Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Sulfur substitution in a Ni(cyclam) derivative results in lower overpotential for CO2 reduction and enhanced proton reduction

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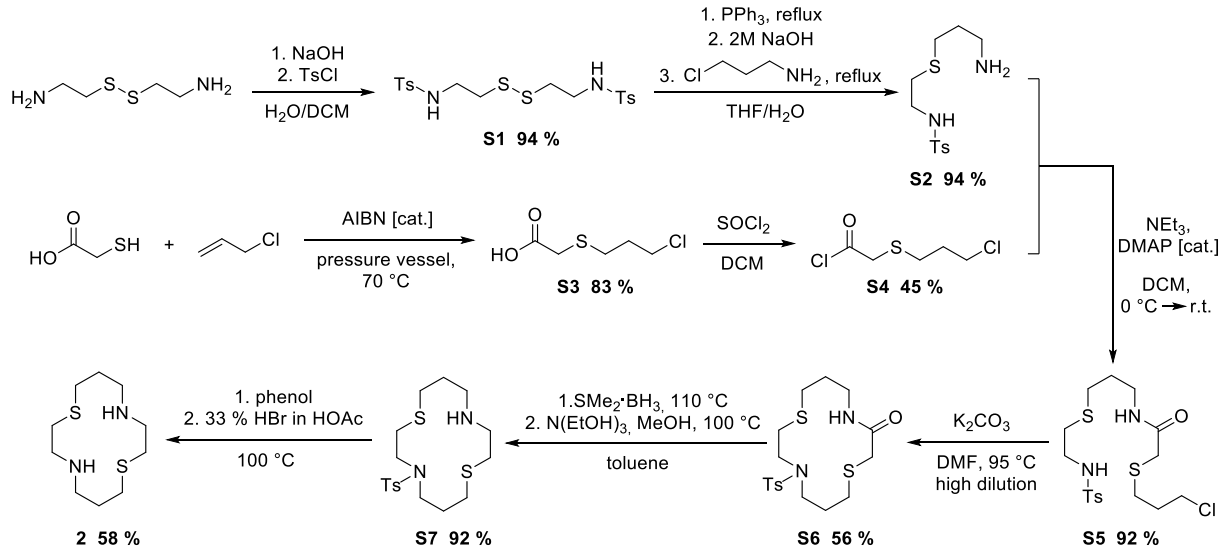
General techniques: All reactions were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques. 1,8-dithia-4,11-diazacyclotetradecane was synthesized according to literature procedures.[1] All other compounds were obtained from commercial vendors and used without further purification. All solvents were dried prior to use according to standard methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker DPX-200 NMR or a Bruker DPX-250 NMR spectrometer at room temperature. Peaks were referenced to residual ^{1}H signals from the deuterated solvent and are reported in parts per million (ppm). IR spectra were measured with a Bruker Tensor 27 FT-IR spectrometer in solution and are reported in wavenumbers (cm^{-1}). Mass spectra were obtained with a Bruker Daltonics Esquire 6000 instrument. UV/vis/NIR spectra were recorded with a Jasco V-670 at 25 °C. Thin-layer chromatography was performed by using Merck TLC aluminum sheets, silica gel 60 F_{254}.



Scheme S1: Schematic overview of the dithiacyclam **2** synthesis.

N,N'-bis-(p-toluenesulfonyl)cystamine (S1): Sodium hydroxide (9.96 g, 249 mmol) was dissolved in water (250 mL) and cystamine dihydrochloride (13.1 g, 58.4 mmol) was added to the stirring solution. Subsequently *p*-toluenesulfonylchlorid (22.2 g, 116.7 mmol) dissolved in DCM (300 mL) was added dropwise to the vigorous stirring mixture. After the addition was complete, the reaction mixture was stirred for an additional 12 h. The organic layer was separated from the aqueous layer, and the organic layer was washed with 3 M HCl (2 x 45 mL), water (2 x 45 mL), saturated NaCl (1 x 45 mL) and dried over Na_2SO_4, filtered and concentrated to give **S1** (25.2 g, 94 %) as a colorless solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.74 (d, 4 H, J = 8.4 Hz, $H_{aromatic}$), 7.30

(d, 4 H, J = 8.4 Hz, $H_{aromatic}$), 5.32 (t, 2 H, J = 6.4 Hz, N*H*), 3.21 (q, 4 H, J = 6.4 Hz, CH_2NH), 2.69 (t, 4 H, J = 6.4 Hz, CH_2S), 2.41 (s, 6 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.8, 136.8, 130.0, 127.2 ($C_{aromatic}$), 41.8 (CH$_2$NH), 38.0 (CH$_2$S), 21.7 (CH$_3$) ppm.

N-[2-(3-Amino-propylthio)-ethyl]-4-methyl-benzenesulfonamide (S2): S1 (11.6 g, 25.1 mol) and triphenylphosphine (7.9 g, 30.1 mmol) were dissolved in deoxygenated THF (94 mL) and water (19 mL). The mixture was refluxed for 5 d, followed by the addition of 2 M deoxygenated NaOH (26.3 mL). A solution of chloropropylamine hydrochloride (6.4 g, 50.2 mmol) in 2 M deoxygenated NaOH (26.3 mL) was added to the mixture and it was refluxed for 12 h. Subsequently, the reaction mixture was cooled to room temperature and the pH was adjusted to 2 using 6 M HCl. The organic layer was separated from the aqueous layer and the aqueous layer was washed with chloroform (2 x 40 mL). The aqueous layer was adjusted to a pH of 10 using 6 M NaOH and washed with chloroform (3 x 40 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated to give **S2** (13.6 g, 94 %) as a colorless solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.75 (d, 2 H, J = 8.2 Hz, $H_{aromatic}$), 7.30 (d, 2 H, J = 8.2 Hz, $H_{aromatic}$), 3.13 (t, 2 H, J = 6.27 Hz, CH_2NH), 2.76 (t, 2 H, J = 6.9 Hz, CH_2NH$_2$), 2.60 (t, 2 H, J = 6.27 Hz, CH_2S), 2.49 (t, 2 H, J = 6.9 Hz, CH_2S), 2.42 (s, 3 H, CH_3), 1.65 (quintet, 2 H, J = 6.9 Hz, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.6, 137.2, 129.9, 127.2 ($C_{aromatic}$), 41.2 (CH$_2$NH), 40.8 (CH$_2$NH$_2$), 32.7 (CH$_2$S), 32.1 (CH$_2$S), 29.2 (CH$_2$$CH_2CH_2$), 21.7 ($CH_3$) ppm.

2-[(3-chloropropyl)sulfanyl]acetic acid (S3): Mercaptoacetic acid (4.6 mL, 66.3 mmol) and allyl chloride (6.0 mL, 73.7 mmol) were added to a resealable glass pressure vessel and purged with argon for 5 min. A catalytic amount of AIBN was added to the solution and the vessel was sealed. The mixture was heated to 70 °C and stirred for 10 h. The reaction was cooled to room temperature and the contents were transferred to a round bottom flask and placed under reduced pressure (1 mbar) for 8 h to give **S3**. The product was used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.64 (t, 2 H, J = 6.65 Hz, CH_2Cl), 3.25 (s, 2 H, SCH_2CO), 2.82 (t, 2 H, J = 6.65 Hz, SCH_2), 2.06 (quintet, 2 H, J = 6.65 Hz, CH$_2$CH_2CH$_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 176.6 ($C_{carbonyl}$), 43.3 (CH$_2$Cl), 33.6 (SCH$_2$CO), 31.6 (SCH$_2$), 29.9 (CH$_2$$CH_2CH_2$) ppm.

2-[(3-chloropropyl)sulfanyl]acetyl chloride (S4): Compound **S3** (10.5 g, 62.5 mmol) was dissolved in DCM (35 mL) and thionyl chloride (4.5 mL, 62.5 mmol) was added dropwise. After the addition was complete, the mixture was stirred for 12 h, whereby the color changed to dark brown. The solution was concentrated and toluene was added (10 mL) and concentrated to remove excess thionyl chloride (2x). Distillation afforded pure **S4** as a yellow oil (5.2 g, 45 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.7 (t, 2 H, J = 6.61 Hz, CH_2Cl), 3.64 (s, 2 H, SCH_2CO), 2.80 (t, 2 H, J =

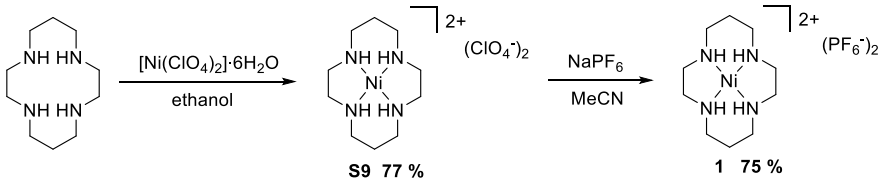
6.61 Hz, SCH_2), 2.04 (quintet, 2 H, J = 6.61 Hz, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.3 ($C_{carbonyl}$), 45.3 (CH_2Cl), 43.0 (SCH_2CO), 31.5 (SCH_2), 29.9 ($CH_2CH_2CH_2$) ppm.

N-{N'-[2-(3-propylthio)ethyl]-4-methylbenzenesulfonamide}-[(3-chloropropyl)thio]-acetamide (S5): Compound **S2** (5.3 g, 18.5 mmol) and a catalytic amount of 4-dimethylaminopyridine were dissolved in DCM (50 mL). Subsequently, freshly distilled triethylamine (2.7 mL, 19.5 mmol) was added and the mixture was cooled to 0 °C. **S4** (3.5 g, 18.5 mmol) was dissolved in DCM (50 mL) and was added to the reaction mixture over a period of 1 h. After the addition was complete, the solution was warmed to room temperature and stirred for an additional 12 h. The reaction mixture was washed with water (2 x 40 mL), 3 M HCl (2 x 40 mL), 3 M NaOH (2 x 40 mL), dried over Na_2SO_4, filtered, and then concentrated to give **S5** (7.47 g, 92 %) as a red/brown oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73 (d, 2 H, J = 8.3 Hz, $H_{aromatic}$), 7.28 (d, 2 H, J = 8.3 Hz, $H_{aromatic}$), 6.97 (bt, 1 H, N*H*), 4.66 (s, 1 H, N*H*Ts), 3.62 (t, 2 H, J = 6.4 Hz, CH_2Cl), 3.35 (q, 2 H, J = 6.8 Hz, CH_2NH), 3.21 (s, 2 H, SCH_2CO), 3.08 (t, 2 H, J = 6.0 Hz, CH_2NHTs), 2.69 (t, 2 H, J = 6.0 Hz, CH_2S), 2.60 (t, 2 H, J = 6.4 Hz, CH_2S), 2.47 (t, 2 H, J = 6.8 Hz, CH_2S), 2.41 (s, 3 H, CH_3), 2.03 (quintet, 2 H, J = 6.4 Hz, $CH_2CH_2CH_2$), 1.76 (quintet, 2 H, J = 6.8 Hz, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.1 ($C_{carbonyl}$), 143.4, 137.4, 129.8, 127.1 ($C_{aromatic}$), 43.3, 42.5, 38.7, 36.1, 32.4, 31.6, 30.0, 29.2, 21.6 (CH_3) ppm.

7-(Toluene-4-sulfonyl)-3,10-dithia-7,14-diazacyclotetradecan-1-one (S6): Vacuum dried K_2CO_3 (7.1 g, 51 mmol) was suspended in DMF (720 mL) and the mixture was heated to 95 °C. **S5** (9 g, 20.5 mmol) was dissolved in DMF (240 mL) and purged with N_2. Subsequently, the amide solution was added to the mixture via syringe pump (25 mL/h). After addition completed, the reaction mixture was stirred for an additional 12 h. The solution was then cooled to room temperature and filtered. The solution was concentrated and the solid was dissolved in chloroform (700 mL). The chloroform solution was washed with 6 M HCl (4 x 100 mL), water (4 x 100 mL), brine (1 x 100 mL), dried over Na_2SO_4, filtered, and concentrated. The yellow residue was washed with hot 100 % ethanol to afford a colorless solid of **S6** (4.6 g, 56 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.66 (d, 2 H, J = 8.3 Hz, $H_{aromatic}$), 7.31 (d, 2 H, J = 8.3 Hz, $H_{aromatic}$), 6.98 (bt, 1 H, N*H*), 3.41 (q, 2 H, J = 6.5 Hz, CH_2NH), 3.22 (s, 2 H, SCH_2CO), 3.15 (t, 2 H, J = 7.5 Hz, CH_2NTs), 3.11 (t, 2 H, J = 7.5 Hz, CH_2NTs), 2.77 (t, 2 H, J = 7.5 Hz, CH_2S), 2.64 (t, 2 H, J = 7.5 Hz, CH_2S), 2.56 (t, 2 H, J = 6.5 Hz, CH_2S), 2.43 (s, 3 H, CH_3), 1.98-1.81 (m, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.2 ($C_{carbonyl}$), 143.7, 135.2, 129.8, 127.3 ($C_{aromatic}$), 49.2, 38.7, 37.6, 31.9, 31.7, 30.3, 29.7, 29.4, 21.5 (CH_3) ppm.

4-(Toluene-4-sulfonyl)-1,8-dithia-4,11-diazacyclotetradecane (S7): Compound **S6** (4.6 g, 11.5 mmol) was dissolved in toluene (80 mL) and borane dimethyl sulfide (9.1 mL, 18.2 mmol) was added dropwise via syringe. After the addition was complete, the mixture was refluxed for 24 h. After the addition was complete, the reaction was heated to 110 °C for 24 h. The reaction was cooled to room temperature and a solution of triethanolamine (0.43 g, 2.85 mmol) in methanol (7 mL) was added slowly to the solution. The reaction was heated to 100 °C and stirred for 48 h. The reaction mixture was cooled to room temperature and concentrated. The solid product was taken up in chloroform (70 mL) and washed with water (2 x 10 mL), dried over Na_2SO_4, filtered, and concentrated to give **S7** (4.1 g, 92 %) as a colorless solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.69 (d, 2 H, J = 8.2 Hz, $H_{aromatic}$), 7.30 (d, 2 H, J = 8.2 Hz, $H_{aromatic}$), 3.27 (t, 2 H, J = 7.9 Hz, CH_2NHTs), 3.23 (t, 2 H, J = 7.9 Hz, CH_2NH), 2.82-2.73 (m, 8 H, CH_2N/ CH_2S), 2.63 (t, 2 H, J = 6.6 Hz, CH_2S), 2.59 (t, 2 H, J = 6.9 Hz, CH_2S), 2.42 (s, 3 H, CH_3), 1.97 (quintet, 2 H, J = 6.9 Hz, $CH_2CH_2CH_2$), 1.79 (quintet, 2 H, J = 6.6 Hz, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.6, 136.1, 129.9, 127.3 ($C_{aromatic}$), 50.1, 48.9, 47.8, 46.7, 34.5, 32.0, 30.4, 30.1, 29.2, 21.7 (CH_3) ppm.

1,8-dithia-4,11-diazacyclotetradecane (2): Compound **S7** (2.5 g, 6.33 mmol) and phenol (3.85 g, 40.9 mmol) were dissolved in 33 % HBr in glacial acetic acid (30 mL) and the mixture was heated to 100 °C for 24 h. An additional 10 mL of 33 % HBr in glacial acetic acid was added to the reaction mixture and stirred for another 24 h. After the reaction was complete, the solution was cooled to room temperature and concentrated. Toluene was added to the remaining oil and concentrated (2 x 40 mL). Water (50 mL) was added to dissolve the oil and the solution was washed several times with methylene chloride to remove excess phenol. The aqueous solution was adjusted to a pH of 10 using 3 M NaOH and the product was extracted with ethyl acetate (4 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give **2** (857 mg, 58 %) as a tan solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.82-2.70 (m, 18 H), 1.87 (quintet, 4 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.8, 46.6, 32.7, 28.3, 27.3 ppm. ESI-MS: calcd. for $[C_{10}H_{23}N_2S_2]^+$: 235.1; found: 235.0.



Scheme S2: Synthesis of the nickel-complexes **S9** and **1**.

[Ni(cyclam)](ClO$_4$)$_2$ (S9): Cyclam (500 mg, 2.5 mmol) was dissolved in ethanol (20 ml) and [Ni(ClO$_4$)$_2$]·6 H$_2$O (900 mg, 2.5 mmol) dissolved in ethanol (40 ml) was added. In course of the reaction a yellow precipitate was formed. The mixture was stirred for 24 h. Subsequently, the mixture was concentrated, dissolved in 40 ml acetone and precipitated by addition of diethyl ether. The solid was filtered, washed with diethyl ether and dried in vacuum to afford **S9** (880 mg, 77 %) as a yellow solid.

[Ni(cyclam)](PF$_6$)$_2$ (1): Compound **S9** (880 mg, 1.9 mmol) was suspended in warm acetonitrile (27 ml) and NaPF$_6$ (1.29 g, 7.68 mmol) was added. The color changed to green and the mixture was stirred for 72 h. Subsequently, the mixture was heated and filtered. Water was added to the green filtrate, followed by evaporation of the solvent. An orange solid was formed, which was recrystallized from water to afford **1** (790 mg, 75 %) as an orange solid.

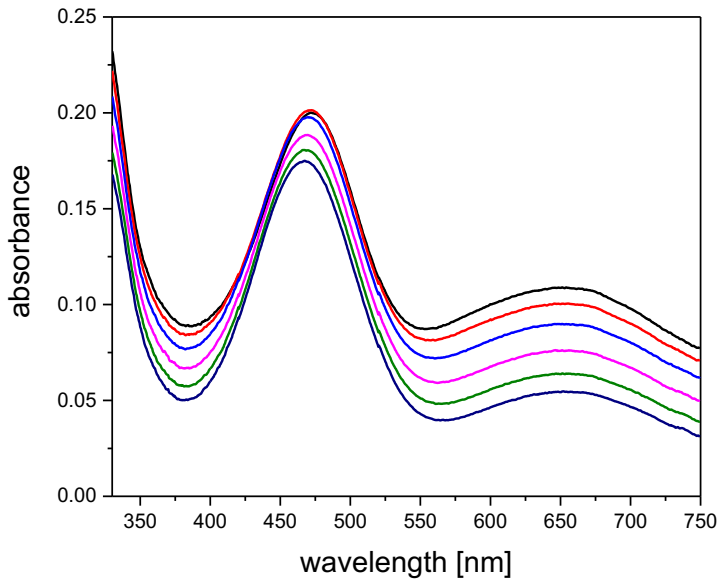


Figure S1: UV/vis titration of [Ni(cyclam)]$^{2+}$ **1** with H$_2$O. The change in absorption results from the dilution during titration.

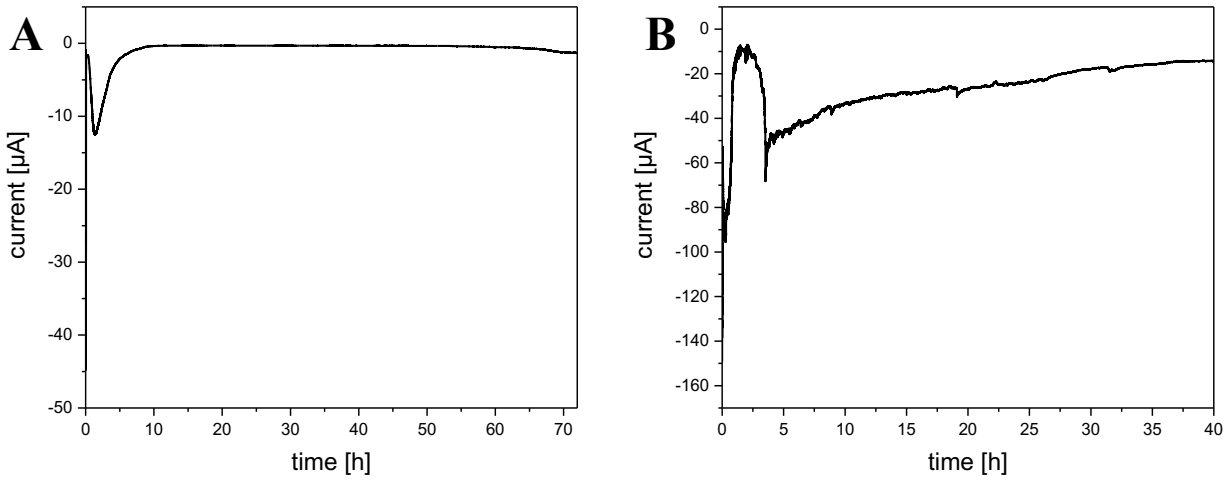


Figure S2: Long-term controlled potential coulometry of (A) 2 mg complex **3** held at -0.9 V vs NHE (after 1st reduction wave) and (B) 12 mg complex **3** held at -1.8 V vs NHE (after 2nd reduction wave). Based on the Faraday law for a 1 e^- reduction of the total amount of substance used in (A) a charge of 0.33 C should have been consumed and 0.23 C was consumed. However, according to the Nernst-equation the species is not fully reduced at this defined potential. For a 2 e^- reduction of the total amount of substance used in (B) a charge of 4.03 C should have been consumed and 3.84 C was consumed, confirming the 2 e^- reduction. Since the current of the two reduction waves of complex **3** are identical each reduction can be assigned as a 1e^- reduction process.

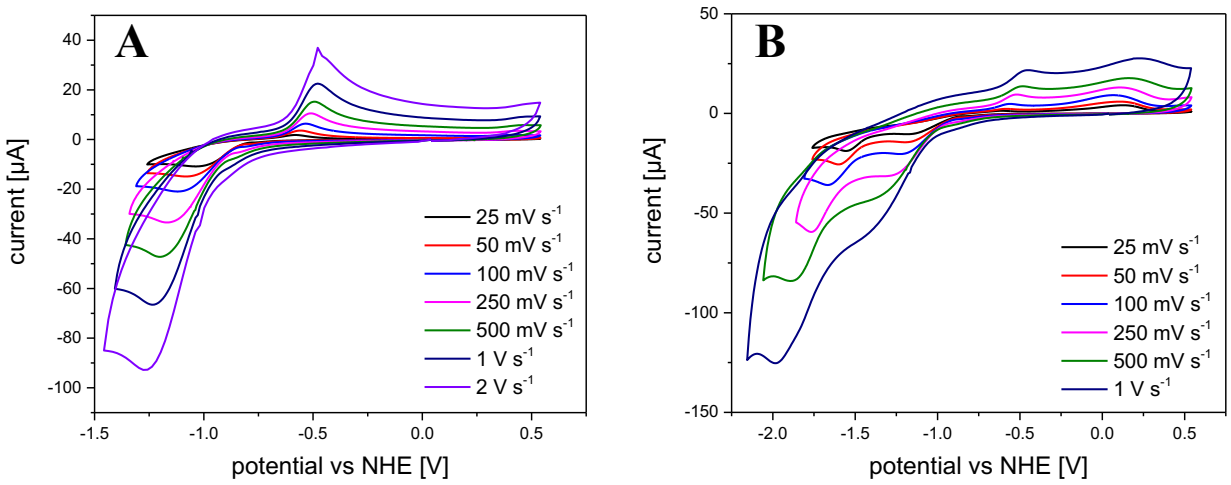


Figure S3: Cyclic voltammograms of 1 mM **3** in acetonitrile, with 0.1 M $[^{n}Bu_4N]^{+}PF_6^{-}$ at different scan rates. (A) Reversed after the first reduction wave, (B) reversed after the second reduction wave.

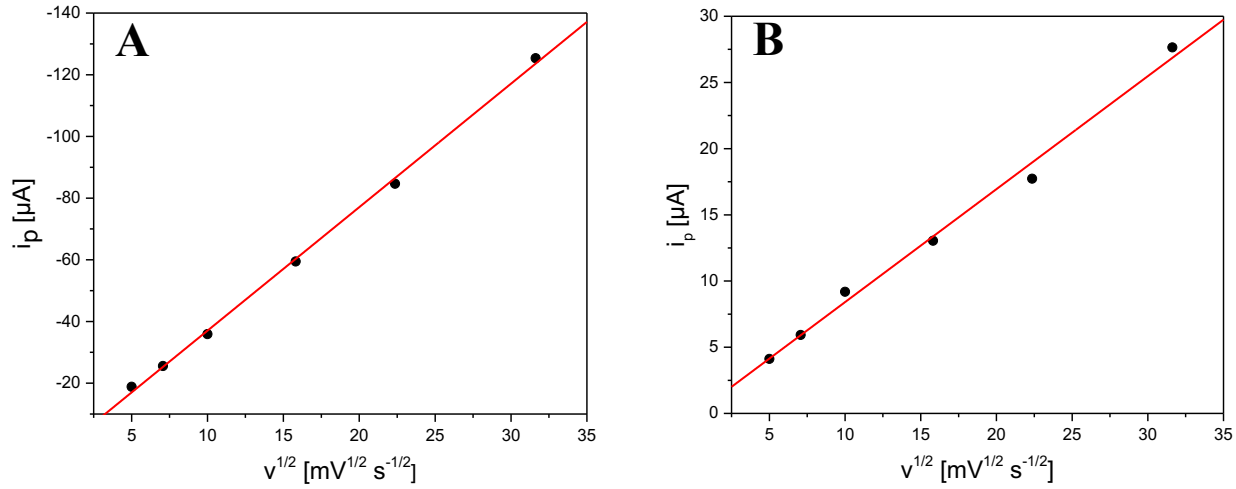


Figure S4: Figure S4: Scan rate dependency of the peak current of the second reduction wave (A) and the oxidation peak of complex **3** (B). Given the linear behavior of the peak current versus the square root of the scan rate, the data suggest that reduction of the electroactive species is diffusion controlled. An adsorbate may, however, still be formed during electrolysis. In addition, based on the rinse tests and surface analyses, a heterogeneous film is formed during electrocatalysis.

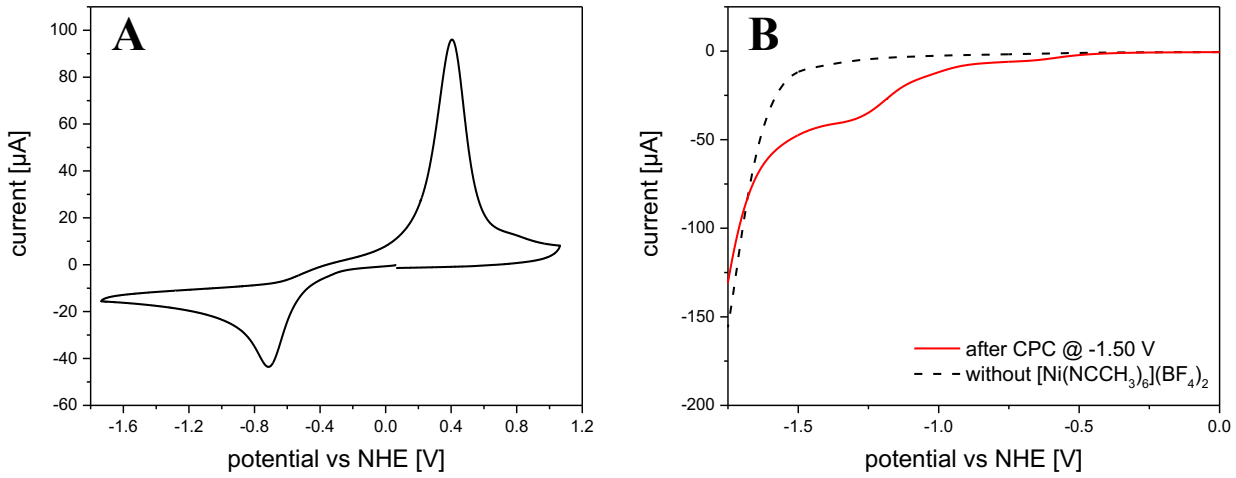


Figure S5: (A) Cyclic voltammogram of 1 mM $[Ni(NCCH_3)_6](BF_4)_2$ in acetonitrile, with 0.1 M $[^nBu_4N]^+PF_6^-$ at 100 mV s^{-1}. (B) Rinse test of $[Ni(NCCH_3)_6](BF_4)_2$.

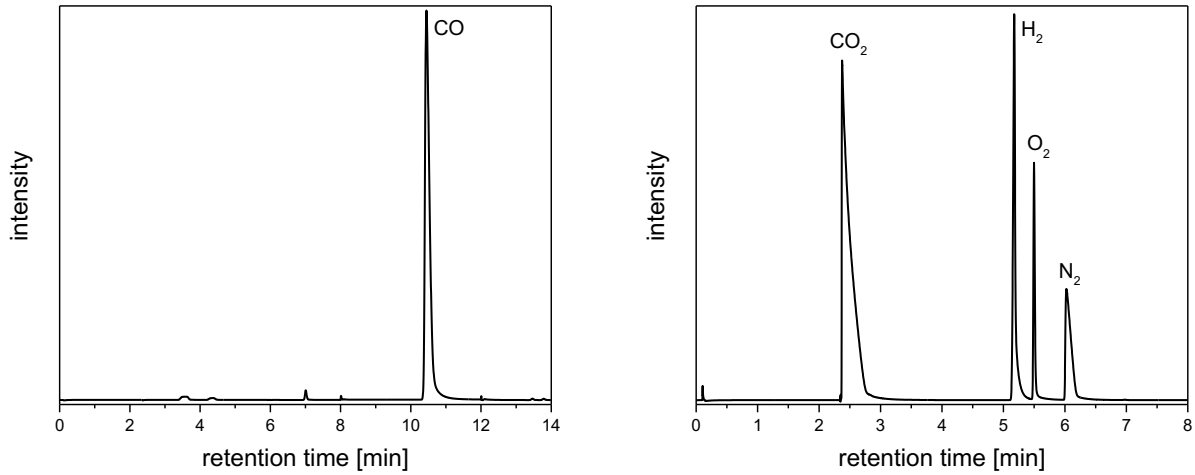


Figure S6: Generic gas chromatogram, recorded during the long-term CPC of 1 mM **3** in CO_2 saturated acetonitrile/water (4:1) and 0.1 M $[^nBu_4N]^+PF_6^-$ at -1.5 V vs NHE.

Table S1: Faradaic efficiencies of the long-term measurement for the CO_2 reduction with complex **3** as electrocatalyst.

Time [h]	CO FE [%]	H_2 FE [%]	Ratio CO/H_2
1	0.53	0.23	2.3
2	0.23	0.40	0.58
4	0.78	3.3	0.24
6	1.8	6.5	0.28
8	3.5	12	0.29
10	5.4	19	0.28
12	8.0	27	0.30
14	10	33	0.30
16	11	36	0.31
18	12	37	0.32
20	11	35	0.31
22	10	31	0.32
24	13	39	0.33
26	20	62	0.32
28	22	70	0.31
30	23	74	0.31
32	21	72	0.29

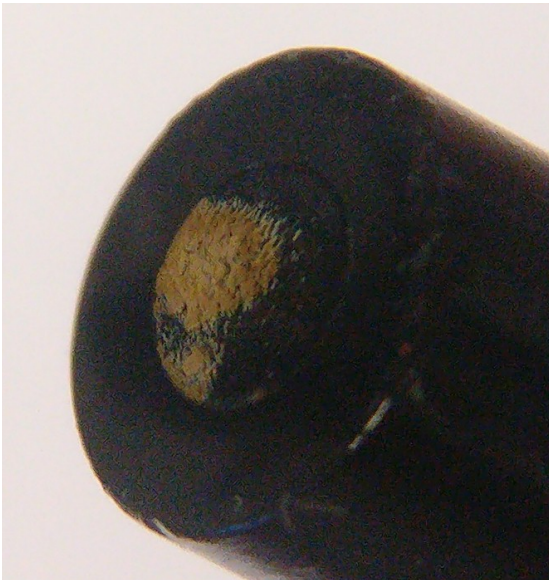


Figure S7: Glassy carbon working electrode with co-deposited species, generated during 15 h CPC of 5 µM **3** in pure acetonitrile with 0.1 M $[^{n}Bu_4N]^{+}PF_6^{-}$ at -1.1 V vs NHE.

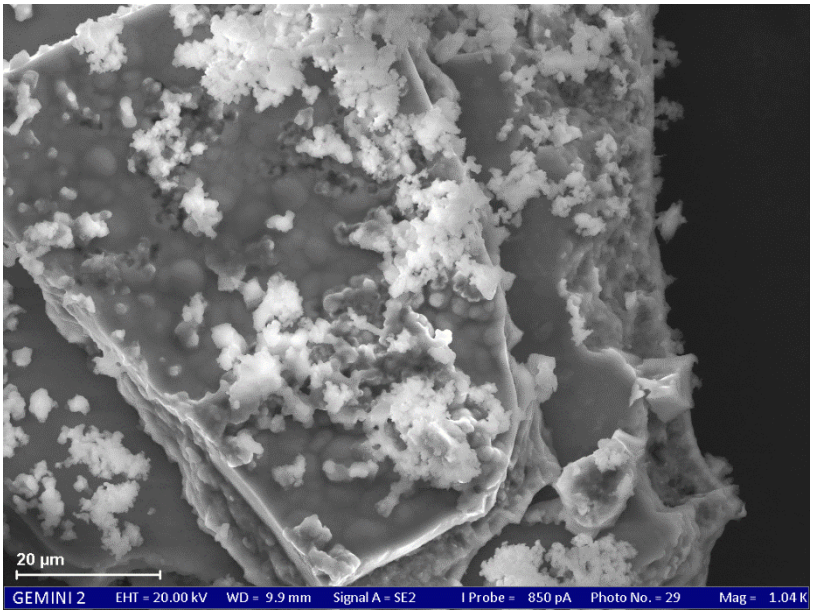


Figure S8: SEM image of the co-deposited species.

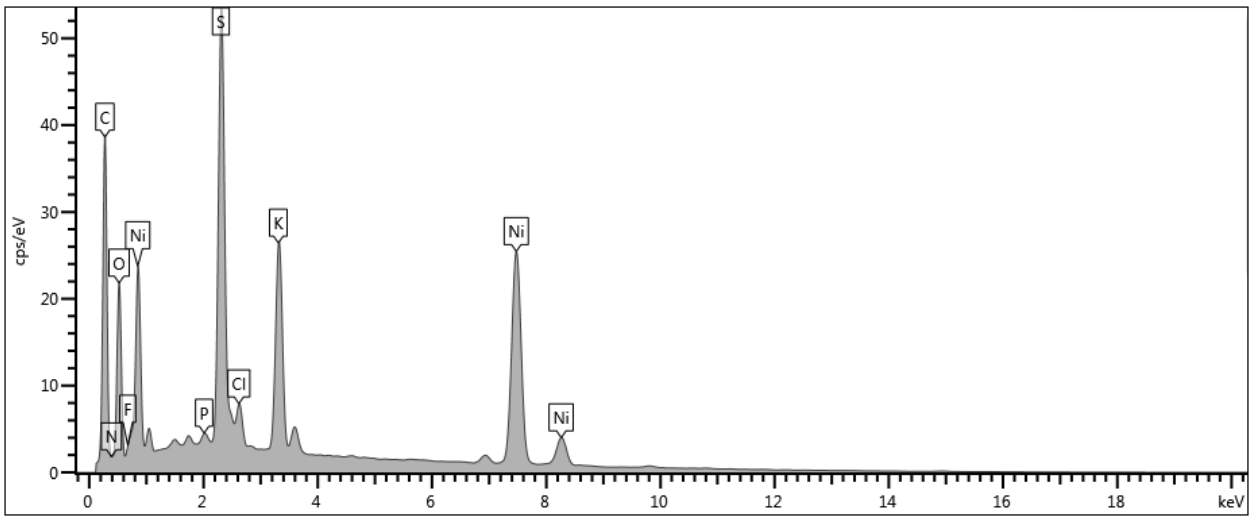


Figure S9: Generic electron dispersive X-ray (EDX) spectrum of the co-deposited species.

Table S2: Mass fractions of the co-deposited species at different spots determined by EDX.

Element	Mass fraction [%] Spot 1	Mass fraction [%] Spot 2	Mass fraction [%] Spot 3
Ni	15.4	32.8	38.7
S	6.4	5.5	5.8
N	3.4	5.8	5.8
C	51.8	32.1	29.3
O	16.5	19.9	17.2
P	0.2	0.1	0.1
F	1.4	2.2	1.4
K	4.1	1.6	1.5
Cl	0.7	0.0	0.2
Ratio $Ni_xS_yN_z$	$Ni_{1.3}S_1N_{1.2}$	$Ni_{3.3}S_1N_{2.4}$	$Ni_{3.6}S_1N_{2.3}$

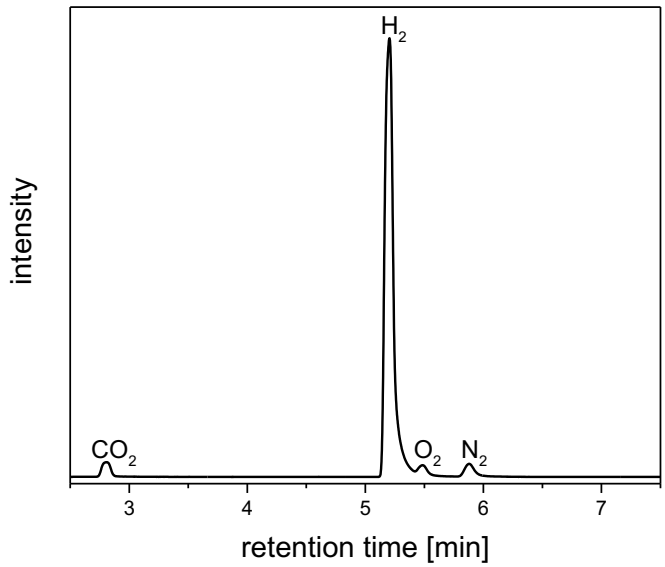


Figure S10: Generic gas chromatogram, recorded during the long-term CPC of 0.5 mM **3** in water with 350 mM acetic acid (HOAc) and 1 M KCl at -0.9 V vs NHE.

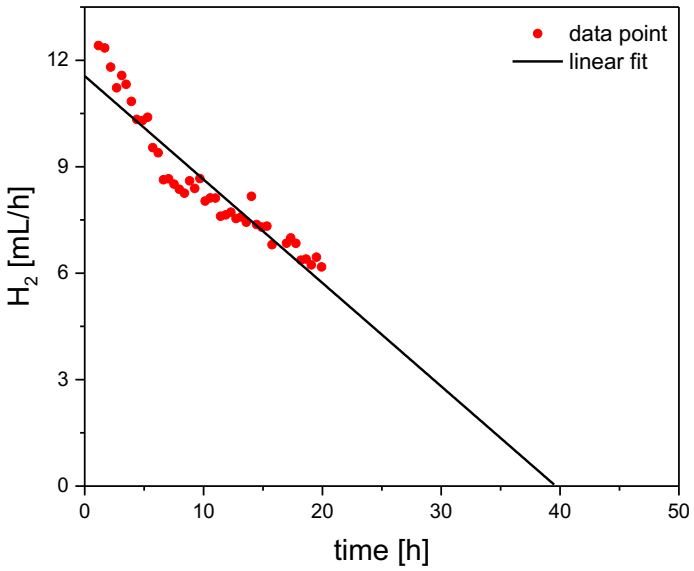


Figure S11: GC quantification of the amounts of H_2 generated by 0.5 mM **3** in water with 350 mM acetic acid (HOAc) and 1 M KCl during a long-term CPC at -0.9 V vs NHE.

X-ray data collection and structure refinement: Data collection for **3** was performed at 100 K using MoK_α radiation, λ = 0.71073 Å on a Bruker D8 Venture area detector. Crystals of compound **3** are pseudo-merohedral twins in space group *I*2/a, with the monoclinic angle β very close to 90 degrees; the relative domain volumes refined to 0.576(4):0.424(4). The structure was solved by intrinsic phasing;[2] a difference Fourier synthesis revealed disorder for the cationic complex, a counter anion and the solvent region. The final structure model was refined on F^2.[2] Two conformations of the macrocyclic ligand involve disorder of the ethylene versus propylene bridges. A perchlorate anion was treated as disordered over two edge-sharing alternative orientations. The sum of the occupancies for three mutually exclusive sites of the solvent water molecule was restrained to unity. All hydrogen atoms were introduced at their idealized positions and were refined using a riding model.

Crystallographic data including structure factors for the structures reported in this paper have been deposited at The Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–1539266.

These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S3: Crystal Data and Refinement Details for the Crystal Structure Analysis of complex **3**.

	3
Empirical formula	$C_{14}H_{28}Cl_2N_4NiO_9S_2$
Formula weight	590.13
Temperature/K	100
Crystal system	Monoclinic
Space group	*I*2/a
a/Å	12.3784(2)
b/Å	19.1075(3)
c/Å	21.1751(3)
β/°	90.0587(7)
Volume/Å^3	5008.34(13)
Z	8
ρ_{calc}/g·cm^{-3}	1.565
μ/mm^{-1}	1.204
F(000)	2448
Crytsal size/mm^3	0.08 x 0.14 x 0.36
2θ range for data collection/°	25.24
Reflection collected	47955
Independent reflections	4464
Data/restraints/parameters	4464/56/228
[a]Goodness-of-fit on F^2	1.080
[b,c]Final R indexes [I≥2σ (I)]	0.0757/ 0.1859
Final R indexes [all data]	0.0817/ 0.1919
Largest diff. peak/hole/e·Å^{-3}	-1.60/ 1.85
CCDC reference	1539266

[a] $S = \{\sum[w(F_o^2-F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$.
[c] $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

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