applied sciences

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Supplementary Materials

Synthesis, Structures, Electrochemistry, and Catalytic Activity towards Cyclohexanol Oxidation of Mono-, Di-, and Polynuclear Iron(III) Complexes with 3-Amino-2-Pyrazinecarboxylate

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Received: 20 March 2020; Accepted: 9 April 2020; Published: date

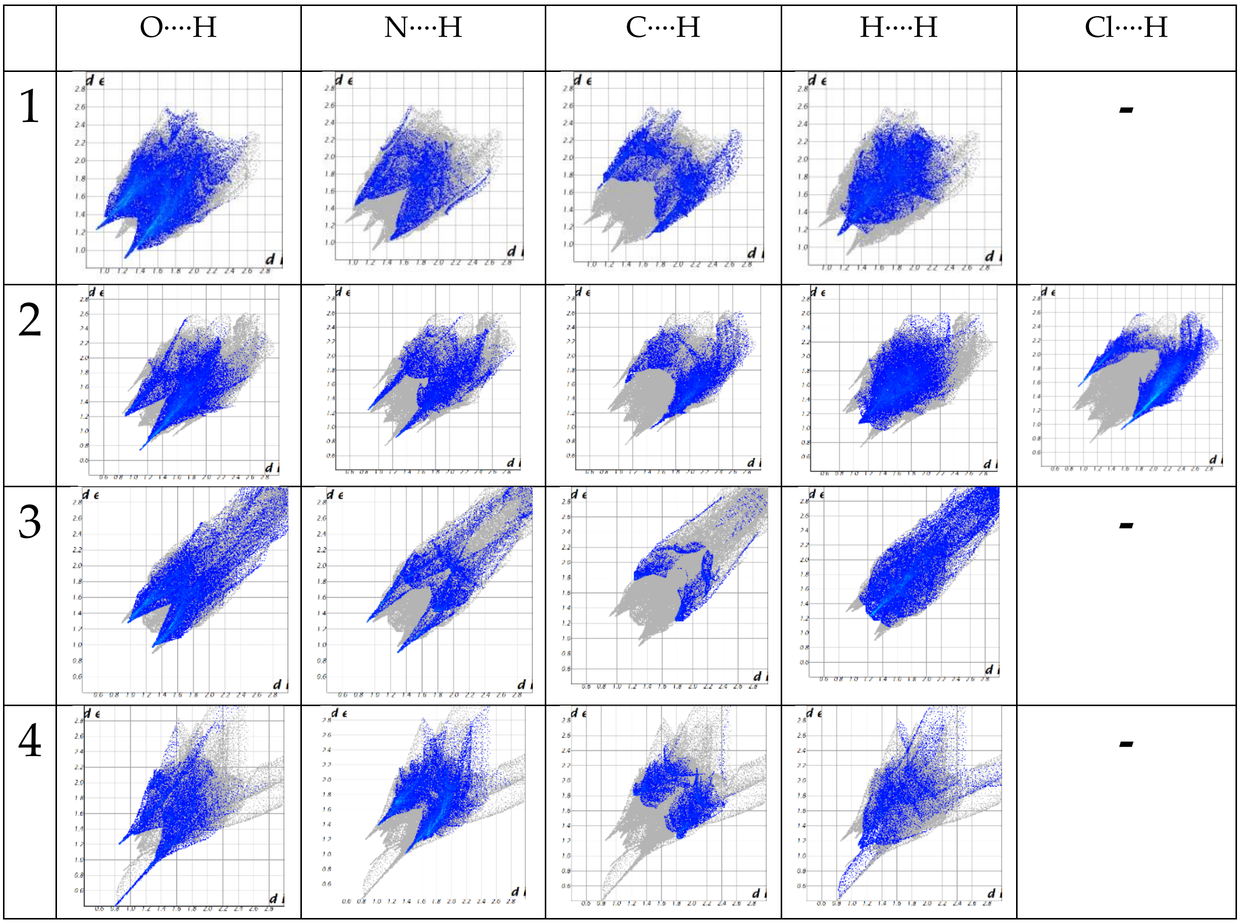

Figure S1 2D fingerprint plots of **1-4**, exhibiting different intermolecular interactions.

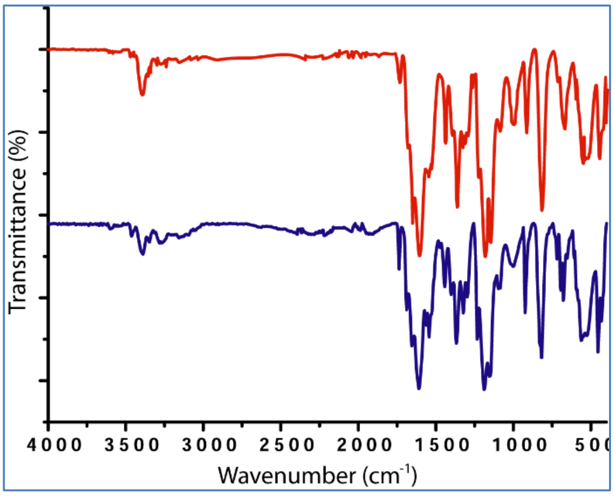

Figure 2. FT-IR spectra of **3** before (in blue), after (in red) the microwave-assisted catalytic peroxidative oxidation of cyclohexanol.

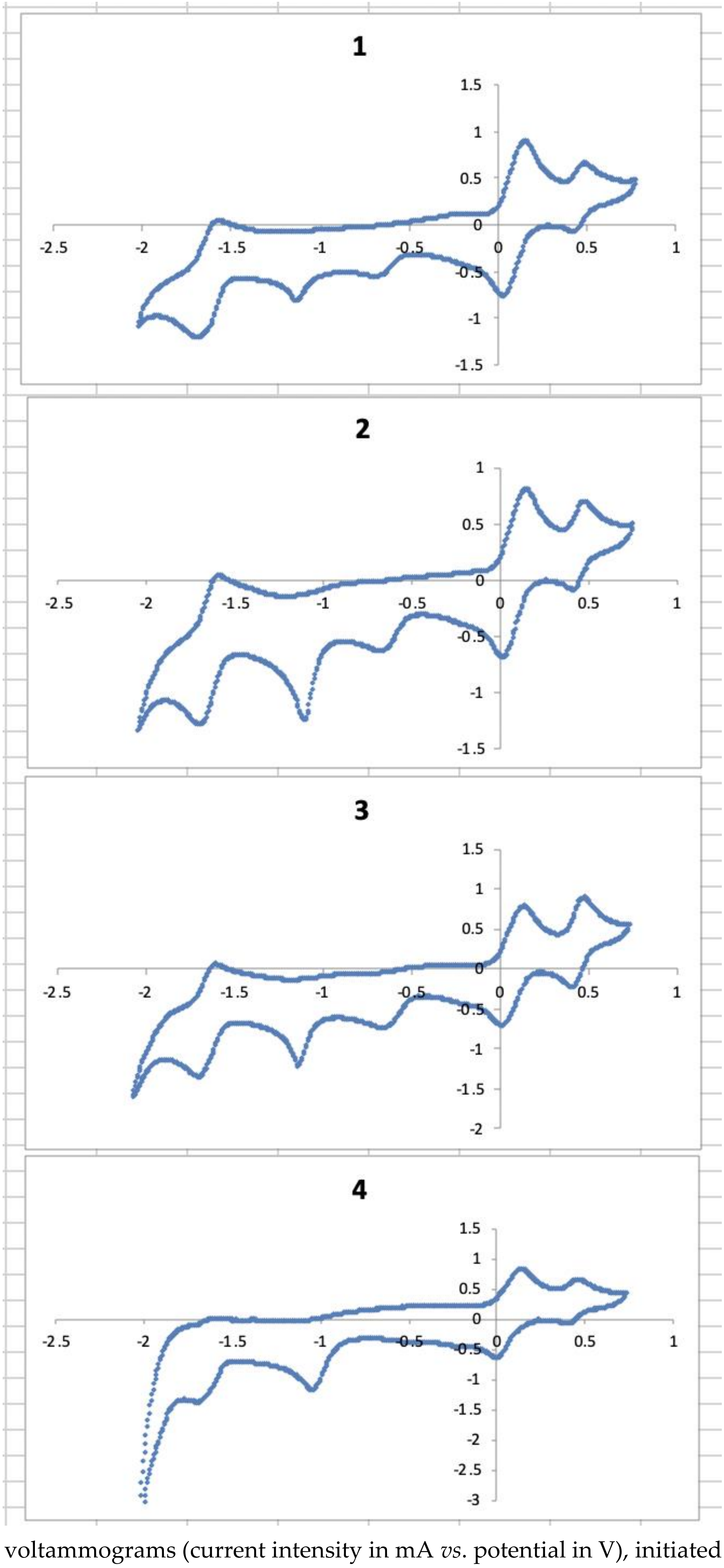

Figure S3 Cyclic voltammograms (current intensity in mA *vs*. potential in V), initiated by the anodic sweep, of compounds **1** - **4** in a 0.2 M [^{n}Bu$_4$N][BF$_4$]/DMSO solution, at a Pt disc working electrode. Internal standard used: [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.42 V vs. SCE)

Table S1: Crystal data and structure refinement details for compounds 1-4				
Identification name	**1**	**2**	**3**	**4**
Formulae	$C_{15}H_{12}FeN_9O_6$	$C_{16}H_{24}Cl_2FeN_7O_4$	$C_{22}H_{22}Fe_2N_{12}O_{10}$	$C_{10}H_9FeN_9NaO_5$
Mol. wt.	470.19	505.17	726.21	414.10
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P-1	C2/c	C2/c
Temperature /K	296	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
a /Å	30.021(4)	7.9489(6)	15.014(9)	23.0847(10)
b /Å	8.3527(11)	16.4168(13)	17.162(10)	9.0844(4)
c /Å	14.4755(19)	17.8085(13)	15.390(11)	15.1865(6)
α/°	90	86.504(3)	90	90
β/°	92.979(5)	79.786(3)	115.92(2)	99.570(2)
γ/°	90	79.198(3)	90	90
V/ $Å^3$	3624.9(8)	2245.6(3)	3567(4)	3140.4(2)
Z	8	4	4	8
Density/Mgm^{-3}	1.723	1.494	1.352	1.752
Abs. Coeff. /mm^{-1}	0.892	0.946	0.876	1.036
F(000)	1912	1044	1480	1672
Refl. collected	23983	26499	11850	23080
Refl. unique	3332	8221	3348	3223
Max. 2θ/°	25.556	25.395	26.055	26.422
Ranges (h, k, l)	-36<= h <=36 -10<= k <=10 -17<= l <= 17	-9<= h <=9 -19<= k <=19 -21<= l <= 21	-16<= h <=18 -20 <= k <=20 -18<= l <=16	-28<= h <=28 -11<= k <=11 -19<= l <= 18
Complete to 2θ (%)	98.3	99.3	99.3	99.5
Refl. with I > 2σ(I)	3016	5130	1651	2741
Data/Restraints/Parameters	3332/0/281	8221/31/545	3348/30/208	3223/0/237
Goof (F^2)	1.113	1.014	1.008	1.067
R1 [I > 2s(I)]	0.1603	0.0598	0.0918	0.0610
wR2 [I > 2s(I)]	0.4508	0.1413	0.2345	0.1698
R1 [all data]	0.1658	0.1123	0.1648	0.0707
wR2 [all data]	0.4533	0.1645	0.2887	0.1789

Table S2: Selected bond distances (Å) and angles (°) for compounds 1-4	
1	Fe01-O5 1.882(12); Fe01-O3 1.962(10); Fe01-O1 1.979(11); Fe01-N1 2.047(14); Fe01-N4 2.134(12); Fe01-N7 2.137(12. <O5-Fe01-O3, 96.6(5); <O5-Fe01-O1, 96.3(5); <O3-Fe01-O1, 166.0(5); <O5-Fe01-N1, 170.5(5); <O3-Fe01-N1, 90.7(5); <O1-Fe01-N1, 77.2(4); <O5-Fe01-N4, 93.6(5); <O3-Fe01-N4, 78.6(5); <O1-Fe01-N4, 95.1(5); <N1-Fe01-N4, 93.8(4); <O5-Fe01-N7, 81.1(4); <O3-Fe01-N7, 93.6(4); <O1-Fe01-N7, 93.7(5); <N1-Fe01-N7, 92.3(4); <N4-Fe01-N7, 170.2(5) .
2	Fe1-O3 1.968(3); Fe1-O1 2.047(3); Fe1-N1 2.200(4); Fe1-N4 2.236(4); Fe1-Cl1 2.2691(16); Fe1-Cl2 2.2725(14); Fe2-O7 1.980(3); Fe2-O5 1.987(3); Fe2-N7 2.186(4); Fe2-N10 2.258(3). <O3-Fe1-O1, 86.83(15); <O3-Fe1-N1, 158.31(15); <O1-Fe1-N1, 75.37(14); <O3-Fe1-N4, 75.96(13); <O1-Fe1-N4, 84.50(14); <N1-Fe1-N4, 89.87(14); <O3-Fe1-Cl1, 102.81(12); <O1-Fe1-Cl1, 164.54(11); <N1-Fe1-Cl1, 92.35(12); <N4-Fe1-Cl1, 86.16(11); <O3-Fe1-Cl2, 93.13(10); <O1-Fe1-Cl2, 93.67(11); <N1-Fe1-Cl2, 100.18(11); <N4-Fe1-Cl2, 169.00(11); <Cl1-Fe1-Cl2, 97.78(6); <O7-Fe2-O5, 160.85(13); <O7-Fe2-N7, 92.79(14); <O5-Fe2-N7, 76.52(13); <O7-Fe2-N10, 75.45(13); <O5-Fe2-N10, 87.04(13) ; <N7-Fe2-N10, 80.71(13); <O7-Fe2-Cl3, 96.62(12); <O5-Fe2-Cl3, 91.36(11); <N7-Fe2-Cl3, 165.69(12); <N10-Fe2-Cl3, 91.23(11); <O7-Fe2-Cl4, 91.93(10); <O5-Fe2-Cl4, 103.70(10); <N7-Cl4, 89.71(10); <N10-Fe2-Cl4, 163.63(11); <Cl3-Fe2-Cl4, 100.69(6).
3	Fe01-O5 1.976(5); Fe01-O1 1.972(6) ; Fe01-O3 1.991(5); Fe01-N4 2.140(6); Fe01-N1 2.167(8). <O5-Fe01-O5, 79.6(2); <O5-Fe01-O1, 92.5(2); <O5-Fe01-O1, 99.6(2); <O5-Fe01-O3, 102.4(3); <O5-Fe01-O3, 92.7(2); <O1-Fe01-O3, 162.2(2); <O5-Fe01-N4, 94.4(2); <O5-Fe01-N4, 168.0(2); <O1-Fe01-N4, 91.0(2); <O3-Fe01-N4, 78.4(2); <O5-Fe01-N1, 166.6(2); <O5-Fe01-N1, 93.4(2); <O1-Fe01-N1, 77.3(3); <O3-Fe01-N1, 89.2(3); <N4-Fe01-N1, 94.4(3).
4	Fe1-O5 1.7720(5); Fe1-O3 2.036(3); Fe1-N7 2.042(4); Fe1-O1 2.052(3); Fe1-N1 2.216(3); Fe1-N4 2.262(4); Na1-O2 2.292(5); Na1-O6 2.372(7); Na1-O3 2.416(4); Na1-O4 2.469(5); Na1-O1 2.962(4). <O5-Fe1-O3, 102.04(9); <O5-Fe1-N7, 96.94(14); <O3-Fe1-N7, 92.82(17); <O5-Fe1-O1, 96.18(8); <O3-Fe1-O1, 156.13(12); <N7-Fe1-O1, 100.20(18); <O5-Fe1-N1, 93.52(8); <O3-Fe1-N1, 75.68(12); <N7-Fe1-N1, 165.87(16); <O1-Fe1-N1, 88.03(12); <O5-Fe1-N4, 170.31(10); <O3-Fe1-N4, 86.57(13); <N7-Fe1-N4, 86.95(17); <O1-Fe1-N4, 74.35(13); <N1-Fe1-N4, 84.24(13); <O2-Na1-O6, 113.7(2); <O2-Na1-O3, 108.56(18); <O6-Na1-O3, 80.48(14); <O2-Na1-N2, 105.07(19); <O6-Na1-N2, 104.6(2); <O3-Na1-N2, 140.35(17); <O2-Na1-O4, 130.5(3); <O6-Na1-O4, 108.10(18); <O3-Na1-O4, 53.74(13); <N2-Na1-O4, 88.30(16); <Fe1-O1-Na1, 160.67(16).

Table S3: Hydrogen bond geometry (Å, °) in compounds 1-4					
Compound	D-H···A	D···H (Å)	H···A (Å)	D···A (Å)	<D–H···A(°)
1	N9-H9A···O1	0.86	2.51	3.169(17)	134.2
	N9-H9B···O6	0.86	2.14	2.77(2)	129.4
	N3-H3A···O1	0.86	2.59	3.345(18)	146.5
	N3-H3B···O2	0.86	2.14	2.764(19)	128.6
	N3-H3B···N8	0.86	2.59	3.24(2)	132.9
	N6-H6B···O4	0.86	2.08	2.70(3)	128.7
	C5-H5···O4	0.93	2.40	3.106(19)	132.1
	C15-H15···O6	0.93	2.29	3.096(19)	144.4
	C14-H14···O2	0.93	2.59	3.36(2)	141.0
2	N12-H12A···N11	0.86	2.27	3.076(5)	156.3
	N12-H12B···O8	0.86	2.13	2.761(5)	130.1
	N12-H12B···O8	0.86	2.26	2.876(5)	128.5
	N9-H9A···Cl4	0.86	2.64	3.445(5)	157.4
	N9-H9B···O6	0.86	2.13	2.755(6)	129.6
	N6-H6A···N5	0.86	2.26	3.114(6)	170.6
	N6-H6B···O4	0.86	2.12	2.746(6)	129.7
	N6-H6B···O4	0.86	2.21	2.834(6)	129.4
	N3-H3A···Cl4	0.86	2.83	3.663(5)	164.5
	N3-H3B···O2	0.86	2.10	2.734(7)	130.6
	N14-H14A···O5	0.98	1.93	2.886(6)	163.0
	N13-H13N···O1	0.93	1.93	2.844(6)	167.0
	C19-H19···O7	0.93	2.45	3.359(6)	164.4
	C9-H9···O3	0.93	2.31	3.238(6)	177.1
	C14-H14···Cl2	0.93	2.75	3.658(6)	165.3
	C4-H4···O6	0.93	2.39	3.167(7)	141.0
	C28-H28A···O6	0.97	2.33	3.179(16)	146.0
3	N3-H3A···N6	0.88	2.71	3.567(17)	164.2
	N3-H3B···O2	0.88	2.10	2.720(14)	126.4
	N6-H6A···N5	0.88	2.30	3.063(10)	144.8
	N6-H6B···O4	0.88	2.10	2.757(10)	130.4
	N6-H6B···O4	0.88	2.43	3.026(10)	125.7
	C4-H4···O2	0.93	2.39	3.166(14)	141.0
	C9-H9···O3	0.93	2.56	3.475(10)	170.1
	C10-H10···O1	0.93	2.49	3.312(9)	148.2
4	N3-H3A···O1	0.86	2.18	2.963(5)	151.3
	N3-H3B···O4	0.86	2.09	2.727(6)	130.6
	N6-H6B···O2	0.86	2.10	2.739(8)	130.1
	C9-H9···O4	0.93	2.48	3.224(6)	137.1
	C4-H4···N9	0.93	2.54	3.396(9)	152.7

Table S4 – MW-assisted oxidation[a] of cyclohexanol to cyclohexanone with TBHP and catalyzed by **1** – **4**.					
Entry	Catalyst	t/h	T /ºC	Yield/% [b]	TOF/h^{-1} [c]
1	**1**	0.5	60	47.6	952
2		1.0	60	87.3	873
3		1.5	60	86.8	579
4		2.0	60	81.3	407
5		2.5	60	79.7	319
6		3.0	60	77.1	257
7		0.5	70	52.1	1.04×10^3
8		1.0	70	91.0	910
9		1.5	70	91.1	607
10		2.0	70	84.2	421
11		2.5	70	80.6	322
12		3.0	70	73.8	246
13		0.5	80	66.2	1.32×10^3
14		1.0	80	89.1	891
15		1.5	80	81.4	543
16		2.0	80	71.8	359
17		2.5	80	60.4	242
18		3.0	80	46.5	155
19	**2**	0.5	60	53.7	1.07×10^3
20		1.0	60	90.8	908
21		1.5	60	89.6	597
22		2.0	60	87.3	437
23		2.5	60	81.1	324
24		3.0	60	74.2	247
25		0.5	70	57.6	1.15×10^3
26		1.0	70	92.5	925
27		1.5	70	91.1	607
28		2.0	70	87.3	437
29		2.5	70	86.2	345
30		3.0	70	82.8	276
31		0.5	80	63.0	1.26×10^3
32		1.0	80	86.1	861
33		1.5	80	80.4	536
34		2.0	80	70.1	351
35		2.5	80	61.4	246
36		3.0	80	49.3	164
37	**3**	0.5	60	51.1	1.02×10^3
38		1.0	60	89.2	892

39		1.5	60	88.8	592
40		2.0	60	85.3	427
41		2.5	60	82.7	331
42		3.0	60	82.1	274
43		0.5	70	66.6	1.33 x 10^3
44		1.0	70	93.1	931
45		1.5	70	93.0	620
46		2.0	70	91.3	457
47		2.5	70	87.2	349
48		3.0	70	83.4	278
49		0.5	80	67.0	1.34 x 10^3
51		1.0	80	88.2	882
52		1.5	80	82.5	550
53		2.0	80	74.6	373
54		2.5	80	66.9	268
55		3.0	80	51.7	172
56	**4**	0.5	60	71.6	1.43 x 10^3
57		1.0	60	90.4	904
58		1.5	60	90.3	602
59		2.0	60	88.3	442
60		2.5	60	86.7	347
61		3.0	60	82.1	273
62		0.5	70	75.2	1.50 x 10^3
63		1.0	70	92.7	927
64		1.5	70	92.5	617
65		2.0	70	89.0	445
66		2.5	70	82.2	328
67		3.0	70	74.1	247
68		0.5	80	67.2	1.34 x 10^3
69		1.0	80	89.0	890
70		1.5	80	82.5	550
71		2.0	80	76.1	381
72		2.5	80	67.3	269
73		3.0	80	53.9	180

[a]Reaction conditions: Cyclohexanol (5 mmol), TBHP (70 % aqueous solution, 10 mmol) and **1** - **4** (5 μmol, 0.1 mol% *vs.* substrate), 10 W of MW irradiation, 60-80^{o}C. [b]Product yield = (moles of cyclohexanone / initial moles of cyclohexanol)*100. [c]Turnover frequency = moles of cyclohexanone per mol of catalyst per hour.