Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Chemoselective and Biomimetic Hydroxylation of Hydrocarbons by Non-heme μ-Oxo-Bridged Diiron(III) Catalysts using *m*-CPBA as Oxidant

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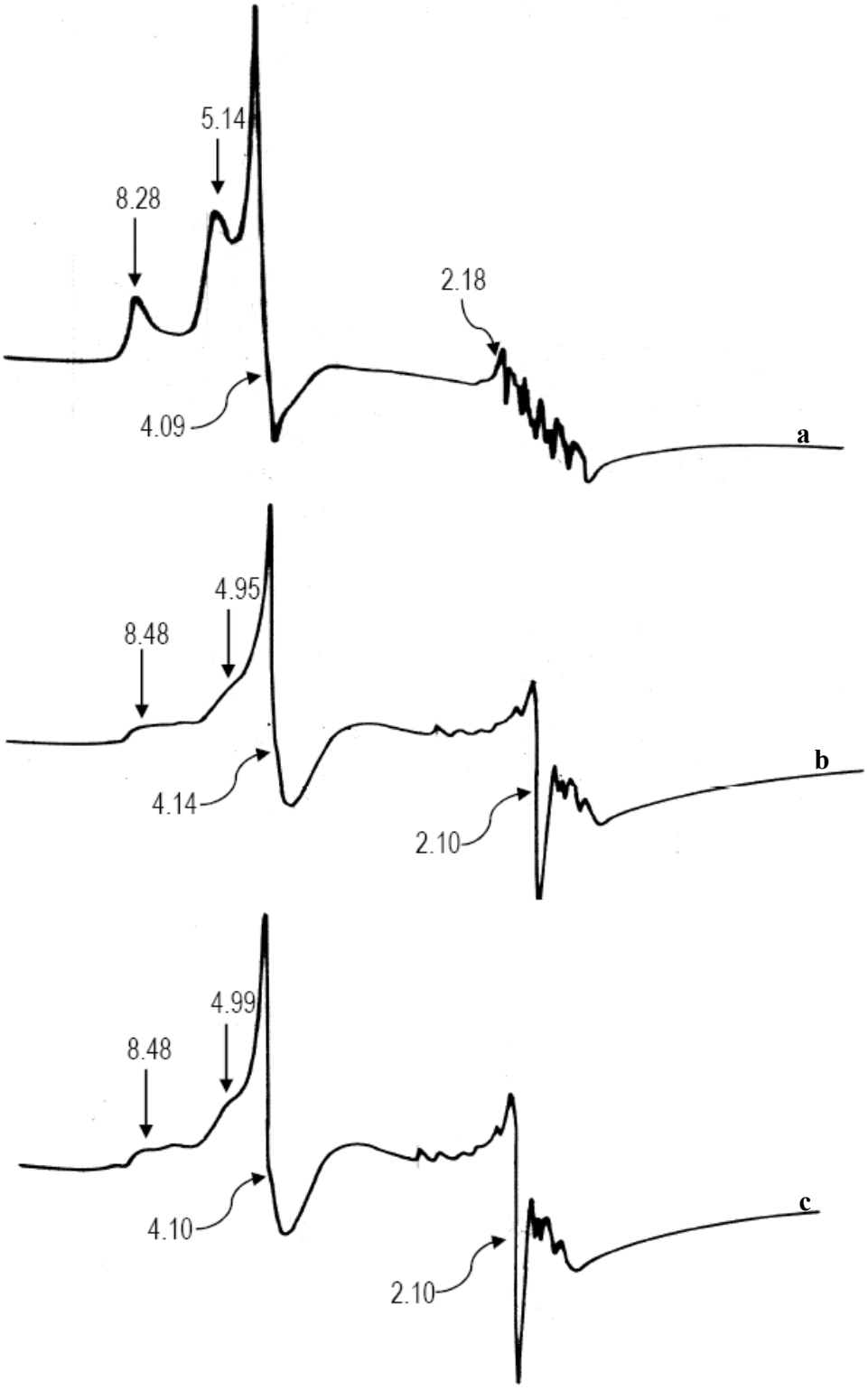

Figure S1. EPR spectra of iron(III) complexes [Fe(L2)Cl] **3** (a) [Fe(L3)Cl] **5** (b) and [Fe(L4)Cl] **7** in frozen acetonitrile /acetone solution at 77 K.

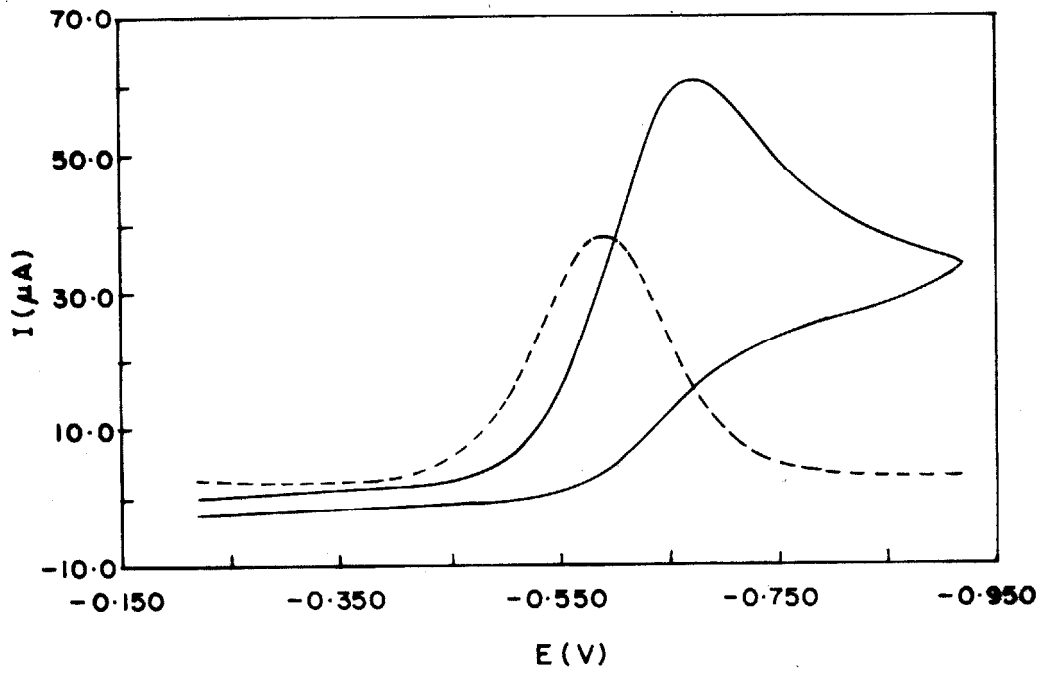

Figure S2. Cyclic (CV) and Differential pulse voltammogram of **2** in acetonitrile at 25 °C. Complex concentration: 0.001 M, Supporting electrolyte: 0.1 M TBAP, Scan rate: 50 (CV) and 5 mV s^{-1} (DPV), Working electrode: Pt sphere; Reference electrode: Ag/Ag^{+}.

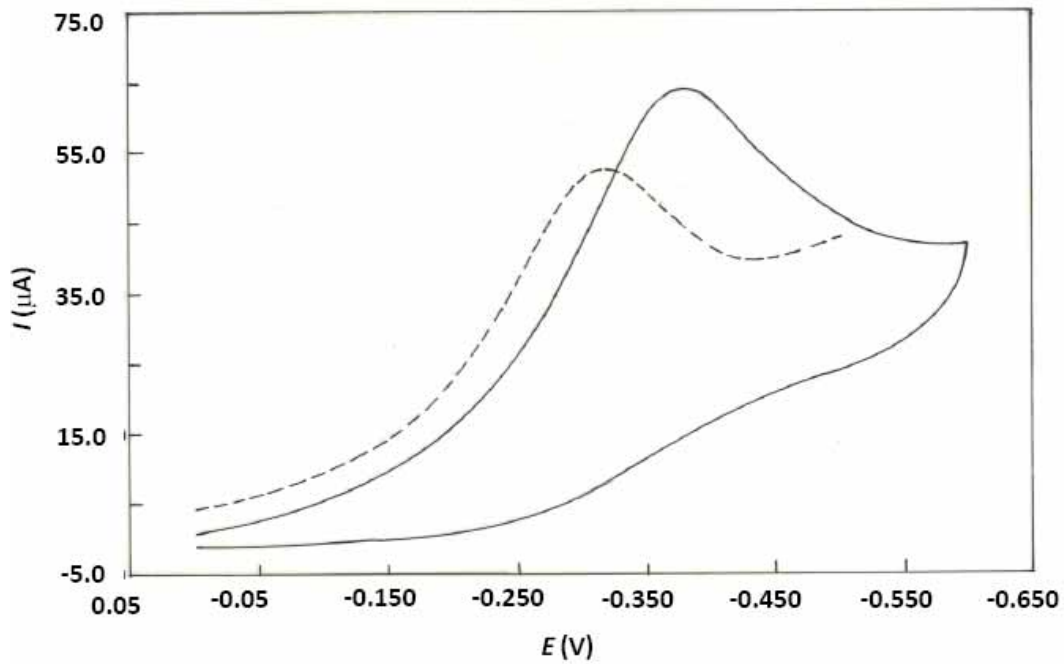

Figure S3. Cyclic (CV) and Differential pulse voltammogram of **4** in acetonitrile at 25 °C. Complex concentration: 0.001 M, Supporting electrolyte: 0.1 M TBAP, Scan rate: 50 (CV) and 5 mV s^{-1} (DPV), Working electrode: Pt sphere; Reference electrode: Ag/Ag^{+}.

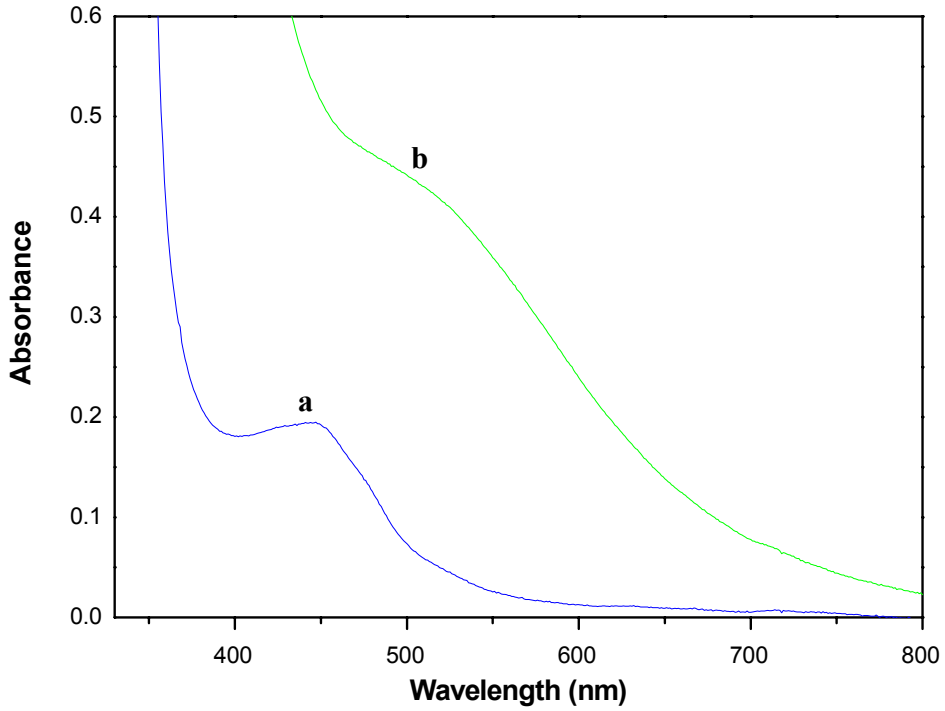

Figure S4. Electronic absorption spectral changes on adding H_2O_2 (a) and *t*-BuOOH (b) to [Fe(L2)Cl] **3** (2.0×10^{-4} M) in acetonitrile.

Table S1. ESI-Mass Spectral data for iron(III) complexes and their hydro/alkyl/arylperoxo intermediates in acetonitrile solution

Complex	Added oxidant	Species identified	Cal. mass (*m/z*)	ESI-Mass (*m/z*)
[Fe(L2)Cl] **3**	-	[Fe(L2)Cl]	630	631
[Fe(L2)Cl] **3**	H_2O_2	[(L2)Fe-OOH]	629	634
[Fe(L2)Cl] **3**	*t*-BuOOH	[(L2)(Cl)Fe-OO-*t*Bu]	720	719,702
[Fe(L2)Cl] **3**	*m*-CPBA	[(L2)(Cl)Fe-OO-OC-C_6H_4Cl]	802	804
[$Fe_2O(L2)_2$] **4**	-	[$Fe_2O(L2)_2$]	1241	1243, 1233
[$Fe_2O(L2)_2$] **4**	H_2O_2	[$(L2)_2(O)Fe_2(OOH)_2$]	1307	1308, 1275
[$Fe_2O(L2)_2$] **4**	*t*-BuOOH	[$(L2)_2(O)Fe_2$(OO-*t*Bu)]	1330	1332
[$Fe_2O(L2)_2$] **4**	*m*-CPBA	[$(L2)_2(O)Fe_2$(OO- OC-C_6H_4Cl)$_2$]	1583	1586, 1575
[Fe(L3)Cl] **5**	-	[Fe(L3)Cl]	400	401
[Fe(L3)Cl] **5**	H_2O_2	[(L3)Fe-OOH]	399	402
[Fe(L3)Cl] **5**	*t*-BuOOH	[(L3)Fe-OO-*t*Bu]	455	457
[Fe(L3)Cl] **5**	*m*-CPBA	[(L3)Fe-OO-OC-C_6H_4Cl]	537	535, 536
[$Fe_2O(L3)_2$] **6**	-	[$Fe_2O(L3)_2$]	748	749
[$Fe_2O(L3)_2$] **6**	H_2O_2	[$(L3)_2(O)Fe_2(OOH)_2$]	815	816, 779
[$Fe_2O(L3)_2$] **6**	*t*-BuOOH	[$(L3)_2(O)Fe_2$(OO-*t*Bu)$_2$]	928	932,829
[$Fe_2O(L3)_2$] **6**	*m*-CPBA	[$(L3)_2(O)Fe_2$(OO- OC-C_6H_4Cl)]	919	922

Table S2. Oxidation products of cyclohexane (% yield)[a,c] by **4** as catalyst and *m*-CPBA

Time (h)	CyOH (%)	CyO(%)	A/K	T.O. N[b]
2	1.68	-	-	4.2
4	2.16	-	-	5.4
6	2.44	0.20	12.2	6.6
8	2.96	0.40	7.4	8.4
10	3.68	0.76	4.8	11.1
12	3.92	1.64	2.4	13.9
12[d]	2.39	2.28	0.96	12.2
12[e]	8.32	12.40	0.68	51.8

[a]Reaction Conditions: cyclohexane (0.2 M), complex (1.0×10^{-4} M), *m*-CPBA (0.05 M), CH_3CN (2 mL), temperature 25 °C, [b]T.O.N = mol product / mol catalyst. [c]Yield based on the oxidant used. [d]H_2O_2 is used as oxidant, [e]*t*-BuOOH is used as oxidant.

Table S3 Oxidation products (% yield)[a,c] of cyclohexane with **3** as catalyst and *m*-CPBA

Time (h)	CyOH	CyO	A/K	T.O.N[b]
2	2.44	1.12	2.2	8.9
4	2.64	1.20	2.2	9.6
6	3.48	2.08	1.7	13.9
8	3.52	1.92	1.8	13.6
10	3.60	2.00	1.8	14.0
12	3.64	2.08	1.8	14.3

[a]Reaction Conditions: cyclohexane (0.2 M), complex (1.0×10^{-4} M), *m*-CPBA (0.05 M), CH_3CN (2 mL), temperature 25 °C, [b]T.O.N = mol product / mol catalyst. [c]Yield based on the oxidant used.