Electronic Supplementary Information

A Tailor-made Ligand to Mimic the Active Site Diiron Enyzmes: An Air-oxidized High-Valent Fe^{III} h.s.(μ-O)$_2$ Fe^{IV} h.s Species**

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Experimental Details

X-Ray Crystallographic Data Collection and Refinement of the Structures.

Crystals of [(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}]•6H$_2$O and [(julia){Fe(DMSO)(μ-O)Fe(DMSO)}]•3DMSO were removed from the mother liquor and immediately cooled to 173(2) K (183(2) K) on a Bruker AXS SMART diffractometer (three circle goniometer with 1K CCD detector, Mo$_{k\alpha}$ radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435 and 230 frames (ϕ = 0, 88 and 180 °) at a detector distance of 5 cm). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10.[1] The structure was solved with the program SHELXS-97[2,3] and refined using SHELXL-97.[3]

All hydrogen atoms for [(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}]•6H$_2$O could be found and individually refined.

The solvent DMSO molecules and one of the coordinated DMSO molecules of [(julia){Fe(DMSO)(μ-O)Fe(DMSO)}]•3DMSO are disordered on two positions. The hydrogen atoms of the minor components of the solvent DMSO molecules could not be located on reasonable positions. That explains the difference between the published sum formula and the formula which can be calculated from the atom list.

Crystal data for [(julia){Fe(DMSO)(μ-O)Fe(DMSO)}]•3DMSO: C$_{26}$H$_{56}$Fe$_2$N$_4$O$_{14}$S$_5$, M_r = 920.75 g mol^{-1}, 0.14 × 0.11 × 0.10 mm^3, monoclinic, $P2_1$/n, a = 14.145(4), b = 15.116(4), c = 19.598(5) Å, β = 94.854(5)°, V=4175.4(19) Å^3, Z = 4, ρ_{calcd} = 1.465 g

cm^{-3}, μ = 1.007 mm^{-1}, Mo$_{k\alpha}$ radiation (0.71073 Å), T = 183(2) K, $2\theta_{max}$ = 50.00°, 20015 reflections measured, 7313 independent reflections, R_{int} = 0.0527, R = 0.0609, $wR2$ = 0.1429, residual max./min. electron densities 1.001 / -0.687 e Å^{-3}, CCDC-743430 contains the supplementary crystallographic data.

Other Physical Measurements.

Infrared spectra (400-4000 cm^{-1}) of solid samples were recorded on a Shimadzu FTIR 8300 as KBr disks. ESI mass spectra were recorded on a Bruker Esquire 3000 mass spectrometer. The exact mass experiments had been performed with a Bruker Apex III Fourier Transform Ion Cyclotron Resonace Mass Spectrometer with an ESI ion source. pH measurements were performed with a Greisinger QpH70 pH-electrode.

UV/vis/NIR absorption spectra of solutions were measured on a Shimadzu UV-3101 PC spectrophotometer in the range 10000-50000 cm^{-1} at ambient temperatures or on a J&M Tidas II diode array spectrometer. The diode array spectrometer was coupled to a Hellma quartz dip-probe 661.087-UVS (1mm opening) by a fibre optic cable.

The spectrum at pH=5.95 was fitted with a minimum number of Gaussians. The overall fit (Figure 2b) gave a perfect reproduction of the experimental data. Gaussians below 22000 cm^{-1} were included to obtain a reasonable background but cannot be interpreted in terms of d-d transition due to the lack of experimental resolution. The band at 36630 cm^{-1} fits this region well but the presence of several unresolved is highly likely. The resulting fit parameters are given in Table S1.

Cyclic voltammograms were measured by use of a VersaStat potentiostat on Ar-flushed aqueous solutions containing 0.05 M KClO$_4$ as 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/AgCl. The potentials are referenced versus methylviologen/methylviologen radical cation (MV^{2+}/MV^+) couple (methylviologen = 1,1-dimethyl-4,4-bipyridiniumdichloride, $E^0(MV^{2+}/MV^+) = -0.448$ V vs NHE[4] used as an internal standard.

Magnetic susceptibility data were measured from powder samples of solid material in the temperature range 2-300 K by using a SQUID magnetometer (Quantum Design MPMS XL-7 EC) with a field of 1.0 T. The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants. The susceptibility data of the dinuclear ferric high-spin complex were analyzed on the basis of the usual spin-Hamiltonian description for the electronic ground state by using the simulation package julX written by Eckhard Bill for exchange coupled systems.[5] The Hamilton operator was:

$$\hat{H} = 2J_{ij}\,\hat{\vec{S}}_i\hat{\vec{S}}_j + g\beta\,\hat{\vec{S}}\cdot\vec{B} \qquad (1)$$

where J_{ij} is the coupling constant and g is the average electronic g value. Magnetic moments were obtained from numerically generated derivatives of the eigenvalues of eq. 1, and summed up over 16 field orientations along a 16-point Lebedev grid to account for the powder distribution of the sample.

[57]Fe 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). [57]Co/Rh was used as the radiation source. Isomer shifts were determined relative to α-iron at room temperature. 1×10^{-3} mmol [57]Fe-enriched complex was dissolved in 1 mL of water. The respective pH-values was set by adding aqueous solutions of NEt$_4$OH at room temperature. Solutions were taken out directly to Mössbauer cups and frozen in liquid nitrogen.

EPR spectra of frozen solutions 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 EPR samples were prepared according to the Mössbauer samples described before except that 5 mM solutions has been used instead of 1 mM solutions. The experimental conditions of the spectrum shown in Fig. 3 are: T = 24.3 K, frequency 9.42668 GHz, power 0.20 mW, modulation amplitude 10.0 G. The spectra were simulated by using effective g-values with the program ESIM written by Eckhard Bill for powder spectra.[6] The simulation was performed with an anisotropic lineshape and g = (2.0066, 2.0066, 2.0982).
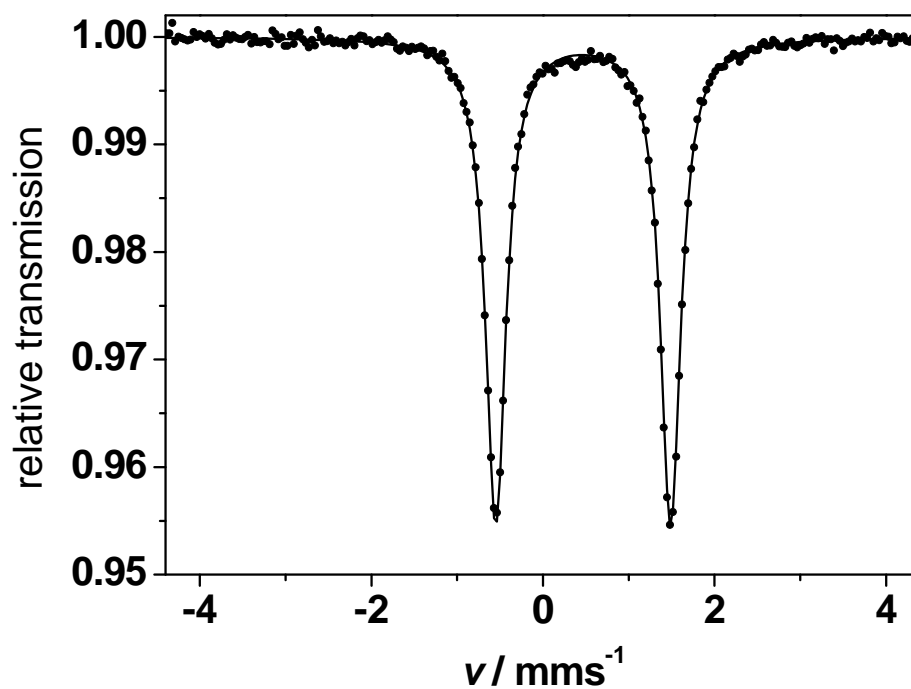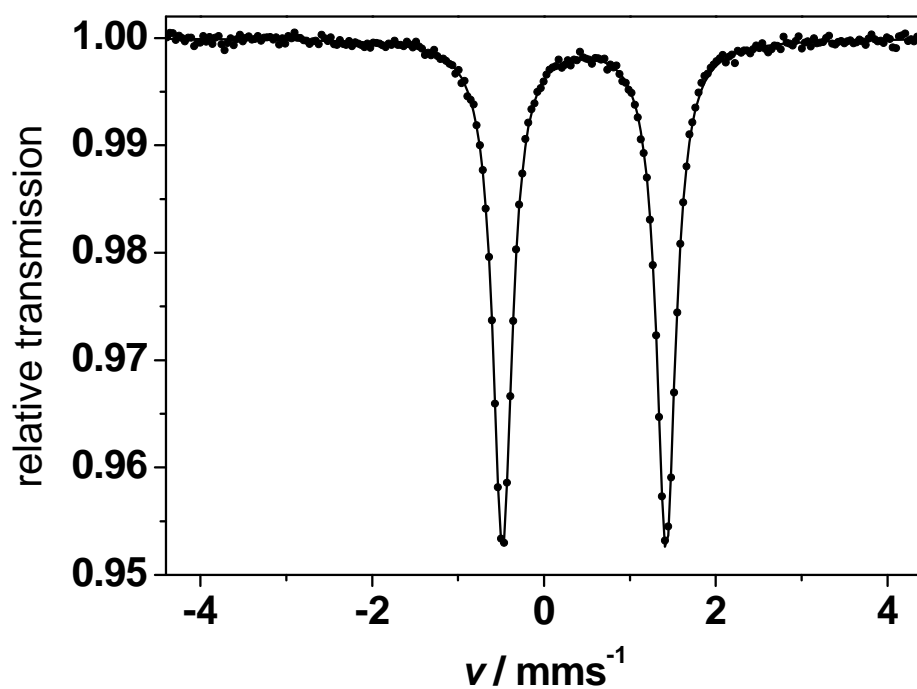
**Figure S1:** Mössbauer spectrum of [(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}] at 80 K.
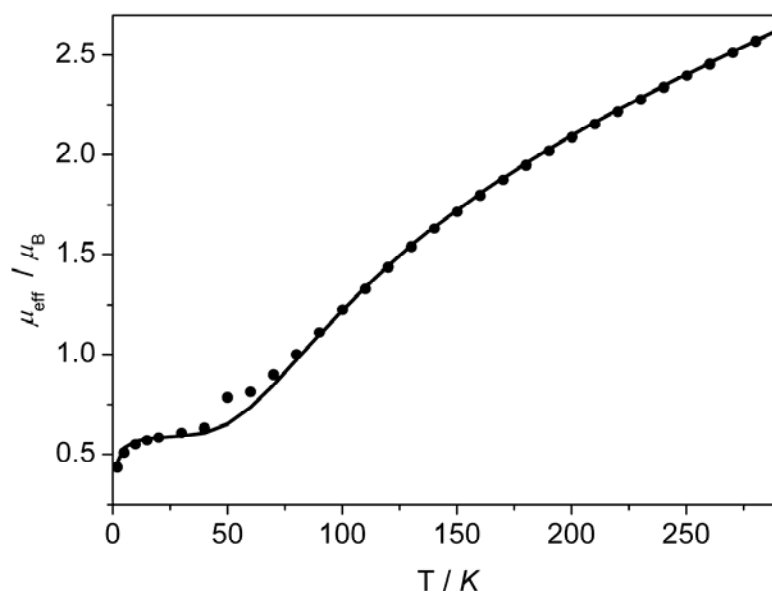
Figure S2: Temperature-dependence of the effective magnetic moment, μ_{eff}, of solid

[(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}]. The solid line is a fit to the experimental data with J =

-101 cm^{-1}, g = 2.00, and p.i. (S = 5/2, same molecular mass) = 1.0%.

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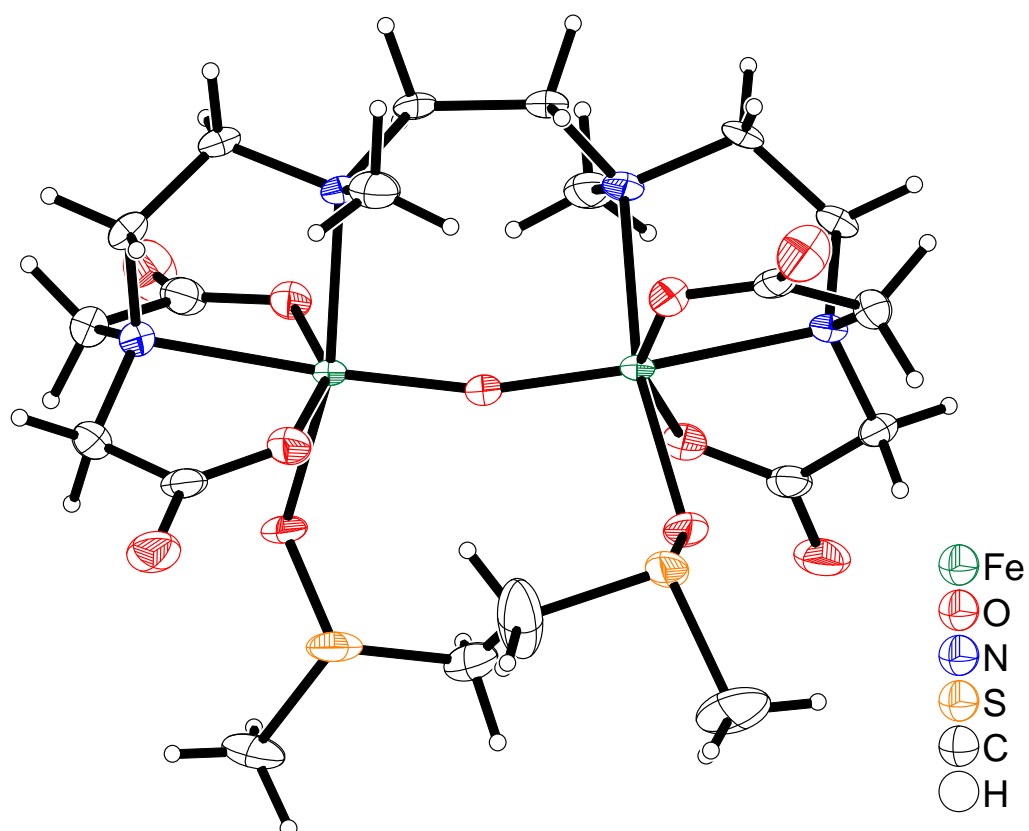
Figure S3: Molecular structure of [(julia){Fe(DMSO)(μ-O)Fe(DMSO)}] in crystals of

[(julia){Fe(DMSO)(μ-O)Fe(DMSO)}]•3DMSO.

Figure S4: Mössbauer spectrum of [(julia){Fe(dmso)(μ-O)Fe(dmso)}] at 80 K.
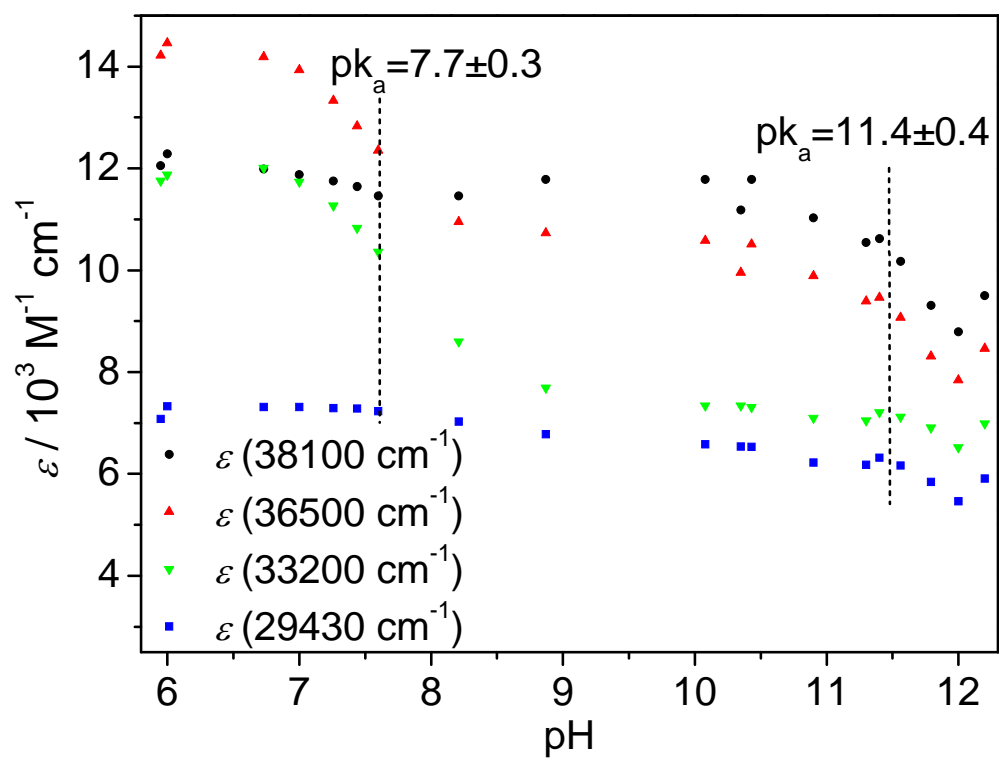
Figure S5: pH-dependence of the absorption spectra an aqueous solution of [(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}]] at ambient temperature at selected wavelengths.
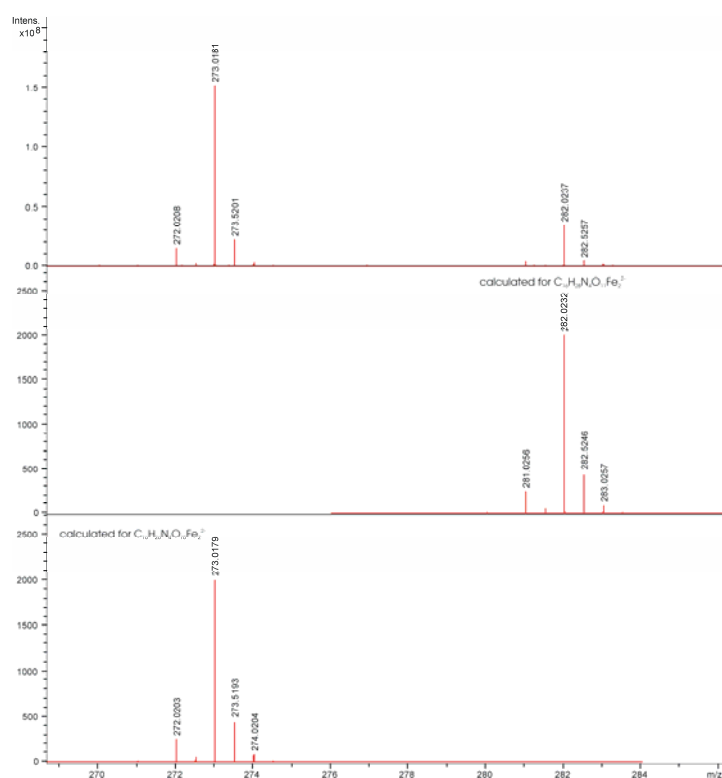
Figure S6: Exact mass ESI-MS of an aqueous solution of [(julia){Fe(H$_2$O)(μ-O)Fe(H$_2$O)}] at pH = 9.8. Top: experimental data, center: simulation for **5a^{2-}**, bottom: simulation for **5b^{2-}**.

Table S1: Result of the Gaussian fit of the Absorption Spectra

Band	v_{max} / cm^{-1}	ε_{max} / M^{-1} cm^{-1}
1	25490	800
2	28930	6400
3	32790	11400
4	36630	14500

Electrostatic model based on the Born equation (1)

$$-\Delta G^0 = E^f F = \frac{n^2 e^2 N_L}{8\pi r \varepsilon_0 \varepsilon_E} \quad (1)$$

where E^f represents the redox potential in volts, N_L is the Avogadro number and F the Faraday constant, $8\pi r$ is a geometric parameter of the spherical particle, $\varepsilon_0 \varepsilon_E$ is the dielectricity constant of the surrounding medium, and ne is the electric charge of the particle.[7]

Assuming that the difference of the redox potentials $[L\{Fe^{III}(\mu\text{-}O)_2Fe^{III}\}]^{n+/(n-1)+}$ is primarily governed by the differing solvation energy of two charged cations, equation (2) was derived[8]

$$\Delta E^f = (2n-1)\frac{e^2 N_L}{8\pi r \varepsilon_0 \varepsilon_E F} \quad (2)$$

By taking the four $n+/(n-1)+$ steps to from charge 2- to the charge 2+ for n, and using an estimate of 10 for an effective dielectricity constant, a radius of 3.0 Å for an approximated sphere surrounding the central $\{Fe^{III}(\mu\text{-}O)_2Fe^{III}\}$ core, results in a shift of the redox potential of 1.68 V.

References

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5   *The program package JulX was used for spin-Hamiltonian simulations and fittings of the data by a full-matrix diagonalization approach (E. Bill, unpublished results).*

6   *The program package ESIM was used for simulation of the EPR spectra by a full-matrix diagonalization approach of the appropriate spin-Hamiltonian (E. Bill, unpublished results).*

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