cathodic compartment, equipped with a glassy carbon working electrode (ϕ = 10 mm) was separated from the anodic compartment via a glass frit of fine porosity. The counter electrode was a 0.5 mm diameter platinum wire and the reference electrode was a saturated Ag/AgCl/KCl electrode.

Synthesis of **1** was reported earlier.[S2]

Synthesis of 4. Under an Ar atmosphere, a solution of $Na_2S_2O_4$ (0.366 mg, 2.1 mmol) in water (3 mL) was added at 0°C to a solution of **1** (1 g, 2.1 mmol) in MeOH (30 mL). This addition was repeated every 15 min. (10 additions in total). The reaction was kept at 0 °C for 30 minutes and was extracted with CH_2Cl_2 three times. The combined organic layers were dried over magnesium sulfate and concentrated *in vacuo*. The crude product was dissolved in chloroform and kept in a fridge for 3 days. Purification of the reaction product by flash chromatography over silica gel with EtOAc/cyclohexane (35 : 65) as eluent gave a pale yellow oil (599 mg, 60 %). IR (cm^{-1}): 1732 ($\nu_{C=N}$), 1660 ($\nu_{C=O}$). ^1H NMR (300 MHz, $CDCl_3$) δ 12.65 (1H, D_2O exchangeable), 7.99 (d, *J* = 8 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8Hz, 1H), 5.90 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 2.18 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.94 (C=O), 157.36 (CONH), 155.69 (C), 146.24 (C), 132.64 (C), 131.04 (C), 130.38 (CH), 129.58 (CH), 124.83 (C), 124.25 (CH), 115.49 (CH), 60.68 (CH_2), 60.42 (CH_2), 51.20 (CH), 34.81(CH_2), 34.29 (CH_2), 30.78 (CH_2), 26.61 (CH_2), 24.68 (CH_3), 22.09 (CH_3), 14.18 (CH_3), 14.12 (CH_3). HRMS: *m/z* calcd. for $C_{23}H_{31}N_2O_5S_2$ $[M + H]^+$: 479.1674 ; found: 479.1668.

Synthesis of 7. Under an Ar atmosphere, $NaBH_4$ (248 mg, 5.96 mmol) was added at 10 °C to a solution of **4** (712 mg, 1.49 mmol) in acetic acid (15 mL). After 30 min, acetaldehyde (940 μL, 15 mmol) and $NaBH_3CN$ (507 mg, 7.5 mmol) were added to the solution. The reaction was kept at 10 °C for 30 minutes and was quenched by adding saturated aq. Na_2CO_3. The usual work-up with CH_2Cl_2 gave a crude yellow oil, which was purified by flash chromatography over silica gel (eluting with AcOEt : cyclohexane, 5 : 95) to furnish **7** (522 mg, 69 %). ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (br s, 1H, D_2O exchangeable), 7.00 (br t, J = 7.4 Hz, 1H), 6.94 – 6.79 (m, 2H), 6.71 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 9.9 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 4.10 (q, J = 7.2 Hz, 2H), 3.95 (d, J = 9.9 Hz, 1H), 3.45 (dq, J = 13.7, 6.8, 1H), 3.16 – 2.92 (m, 3H), 2.71 – 2.54 (m, 4H), 2.49 – 2.40 (m, 2H), 2.08 (s, 3H), 1.31 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.0 Hz, 3H).13C NMR (75 MHz, $CDCl_3$) δ 172.00 (C=O), 171.60 (C=O), 164.83 (CONH), 145.90 (C), 132.87 (C), 127.39 (C), 126.82 (C), 123.99 (CH), 119.63 (CH), 115.83 (CH), 115.43 (CH), 64.50 (CH), 60.64 (CH_2), 48.24 (CH), 46.14 (CH_2), 34.52 (CH_2), 34.38 (CH_2), 32.26 (CH_2), 26.78

(CH_2), 24.69 (CH_3), 20.71 (CH_3), 14.16 (CH_3), 13.42 (CH_3). HRMS: *m/z* calcd. for $C_{25}H_{37}N_2O_5S_2$ [M + H]$^+$: 509.2144; found: 509.2143.
Single crystals suitable for X-ray diffraction were obtained by slow diffusion of cyclohexane into a solution of EtOAc containing **7.**

Synthesis of 9. Under an Ar atmosphere, Cs_2CO_3 (310 mg, 0.951 mmol) and MeI (120 μL, 1.9 mmol) were added at 10 °C to a solution of **7** (322 mg, 0.634 mmol) in anhydride DMF (4 ml). After 3.5 h, Et_2O (30 mL) was added and the mixture was washed with H_2O (3 x 5 mL). The organic layer was dried over $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by flash chromatography over silica gel (eluting with AcOEt/cyclohexane, 1:9) to afford **9** (280 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08 – 6.96 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.69 (d, J = 7.7 Hz, 1H), 4.35 (d, J = 9.9 Hz, 1H), 4.23 (q,J = 7 Hz, 2H), 4.04 (q,J = 7 Hz, 2H), 3.87 (d, J = 9.9 Hz, 1H), 3.43 (s, 3H), 3.49 (m, 1H), 3.13 – 2.93 (m, 3H), 2.68 – 2.60 (m, 2H), 2.56 – 2.46 (m, 2H), 2.46 – 2.36 (m, 2H), 2.06 (s, 3H), 1.32 – 1.19 (m, 6H), 1.11 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.00 (C=O), 171.55 (C=O), 163.97 (C=O), 145.65 (C), 134.18 (C), 130.89 (C), 126.91 (C), 123.58 (CH), 119.46 (CH), 115.10 (CH), 114.98 (CH), 64.51 (CH), 60.62 (CH_2), 47.81 (CH), 45.65 (CH_2), 34.58 (CH_2), 34.36 (CH_2), 32.20 (CH_2), 29.66 (CH_3), 26.62 (CH_2), 24.65 (CH_3), 20.64 (CH_3), 14.19 (CH_3), 13.38 (CH_3). HRMS: *m/z* calcd. for $C_{26}H_{39}N_2O_5S_2$ [M + H]$^+$: 523.2300; found: 523.2295.

Synthesis of 10. The experiment was carried out under Ar using Schlenk tubes and all solutions were degassed prior to use. *t*BuOK (234 mg, 2.08 mmol) was added to a solution of **9** (272 mg, 0.521 mmol) in anhydrous THF (10 mL) at 0°C. After 30 min at room temperature, [Co^{III}CpI$_2$(CO)]^{S3} (212 mg, 0.522 mmol) in THF (15 mL) was added dropwise *via* a cannula needle to the orange suspension. An immediate color change to black was observed. After 1.5 h, water was added and the product was extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and evaporated to dryness. The crude product was purified by flash chromatography over silica gel (eluting with CH_2Cl_2) to afford **12** as a dark brown solid (74 mg, 31 %). UV-Vis (CH_2Cl_2), λ_{max} nm (ε M^{-1}.cm^{-1}): 402 (2900), 310 (7600), 285 (8500). Positive-ion Electrospray MS (MeOH) *m/z*: 889 [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 – 6.99 (m, 2H), 6.85 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 4.98 (s, 5H), 4.01 (d, J

= 9.8 Hz, 1H), 3.61 (td, J = 14.1, 7.1 Hz, 1H), 3.47 (s, 1H), 3.44 – 3.36 (m, 1H), 2.98 (d, J = 9.8 Hz, 1H), 2.27 (s, 3H), 1.34 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.38 (C), 140.03 (C), 134.28 (C), 129.25 (C), 128.67 (C), 123.53 (CH), 118.00 (CH), 115.43 (CH), 113.24 (CH), 85.03 (5*CH), 64.90 (CH), 53.95 (CH), 44.77 (CH_2), 30.66 (CH_3), 25.38 (CH_3), 23.91 (CH_3), 13.31 (CH_3). *Anal.* Calc. for: $C_{43}H_{52}Cl_2Co_2N_4O_2S_4$ (**12**.CH_2Cl_2, 972.1014) C 53.03, H 5.38, N 5.75, S 13.17; Found: C 52.87, H 5.35, N 5.70, S 12.93. Single crystals suitable for X-ray diffraction were obtained by layering pentane over a solution of CH_2Cl_2 containing the complex at room temperature.

Synthesis of [CpCo^{III}(qpdt)] (**2**). This complex was synthesized according to the same procedure as complex **10**, with *t*BuOK (94 mg, 0.840 mmol), **1** (100 mg, 0.211 mmol) and [Co^{III}CpI$_2$(CO)] (86 mg, 0.211 mmol). The crude product was purified by flash chromatography over silica gel (eluting with CH_2Cl_2) to afford **2** as a dark blue solid (67 mg, 80 %). UV-Vis (CH_3CN), λ_{max} nm (ε, M^{-1} cm^{-1}): 617 (12800), 401 (13880), 367 (15600), 290 (27550). Positive-ion Electrospray MS (MeOH) *m/z*: 399 [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.78 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.3, 1H), 7.57 (dt, *J* = 7.6, 1.3, 1H), 5.47 (s, 5H), 1.89 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.09 (C), 154.39 (C), 153.10 (C), 141.42 (C), 140.79 (C), 140.42 (C), 129.26 (CH), 129.00 (CH), 127.48 (CH), 127.41 (CH), 86.19 (C), 79.91 (5 x CH), 30.85 (2 x CH_3). *Anal.* Calcd. for $C_{18}H_{15}CoN_2OS_2$ (398.3842): C 54.27, H 3.80, N 7.03, S 16.10; Found: C 54.4, H 4.03, N 6.65, S 15.38. Single crystals suitable for X-ray diffraction were obtained as dark blue plates by layering a CH_3CN solution containing the complex over water at room temperature.

Synthesis of complex 11. AcOH (140 μL, 2.45 mmol) was added to a solution of **2** (19 mg, 0.048 mmol) in anhydrous CH_3CN (11 mL) containing tetrabutylammonium perchlorate (0.1 M). They were purged with N2 gas for 15 min before electrolysis and were constantly stirred. The solution was degassed with N_2 for 20 minutes. The controlled-potential electrolysis was carried out at -1.1 V *vs.* Ag/AgCl/KCl (sat) over a period of 2 h with stirring. Water was added and the product was extract with CH_2Cl_2, the combined extracts were dried over sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography over silica gel (eluting with

AcOEt/cyclohexane, 1:9) to afford **9** as a purple solid (6 mg, 32 %). UV-Vis (CH_3CN), λ_{max} nm (ε, M^{-1} cm^{-1}): 573 (3600), 287 (11800). IR (cm^{-1}): 1680 ($\nu_{C=O}$). Electronic Ionization MS (CH_2Cl_2) *m/z*: 402. $[M\bullet]^+$. ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (br, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.80 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 5.51 (s, 1H), 5.26 (s, 5H), 3.49 (m, 1H), 1.41 (d, J = 7.0 Hz, 3H), 1.39 (d, J = 7.0 Hz, 3H). Single crystals suitable for X-ray diffraction were obtained by layering a CH_3CN solution containing the complex over water at room temperature.

X-ray crystallographic data

For compounds **7** and **10**: A single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with either graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) or a copper microfus source (λ = 1.54178 Å). Data collections were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections.

In the WinGX suite of programs,[S4] the structure were solved with SHELXT[S5] program and refined by full-matrix least-squares methods using SHELXL-14.[S6]

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions or from a Fourier difference map and mostly refined with a riding model, except for NH group. and refined with a riding model. A SQUEEZE[S7] procedure was applied for complex **10** because of the presence of disordered solvent. The crystallographic data were summarized in Table S1.

Table S1. Crystallographic data of the compounds **7** and **10**.

Compound	**7**	**10**
Chemical formula	$C_{25}H_{36}N_2O_5S_2$	$C_{42}H_{50}Co_2N_4O_2S_4\cdot1.5(C_5H_{12})$
MW	508.68	913.01
Crystal system, space group	Triclinic, $P\bar{1}$	Trigonal, $R\bar{3}$:
Temperature (K)	200	200
a, *b*, *c* (Å)	9.8222 (5), 11.7774 (6), 13.4213 (7)	32.4643 (17), 10.4380 (5)
α, β, γ (°)	66.426 (2), 72.546 (2), 70.537 (2)	
V (Å^3)	1316.50 (12)	9527.1 (11)
Z	2	9
Radiation type	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.14	1.02
Crystal size (mm)	0.31 × 0.09 × 0.06	0.17 × 0.09 × 0.08
T_{min}, T_{max}	0.631, 0.753	0.691, 0.746
No. of measured, independent, observed [$I > 2\sigma(I)$] reflections	27977, 4817, 4488	23401, 6170, 4543
R_{int}	0.030	0.035
(sin θ/λ)$_{max}$ (Å^{-1})	0.607	0.703
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.094, 1.04	0.036, 0.102, 0.98
No. of reflections	4817	6170
No. of parameters	317	248
No. of restraints	0	0
$\Delta>_{max}$, $\Delta>_{min}$ (e Å^{-3})	0.27, -0.43	0.45, -0.26
CCDC number	1523010	1523011

For compounds **2** and **11**: The measurements were made on a Rigaku XtaLabPro diffractometer equipped with an HPAD Dectris Pilatus 200K area detector and with Rigaku mm003 microfocus Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K. All calculations were performed using the CrysAlis Pro 1.171.39.7b[S7] and Olex2 1.2 (compiled 2016.11.30 svn.r3368 for OlexSys, GUI svn.r5269)[S9] crystallographic software packages, including SHELXT[S5] and SHELXL-7/2014.[S6] The crystallographic data were summarized in Table S2.

CCDC 1522379 (**2**), 1523010 (**7**), 1523011(**10**), and 1522380 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystallographic data of the compounds **2** and **11**.

Compound	**2**	**11**
Chemical formula	$C_{18}H_{15}CoN_2OS_2$	$C_{18}H_{19}CoN_2OS_2$
Formula weight	398.37	402.40
Temperature (K)	173 (2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Monoclinic, $P\ 2_1/n$	Monoclinic, $P\ 2_1/n$
Unit cell dimensions	a = 10.1653(2), α= 90	a = 17.498(4), α = 90
(Å, °)	b = 19.6347(6), β = 95.169(2)	b = 5.5628(14), β = 98.08(2)
	c = 16.9400(5), γ = 90	c = 17.846(5), γ = 90
Volume (Å^3)	3367.36(16)	1719.9(7)
Z	8	4
Calc. Density (Mg/m^{-3})	1.572	1.554
Abs. coefficient (mm^{-1})	1.274	1.248
F(000)	1632	832
Crystal size (mm)	0.30 x 0.24 x 0.14	0.20 x 0.05 x 0.02
θ range for data coll. (°)	3.649 to 30.742	3.518 to 25.349
Limiting indices	$-14 \leq h \leq 14$, $-28 \leq k \leq 27$, $-21 \leq l \leq 24$	$-21 \leq h \leq 21$, $-6 \leq k \leq 6$, $-21 \leq l \leq 20$
Refl. collected / unique	54264 / 9670	13572 / 3131
R(int)	0.0286	0.1247
Completeness to θ_{full} (%)	99.64	99.1
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.55077	1.689 and 0.740
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9665 / 0 / 437	3131 / 2 / 225
Goodness-of-fit on F^2	1.045	0.987
Final R indices [I>2σ(I)]	R1 = 0.0242, wR2 = 0.0634	R1 = 0.0542, wR2 = 0.1048
R indices (all data)	R1 = 0.0287, wR2 = 0.0652	R1 = 0.0979, wR2 = 0.1189
Largest $\Delta_{\text{peak and hole}}$ (e.A^{-3})	0.420 and -0.243	0.517 and -0.483
CCDC number	1522379	1522380

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