

Electronic Supporting Information

“Highly Oxidized Diiron Complexes: Generation, Spectroscopy, and Stabilities”

Julia B. H. Strautmann, Carl-Georg Freiherr von Richthofen, Serena DeBeer

George, Eberhard Bothe, Eckhard Bill, Thorsten Glaser*

Methods and materials.

Solvents and starting materials were of the highest commercially available purity and used as received except of the CH₂Cl₂ used for the chemical oxidations. CH₂Cl₂ was dried over CaH₂ and distilled under argon atmosphere before use. All manipulations were performed using standard Schlenk-conditions.

Synthetic procedures.

Complex **1** was synthesized as described previously.¹

Oxidation of 1 to 1⁺ with [(C₆H₄Br)₃N](SbCl₆) (AR) and monitoring of the conversion of 1⁺ by UV/vis spectroscopy. The reaction was carried out using two temperable 50 mL Schlenk flasks which were cooled in-line by one circulation cryostat (Julabo F81-ME). A dip probe (Hellma 661.087-UVS) connected to a diode-array UV/vis spectrometer (J&M TIDAS II) via fibre optics was placed in one of the temperable Schlenk flasks, so that it resides in the upper half of the Schlenk flask. Dried CH₂Cl₂ (40 mL in the Schlenk flask equipped with the dip probe to ensure that the slit of the dip probe was covered completely with CH₂Cl₂ and 5 mL in the other Schlenk flask) was cooled down to the temperature of the measurement (−30°C, ..., −60°C) under argon atmosphere. Before each measurement, the background spectrum of CH₂Cl₂ at the respective temperature was

taken. CH₂Cl₂ was warmed to room temperature and **AR** (18.7 mg, 22.9 μmol) was transferred into the Schlenk flask without the dip probe. CH₂Cl₂ (20 mL) was taken out of the Schlenk flask equipped with the dip probe and filled into the Schlenk flask containing **AR. 1** (21.5 mg, 18.3 μmol) was filled in the flask with the dip probe. Both Schlenk flasks were heated to 35°C using the cryostat and stirred for 1 h at this temperature to ensure that both solids were dissolved completely. Both solutions were cooled down to the respective temperature. The solution of **AR** (20 mL, 18.3 μmol) was quickly added to the solution of **1** and UV/vis spectra were taken at fixed intervals (1 – 10 s).

Oxidation of 1 to 1²⁺ with [(C₆H₄Br)₃N](SbCl₆) (AR) and monitoring of the conversion of 1²⁺ by UV/vis spectroscopy. The reaction was carried out using the same equipment as described above. Dried CH₂Cl₂ (30 mL in the Schlenk flask equipped with the dip probe to ensure that the slit of the dip probe was covered completely with CH₂Cl₂ and 12.5 mL in the other Schlenk flask) was cooled down to the temperature of the measurement (–40°C, ... , -20 °C) under argon atmosphere and the background spectrum was taken. CH₂Cl₂ was warmed to room temperature, **AR** (28.5 mg, 34.9 μmol) was filled in the Schlenk flask with the dip probe and CH₂Cl₂ (5 mL) was added. **1** (25.6 mg, 21.8 μmol) was filled in the flask without the dip probe. Both Schlenk flasks were stirred for 1 h at this temperature to ensure that both solids were dissolved completely. Both solutions were cooled down to the respective temperature. The solution of **1** (10 mL, 17.5 μmol) was quickly added to the solution of **AR** and UV/vis spectra were taken every 1-10 seconds.

Oxidation of 1 to 1⁺ with [(C₆H₄Br)₃N](SbCl₆) (AR) for XAS measurements. **1** (18.77 mg, 16.00 μmol) was dissolved in CH₂Cl₂ (4.00 mL) and **AR** (2.45 mg, 3.00 μmol) was suspended in CH₂Cl₂ (0.75 mL) in a glove box. Both flasks were cooled down to –45°C using a aluminium cooling block and CH₂Cl₂ as a conductor of heat. They were stirred for 10 min for equilibration of temperature. The solution of **1** (0.75 mL, 3.00 μmol) was added with a pre-cooled Pasteur pipette to the suspension of **AR** during which a reddish solution formed. Samples were transferred into

¹ Glaser, T.; Pawelke, R. H.; Heidemeier, M. *Z. Anorg. Allg. Chem.* **2003**, 629, 2274-2281.

modified Moessbauer cells made of Delrin[®] with a polypropylene film window after 4 min, 8 min, or 12 min using pre-cooled Pasteur pipettes and frozen immediately in liquid nitrogen in the glove box. The XAS data for the 4 minutes and 8 minutes samples are identical within noise, while the 12 minutes point starts to show subtle changes. Thus, the 4 minutes and 8 minutes data were averaged.

Oxidation of 1 to 1²⁺ with [(C₆H₄Br)₃N](SbCl₆) (AR) for XAS measurements. **1** (14.08 mg, 12.00 μmol) was dissolved in dichloromethane (4.00 mL) and **AR** (3.67 mg, 4.50 μmol) was suspended in dichloromethane (0.75 mL) in a glove box. Both flasks were cooled down to -45°C using a aluminium cooling block and CH₂Cl₂ as a conductor of heat. They were stirred for 10 min for equilibration of temperature. The solution of **1** (0.75 mL, 2.25 μmol) was added with a pre-cooled Pasteur pipette to the suspension of **AR** during which a reddish solution formed. Samples were transferred into modified Mössbauer cells made of Delrin[®] with a polypropylene film window after 6 min, 10 min, or 12 min using pre-cooled Pasteur pipettes and frozen immediately in liquid nitrogen in the glove box. The XAS data for all three samples are identical within the noise. The finale average therefore represents the average of all three samples.

As indicated above, we have tried to reproduce the chemical oxidation for the UV/vis control as closely as possible at the beam line. However, in order to obtain high enough concentrations for XAS, the oxidant was only suspended and not completely dissolved. Complete dissolution of the oxidant under these conditions requires ~2 minutes. The first samples were therefore not taken until at least 4 minutes and were then frozen in liquid nitrogen. Therefore, the XAS data may already contain a few percent of the decay product.

Oxidation of 1 to 1²⁺ with [(C₆H₄Br)₃N](SbCl₆) (AR) for Mössbauer measurements of 1²⁺ and the conversion products. ⁵⁷Fe-enriched **1** (9.87 mg, 8.40 μmol) was dissolved in CH₂Cl₂ (1.40 mL) and **AR** (9.82 mg, 12.00 μmol) was suspended in CH₂Cl₂ (1.00 mL). Both flasks were cooled down to -30°C. 1 mL of the solution of **1** was transferred with a pre-cooled syringe to the suspension of **AR** resulting in complete dissolution of **AR**. This procedure results in a 3 mM CH₂Cl₂ solution of

^{57}Fe -enriched $\mathbf{1}^{2+}$, i.e. a CH_2Cl_2 solution which is 6 mM in ^{57}Fe . Samples (0.05 mL) were taken after 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min, and 180 min with a pre-cooled syringe and were transferred into a Mössbauer cell. The Mössbauer cell was cooled with liquid nitrogen using a metal block to guarantee heat exchange and to orient the Mössbauer cell properly for filling with the reaction solution. The solutions froze on contact directly and the samples were maintained in liquid nitrogen.

Optimized Absorber Thickness

The sample layers prepared under this protocol have been 1.5-2.0 mm thick. As the chlorine atoms of CH_2Cl_2 strongly absorb the γ -radiation, the Mössbauer acquisition times were in the range from 5 to 6 weeks. The optimized sample thickness was obtained from the procedure described by G. Long et al.,² which suggests for the area density a low background absorber $t'_{\text{opt}} = 2/\mu_e$, where μ_e is the electronic mass absorption coefficient ($16.83 \text{ cm}^2/\text{g}$ for DCM^3 [2]). Since the concentration of the compound was low, we neglected its contribution to mass absorption and obtained $t'_{\text{opt}} = 2 / 16.83 \text{ g/cm}^2 = 0.1188 \text{ g/cm}^2$, or with the density of DCM ($\rho = 1.33 \text{ g/cm}^3$), $t'_{\text{opt}}/\rho = 0.09 \text{ cm}^3/\text{cm}^2$, the layer thickness $x = 0.9 \text{ mm}$. As evidenced during the course of the measurements, thinning down the absorber by simply scratching the frozen samples to approximately 1 mm, has led to reasonable signal-to-noise ratios within 2 to 3 weeks (source activity $\approx 1 \text{ GBq}$). This demonstrates that not the low content of ^{57}Fe but the high chlorine cross section for mass absorption is limiting the measuring time of frozen DCM solutions..

Physical measurements.

Cyclic and square-wave voltammograms were measured by use of an EG&G potentiostat/galvanostat 273A on Ar-flushed CH_2Cl_2 solutions containing 0.2 M $[\text{NBu}_4]\text{PF}_6$ as

² Long, G. J.; Cranshaw, T. E.; Longworth, G., In Mössbauer Effect Reference and Data Journal, Stevens, J. G.; Stevens, V. E.; White, R. M.; Gibson, J. L., Eds. Mössbauer Effect Data Center: North Carolina, 1983; Vol. 6, 42-49.

³ Münck, E., In Methods in Enzymology, Fleischer, S.; Parker, L., Eds. Academic Press: New York, 1978; Vol. LIV, 346-379.

supporting electrolyte in a conventional electrochemical cell. The working electrode was a glassy carbon disk electrode, the counter electrode a platinum wire, and the reference electrode was Ag/0.01 M AgNO₃/CH₃CN. The potentials are referenced versus the ferrocenium/ferrocene (Fc⁺/Fc) couple used as an internal standard. Spectroelectrochemical measurements were performed by using an optically transparent thin-layer electrochemical cell (OTTLE cell, $d = 0.018$ cm). During oxidations/reductions in the OTTLE cell spectral changes were recorded on a Hewlett-Packard HP 8453 diode array spectrophotometer in the range 190-1100 nm.

⁵⁷Fe Mössbauer spectra were recorded on an alternating constant-acceleration spectrometer. The minimal line-width was 0.24 mm s⁻¹ full-width at half-height. The sample temperature was maintained constant in a bath cryostat (Wissel MBBC-HE0106). ⁵⁷Co/Rh was used as the radiation source. Isomer shifts were determined relative to α -iron at room temperature.

EPR spectra of frozen solutions of electrochemically generated **1**⁺ were recorded on a Bruker ELEXSYS E500 X-band cw-spectrometer equipped with a helium flow cryostat (Oxford Instruments ESR 910). The resonator was a standard rectangular cavity ER4102. The experimental conditions of the spectrum shown as inset in Fig. 1B are: $T = 10.0$ K, frequency 9.6353 GHz, power 50.5 μ W, modulation amplitude 7.5 G. The spectra were simulated by using effective g -values with our program GFIT written by E. B. for powder spectra. The simulation was performed with an isotropic lineshape and $\mathbf{g} = (2.0050, 2.0050, 2.0050)$.

XAS data were recorded at the Stanford Synchrotron Radiation Lightsource (SSRL) on focused beam line 9-3, under ring conditions of 3 GeV and 60-100 mA. A Si(220) double-crystal monochromator was used for energy selection and a Rh-coated mirror (set to an energy cutoff of 10 keV) was used for harmonic rejection. Internal energy calibration was performed by assigning the first inflection point of the Fe foil spectrum to 7111.2 eV. The solid samples were prepared by dilution in boron nitride, pressed into a pellet and sealed between 38 μ m Kapton tape windows in a 1 mm aluminium spacer. The solution samples were prepared by dilution in dichloromethane (~5 mM) and loaded into a Delrin Mössbauer/XAS sample holder, with a 6 μ m polypropylene window. All samples were maintained at 10 K during data collection using an Oxford Instruments CF1208

continuous flow liquid helium cryostat. Solid and solution data were measured in transmission and fluorescence mode (using a Canberra Ge 30-element array detector), respectively.

XAS data were measured to $k = 15 \text{ \AA}^{-1}$ for solid samples and $k = 11 \text{ \AA}^{-1}$ for solution samples. The solution data range is truncated due to the highly absorbing nature of the solvent (dichloromethane), which made collection of higher k data prohibitive. Samples were monitored for photoreduction throughout the course of data collection. Only those scans which showed no evidence of photoreduction were used in the final average.

The data were calibrated and averaged using EXAFSPAK.⁴ Pre-edge subtraction and splining were carried out using PYSPLINE.⁵ A three-region cubic spline of order 2, 3, 3 was used to model the smooth background above the edge. Normalization of the data was achieved by subtracting the spline and normalizing the post-edge region to 1. The resultant EXAFS was k^3 -weighted to enhance the impact of high- k data.

Theoretical EXAFS signals $\chi(k)$ were calculated using FEFF (version 7.0)^{6,7} and fit to the data using EXAFSPAK.⁴ The non-structural parameter E_0 was also allowed to vary but was restricted to a common value for every component in a given fit. The structural parameters varied during the refinements were the bond distance (R) and the bond variance (σ^2). The σ^2 is related to the Debye-Waller factor, which is a measure of thermal vibration and to static disorder of the absorbers/scatterers. Coordination numbers were systematically varied in the course of the analysis, but they were not allowed to vary within a given fit.

⁴ George, G. N. *EXAFSPAK*, Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University: Stanford, CA.

⁵ Tenderholt, A. *PySpline*, Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University: Stanford, CA..

⁶ Mustre de Leon, J.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. B* **1991**, *44*, 4146-4156.

⁷ Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135-5140.

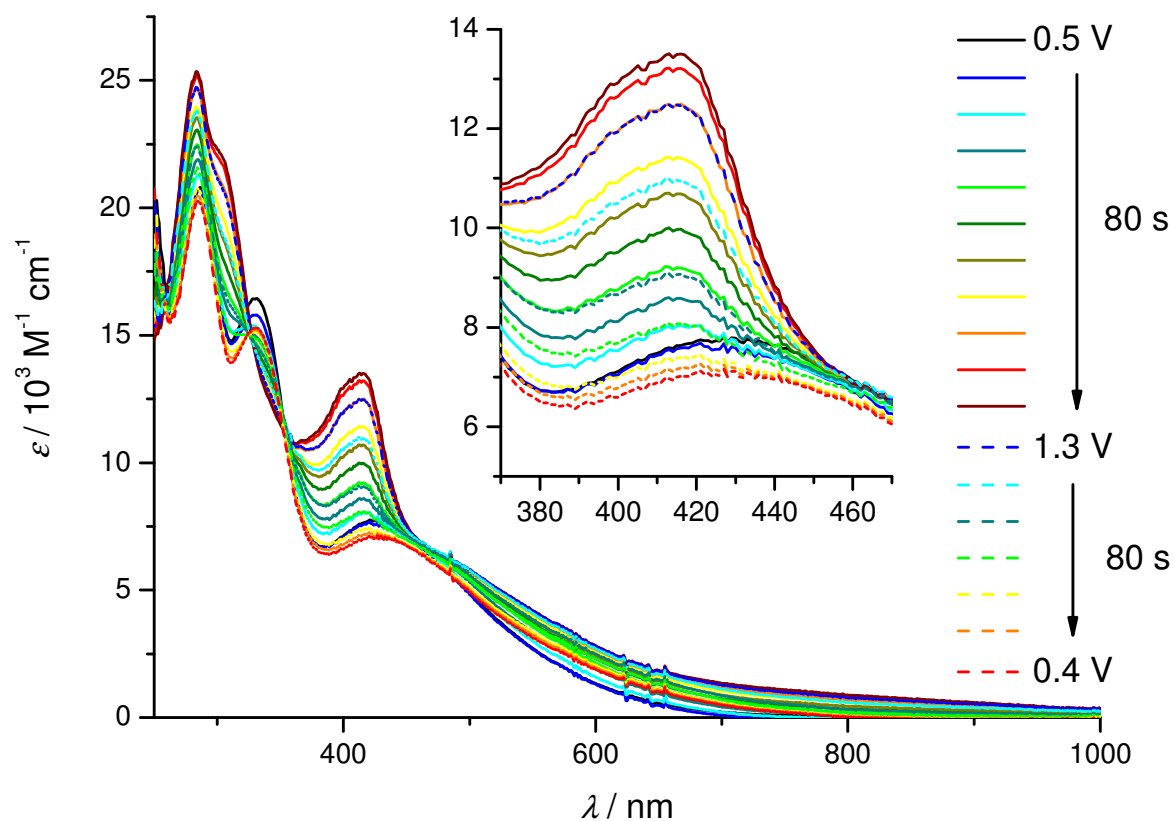


Figure S1. UV/vis spectra recorded during a chronoamperometry of **1** in CH_2Cl_2 (0.2 M $[\text{N}(n\text{-Bu})_4]\text{PF}_6$) in an OTTLE cell at -20°C . A glassy carbon working electrode and an Ag wire reference electrode were used. The UV/vis spectra recorded at the beginning and at the end of the chronoamperometry are almost identical.

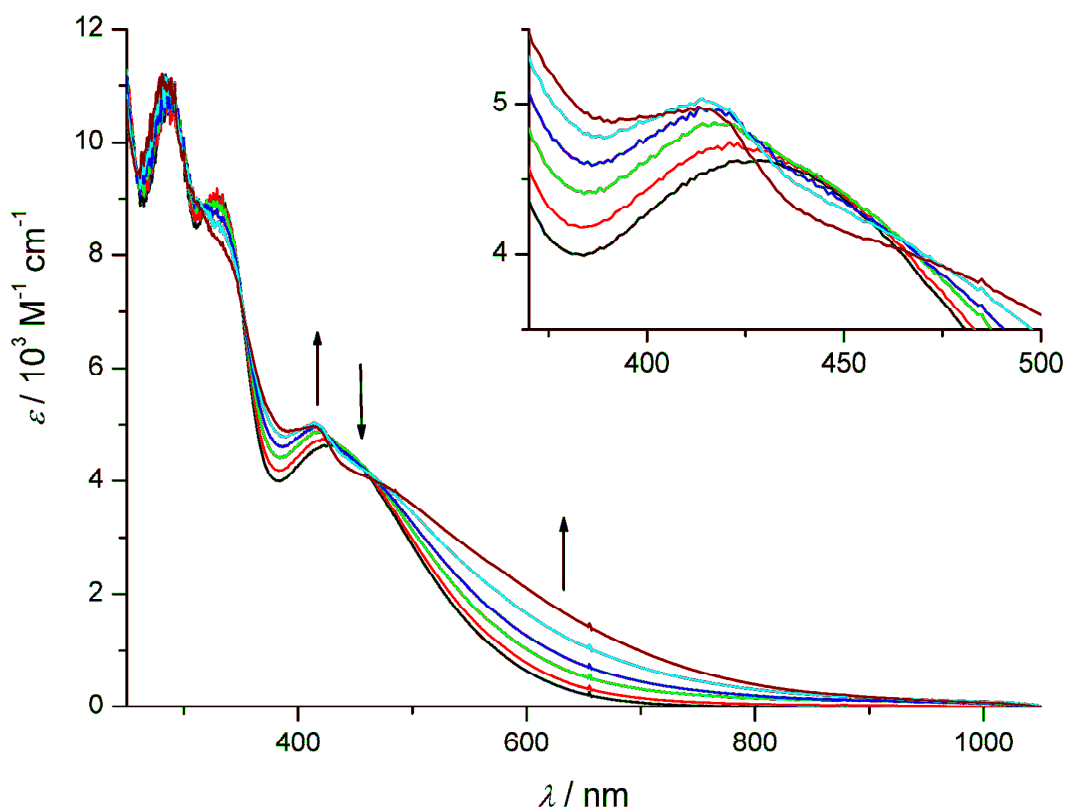


Figure S2. Spectroscopic observation of potentiostatic electrolysis of the one-electron oxidation of **1** in CH_2Cl_2 (0.2 M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$) at 580 mV versus Ag/AgNO_3 at -40°C . A glassy carbon working electrode and an Ag wire reference electrode were used. The expected charge flow for the one-electron oxidation of **1** to $\mathbf{1}^+$ was 188 mC. Black line: 0 mC, red: 30 mC, green: 60 mC, blue: 90 mC, light blue: 120 mC, wine: 150 mC. The conversion of $\mathbf{1}^+$ starts between 120 and 150 mC. Therefore, the oxidation was discontinued. Cyclic voltammograms before and after electrolysis were recorded and found to be nearly identical. This experiment is on the time scale of approximately 10 min.

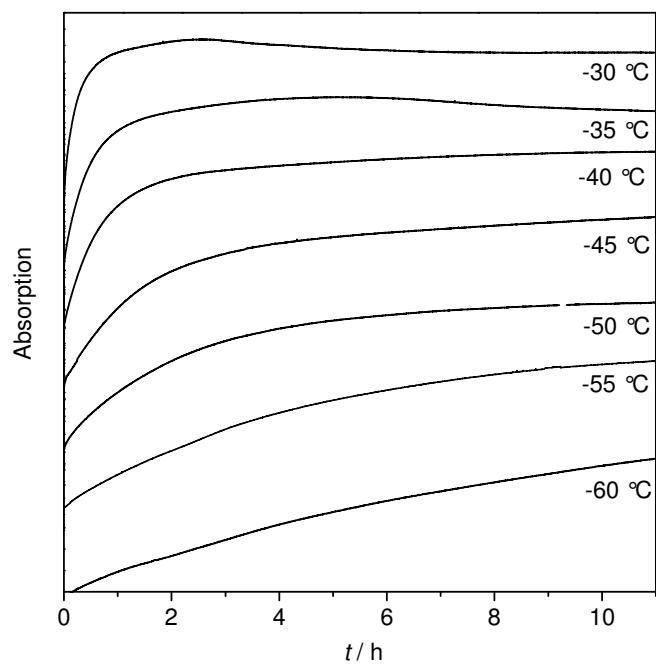


Figure S3. Course of the absorption at 580 nm during the follow-up reaction of 1^+ at different temperatures.

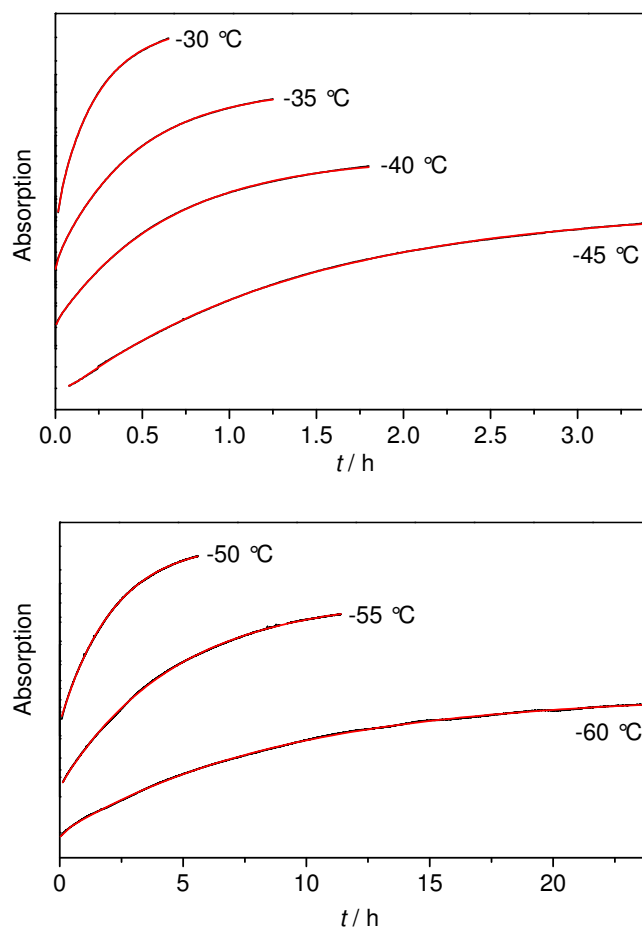


Figure S4.: Course of the absorption at 580 nm during the follow-up reaction of 1^+ at different temperatures (black lines) and the corresponding fits using $E = \Delta_1 \cdot e^{-k_1 t} + \Delta_2 \cdot e^{-k_2 t} + E_\infty$ (red lines). The second exponential is used to account for follow-up reactions occurring later. As these constitute complicated combinations of follow-up and parallel reactions, the second exponential was not analyzed.

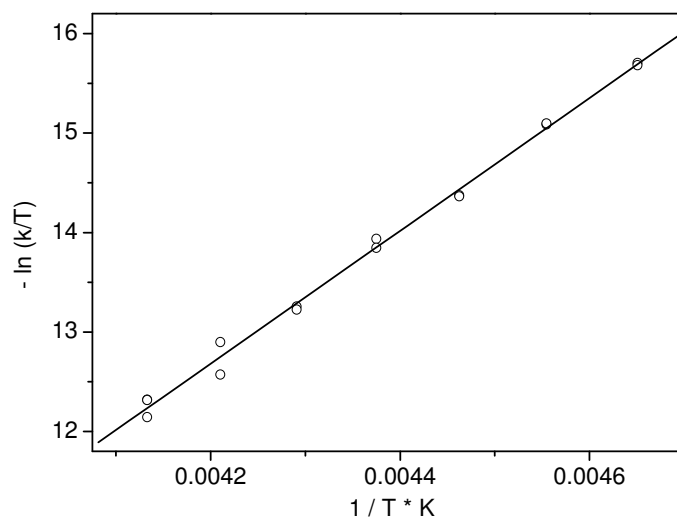


Figure S5. Eyring-plot to determine $\Delta H^{\ddagger,0} = 51 \pm 1$ kJ/mol and $\Delta S^{\ddagger,0} = -90 \pm 6$ J/(mol•K) using the equation $-\ln(k/T) = \Delta H^{\ddagger,0} / (RT) - \Delta S^{\ddagger,0} / R - \ln(k_B/h)$ and the values listed in Ttable S1.

T	k_1 / s^{-1}	$t_{1/2} / \text{min}$
-30 °C	$(1.2 \pm 0.2) \cdot 10^{-3}$	9.4 ± 0.8
-35 °C	$(7.3 \pm 1.2) \cdot 10^{-4}$	16 ± 3
-40 °C	$(4.2 \pm 0.1) \cdot 10^{-4}$	27 ± 1
-45 °C	$(2.1 \pm 0.1) \cdot 10^{-4}$	55 ± 3
-50 °C	$(1.3 \pm 0.1) \cdot 10^{-4}$	90 ± 1
-55 °C	$(6.0 \pm 0.1) \cdot 10^{-5}$	195 ± 2
-60 °C	$(3.1 \pm 0.1) \cdot 10^{-5}$	369 ± 4

Table S1: Rate constants for the follow-up reaction of 1^+ at different temperatures, which are calculated using $E = \Delta_1 \cdot e^{-k_1 t} + \Delta_2 \cdot e^{-k_2 t} + E_\infty$, and the corresponding half-lives.

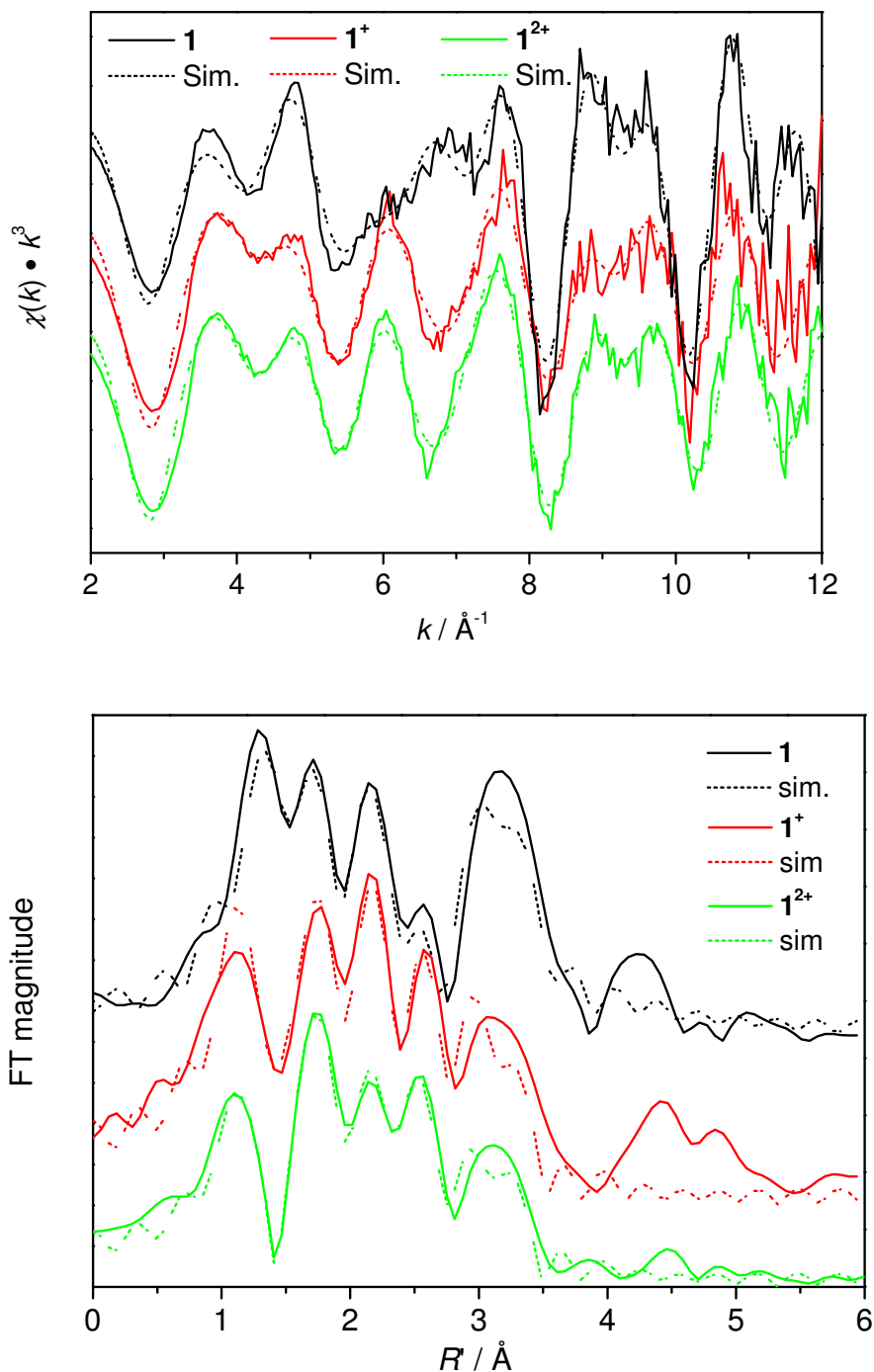


Figure S6. top: Extended X-ray absorption fine structure (Fe K) of **1** (black line, Simulation: black dashes), **1⁺** (red line, Simulation: red dashes), and **1²⁺** (green line, Simulation: green dashes). bottom: Fourier transforms of the EXAFS (Fe K) of **1** (black line, Simulation: black dashes), **1⁺** (red line, Simulation: red dashes), and **1²⁺** (green line, Simulation: green dashes).

Table S2. EXAFS derived Fe-O/N and Fe-Fe distances for **1**, **1⁺** and **1²⁺**.

compound	vector	length / Å	$\sigma^2 / \text{Å}^2$
1 in BN	3 Fe-O/N	1.88	0.0068
	2 Fe-O/N	2.25	0.0056
	1 Fe-Fe	3.59	0.0012
1 in DCM solution	3 Fe-O/N	1.86	0.0094
	2 Fe-O/N	2.14	0.0019
	1 Fe-Fe	3.55	0.0018
1⁺	1 Fe-O/N	1.78	0.0019
	2 Fe-O/N	1.98	0.0010
	2 Fe-O/N	2.17	0.0012
	1 Fe-Fe	3.51	0.0073
1²⁺	1 Fe-O/N	1.78	0.0025
	2 Fe-O/N	1.99	0.0029
	2 Fe-O/N	2.18	0.0040
	1 Fe-Fe	3.50	0.0056