Supporting Information for:

Bioinspired Symmetrical and Unsymmetrical Diiron Complexes for Selective Oxidation Catalysis with Hydrogen Peroxide

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Synthesis of ligands

***N,N*-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol:** was synthesized as previously described by Suzuki *et al.*[1]

***N,N,N',N'*-tetrakis(2-pyridylmethyl)-1,3-diaminopropan-2-ol (L_1) :** was synthesized as previously described[2] *via* a method adapted from the original synthesis developed by Suzuki *et al.*[1]

***N,N*-bis((2,4-dimethyl-3-methoxy-2-pyridyl)methyl)-*N',N'*-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol (L_2):** 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine hydrochloride was dehydrochlorinated by dissolution in an aqueous solution saturated with sodium carbonate and then extracted with dichloromethane. A solution of 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine (830 mg) in 5 mL acetonitrile was then added dropwise to a solution of *N,N*-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol (608 mg) in 5 mL acetonitrile, and 2.5 mL of triethylamine were added dropwise to the reaction mixture which was stirred at room temperature for 3 days. After removing the solvent under reduced pressure, the mixture was dissolved in dichloromethane and washed three times with water. Purification by chromatography on a silica gel column ($CHCl_3/CH_3OH$) yielded 960 mg (75 %) of the expected product as a pale-yellow oil. ^1H NMR analysis ($CDCl_3$, 250 MHz): δ (ppm): 8.519 (2H, d, J_{HH} = 5.0 Hz), 8.115 (2H, s), 7.625 (2H, td, J_{HH} = 7.5 Hz), 7.441 (2H, d, J_{HH} = 7.5 Hz), 7.145 (2H, t, J_{HH} = 6.3 Hz), 3.851 (8H, s), 3.750 (1H, m), 3.515 (6H, s), 2.698 (2H, dd, J_{HH} = 7.5 Hz), 2.556 (2H, d, J_{HH} = 5.8 Hz), 2.181 (6H, s), 2.101 (6H, s). HR ESI-MS analysis: *m/z* 571.3399, calculated *m/z* 571.3391.

***N,N,N',N'*-tetrakis*((2,4-dimethyl-3-methoxy-2-pyridyl)methyl)*-1,3-diaminopropan-2-ol (L3):** 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine hydrochloride was dehydrochlorinated by dissolution in an aqueous solution saturated with sodium carbonate and then extracted with dichloromethane. A solution of 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine (789 mg) in 5 mL acetonitrile was added dropwise to a solution of 1,3-diamino-2-propanol (90 mg) in 5 mL acetonitrile. Then, 1.10 mL of triethylamine were added dropwise to the reaction mixture which was then allowed to stir at room temperature for 3 days. After removing the solvent under reduced pressure, the mixture was dissolved in dichloromethane and washed three times with water. Purification by chromatography on a silica gel column ($CHCl_3/CH_3OH$) yielded 424 mg (62 %) of the expected

product as a pale-yellow oil. ^{1}H NMR analysis ($CDCl_3$, 250 MHz): δ (ppm): 8.142 (4H, s), 3.844 (8H, m), 3.756 (1H, m), 3.692 (12H, s), 2.559 (4H, m), 2.209 (12H, s), 2.104 (12H, s). HR ESI-MS analysis: *m/z* 687.4241, calculated *m/z* 687.4228.

Synthesis of complexes.

$[Fe_2(L_1)(CH_3O)(CH_3OH)_3](ClO_4)_4$ [1]: was synthesized as previously described.[2]

$[Fe_2(L_2)(H_2O)_2(HO)(CH_3O)](ClO_4)_3$ [2]: a 5 mL methanol solution of iron(III) perchlorate hexahydrate ($Fe(ClO_4)_3$, 6 H_2O) (373 mg) was added dropwise to a 15 mL methanol solution of *N,N*-((2,4-dimethyl-3-methoxy-2-pyridyl)methyl)-*N',N'*-bis(2-pyridylmethyl)-1,3-diaminopropan-2-ol L_2 (259 mg) under stirring at room temperature. Liquid-liquid diffusion of diethyl ether into the orange solution yielded orange crystals of the desired complex. HR ESI-MS analysis $[Fe^{III}_2(L_2)(CH_3O)_3(ClO_4)]^+$: *m/z* 873.1938 ; Calculated : *m/z* 873.1972. Elemental Analysis: calculated for $[Fe_2(L_2)(H_2O)_2(HO)(CH_3O)](ClO_4)_3$ ($C_{34}H_{52}Cl_3Fe_2N_6O_{19}$), C 38.28%, H 4.91%, N 7.88%. Found, C 38.58%, H 4.78%, N 7.19%.

$[Fe_2(L_3)(H_2O)_2(CH_3OH)(CH_3O)](ClO_4)_4$ [3]: a 5 mL solution of iron(III) perchlorate hexahydrate ($Fe(ClO_4)_3$, 6H_2O) (544 mg) was added dropwise to a 20 mL methanol solution of *N,N,N',N'*-tetrakis((2,4-dimethyl-3-methoxy-2-pyridyl)methyl)-1,3-diaminopropan-2-ol (404 mg) under stirring at room temperature. Slow vapor diffusion of diethyl ether into the orange solution yielded orange crystals of the desired complex. HR ESI-MS analysis $[Fe^{III}_2(L_3)(CH_3O)_3(ClO_4)]^+$: *m/z* 989.2821 ; Calculated : *m/z* 989.2813. Elemental Analysis: calculated for $[Fe_2(L_3)(H_2O)_3(OH)](ClO_4)_4$ ($C_{39}H_{64}Cl_4Fe_2N_6O_{25}$), C 36.87%, H 5.08%, N 6.62%. Found, C 35.97%, H 4.93%, N 6.53%.

Physical measurements.

Electrospray ionization mass spectrometry experiments were carried on a MicrOTOF-Q Bruker instrument using a source acceleration voltage of 3 kV and transfer capillary temperature (i.e. Dry heater on this particular instrument) of 140°C. About 1 pM solutions of the compounds in methanol were injected without addition of charge carriers. Data were calibrated internally with ESI-L Low Concentration Tuning Mix (Agilent-Technologies).

Gaz chromatography analysis were performed using a SHIMADZU GC-2014A.

Electronic spectra were measured on a Varian Cary 300-bio spectrophotometer.

X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in

a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ± 1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[3] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[4] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations for complex2 were performed by using the Crystal Structure crystallographic software package WINGX.[5] For complex3 the disorder of the $[ClO_4]^-$ anions was treated by using DSR[6] in ShelXle[7].

The crystal data collection and refinement parameters are given in Table S1.

CCDC 1406272-1406273 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

For ^{1}H NMR analysis, organic compounds were dissolved in deuterated chloroform and spectra were recorded on a Bruker AC250 (250 MHz) or AC300 (300 MHz) or AC360 (360 MHz). Chemical shifts δ are expressed in ppm (parts per million).
Mössbauer spectra were recorded at 5 K on a low-field Mössbauer spectrometer equipped with a Janis CCR 5K cryostat. The spectrometer was operated in a constant-acceleration mode in transmission geometry. The isomer shifts are referenced against that of a metallic iron foil at room temperature. Analysis of the data was performed with the program WMOSS (WMOSS4 Mössbauer Spectral Analysis Software, www.wmosss.org, 2009−2015).

Catalysis experiments. All experiments were realized under the following conditions. To a solution of 0.7 µmol of complex and 0.7 mmol of substrate in 0.9 mL acetonitrile, were injected 0.1 mL of 0.7 M hydrogen peroxide (1.4 M for the cyclooctene catalysis experiment), using a syringe pump system, over 30 min, under vigorous stirring at room temperature. After 30 min of injection, the solution was left 5 min under vigorous stirring at room temperature. Before GC analysis, internal standard was added to the solution and the solution was filtered off on silica (1 cm in Pasteur pipette) and eluted with 1 mL of acetonitrile. Finally, 3 µL of this solution were injected in a Zebron ZB Semi Volatiles column (30 m x 0.25 mm x 0.25 µm). Depending on the substrate, the following conditions were used: Thioanisole: 100°C to 130°C, 5°C/min, then 130°C to 300°C, 50°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: acetophenone. Retention times (min.): acetophenone (4.03), thioanisole (4.32), thioanisole sulfoxide (7.56), thioanisole sulfone (8.04).

Cyclooctene: 100°C to 160°C, 20°C/min, then hold for 1 min, then 160°C to 300°C, 40°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: acetophenone. Retention times (min.): cyclooctene (2.36), acetophenone (3.04), cyclooctene oxide (3.36), cis-cyclooctanediol (4.95). Cyclohexene: 50°C to 180°C, 20°C/min, then 180°C to 300°C, 50°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: anisole. Retention times (min.): cyclohexene (2.09), cyclohexene oxide (3.17), 2-cyclohexenol (3.40), anisole (3.63), 2-cyclohexenone (3.75), cis-cylclohexanediol (4.92). Diphenylmethane: 100°C to 270°C, 50°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: acetophenone. Retention times (min.): acetophenone (2.55), diphenylmethane (3.70), benzophenone (4.30). Ethylbenzene: 100°C to 130°C, 3°C/min, then 130°C to 250°C, 50°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: anisole. Retention times (min.): ethylbenzene (2.42), anisole (2.72), acetophenone (4.33), phenylethan-1-ol (4.19). Toluene: 50°C to 250°C, 25°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard: anisole. Retention times (min.): toluene (2.45), anisole (3.35), benzaldehyde (3.73), benzyl alcohol (4.22). Cyclohexane: 50°C to 70°C, 2°C/min, then 70°C to 250°C, 50°C/min, then hold for 3 min. Injector and FID temperature: 300°C. Internal standard : acetophenone. Retention times (min.): cyclohexane (2.26), cyclohexanol (6.43), cyclohexanone (6.69), acetophenone (11.71).

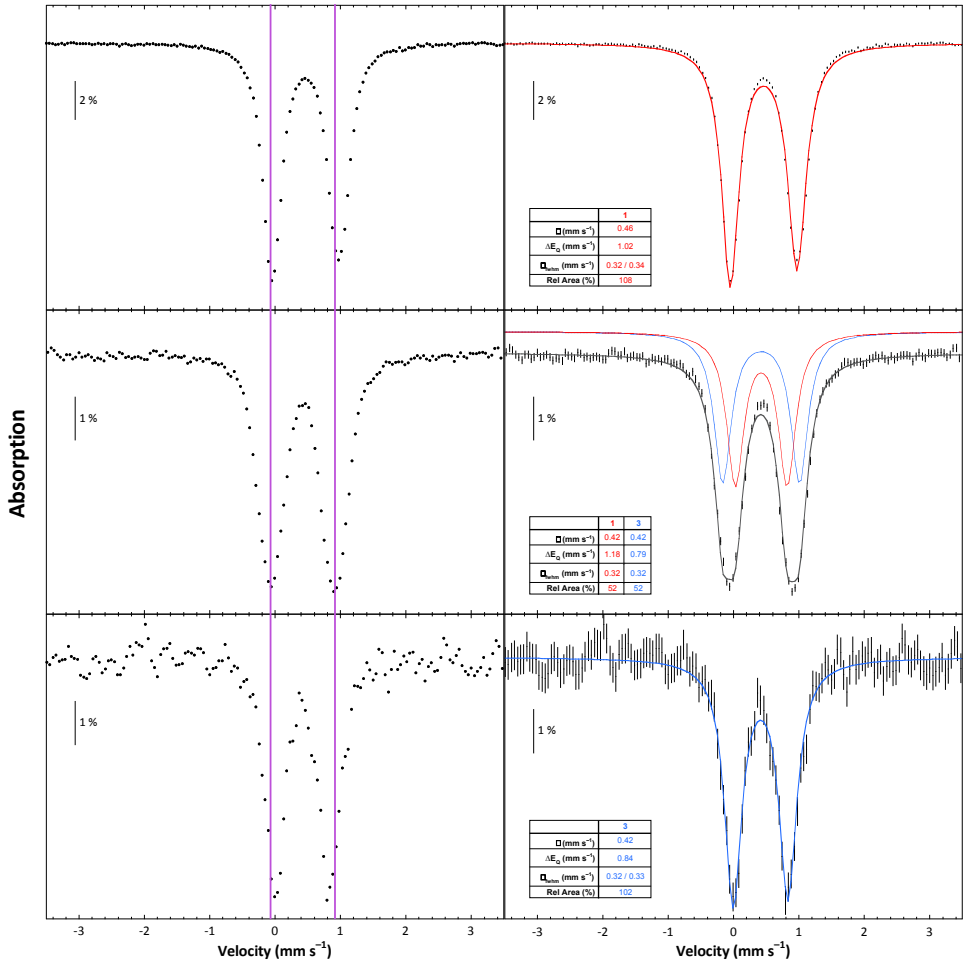

Figure S1. Left panel: Experimental Mössbauer spectra in solid state (dots) recorded at 5 K of complexes **[1]** (top), **[2]** (middle) and **[3]** (bottom). The two vertical lines located at the absorption minima of complex **[2]** (middle) visualize the changes of the line positions for **[1]** (top) and **[3]** (bottom). Right panel respective simulations (right panel) with the parameters indicated on the figure.

Table S1. Crystallographic data and structure refinement details for compounds 2 and 3.

Complex	**2**	**3**
CCDC	1406272	1406273
Empirical Formula	C_{35} H_{57} Cl_3 Fe_2 N_6 O_{22}	C_{41} H_{64} Cl_4 Fe_2 N_6 O_{26}
M_r	1131.91	1310.48
Crystal size, mm^3	0.16 x 0.09 x 0.02	0.31 x 0.20 x 0.18
Crystal system	monoclinic	monoclinic
Space group	*P* $2_1/c$	*C* 2/*m*
a, Å	11.9932(3)	28.7372(12)
b, Å	32.6022(8)	12.3704(5)
c, Å	13.3067(3)	19.2633(7)
α, °	90	90
β, °	113.7520(10)	109.3840(10)
γ, °	90	90

Cell volume, $Å^3$	4762.3(2)	6459.7(4)
Z ; Z'	4 ; 1	4 ; 1/2
T, K	100(1)	100(1)
F_{000}	2352	2720
μ, mm^{-1}	0.864	0.691
θ range, °	1.249 – 30.652	1.502 – 28.332
Reflection collected	84 636	47 118
Reflections unique	14 684	8 160
R_{int}	0.0709	0.0187
GOF	1.014	1.076
Refl. obs. ($I>2\sigma(I)$)	9 196	6 733
Parameters	680	465
wR_2 (all data)	0.1702	0.2963
R value ($I>2\sigma(I)$)	0.0586	0.0930
Largest diff. hole and peak (e-.$Å^{-3}$)	-0.854; 1.342	-2.120; 2.613

Table S2. Selected bond lengths [Å] for the crystal structures of complexes [2] and [3]:

Complex [2]				**Complex [3]**	
Site 1		**Site 2**			
Fe1-N1	2.179(2)	Fe2-N4	2.203(3)	Fe1-N1	2.150(3)
Fe1-N2	2.116(2)	Fe2-N5	2.108(3)	Fe1-N2	2.088(3)
Fe1-N3	2.110(2)	Fe2-N6	2.098(3)	Fe1-N3	2.084(3)
Fe1-O1	2.038(2)	Fe2-O1	2.013(2)	Fe1-O1	2.0026(14)
Fe1-O12(w)	2.026(2)	Fe2-O14(MeO^-)	1.824(2)	Fe1-O4(w)	2.060(4)
Fe1-O13(OH^-)	1.859(2)	Fe2-O15(w)	2.082(2)	Fe1-O5($MeOH_{1/2}$)	1.909(3)

References:

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