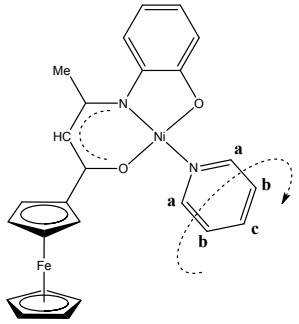
Electronic Supplementary Information

Four-Coordinate Nickel(II) and Copper(II) Complexes Based ONO Tridentate Schiff Base Ligands: Synthesis, Molecular Structure, Electrochemical, Linear and Nonlinear Properties, and Computational Study

Nestor Novoa, Thierry Roisnel, Paul Hamon, Samia Kahlal, Carolina Manzur, Hoang Minh Ngo, Isabelle Ledoux-Rak, Jean-Yves Saillard, David Carrillo and Jean-René Hamon



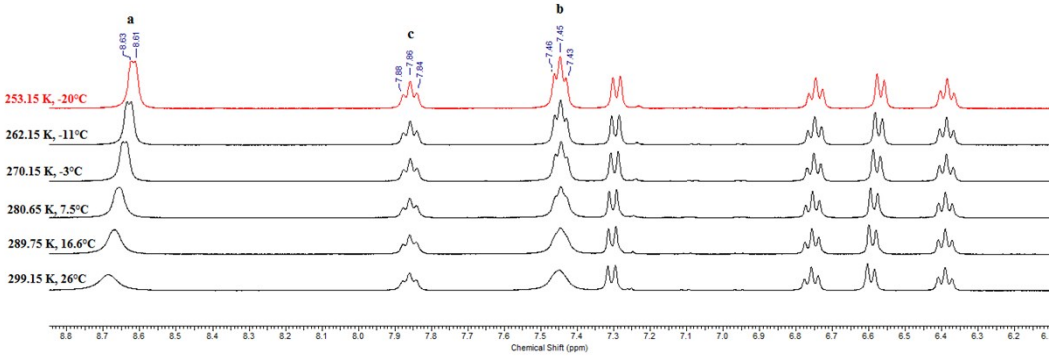


Fig. S1 VT ^{1}H NMR spectra of complex **7** registered in CD_2Cl_2 in the 253-299 K temperature range.

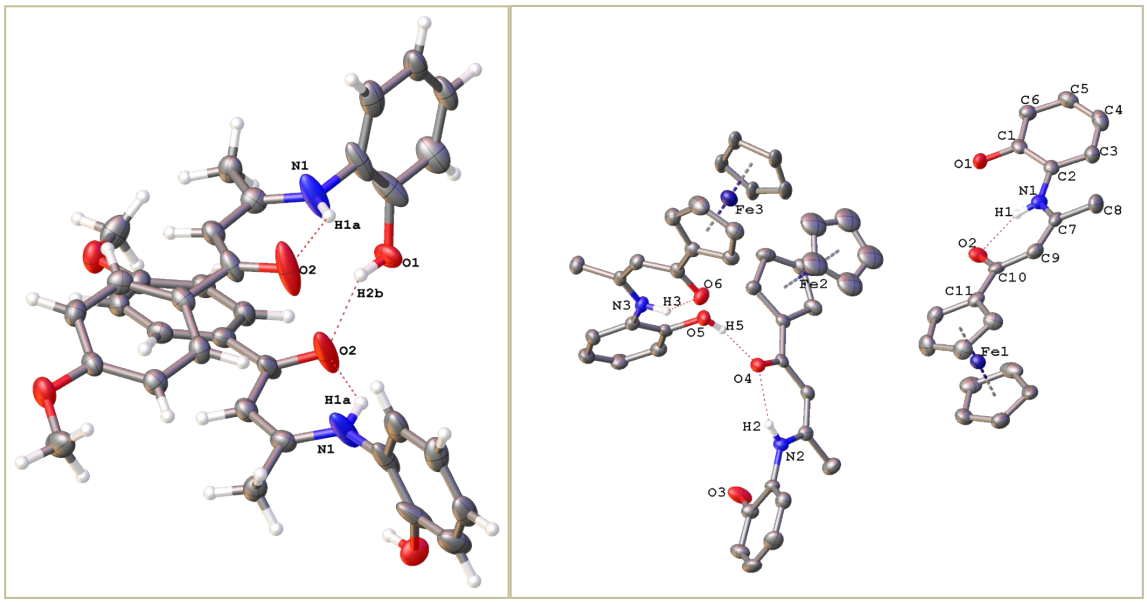


Fig. S2 Packing diagrams of **3** (left) and **4** (right) showing the molecular arrangement within the crystal lattice through intra- and intermolecular hydrogen bonds.

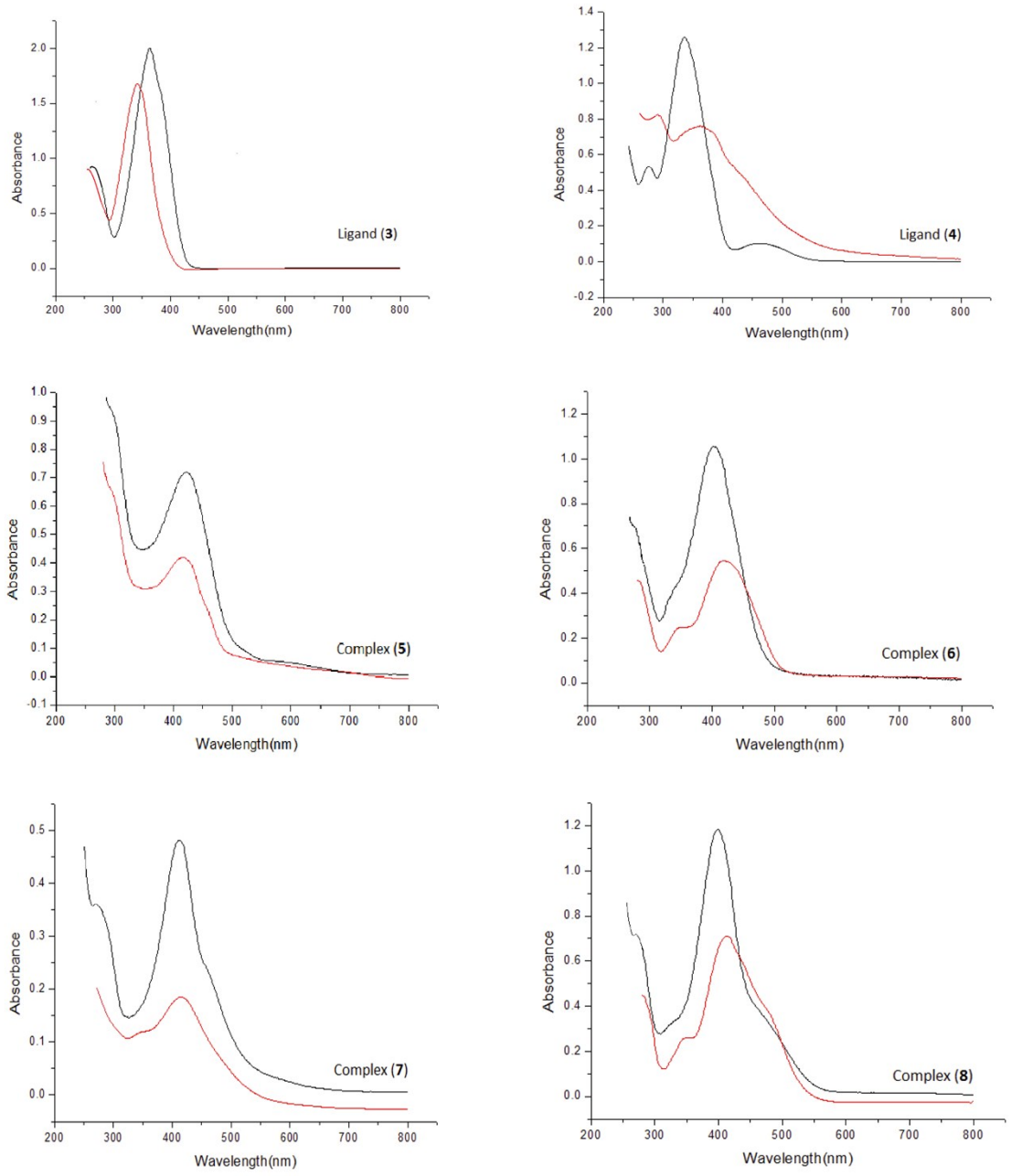
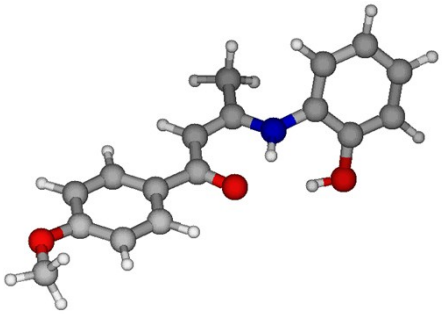
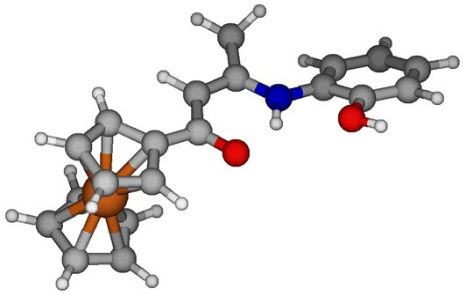


Fig. S3 Experimental UV-Vis spectra of **3-8** recorded in CH_2Cl_2 (black line) and in DMSO (red line).



3



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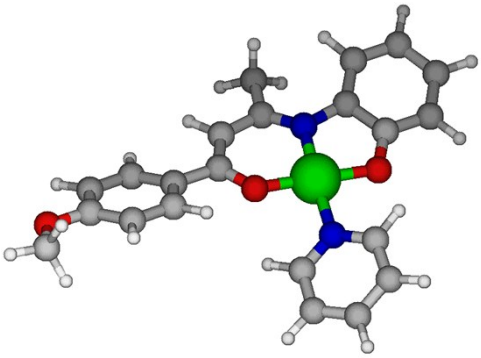
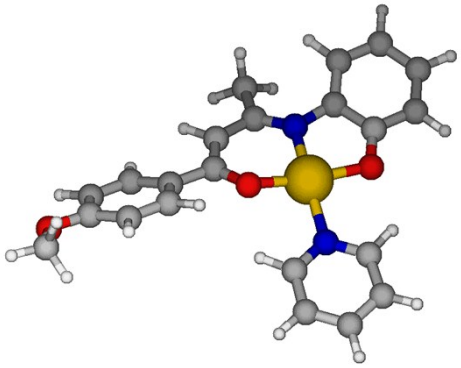
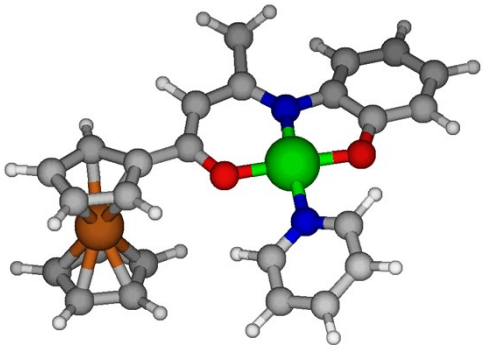


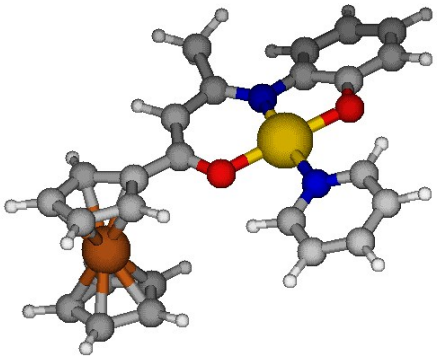
5



6’



7



8

Fig. S4 Optimized geometries of **3**-**5**, **6’**, **7** and **8**.

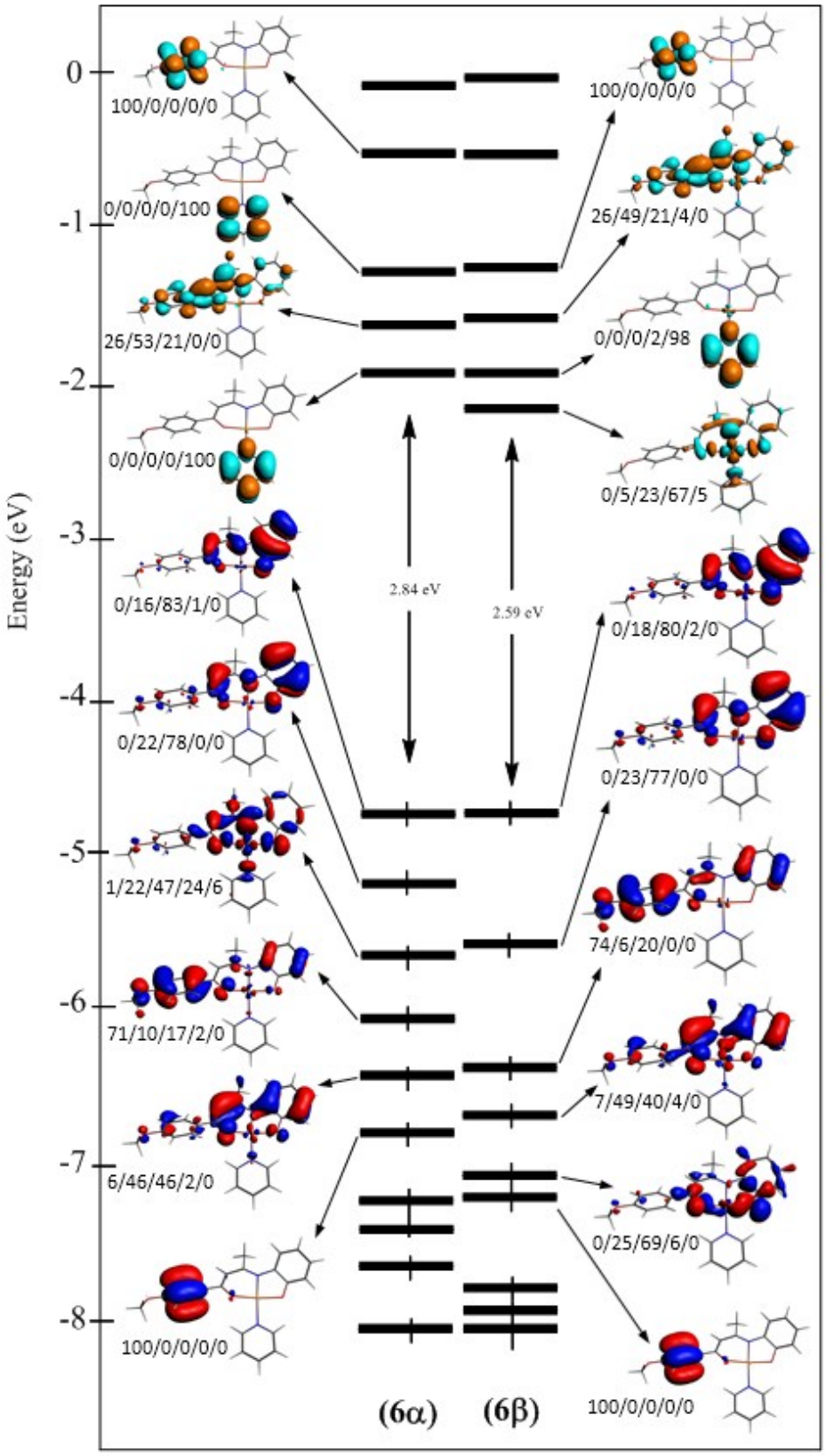


Fig. S5 MO diagram of **6'**. The MO localizations (in %) are given in the following order: R_1/C(10)[O(2)]-C(9)-C(7)[C(8)]-/-N(1)-C_6H_4-O(1)/Cu/pyridine.

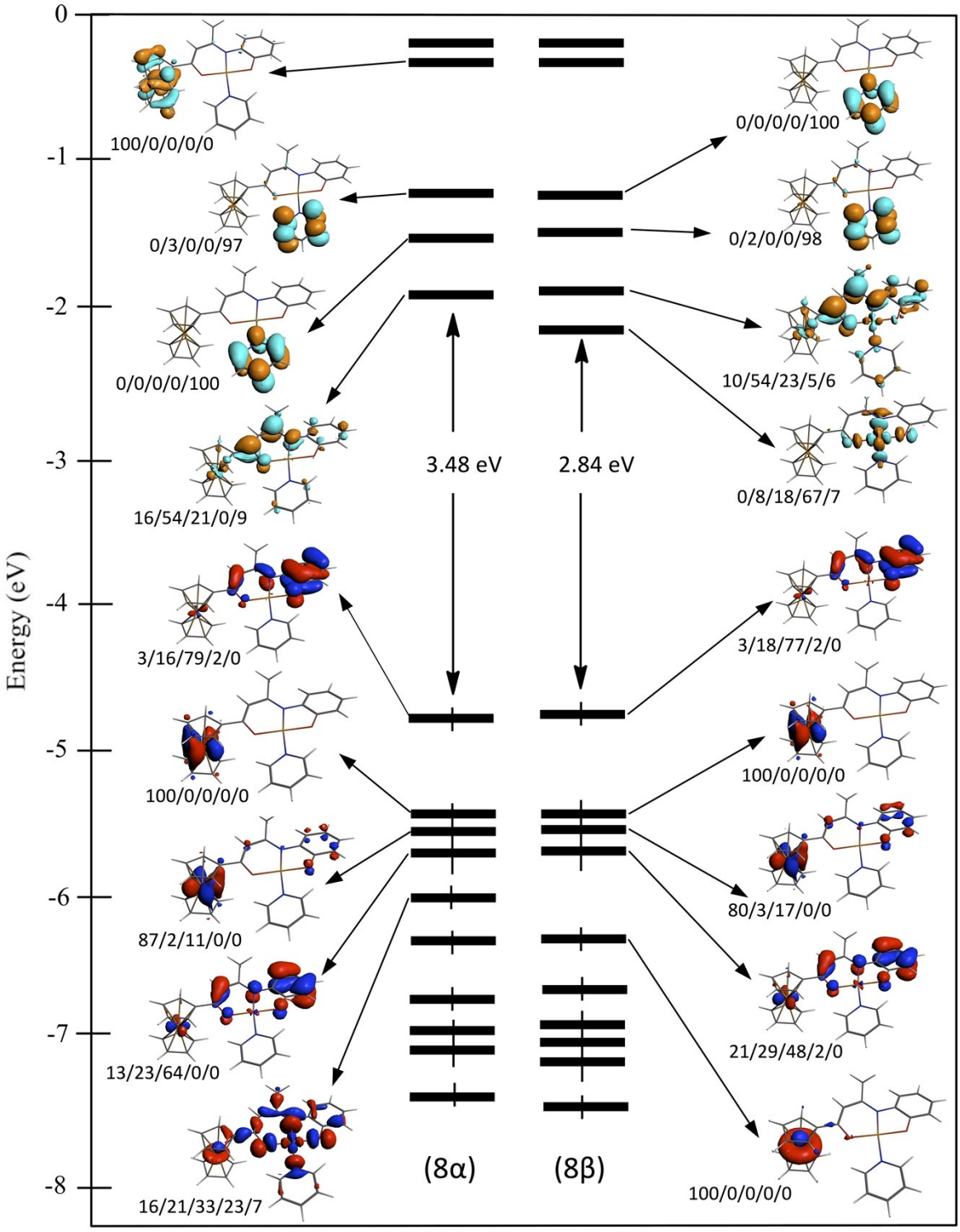
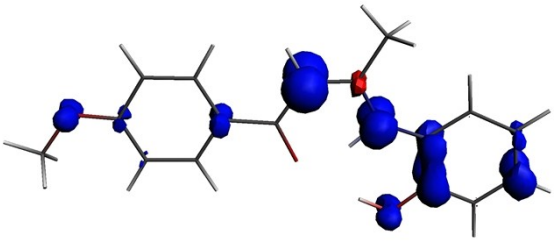
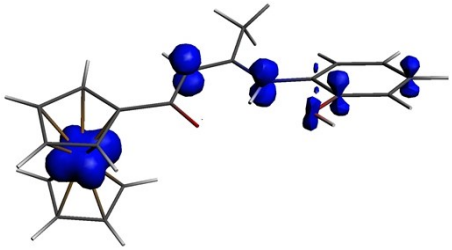


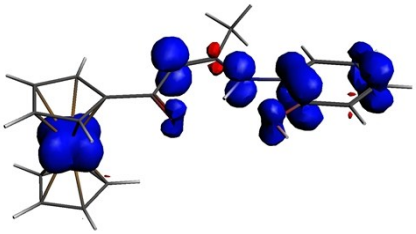
Fig. S6 MO diagram of **8**. The MO localizations (in %) are given in the following order: R_1/C(10)[O(2)]-C(9)-C(7)[C(8)]-/-N(1)-C_6H_4-O(1)/Cu/pyridine.



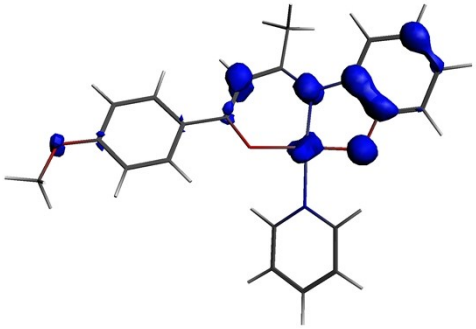
3^+ S=1/2



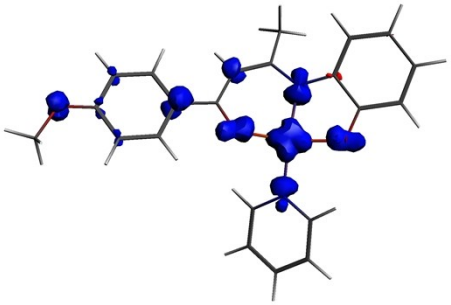
4^+ S=1/2



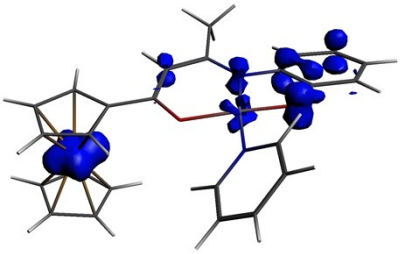
4^{2+} S=1



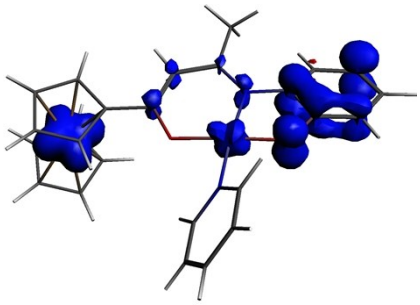
5^+ S=1/2



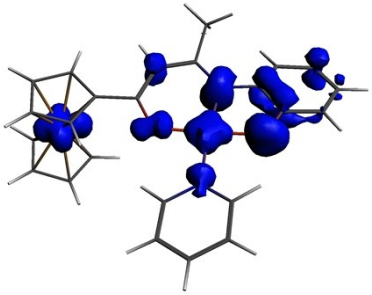
6^{2+} S=1/2



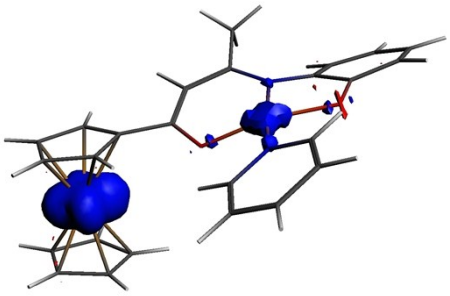
7^+ S=1/2



7^{2+} S=1



8^+ S=1



8^{2+} S=1/2

Fig. S7 Spin density plots of **3^+** , **5^+** , **4^+** , **4^{2+}**, **6^{2+}**, **7^+**, **7^{2+}**, **8^+** and **8^{2+}** in their lowest open-shell configurations (see text).

Table S1 Experimental and Computed (into brackets) infrared frequencies in cm^{-1} for compounds 3-8

	3	**5**	**6**[a]
ν(O–H)	3150(m) [3605(w)]	-	-
ν(N–H)	3073(w) [2855(m)]	-	-
ν(C–H aryl)	3044(w) [3114(w)]	3114(w) [3081(w)]	3040(w) [3080(w)]
ν(C–H, -OCH_3)	2928(w) [2981(w)]	2932(w) [2945(w)]	2926(w) [2945(w)]
ν_{sym}(CH_3)	2844(w) [2948(w)]	2832(w) [2977(w)]	2864(w) [2977(w)]
ν(C=O) and ν(C=C)	1593(s)-1532(m, br) [1609(s)-1491(s)]	-	-
ν(C···O), ν(C···N), ν(C···C)	-	1604(s)-1582(s) [1603(s)-1433(s)]	1604(s)-1584(s) [1603(s)-1440(s)]
ν_{asym}(C-H, C_6H_4-O-CH_3)	1257(s) [1300(m)-1240(m)]	1244(s) [1234(m)-1203(m)]	1242(m) [1240(m)-1208(m)]
δ(C–H)	708(m) [718(m)]	736(m) [721(m)]	734(m) [719(m)]
	4	**7**	**8**
ν(O–H)	3427(w) [3726(w)]	-	-
ν(N–H)	3377(m) [2978(m)]	-	-
ν(C–H aryl)	3088(w) [3136(w)]	3118(w) [3121(w)]	3111(w) [3103(w)]
ν_{sym}(CH3)	2963(w) [2980(w)]	2926(w) [2979(w)]	2980(w) [2978(w)]
ν(C=O) and ν(C=C)	1592(s)-1537(m, br) [1615(s)-1480(s)]	-	-
ν(C···O), ν(C···N), ν(C···C)	-	1606(s)-1473(s) [1601(s)-1415(s)]	1607(w)-1505(w) [1590(s)-1401(s)]
ν_{asym}(C-H)	1298(m) [1264(m)]	1296(m) [1286(m)]	1295(m) [1272(m)]
ν_{asym}(C-H; ferrocenyl)	1032(w) [1024(w)]	1039(w) [1026(w)]	1040(w) [1030(w)]
δ(C–H)	752(s) [722(m)]	754(s) [670(m)]	753(s) [737(m)]

[a] Data taken from Ref. 23.

Table S2 Selected bond distances (Å) and angles (°) for compounds 3 and 4 with their theoretically computed values into brackets.

	3	**4A**	**4B**	**4C**
Bond distances				
O(1)-C(1)	1.492(8) [1.364]	1.369(3) [1.370]	1.354(4)	1.365(3)
N(1)-C(2)	1.432(6) [1.417]	1.412(4) [1.397]	1.429(3)	1.422(4)
C(1)-C(2)	1.373(9) [1.410]	1.402(4) [1.416]	1.410(4)	1.390(4)
N(1)-C(7)	1.339(6) [1.358]	1.351(4) [1.360]	1.341(4)	1.344(4)
C(7)-C(9)	1.380(6) [1.384]	1.386(4) [1.384]	1.393(4)	1.387(4)
C(9)-C(10)	1.411(6) [1.435]	1.414(4) [1.440]	1.411(4)	1.416(4)
C(10)-O(2)	1.259(5) [1.265]	1.277(3) [1.260]	1.260(3)	1.277(4)
C(10)-C(11)	1.495(5) [1.490]	1.476(4) [1.480]	1.481(4)	1.483(4)

O(3)-C(14)	1.371(5) [1.364]			
O(3)-C(17)	1.431(5) [1.426]			
Fe(1)-C(Cp)*avg*		2.048(3) [2.075]	2.036(4)	2.048(8)
Fe(1)-C(Cp')*avg*		2.048(3) [2.071]	2.044(3)	2.048(3)
Angles				
O(1)-C(1)-C(2)	128.3(5) [121]	116.8(3) [116]	116.9(3)	117.3(3)
N(1)-C(2)-C(1)	120.9(6) [117]	115.5(3) [117]	119.1(2)	116.4(2)
C(2)-N(1)-C(7)	124.7(4) [127]	132.1(2) [131]	124.9(2)	130.7(2)
N(1)-C(7)-C(9)	121.3(4) [120]	120.3(3) [119]	122.3(3)	120.3(3)
C(7)-C(9)-C(10)	124.6(4) [121]	124.8(3) [124]	124.1(3)	124.5(3)
C(9)-C(10)-O(2)	122.7(4) [121]	121.9(3) [122]	122.3(3)	122.7(3)

Table S3 Selected bond distances (Å) and angles (°) for compounds (5) and (6) with their theoretically computed values into brackets.

	5[a]	**5B**	**6**[a]
	Bond distances		
M(1)[b]-O(1)	1.8336(15) [1.857]	1.8312(15)	1.9247(11) [1.963]
M(1)[b]-O(2)	1.8240(15) [1.854]	1.8229(14)	1.9155(11) [1.960]
M(1)[b]-N(1)	1.8801(18) [1.892]	1.8797(19)	1.9729(13) [1.991]
M(1)[b]-N(2)	1.9315(17) [1.962]	1.9380(17)	2.0467(13) [2.084]
O(1)-C(1)	1.333(3) [1.327]	1.335(3)	1.3349(18) [1.317]
C(1)-C(2)	1.413(3) [1.418]	1.416(3)	1.424(2) [1.437]
N(1)-C(2)	1.427(3) [1.413]	1.427(3)	1.422(2) [1.397]
N(1)-C(7)	1.339(3) [1.334]	1.336(3)	1.323(2) [1.329]
C(7)-C(9)	1.399(3) [1.410]	1.412(3)	1.417(2) [1.415]
C(9)-C(10)	1.382(3) [1.390]	1.371(3)	1.391(2) [1.396]
O(2)-C(10)	1.299(2) [1.300]	1.303(2)	1.289(19) [1.295]
C(10)-C(11)	1.493(3) [1.481]	1.492(3)	1.496(2) [1.488]
O(3)-C(14)	1.377(3) [1.366]	1.371(3)	1.3639(19) [1.366]
O(3)-C(17)	1.430(3) [1.424]	1.424(3)	1.429(2) [1.424]
	Angles		
O(1)-M(1)[b]-N(1)	87.42(7) [87]	87.33(7)	84.60(5) [85]
O(1)-M(1)[b]-N(2)	88.01(7) [89]	88.32(7)	90.86(5) [92]
O(2)-M(1)[b]-N(1)	97.61(7) [97]	97.43(7)	95.20(5) [94]
O(2)-M(1)[b]-N(2)	87.00(7) [88]	87.02(7)	90.78(5) [91]
O(1)-M(1)[b]-O(2)	174.52(7) [175]	174.88(7)	174.93(5) [169]
N(1)-M(1)[b]-N(2)	175.29(8) [174]	174.92(8)	162.66(5) [168]
M(1)[b]-O(1)-C(1)	112.04(15) [112]	112.41(14)	111.99(10) [111]
M(1)[b]-O(2)-C(10)	125.28(14) [125]	125.41(14)	124.36(10) [122]
M(1)[b]-N(1)-C(2)	110.47(15) [111]	110.62(15)	110.34(10) [110]
M(1)[b]-N(1)-C(7)	123.01(15) [123]	123.27(16)	122.77(11) [121]
C(7)-C(9)-C(10)	127.2(2) [127]	126.3(2)	128.19(15) [128]

C(9)-C(10)-O(2)	123.6(2) [123]	124.4(2)	124.46(15) [125]
O(1)-C(1)-C(2)	118.3(2) [118]	117.8(2)	119.05(14) [120]
N(1)-C(2)-C(1)	111.2(2) [112]	111.3(2)	112.59(13) [114]

[a]Data taken from ref. 23. [b]M= Ni **5**; M= Cu **6**.

Table S4 Selected bond distances (Å) and angles (°) for compounds 7 and 8 with their theoretically computed values into brackets.

	7	**8A**	**8B**
Bond distances			
M(1)[a]-O(1)	1.848(2) [1.854]	1.907(2) [1.952]	1.896(2)
M(1)[a]-O(2)	1.827(2) [1.851]	1.892(2) [1.951]	1.880(2)
M(1)[a]-N(1)	1.875(3) [1.899]	1.950(3) [1.990]	1.951(3)
M(1)[a]-N(2)	1.964(3) [1.968]	2.023(2) [2.102]	2.028(2)
O(1)-C(1)	1.342(4) [1.327]	1.334(4) [1.321]	1.338(4)
N(1)-C(2)	1.426(4) [1.417]	1.415(4) [1.404]	1.412(4)
C(1)-C(2)	1.410(4) [1.419]	1.415(4) [1.432]	1.415(5)
N(1)-C(7)	1.330(4) [1.336]	1.320(4) [1.328]	1.330(4)
C(7)-C(9)	1.416(5) [1.410]	1.425(4) [1.415]	1.410(4)
C(9)-C(10)	1.370(4) [1.390]	1.381(4) [1.396]	1.379(4)
C(10)-O(2)	1.307(4) [1.299]	1.303(4) [1.297]	1.297(4)
C(10)-C(11)	1.481(4) [1.470]	1.477(4) [1.476]	1.487(4)
Fe(1)-C(Cp)*avg*	2.036(8) [2.070]	2.028(4) [2.070]	2.039(4)
Fe(1)-C(Cp')*avg*	2.050(3) [2.075]	2.043(4) [2.075]	2.043(3)
Angles			
O(1)-M(1)[a]-N(1)	86.93(10) [87]	85.16(10) [85]	85.24(10)
O(1)-M(1)[a]-N(2)	89.89(10) [89]	92.26(10) [90]	92.22(10)
O(2)-M(1)[a]-N(1)	94.93(10) [97]	93.92(10) [96]	93.69(10)
O(2)-M(1)[a]-N(2)	88.27(10) [87]	89.00(10) [90]	89.18(10)
O(1)M(1)[a]-O(2)	177.08(10) [176]	174.52(10) [179]	175.46(10)
N(1)-M(1)[a]-N(2)	176.80(11) [175]	175.39(10) [174]	174.90(10)

M(1)[a]-O(1)-C(1)	111.7(2) [112]	110.9(2) [111]	110.3(2)
M(1)[a]-O(2)-C(10)	125.7(2) [125]	124.9(2) [123]	124.4(2)
M(1)[a]-N(1)-C(2)	110.1(2) [110]	109.0(2) [110]	109.6(2)
M(1)[a]-N(1)-C(7)	124.9(2) [123]	123.8(2) [122]	123.6(2)
C(2)-N(1)-C(7)	124.3(3) [127]	126.0(3) [128]	125.8(3)
N(1)-C(7)-C(9)	121.3(3) [123]	121.7(3) [123]	122.0(3)
C(7)-C(9)-C(10)	125.0(3) [127]	126.4(3) [129]	125.5(3)
C(9)-C(10)-O(2)	124.8(3) [124]	124.9(3) [125]	126.1(3)
O(1)-C(1)-C(2)	117.5(3) [118]	118.5(3) [120]	119.5(3)
N(1)-C(2)-C(1)	111.6(3) [112]	113.1(3) [113]	111.9(30)

[a]M = Ni **7**; M = Cu **8**. Abbreviations: Cp = C_5H_5, Cp' = C_5H_4

Table S5 Metrical parameters of the ferrocenyl units in compounds 4, 7 and 8

Compd	Fe-Cp_{CNT} (Å)	Fe-Cp'_{CNT} (Å)	Cp_{CNT}-Fe-Cp'_{CNT}(°)	Cp/Cp' (°)
4A	1.656	1.652	178.03	0
4B	1.647	1.651	179.26	12.
4C	1.648/1.679	1.652	172.9/175.3	22/12.5
7	1.657	1.653	178.59	8.6
8A	1.649	1.647	178.97	3.0
8B	1.650	1.658	178.98	4.9

Abbreviations: Cp = C_5H_5, Cp' = C_5H_4, CNT = centroid.

Table S6 Hydrogen Bonding interaction parameters for 3 and 4

Compd	D-H···A (Å)	D-H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
3	N(1)—H(1)···O(2)	0.97(6)	1.92(5)	2.667(5)	132(5)
	O(1A)—H(1A)···O(2)[#1]	0.84	1.89	2.645(6)	149.6
	O(1B)—H(1B1)···O(2)[#2]	0.84	2.22	2.961(9)	147.5
4	N(3)-H(3a)…O(5)	0.88	1.926	2.652	138.7
	N(1)−H(1a)…O(1)	0.88	1.916	2.642	167.4
	O(4)-H(4a)…O(1)	0.84	1.798	2.625	129.7
	N(2)−H(2a)…O(3)	0.88	2.030	2.680	129.7
	O(6)-H(6a)…O(3)	0.84	1.823	2.648	167.2
	N(3)−H(3a)…O(5)'	0.88	1.926	2.652	138.8

Symmetry transformations: #1 -y+1/2, -x+1/2, z+1/2; #2 -y+1/2, -x+1/2, z-1/2

Table S7 Comparison of the bond distances of the N(1)-C(7)-C(9)-C(10)-O(2) core in the ligands (3, 4) and in their complexes (5-8)

Compd	**N(1)-C(7)**	**C(7)-C(9)**	**C(9)-C(10)**	**C(10)-O(2)**
3	1.339(6)	1.380(6)	1.411(6)	1.259(5)
4[a]	1.345(4)	1.388(4)	1.414(4)	1.271(4)
5[a]	1.337(3)	1.405(3)	1.376(3)	1.301(2)
6	1.323(2)	1.417(2)	1.391(2)	1.289(2)
7	1.330(4)	1.416(5)	1.370(4)	1.307(4)
8[a]	1.325(4)	1.417(4)	1.380(4)	1.300(4)

[a] Averaged values.