SUPPORTING INFORMATION FOR:

Toward Understanding Macrocycle Specificity of Iron on the Dioxygen-Binding Ability: A Theoretic Study

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Table S1 Key geometric features for the close-shell singlets, triplets and quintets of the oxy-systems. Abbreviation definition is the same with Figure 1.

Compound	O-O (Å)	O-Fe (Å)	<O-O-Fe (º)
O_2-FePor	1.321 (1.286) [1.256]	1.737 (2.031) [2.774]	121.4 (126.5) [113.7]
O_2-FePz	1.320 (1.282) [1.274]	1.737 (2.050) [2.576]	120.8 (125.9) [120.2]
O_2-FePc	1.320 (1.283) [1.271]	1.741 (2.185) [2.594]	120.3 (119.9) [121.2]
O_2-FeTAA	1.279 (1.255) [1.213]	1.708 (2.063) [3.299]	121.6 (121.1) [148.5]
O_2-FeTMTAA	1.282 (1.263) [1.222]	1.701 (2.016) [2.984]	123.9 (120.5) [118.8]
O_2-FeAcacen	1.339 (1.313) [1.279]	1.737 (1.993) [2.362]	121.6 (117.8) [130.2]
O_2-FeSalen1	1.334 (1.265) [1.292]	1.746 (2.275) [2.275]	117.8 (120.7) [129.2]
O_2-FeSalen2	1.330 (1.266) [1.280]	1.743 (2.231) [2.352]	118.2 (120.8) [128.6]

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Table S2 AIM analysis results for the open-shell singlets of each oxy-systems.
Abbreviation definition is the same with Figure 1.

Compound	O-O [a]			O-Fe [a]		
	CD	$\nabla^2\rho(r)$	$H_{(r)}$	CD	$\nabla^2\rho(r)$	$H_{(r)}$
$^1O_2$-FePor	0.392	0.0337	-0.3432	0.0433	0.2053	-0.0003
$^1O_2$-FePz	0.4027	0.0099	-0.3589	0.0358	0.1530	-0.0019
$^1O_2$-FePc	0.4015	0.0157	-0.3577	0.0379	0.1717	-0.0079
$^1O_2$-FeTAA	0.3717	0.0742	-0.3141	0.0607	0.2907	-0.0047
$^1O_2$-FeTMTAA	0.3526	0.1238	-0.2871	0.0718	0.3125	-0.0009
$^1O_2$-FeAcacen	0.3835	0.0516	-0.3311	0.0524	0.2332	-0.0031
$^1O_2$-FeSalen1	0.3794	0.0606	-0.3253	0.0563	0.2500	-0.0033
$^1O_2$-FeSalen2	0.3846	0.0494	-0.3327	0.0527	0.2269	-0.0037

[a] CD is the electronic charge density between the two nuclei; $\nabla^2\rho(r)$ is the Laplacian of the charge density; $H_{(r)}$ is the total local energy density.

Table S3 AIM analysis results for the close-shell singlets of oxy-systems.

Abbreviation definition is the same with Figure 1.

Compound	O-O [a]			O-Fe [a]		
	CD	$\nabla^2\rho(r)$	$H_{(r)}$	CD	$\nabla^2\rho(r)$	$H_{(r)}$
$^1O_2$-FePor	0.3425	0.1699	-0.2731	0.1494	1.0073	-0.0145
$^1O_2$-FePz	0.3425	0.1699	-0.2731	0.1494	1.0073	-0.0145
$^1O_2$-FePc	0.343	0.1707	-0.2738	0.1478	0.9875	-0.0139
$^1O_2$-FeTAA	0.3836	0.0683	-0.3331	0.1638	1.0836	-0.0242
$^1O_2$-FeTMTAA	0.3804	0.0778	-0.3285	0.1663	1.1068	-0.0263
$^1O_2$-FeAcacen	0.325	0.1988	-0.2491	0.1516	0.9695	-0.0177
$^1O_2$-FeSalen1	0.3299	0.1932	-0.2559	0.1488	0.9482	-0.0160
$^1O_2$-FeSalen2	0.3336	0.1873	-0.261	0.1490	0.9694	-0.0157

[a] CD is the electronic charge density between the two nuclei; $\nabla^2\rho(r)$ is the Laplacian of the charge density; $H_{(r)}$ is the total local energy density.

Table S4 AIM analysis results for the triplets of each oxy-systems. Abbreviation definition is the same with Figure 1.

Compound	O-O			O-Fe		
	CD	$\nabla^2\rho(r)$	$H_{(r)}$	CD	$\nabla^2\rho(r)$	$H_{(r)}$
$^1O_2$-FePor	0.3763	0.0522	-0.321	0.0693	0.3474	-0.0033
$^1O_2$-FePz	0.3763	0.0522	-0.321	0.0693	0.3474	-0.0033
$^1O_2$-FePc	0.3803	0.0442	-0.3269	0.0579	0.1615	-0.0114
$^1O_2$-FeTAA	0.4101	-0.032	-0.3716	0.0682	0.2952	-0.0050
$^1O_2$-FeTMTAA	0.4019	-0.0141	-0.3594	0.0766	0.3567	-0.0040
$^1O_2$-FeAcacen	0.3494	0.1146	-0.2828	0.0829	0.3707	-0.0038
$^1O_2$-FeSalen1	0.3995	-0.0031	-0.3548	0.0401	0.1579	-0.0058
$^1O_2$-FeSalen2	0.3971	-0.0092	-0.3519	0.0531	0.1923	-0.0108

[a] CD is the electronic charge density between the two nuclei; $\nabla^2\rho(r)$ is the Laplacian of the charge density; $H_{(r)}$ is the total local energy density.

Table S5 AIM analysis results for the quintets of each oxy-systems. Abbreviation definition is the same with Figure 1.

Compound	O-O [a]			O-Fe [a]		
	CD	$\nabla^2\rho(r)$	$H_{(r)}$	CD	$\nabla^2\rho(r)$	$H_{(r)}$
$^1O_2$-FePor	0.4111	0.0002	-0.3711	0.0213	0.0651	0.0011
$^1O_2$-FePz	0.4111	0.0002	-0.3711	0.0225	0.0696	0.0011
$^1O_2$-FePc	0.3939	0.0382	-0.3456	0.0215	0.0676	-0.0011
$^1O_2$-FeTAA	0.4605	-0.1541	-0.45	0.0037	0.0155	0.0010
$^1O_2$-FeTMTAA	0.4517	-0.1367	-0.4359	0.0093	0.0316	0.0009
$^1O_2$-FeAcacen	0.3843	0.0504	-0.3319	0.0353	0.1107	-0.0055
$^1O_2$-FeSalen1	0.3708	0.074	-0.3125	0.0463	0.1230	-0.0089
$^1O_2$-FeSalen2	0.3836	0.0499	-0.331	0.0411	0.1055	-0.0069

[a] CD is the electronic charge density between the two nuclei; $\nabla^2\rho(r)$ is the Laplacian of the charge density; $H_{(r)}$ is the total local energy density.
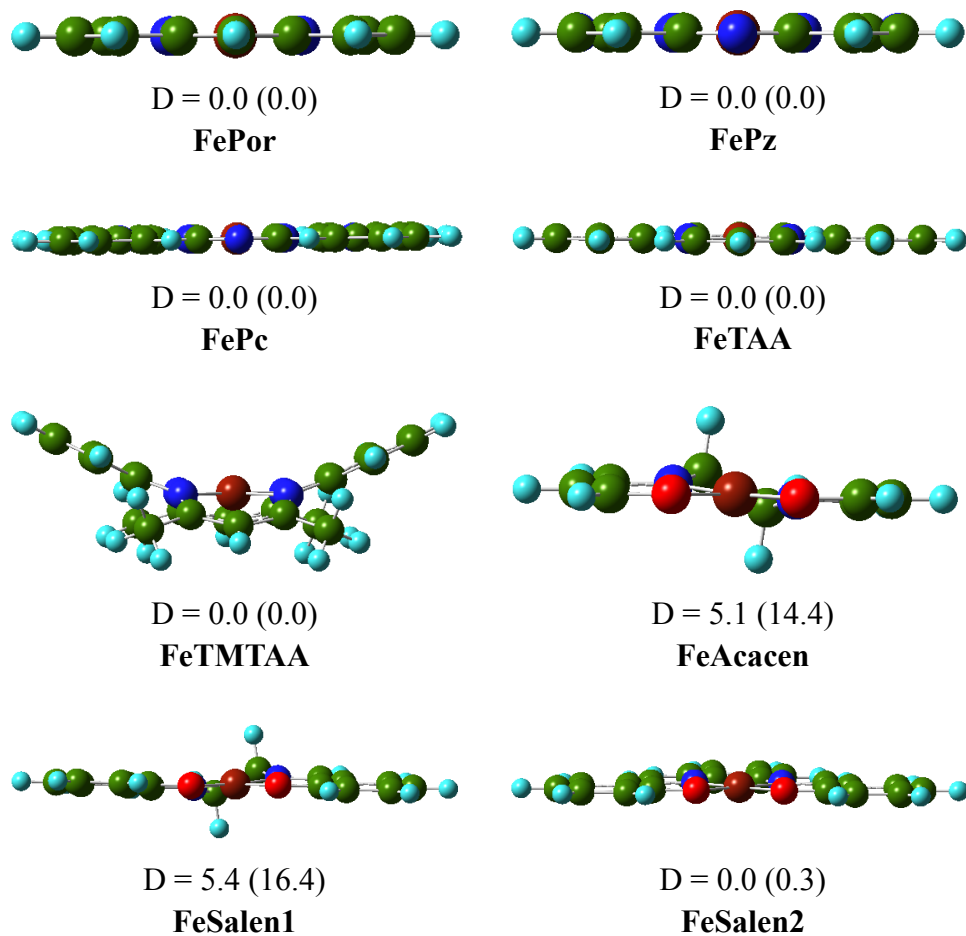
D = 0.0 (0.0)
FePor

D = 0.0 (0.0)
FePz

D = 0.0 (0.0)
FePc

D = 0.0 (0.0)
FeTAA

D = 0.0 (0.0)
FeTMTAA

D = 5.1 (14.4)
FeAcacen

D = 5.4 (16.4)
FeSalen1

D = 0.0 (0.3)
FeSalen2

Figure S1. The side-view structures for the systems under study. Abbreviation definition is the same with Figure 1. The maroon balls are iron atoms, the blue balls are nitrogen atoms, the red balls are oxygen atoms, the green-black balls are carbon atoms, and the turquoise balls are hydrogen atoms. D is the abbreviation of dihedral angle (in degree) of the four coordinated atoms to Fe.