Supplementary Information

Evaluation of Iron-based electrocatalysts for water oxidation – an on-line mass spectrometry approach

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1. Experimental

1.1 General

All chemicals were used as received and without further purification. Cyclam was obtained from Alfa Aesar and iodoacetic acid was obtained from Acros Organics. $FeCl_2 \cdot 4H_2O$ was obtained from Sigma Aldrich and stored under Argon. Cylcamacetate·4HCl and *cis*-$[Fe(cyclam)Cl_2]Cl$ (**1**) were synthesized according to literature procedures.[1] The syntheses of complexes **2** and **3** were performed using standard Schlenk-line techniques. Acetonitrile was degassed according to standard freeze-pump-thaw protocols.

IR spectra were recorded on a Perkin Elmer UATR (Single Reflection Diamond) Spectrum Two device. Mass spectra were measured on a Finnigan Aqua Mass ESI spectrometer. NMR spectra were measured on a Bruker DPX 300 spectrometer. EPR spectra were recorded on a Bruker EMXplus X-band spectrometer. Elemental analyses were performed by Mikroanalytisches Laboratorium Kolbe in Germany.

1.2 Electrochemical experiments

Electrochemical measurements were performed in a custom made single-compartment glass cell on Ivium potentiostats, operated by IviumSoft software, using a three-electrode setup. The working electrode was a pyrolytic graphite (PG) disc with a (geometric) surface area of 0.2 cm^2 used in hanging meniscus configuration. A large surface area gold plate was used as a counter electrode. The reference electrode was a reversible hydrogen electrode (RHE) made up of a platinum mesh in H_2-saturated electrolyte at the same pH as the working solution. The cell and the reference electrode were connected via a Luggin capillary. A fresh PG surface was prepared before each experiment by polishing the working electrode with sandpaper and subsequent removal of excess debris by sonication in Milli-Q grade water for at least 5 minutes.

All glassware used in electrochemical measurements was routinely cleaned of any organic contamination by boiling in 3:1 mixture of concentrated sulfuric and nitric acid. Prior to each experiment the glassware was cleaned by threefold rinsing and boiling in Milli-Q grade water. The electrolyte solutions were prepared from p.a. grade chemicals obtained from Merck (Suprapur®) and Milli-Q grade water.

Prior to measurements, the electrolyte solution was purged of air by bubbling with Argon (Linde, Ar 6.0) for at least 20 minutes. During the measurements, the cell was constantly kept under Argon flow to prevent air from entering.

Complete dissolution of crystalline complex **1** in the electrolyte solution was achieved by sonication for at least 20 minutes. Since the solubility of **1** in 0.1 M $NaClO_4$ solution appears to be substantially lower compared to 0.1 M phosphate buffer, for the experiments in $NaClO_4$ media the complex was dissolved in Milli-Q water instead and subsequently added to the electrolyte solution. In these experiments, the concentration of electrolyte in the cell was adjusted to account for the resulting dilution.

In all cases a 1.1 mM concentration of catalyst and a pyrolytic graphite working electrode were used unless stated otherwise.

For the OLEMS measurements, the gasses formed at the working electrode were collected via a hydrophobic tip (KEL-F with a porous Teflon plug) in close proximity to the surface of the working electrode and analyzed in a QMS 200 mass spectrometer. A detailed description of the OLEMS setup is available elsewhere.[2] All electrochemical potential cycling in combination with OLEMS was done at a scan rate of 1 mV/s.

For the mass spectrometry data recorded during cylic voltammetry, background correction was done by assuming an exponential decay fit (concerns Figures 2b, 3, 4, S14, S17 and S19).

1.3 Synthesis of [Fe(cyclamacetate)Cl] (2)

Cyclamacetate·4HCl (112 mg, 0.28 mmol) was suspended in 5 mL acetonitrile and dissolved upon addition of triethylamine (0.2 mL, 1.42 mmol). Subsequently $FeCl_2 \cdot 4H_2O$ (60 mg, 0.30 mmol) dissolved in 5 mL acetonitrile was added. The mixture was left to stir over night. The white precipitate was subsequently filtered off, washed with acetonitrile (3 x 5 mL) and dried in vacuo to give **2** as a white solid. Yield: 67 mg (0.19 mmol, 69%)

ESI-MS (1:1 MeOH:H_2O) calcd. for $C_{12}H_{25}ClFeN_4O_2$ $[M]^+$ 348.1; Found: $[M-Cl]^+$ 313.1, $[M-Cl+OH]^+$ 330.1, $[M-Cl+OMe]^+$ 344.2

Elemental analysis calcd. (%) for $C_{12}H_{25}ClFeN_4O_2$ (348.65 g/mol): C 41.34, H 7.23, N 16.07 Found: C 41.16, H 7.47, N 15.87

1.4 Synthesis of *trans*-[Fe(cyclam)Cl_2] (3)

To a suspension of cyclam (40 mg, 0.20 mmol) in 5 mL acetonitrile, $FeCl_2 \cdot 4H_2O$ (40 mg, 0.20 mmol) dissolved in 5 mL acetonitrile was added. The mixture was left to stir over night. The pale pink solid was subsequently filtered off, washed with acetonitrile (3 x 5 mL) and dried in vacuo to give **3** as a pale pink solid. Yield: 42 mg (0.13 mmol, 64%)

ESI-MS (MeOH) calcd. for $C_{10}H_{24}Cl_2FeN_4$ $[M]^+$ 327.1; Found: $[M\text{-}H\text{-}Cl]^+$ 290.1, $[M\text{-}H]^+$ 326.0

Elemental analysis calcd. (%) for $C_{10}H_{24}Cl_2FeN_4$ (327.07 g/mol): C 36.72, H 7.40, N 17.13 Found: C 38.31, H 8.08, N 16.48

1.5 Elemental analysis of *cis*-[Fe(cyclam)Cl_2]Cl (1)

Elemental analysis calcd. (%) for $C_{10}H_{24}Cl_3FeN_4$ (362.52 g/mol): C 33.13, H 6.67, N 15.45 Found: C 33.33, H 6.50, N 15.38

1.6 Sample preparation

For experiments with the in situ oxidized complexes **2** and **3**, the respective Fe^{II}-complex was dissolved in air-saturated solvent and measured within minutes. In case of EPR and NMR experiments, the solution was kept under air for the entire duration. Glycerol was added to the EPR samples prior to freezing to sample at 77 K to obtain a better glass. Electrochemistry experiments with samples of oxidized complexes **2** and **3** were purged with argon after the Fe^{III} state was obtained and used as described earlier.

2. Figures

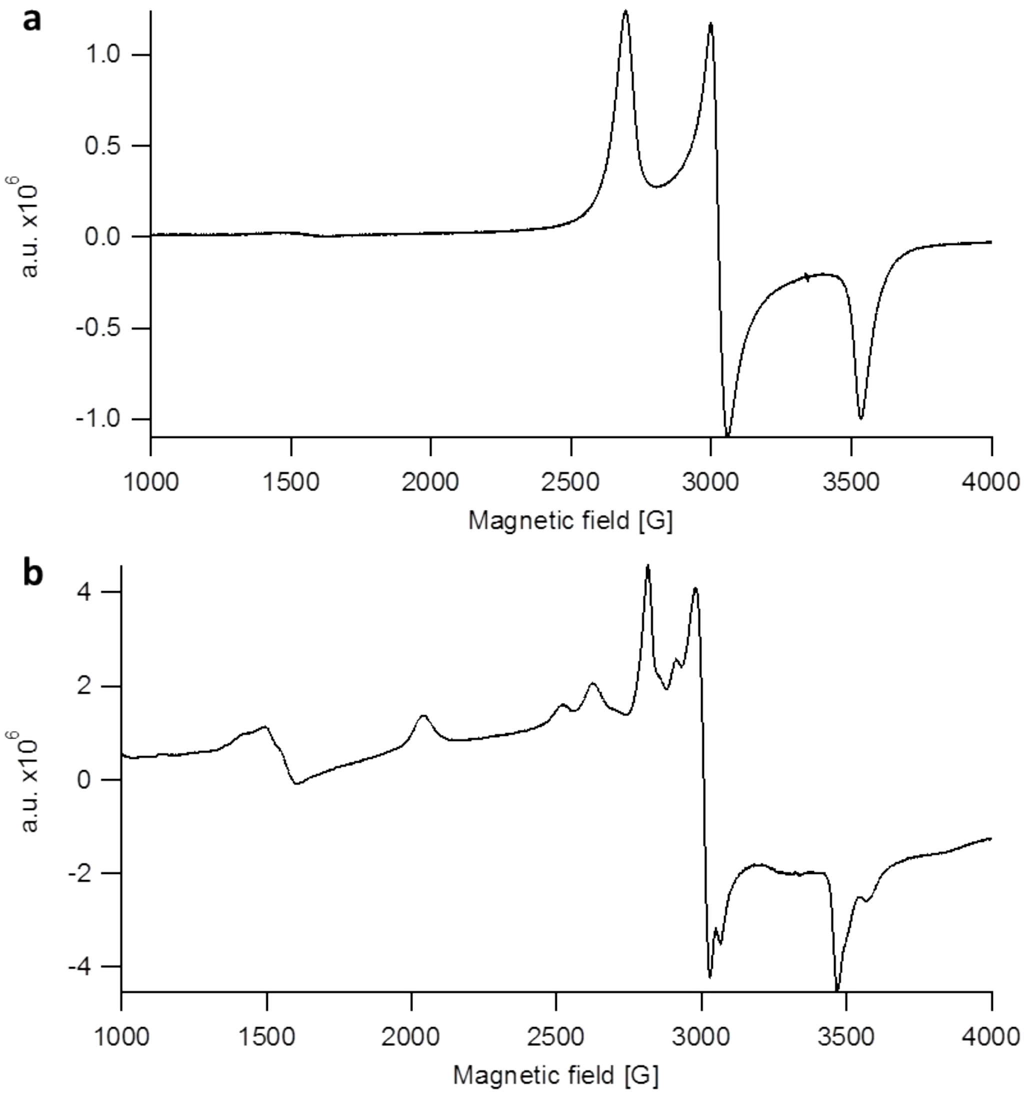

Fig. S1: X-band EPR spectra of the *in situ* oxidized complexes **2** and **3** in water/glycerol at 77K. (a) Oxidized complex **2**; ν = 9.348 GHz; g-values: 2.48, 2.21, 1.89 (b) Oxidized complex **3**; ν = 9.354 GHz; g-values: 2.38, 2.23, 1.92

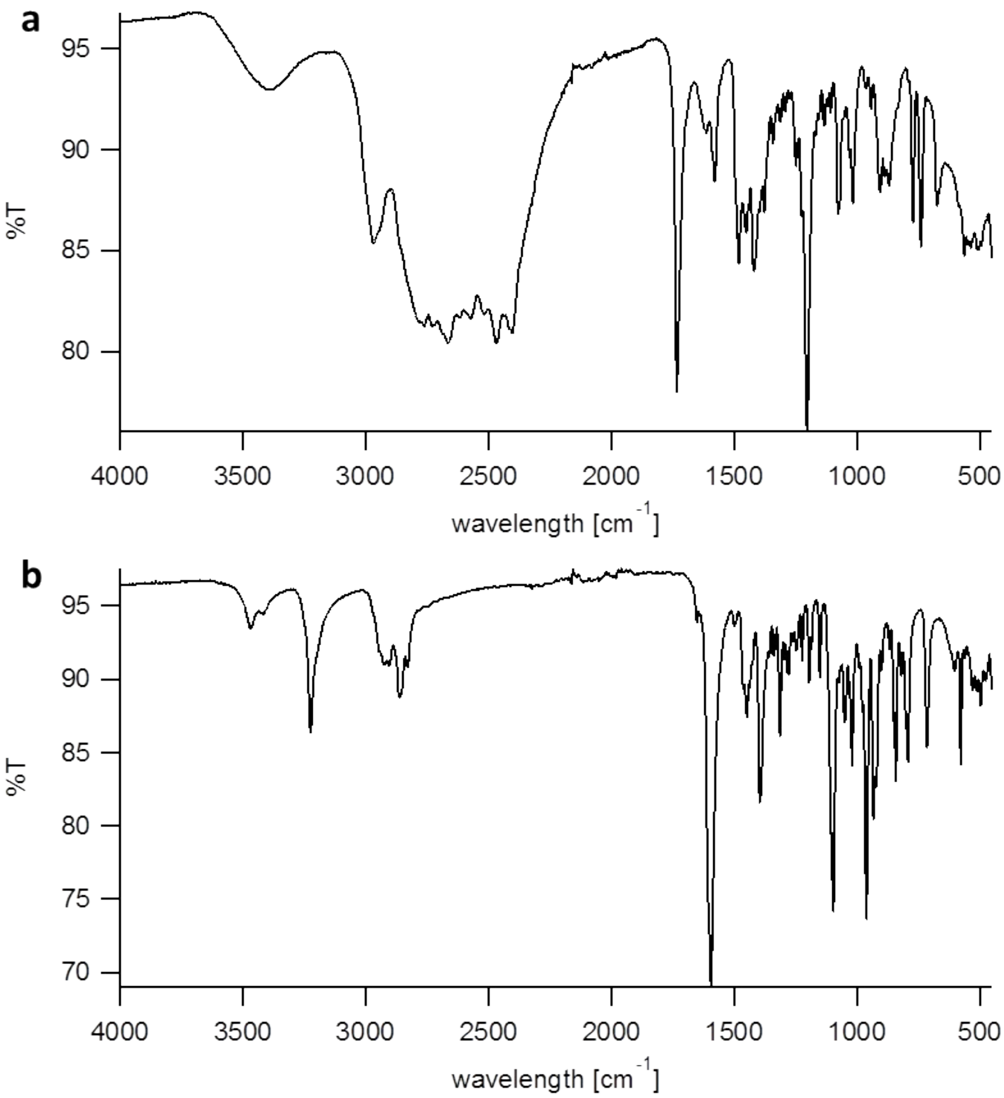

Fig. S2: IR spectrum of (a) cyclamacetate·4HCl (b) [Fe(cyclamacetate)Cl] (**2**); with C=O stretch frequencies of (a) 1734[1b] cm^{-1} and (b) 1595 cm^{-1}.

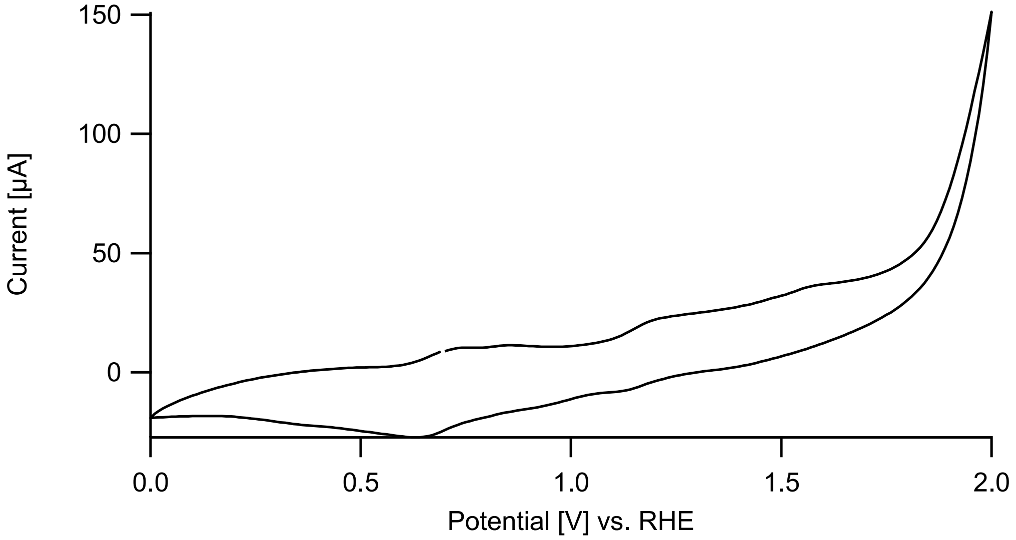

Fig. S3: Voltammogram of *cis*-[Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s

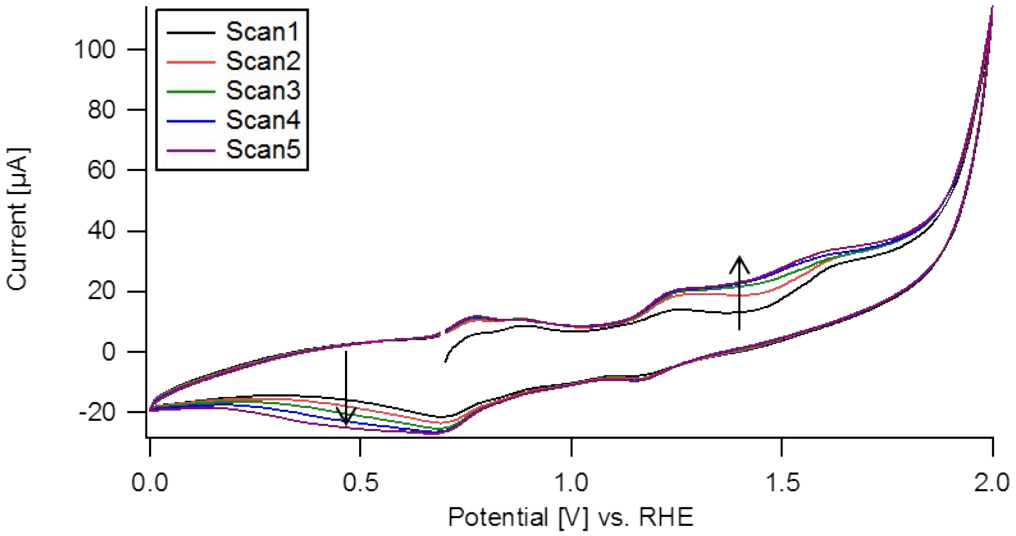

Fig. S4: Voltammogram of *cis*-[Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s before chronoamperometry (1.9V, 180 s). We assign the buildup of reductive current below 0.5 V in the cathodic scan to the reduction of the generated oxygen.

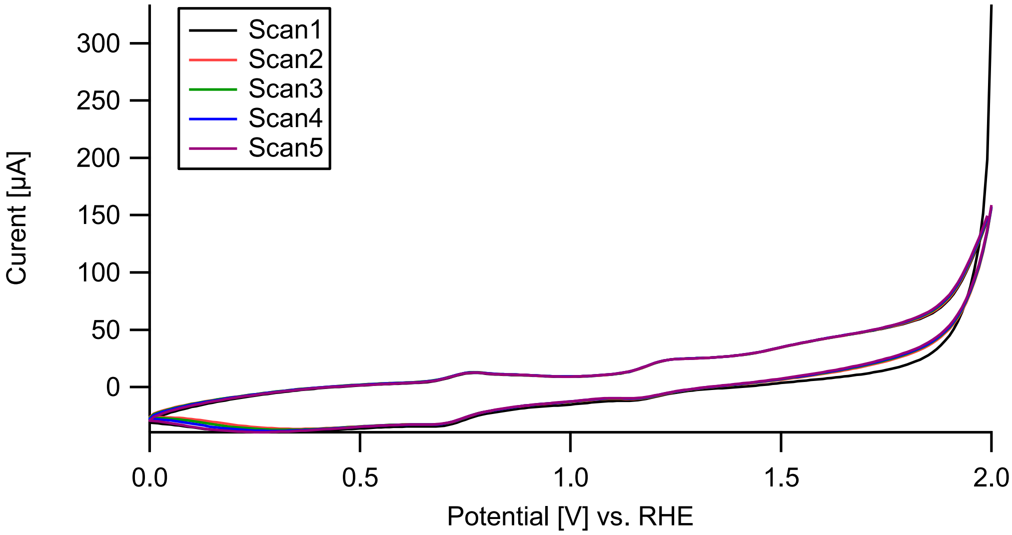

Fig. S5: Voltammogram of *cis*-[Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s recorded immediately (<10 s) after chronoamperometry (1.9V, 180 s). The peak at 2 V in scan one is a result of the jump from the resting potential (0.7 V) to 2 V for the cathodic scan.

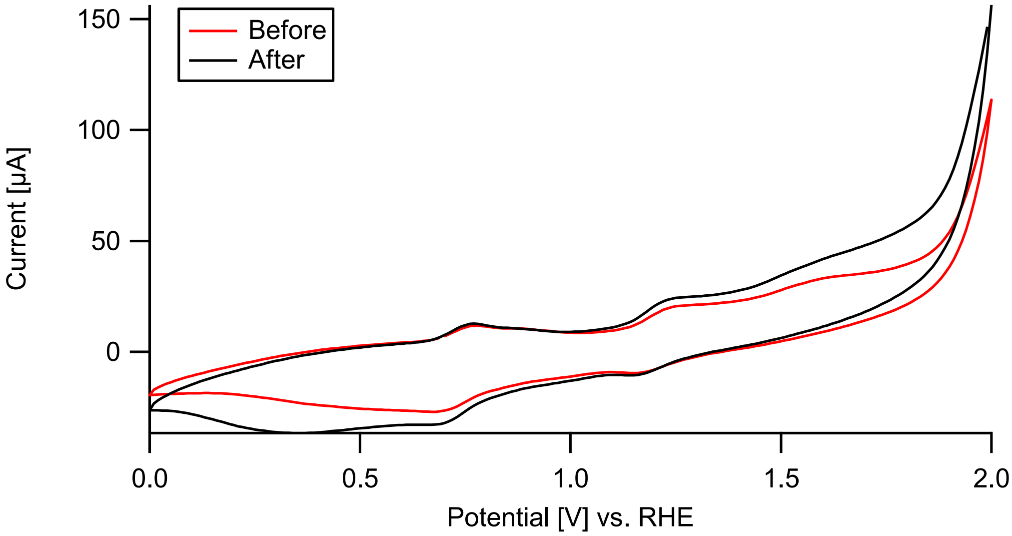

Fig. S6: Comparison of voltammograms of *cis*-[Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s before and after chronoamperometry (1.9 V, 180 s); aside from the reductive current below 0.5 V and a slightly higher oxidative current beyond 1.5 V, the basic features of the CV are identical before and after the chronoamperometry experiment, indicating the complex remains mostly intact. We assign the reductive current below 0.5 V to the oxygen reduction reaction, as oxygen levels have significant increased after the amperometry experiment. We assigned the slightly higher oxidative current to oxidative modifications of the carbon electrode.

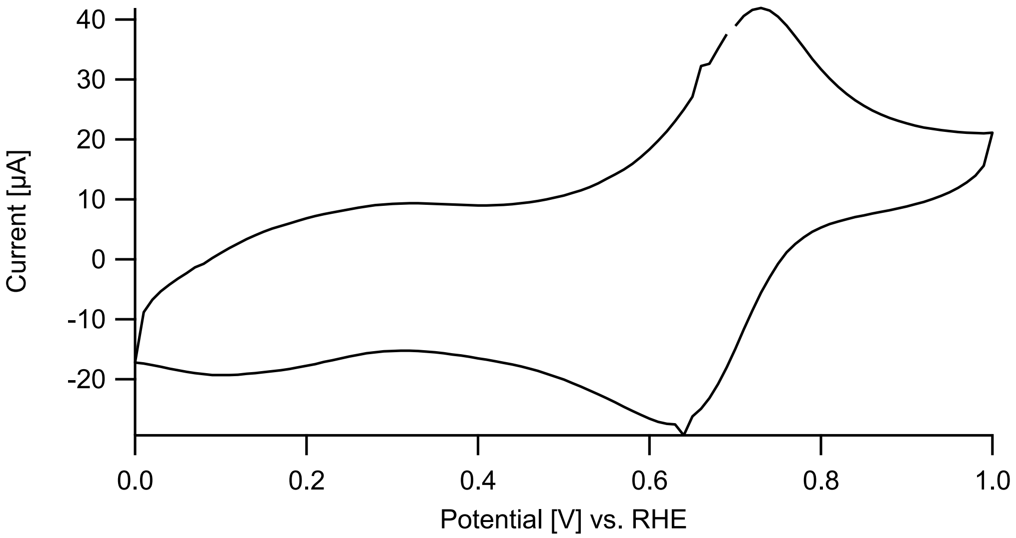

Fig. S7: Voltammogram showing the Fe$^{II/III}$ redox-couple of [Fe(cyclamcetate)Cl] (**2**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s

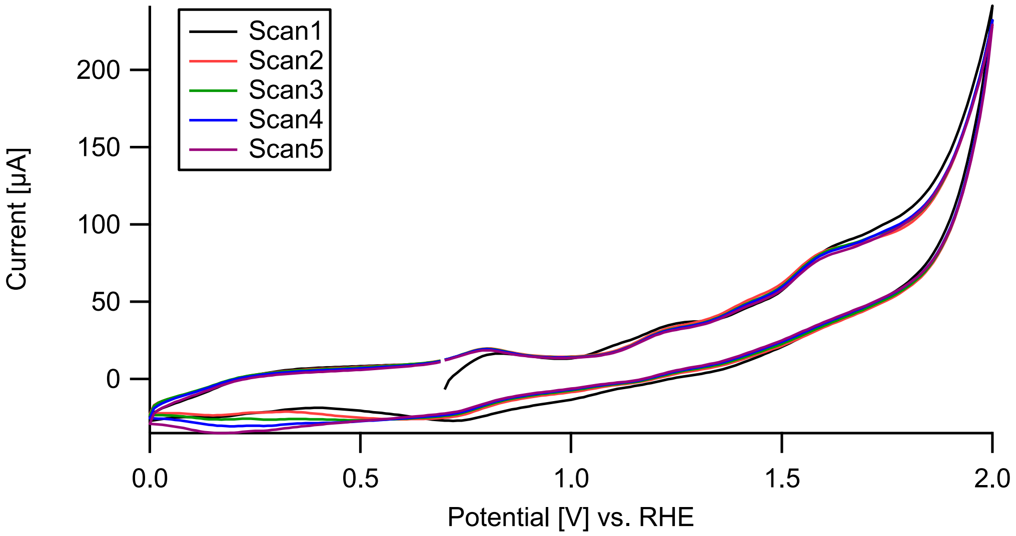

Fig. S8: Voltammograms of [Fe(cyclamacetate)Cl] (**2**) in 0.1 M $NaClO_4$ at a scan rate of 10 mV/s; besides the noticeable buildup of reductive current between 0.5 V, which we assign to reduction of the generated oxygen, the voltammogram does not change considerably over the course of at least five scans, indicating that the complex remains largely intact without the formation of any detectable decomposition products on that time scale.

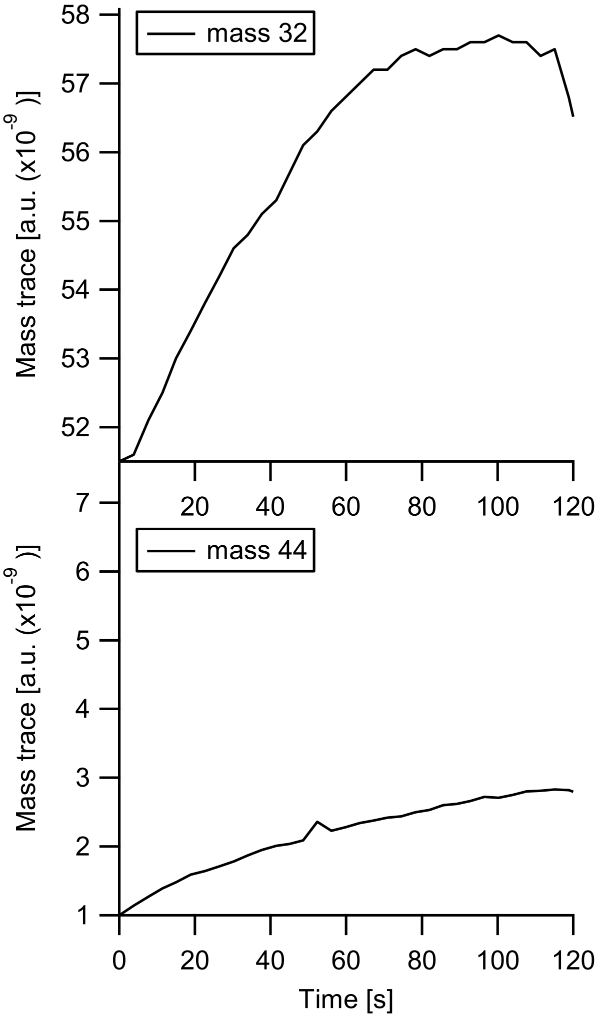

Fig. S9: The m/z traces for [Fe(cyclamacetate)Cl] (**2**) recorded via OLEMS during chronoamperometry measurement at 1.9 V vs. RHE in 0.1 M $NaClO_4$. Depicted are the O_2 trace (top) and CO_2 trace (bottom).

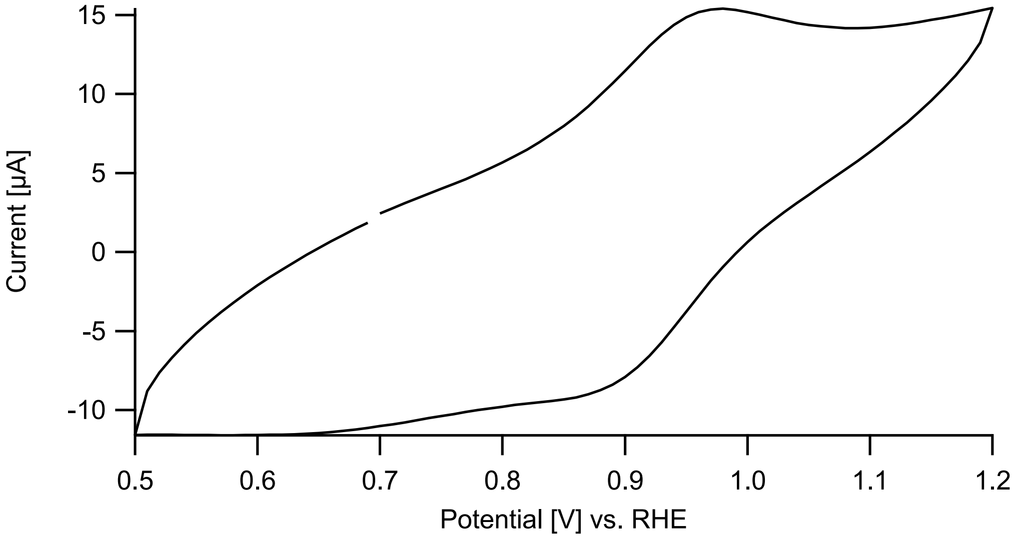

Fig. S10: Voltammogram showing the Fe$^{II/III}$ redox-couple of [Fe(cyclam)Cl$_2$] (**3**) in 0.1 M NaClO$_4$ at a scan rate of 10 mV/s

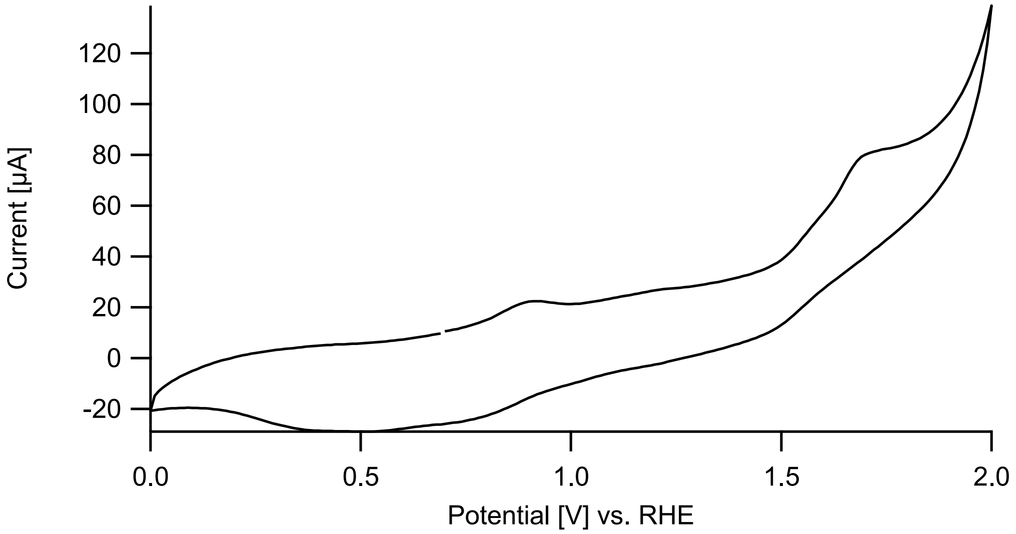

Fig. S11: Voltammogram of *trans*-[Fe(cyclam)Cl$_2$] (**3**) in 0.1 M NaClO$_4$ at a scan rate of 10 mV/s

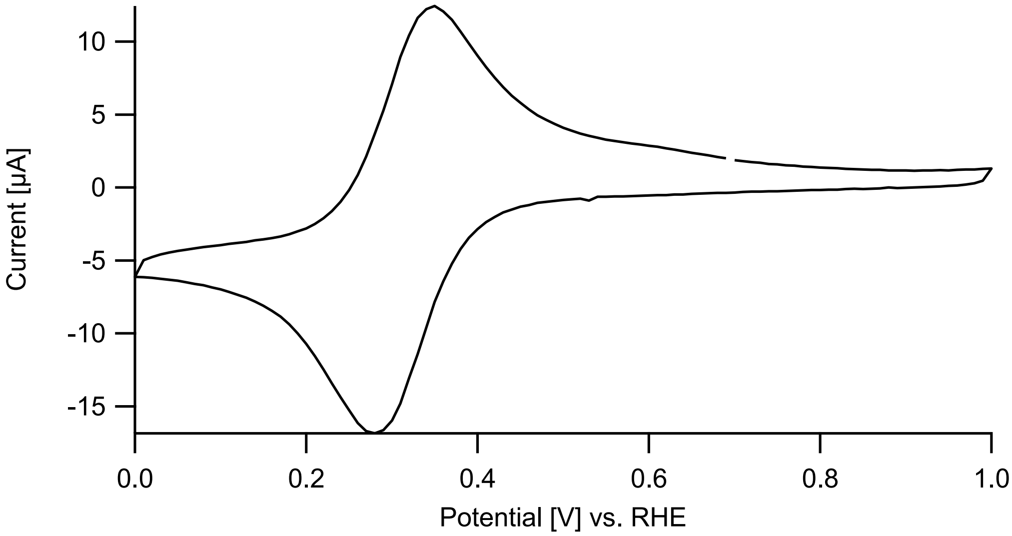

Fig. S12: Voltammogram showing the Fe$^{II/III}$ redox-couple of *cis*-[Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M phosphate buffer (pH 7.5) at a scan rate of 10 mV/s

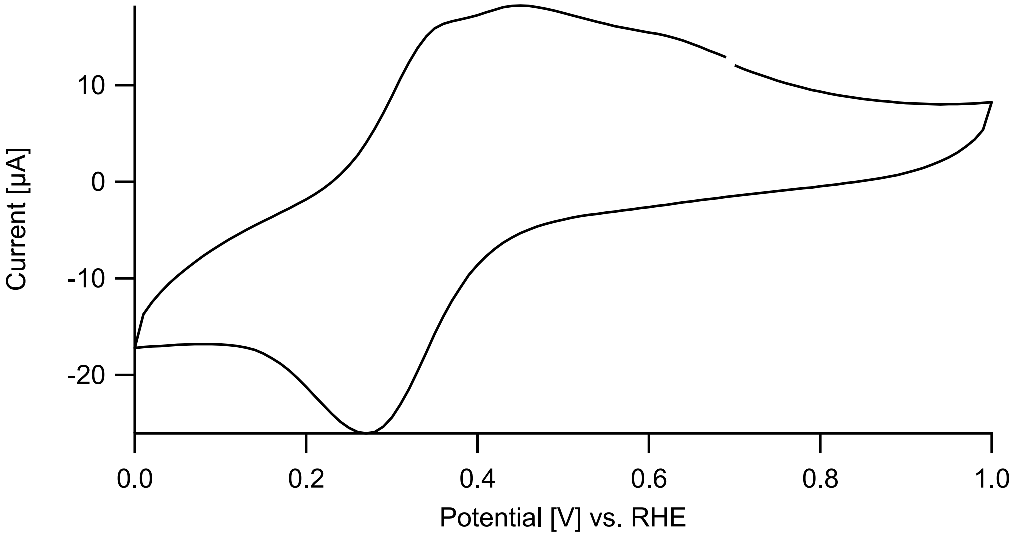

Fig. S13: Voltammogram showing Fe$^{II/III}$ redox-couple of *trans*-[Fe(cyclam)Cl_2] (**3**) in 0.1 M phosphate buffer (pH 7.5) at a scan rate of 10 mV/s

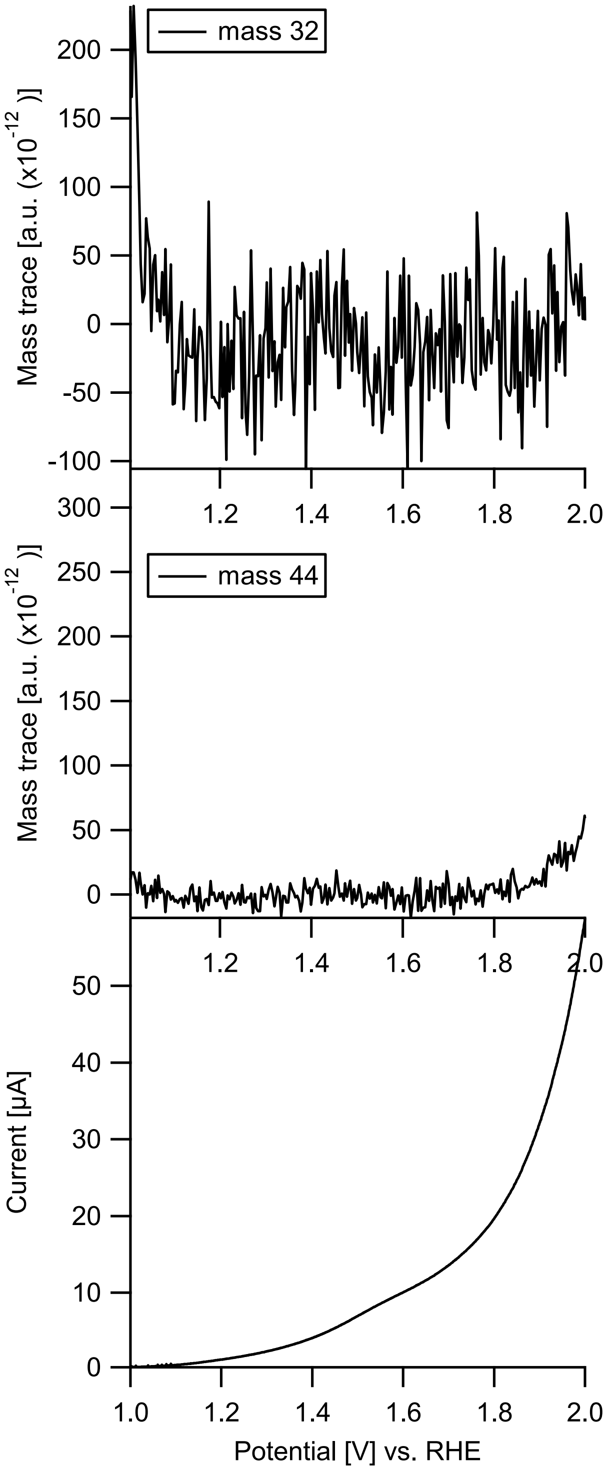

Fig. S14: OLEMS measurements of [Fe(cyclam)Cl_2]Cl (**1**) in 0.1 M phosphate buffer (pH 7.5). Depicted is the forward scan of the cyclic voltammetry experiment with the m/z trace for O_2 (top), m/z trace for CO_2 (middle) and corresponding current (bottom).

Fig. S15: Solid material deposited onto the PG electrode surface during OLEMS measurement of *trans*-[Fe(cyclam)Cl_2] (**3**) in 0.1 M phosphate buffer (pH 7.5)

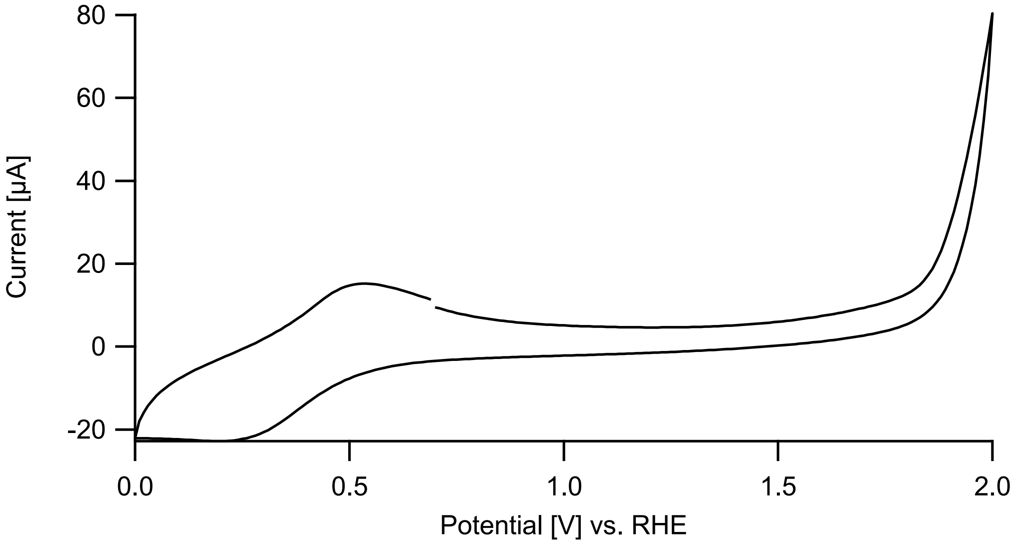

Fig. S16: Voltammogram of the deposit after OLEMS measurement of *trans*-[Fe(cyclam)Cl_2] (**3**) in phosphate buffer (pH 7.5) at a scan rate of 10 mV/s

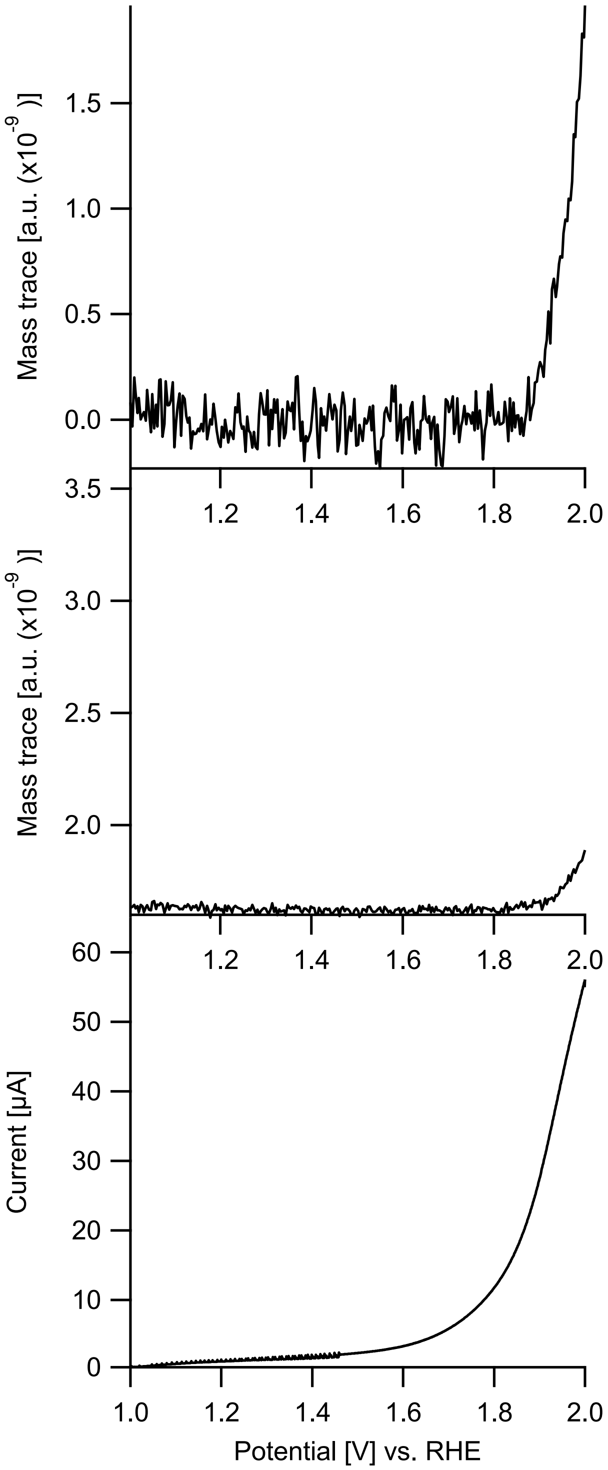

Fig. S17: OLEMS measurements of the blue deposit in 0.1 M phosphate buffer (pH 7.5). Depicted is the forward scan of the cyclic voltammetry experiment with the m/z trace for O_2 (top), m/z trace for CO_2 (middle) and corresponding current (bottom).

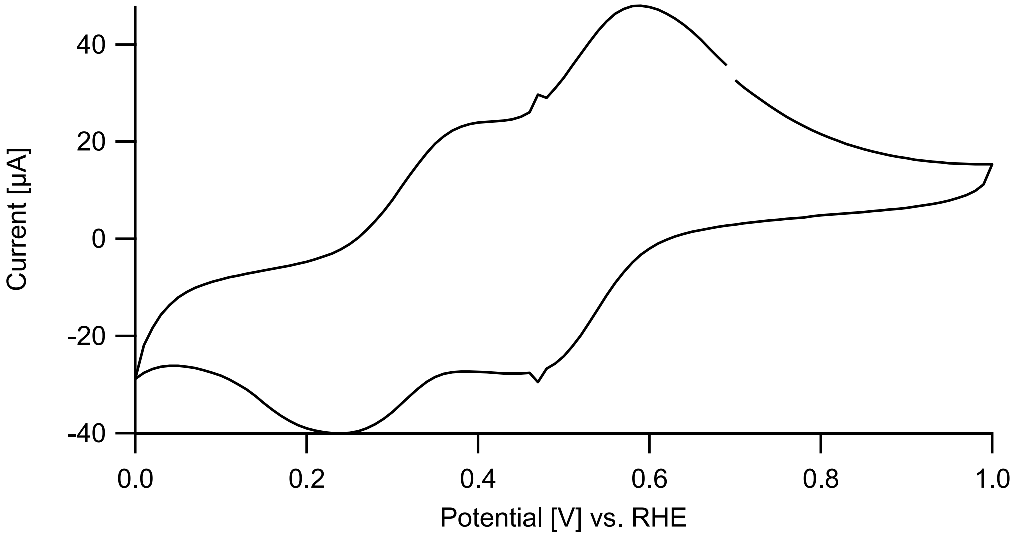

Fig. S18: Voltammogram showing the Redox-couples of [Fe(cyclamacetate)Cl] (**2**) in 0.1 M phosphate buffer (pH 7.5) at a scan rate of 10 mV/s

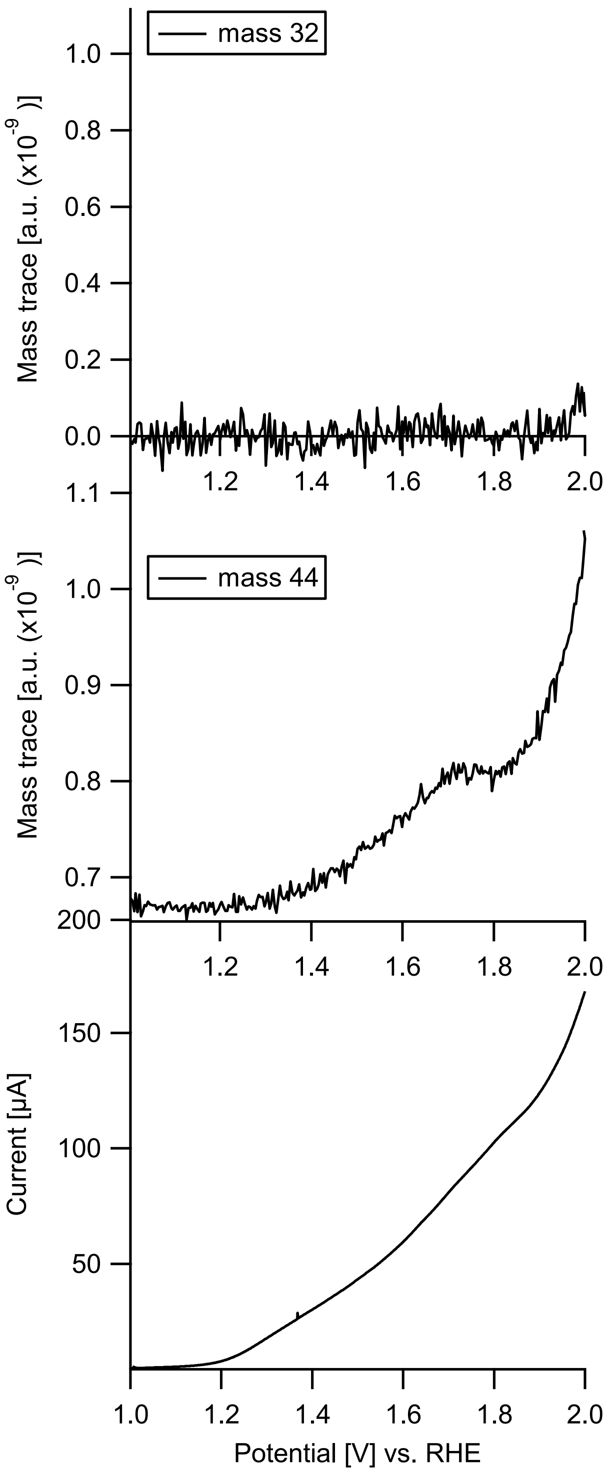

Fig. S19: OLEMS measurements of [Fe(cyclamacetate)Cl] (**2**) in 0.1 M phosphate buffer (pH 7.5). Depicted is the forward scan of the cyclic voltammetry experiment with m/z trace for O_2 (top), m/z trace for CO_2 (middle) and corresponding current (bottom).

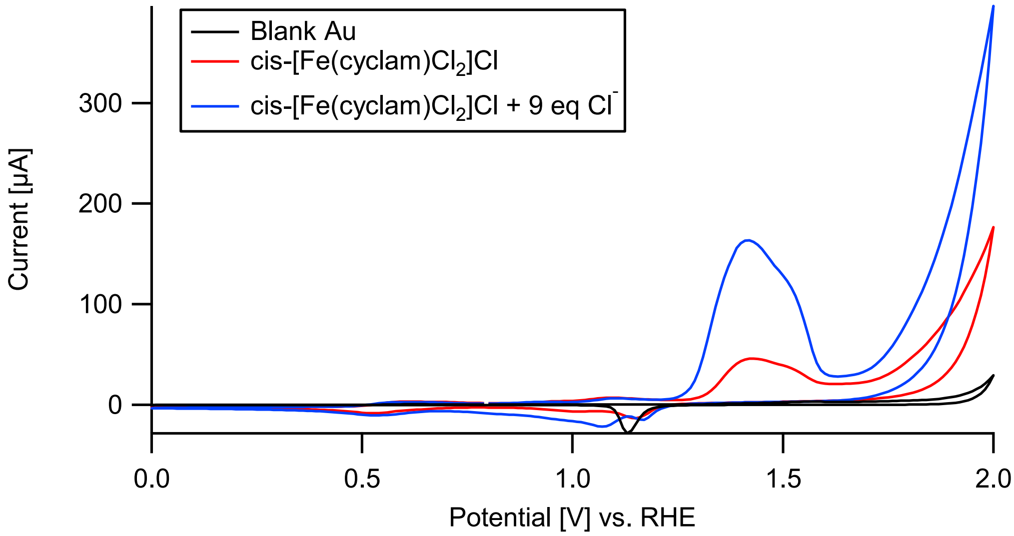

Fig. S20: Voltammogram showing a blank gold working electrode (black) as well as complex **1** on gold (red) with the addition of NaCl (blue). The current of the oxidation peak at 1.5 V vs. RHE correlates directly with the concentration of Cl$^-$ ions, indicating that chloride oxidation takes place on gold. The difference in current above 1.7 V is likely due to the roughness of the electrode surface.

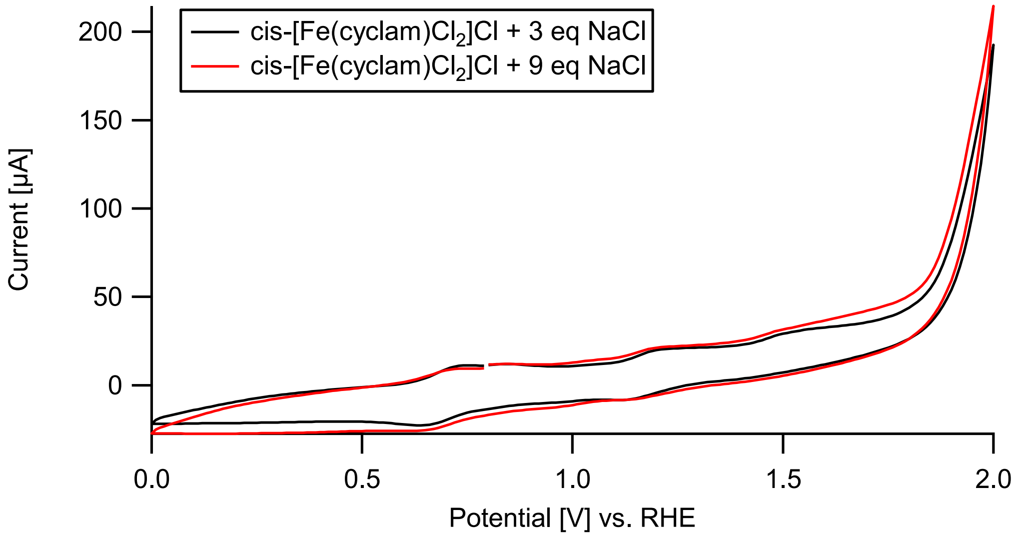

Fig. S21: Voltammogram of complex **1** on PG with added NaCl. In contrast to the observed chloride oxidation on gold (Fig. S20), the addition of several equivalents of NaCl produces no noticeable difference in the voltammogram recorded for complex **1** on pyrolytic graphite.

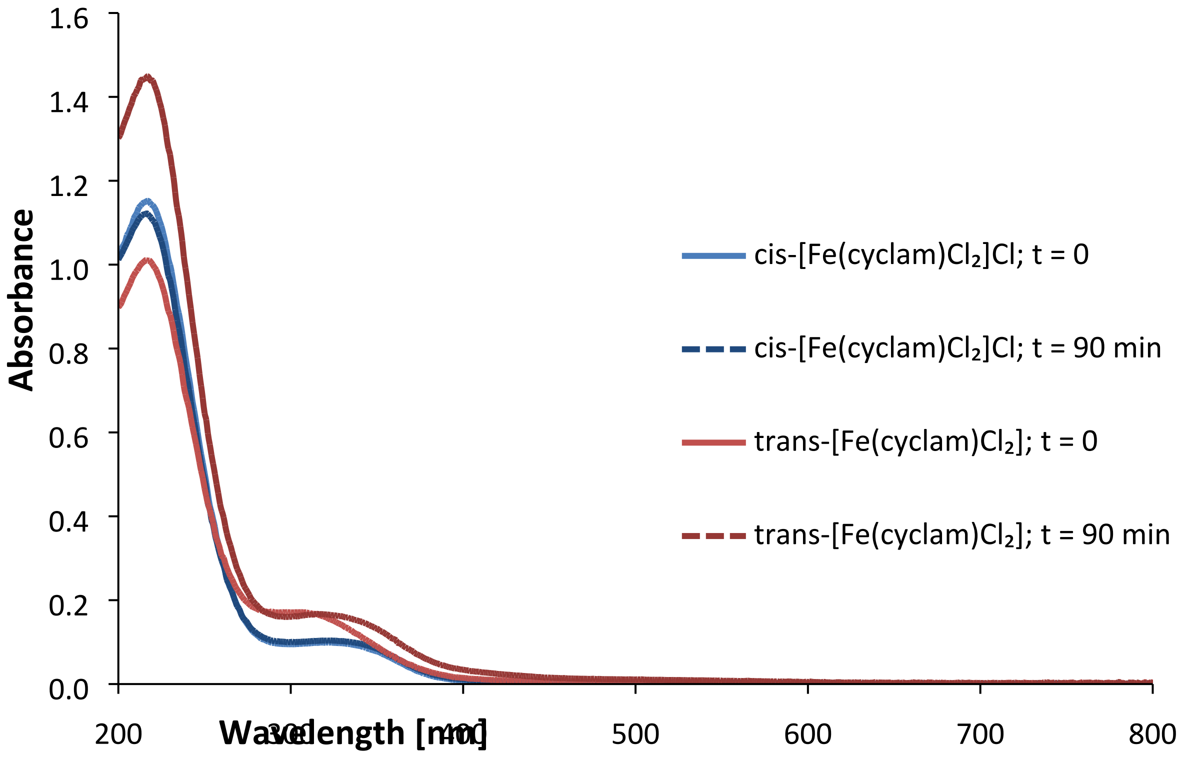

Fig. S22: UV-vis spectra of complexes **1** and **3** over time (t = 0 min → t = 90 min). Complex **1** is stable over the observed time span, whereas complex **3** changes noticeably within the first hour, likely due to oxidation from Fe^{II} to Fe^{III}. Both complexes give clearly different absorption spectra and show no signs of cis-trans-isomerization on the timescale of our experiments. Both complexes were used in identical concentrations of 0.11 mM.

3. References

1 (a) R. Guilard, O. Siri, A. Tabard, G. Broeker, P. Richard, D. J. Nurco and K. M. Smith, *Journal of the Chemical Society, Dalton Transactions*, 1997, 3459; (b) M. Studer and T. A. Kaden, *Helvetica Chimica Acta*, 1986, **69**, 2081.

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