

Electronic supplementary information

for

Synthesis and Characterization of an Fe(I) Cage Complex with High Stability Towards Strong H-Acids

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Materials

The reagents used, 18-crown-6, sorbents and organic solvents were obtained commercially (SAF). Complex $(\text{Fe}^{2+})@L$ was prepared as described in Ref. S1. C_8K (potassium graphite) was obtained as described in Ref. S2. All synthetic manipulations using C_8K were performed in prepurified argon atmosphere using inert-gas glove box technique (Specs GB02M; <8 ppm O_2 , <1 ppm H_2O). THF was predried over NaOH and distilled over potassium/benzophenone ketyl; hexane was distilled over Na/K alloy.

Analytical and spectral methods

Elemental analysis was performed in INEOS RAS under inert atmosphere. Analytical data for C, H, N contents were obtained with a Carlo Erba model 1106 microanalyzer. Iron content was obtained both by spectrophotometry and by X-ray fluorescence method. Potassium content was obtained both by flame photometry and by X-ray fluorescence method. Boron content was obtained spectrophotometrically. Chlorine content was obtained by Shöniger method.

MALDI-TOF mass spectrum of $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$ was recorded in both the positive and negative ranges with a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in a reflecto-mol mode. The ionization was induced by an UV-laser with the wavelength of 337 nm. The sample was applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix.

UV-Vis spectrum of the solution of $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$ in THF was recorded in the range 230 – 900 nm with a Varian Cary 50 spectrophotometer.

Analytical and spectral data for $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$:

Anal. Calc. for $\text{C}_{34}\text{H}_{58}\text{N}_6\text{B}_2\text{Cl}_6\text{FeKO}_{14}$ (%): C, 36.99; H, 5.30; N, 7.61; Fe, 5.06; B, 1.96; K, 3.54; Cl, 19.27.

Found (%): C, 36.95; H, 5.38; N, 7.46; Fe, 4.87 (spectrophotometry), 4.89 (X-ray fluorescence); B, 1.96; K, 3.50 (flame photometry), 3.60 (X-ray fluorescence); Cl, 19.01.

MS(MALDI-TOF, negative range): m/z : – 656 $[(\text{Fe}^+)@L]^-$.

UV-Vis (THF): λ_{\max}/nm ($\epsilon \cdot 10^{-3}, \text{mol}^{-1} \text{l cm}^{-1}$): 250(28), 303(1.4), 317(2.5), 338(5.3), 372(3.2), 457(4.3), 473(10), 581(11), 657(0.8).

Crystallographic data: Crystals of $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$ ($\text{C}_{34}\text{H}_{58}\text{B}_2\text{Cl}_6\text{FeKN}_6\text{O}_{14}$, $M = 1104.13$) are triclinic, space group P-1, at 120 K: $a = 12.1407(14)$, $b = 12.3264(15)$, $c = 18.962(2)$ Å, $\alpha = 76.882(2)$, $\beta = 79.997(2)$, $\gamma = 62.072(2)^\circ$, $V = 2434.2(5)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.506 \text{ gcm}^{-3}$, $\mu(\text{MoK}\alpha) = 7.90 \text{ cm}^{-1}$, $F(000) = 1146$. Intensities of 97386 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [$\lambda(\text{MoK}\alpha) = 0.71072$ Å, ω -scans, $2\theta < 60^\circ$], and 14192 independent reflections [$R_{\text{int}} = 0.0350$] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. After taking the disorder of *n*-butyl groups and coordinated THF molecules into account, the refinement converged to $wR2 = 0.2158$ and $\text{GOF} = 1.317$ for all the independent reflections ($R1 = 0.0676$ was calculated against F for 11270 observed reflections with $I > 2\sigma(I)$). An elongated thermal ellipsoid of the iron(I) ion and an accumulation of residual electron density near it was suggestive of its disorder over three positions around the molecular B...B C_3 -pseudoaxis. The occupations if the three positions by the iron(I) ion were freely refined to be 0.52, 0.38 and 0.10. After accounting for this disorder, the refinement converged to $wR2 = 0.1816$, $\text{GOF} = 1.105$ and $R1 = 0.0555$. All calculations were performed using SHELXTL PLUS 5.0 [S3]. CCDC 1568417 and 1568418 contain the supplementary crystallographic data for $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$ with the disorder of the iron(I) ion ignored and taken into account, respectively.

Cyclic voltammetry (CV) experiments were performed using a Metrohm Autolab PGSTAT128N potentiostat with a conventional one-compartment three-electrode cell (5 ml of solution). Glassy carbon electrode (MF-2012, BASi), which was used as a working electrode, was thoroughly polished with alumina slurry, sonicated for 2 minutes and rinsed before every measurement. A platinum wire

counter electrode and a standard Ag/AgCl/NaCl_{aq} reference electrode (RE-5B, BASi) were used. To account for a drift of the reference electrode, ferrocene was used as an internal standard, and all the measured potentials are reported relative to the Fc/Fc⁺ redox couple. The solutions were thoroughly deaerated by passing argon through them before the CV experiments and above these solutions during the measurements.

UV/Vis spectroelectrochemical cell with patterned honeycomb platinum working electrode (PINE research) with 1.7 mm electrode path length was used for spectroelectrochemical experiments.

Gas chromatography analysis of gases evolved during the electrolysis was performed with a Chromatek-Crystal 5005.2 gas chromatograph equipped with a thermal conductivity detector. Hydrogen content in gaseous mixture was quantitatively detected using a 0.5 m-in-length 60/80 Carboxen-1000 column with an internal diameter 3 mm at 200°C for the detector and at 60°C for the oven. The carrier gas was argon flowing at a rate of 15 ml min⁻¹. The injections (250 μL) were performed via a sampling loop. The retention time of gaseous H₂ was 1.61 min.

Magnetic measurements have been performed using a Quantum Design PPMS-9 device under an applied d.c. field of 1 kOe. Finely ground microcrystalline powders were immobilized in a mineral oil matrix inside a polyethylene capsule. The magnetic data were corrected for the sample holder, the mineral oil and the diamagnetic contribution.

Zero-field ⁵⁷Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer MRG-500 at 77 K in constant acceleration mode. ⁵⁷Co/Rh was used as radiation source. WinNormos for Igor Pro software was used for the quantitative evaluation of the spectral parameters (least squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.21 mm s⁻¹. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N₂ cryostat within an accuracy of ±0.3 K. Isomeric shifts were determined relative to α-Fe at 298 K.

CW EPR spectra was acquired on a Bruker Eleksys-II E580 X-band EPR spectrometer equipped with helium flow cryostat (CF935, Oxford Instruments) and dielectric resonator (ER4118X-MD5, Bruker). The EPR spectra were recorded using the following settings: microwave frequency 9.82 GHz, microwave power 0.02 mW, modulation frequency 100 kHz, modulation amplitude 0.3 mT, conversion time 20 ms, resolution 2048 points. Simulations of the spectra were performed using EasySpin toolbox for the Matlab program package [S4]

Supplementary Figures

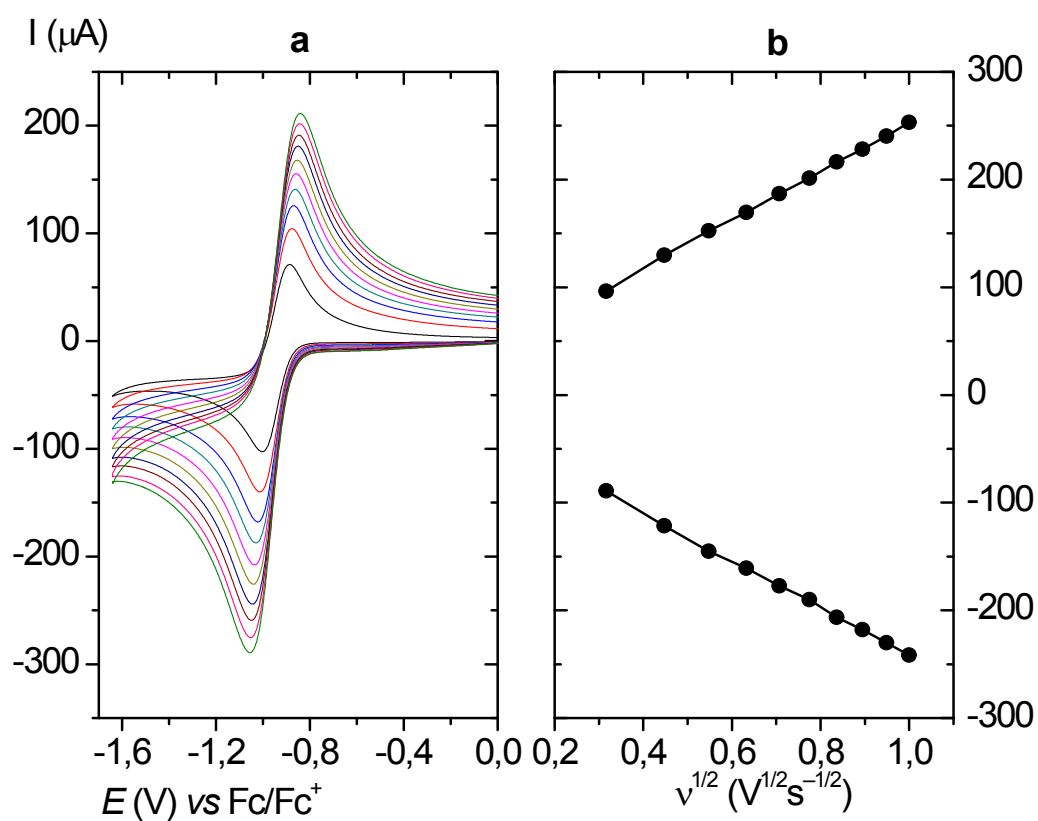


Figure S1. CVs (a) and the plots of the reduction and oxidation peak currents *versus* the square root of the scan rate (b) for 5 mM acetonitrile solution of the clathrochelate (Fe²⁺)@L. Scan rates are from 0.1 to 1 V s⁻¹ (T = 298K).

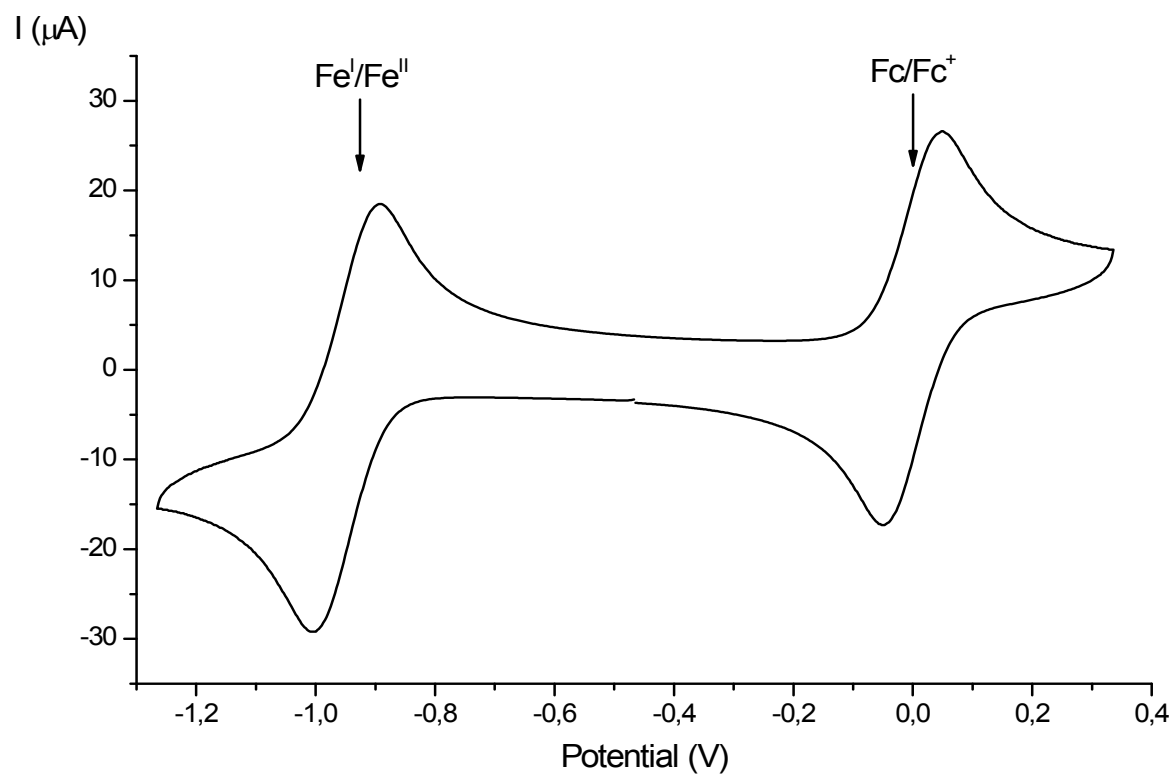


Figure S2. Cyclic voltammogram of 1 mM solution of $(\text{Fe}^{2+})@L$ and ferrocene in dichloromethane. Conditions: 25°C, scan rate 0.1 V/s, 0.1 M $(n\text{-Bu}_4\text{N})\text{ClO}_4$ in dichloromethane, glassy carbon working electrode, potentials are given relative to Fc/Fc^+ couple.

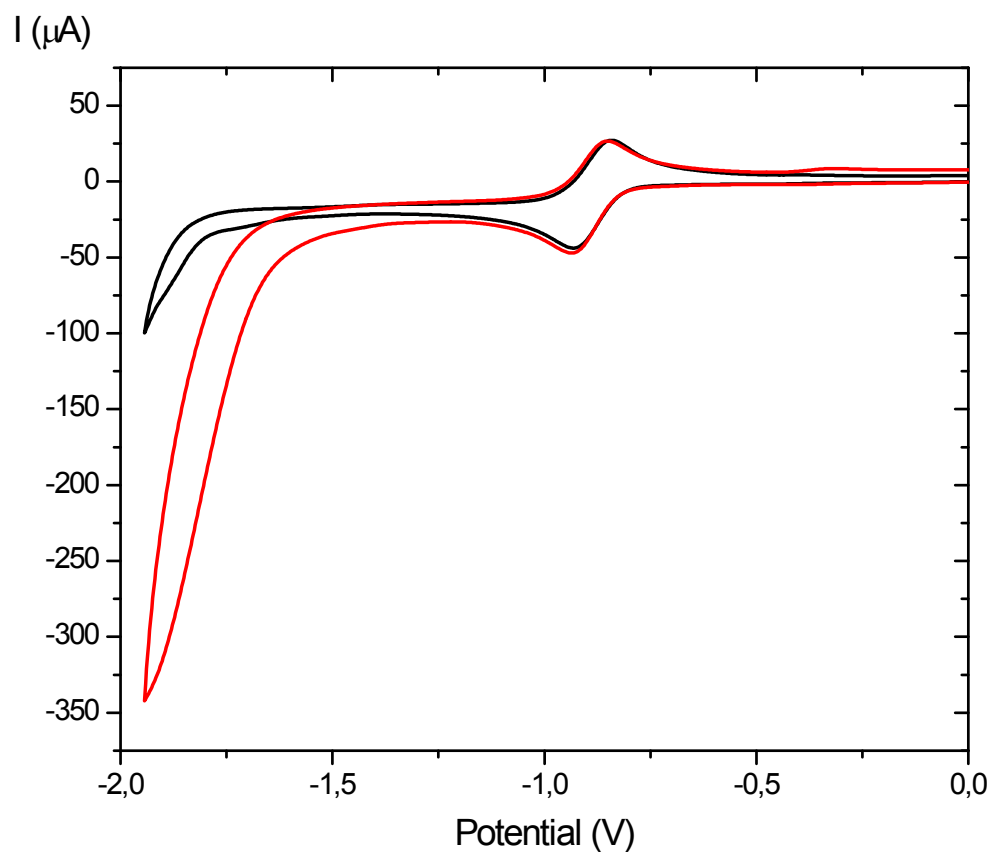


Figure S3. Cyclic voltammogram of 1 mM solution of $(\text{Fe}^{2+})@L$ in the absence (in black) and in the presence (in red) of 10 equivalents of trifluoroacetic acid. Conditions: 25°C, scan rate 0.1 V/s, 0.1M $(n\text{-Bu}_4\text{N})\text{ClO}_4$ in acetonitrile, glassy carbon working electrode, potentials are given relative to Fc/Fc^+ couple.

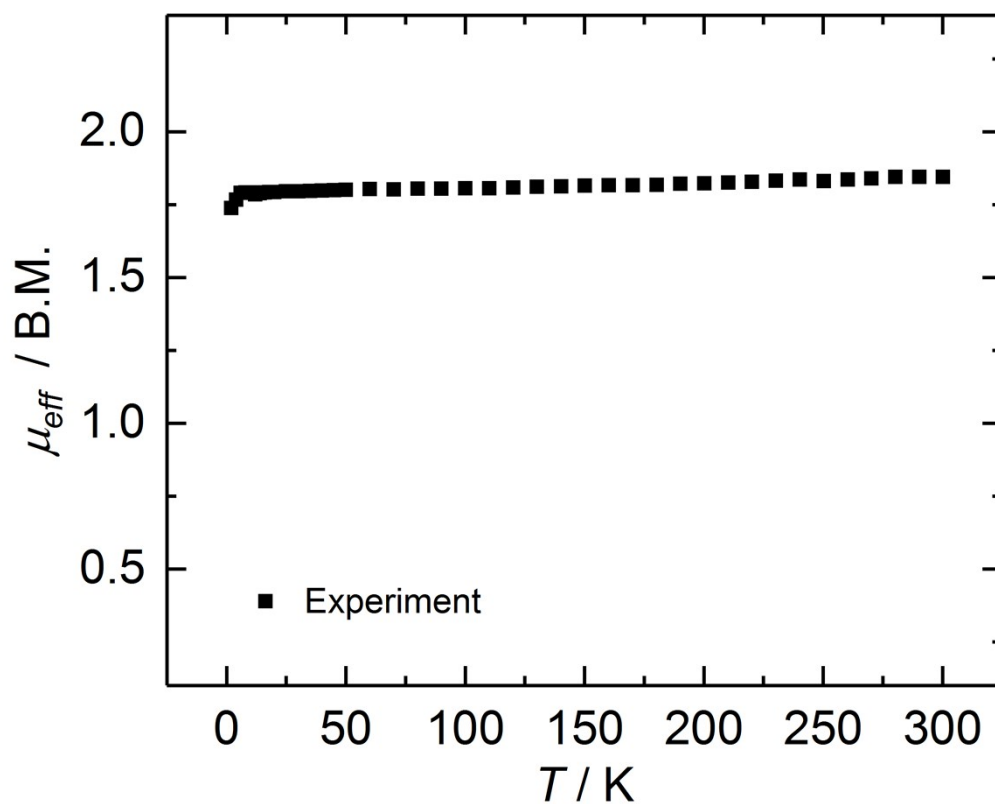


Figure S4. Temperature-dependent SQUID magnetization data for $(\text{K18C6THF}_2)(\text{Fe}^+)@L$ with an applied magnetic field of 1 T, plotted as a function of magnetic moment (μ_{eff}) vs temperature (T, 2 – 300 K).

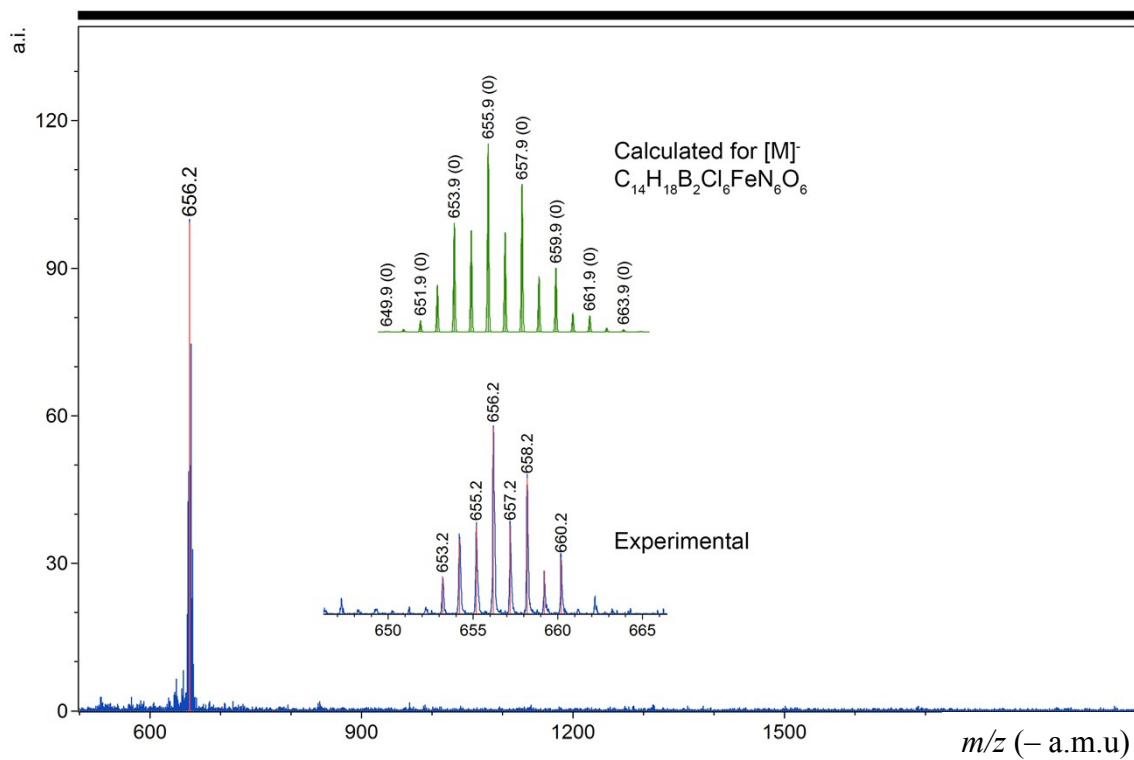


Figure S5. Fragment of the MALDI-TOF mass spectrum of the complex $(\text{K18cw6THF}_2)(\text{Fe}^+)@L$ in its negative range.

Supporting Information References

- S1. Y.Z. Voloshin, O.A. Varzatskii, T.E. Kron, V.K. Belsky, V.E. Zavodnik, N.G. Strizhakova, A.V. Palchik, *Inorg. Chem.* 2000, 39, 1907–1918.
- S2. D.Ottmers, H.Rase, *Carbon* 1966, 4, 125–127
- S3. G.M. Sheldrick, *Acta Cryst. A.* 2008, 64, 112–122
- S4. S.Stoll, A.Schweiger, *J.Magnetic Resonance* 2006, 178, 42–55.