Pages S1-S55

Electronic Supplementary Information (ESI)

Low-spin $[M^{II}(L)_2]$ and $[M^{III}(L)_2]^+$ (M = Fe and Co) complexes of tridentate azo-containing pyridine/pyrazine amide ligands: structures, properties and redox potential correlations

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Figues and Tables

Fig. S33 Least-squares plot of $E_{1/2}$s between $[M^{III}(L^7)_2]^+$ / $M^{II}(L^7)_2]$ and $[M^{III}(bpy)_3]^{3+}$ / $M^{II}(bpy)_3]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line ($y = 1.54827x + 0.23329$) is ±0.08. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(bpy)_3]^{2+}$ (1.06 V), $[Co(bpy)_3]^{2+}$ (0.42 V) and $[Ni(bpy)_3]^{2+}$ (1.79 V). $E_{1/2}$ (CH_2Cl_2; V *vs.* SCE): $E_{1/2}$ (*vs.* SCE, CH_2Cl_2): $[Fe(L^7)_2]$ (0.61 V), $[Co(L^7)_2]^{2+}$ (0.10 V) and $[Ni(L^7)_2]^{2+}$ (0.94 V).

Fig. S34 Least-squares plot of $E_{1/2}$s between $[M^{III}(L^7)_2]^+$ / $[M^{II}(L^7)_2]$ and $[M^{III}(trpy)_2]^{3+}$ / $[M^{II}(trpy)_2]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line ($y = 1.58697x + 0.12854$) is ±0.004. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(trpy)_2]^{2+}$ (1.10 V), $[Co(trpy)_2]^{2+}$ (0.27 V) and $[Ni(trpy)_2]^{2+}$ (1.65 V). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2): $[Fe(L^7)_2]$ (0.61 V), $[Co(L^7)_2]^{2+}$ (0.10 V) and $[Ni(L^7)_2]^{2+}$ (0.94 V).

Fig. S35 Least-squares plot of $E_{1/2}$s between $[M^{III}(trpy)_2]^{3+}$ / $M^{II}(trpy)_2]^{2+}$ and $[M^{III}(bpy)_3]^{3+}$ / $M^{II}(bpy)_3]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line ($y = 0.97496x + 0.10854$) is ±0.08. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(bpy)_3]^{2+}$ (1.06 V), $[Co(bpy)_3]^{2+}$ (0.42 V) and $[Ni(bpy)_3]^{2+}$ (1.79 V). $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(trpy)_2]^{2+}$ (1.10 V), $[Co(trpy)_2]^{2+}$ (0.27 V) and $[Ni(trpy)_2]^{2+}$ (1.65 V).

Table S1 Data collection and structure refinement parameters for $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1), $[Fe^{II}(L^8)_2]$ (2) and $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot H_2O$ (5)

Table S2 Data collection and structure refinement parameters for $[Co^{II}(L^7)_2]$ (3), $[Co^{II}(L^8)_2]$ (4) and $[Co^{III}(L^8)_2][ClO_4]$ (6)

Table S3 Selected bond Lengths (Å) and bond Angles (deg) in for $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ **(1),** $[Fe^{II}(L^8)_2]$ (2) and $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot H_2O$ (5)

Table S4 Selected bond lengths (Å) and bond angles (deg) in for $[Co^{II}(L^7)_2]$ (3), $[Co^{II}(L^8)_2]$ (4) and $[Co^{III}(L^7)_2][ClO_4]$ (6)

Table S5 DFT-optimized cartesian coordinates of $[Fe^{II}(L^7)_2]$ (1).

Table S6 DFT-optimized cartesian coordinates of $[Fe^{II}(L^8)_2]$ (2).

Table S7 DFT-optimized cartesian coordinates of $[Co^{III}(L^7)][ClO_4]$ (6).

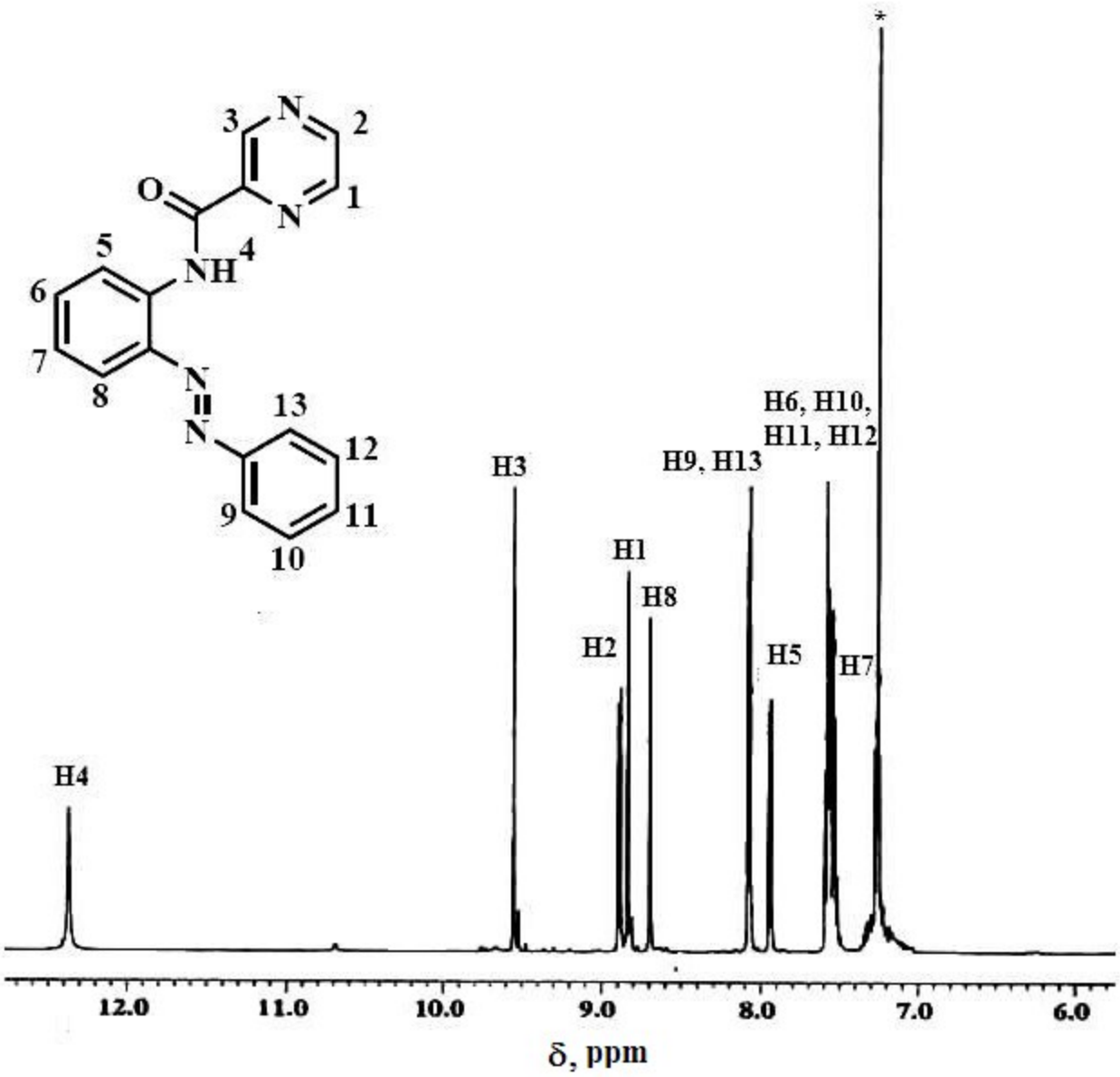


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of HL^8. Peak denoted by * is due to $CHCl_3$.

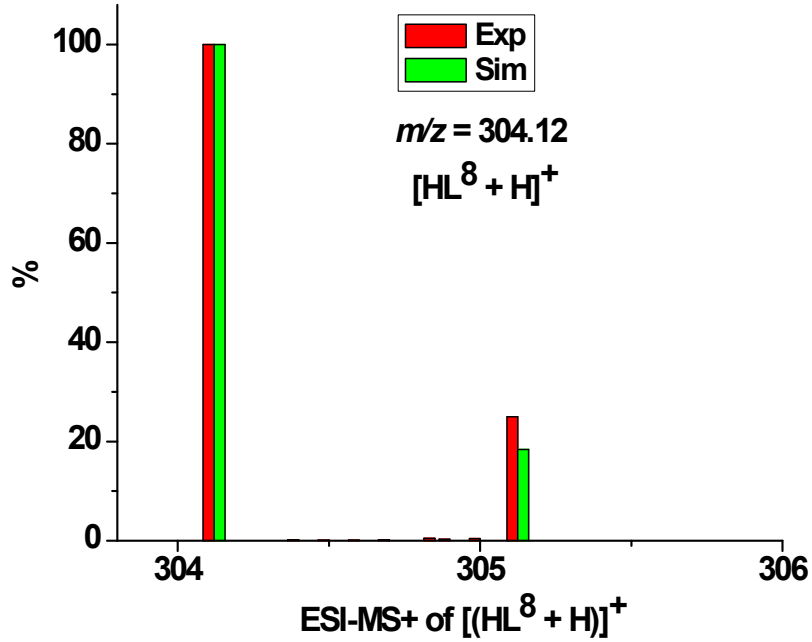


Fig. S2 Positive-Ion ESI-MS spectrum of HL^8.

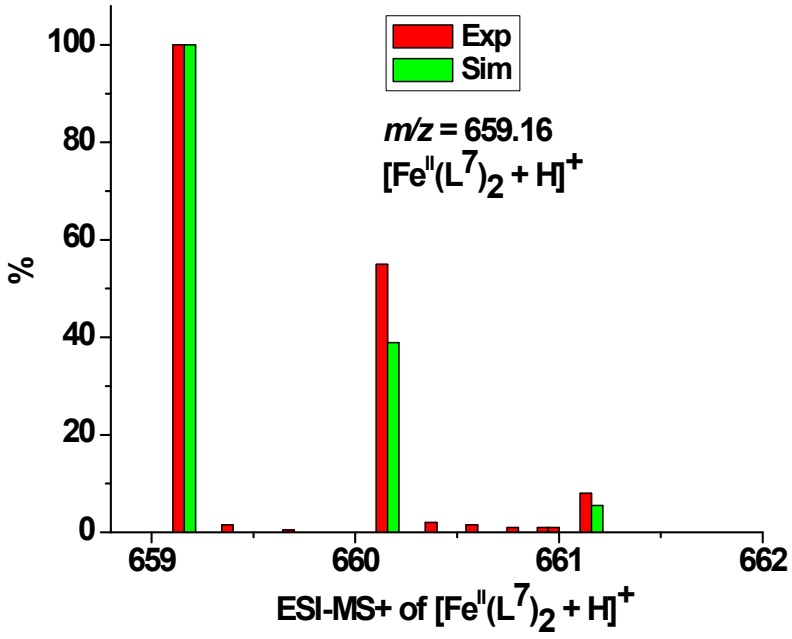


Fig. S3 Positive-Ion ESI-MS spectrum of $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1).

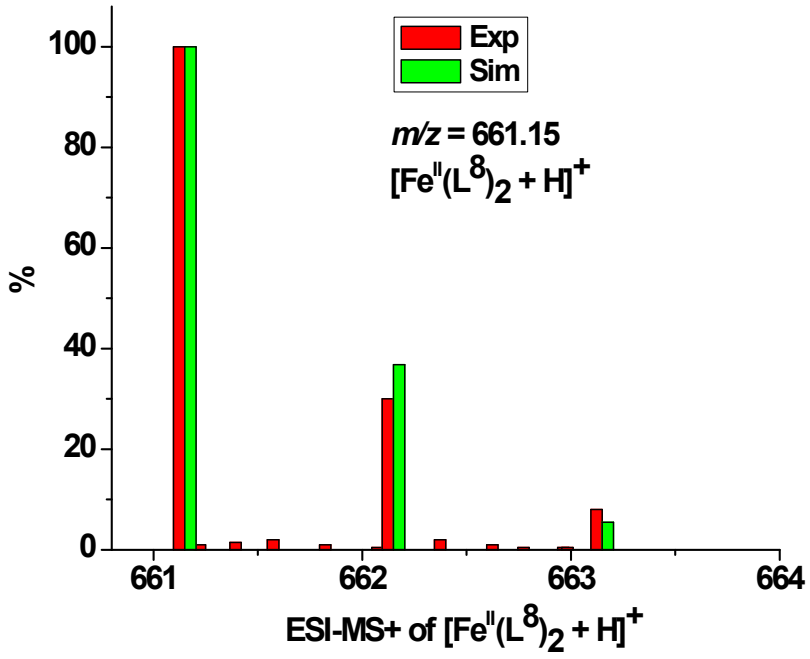


Fig. S4 Positive-Ion ESI-MS spectrum of $[Fe^{II}(L^8)_2]$ (2).

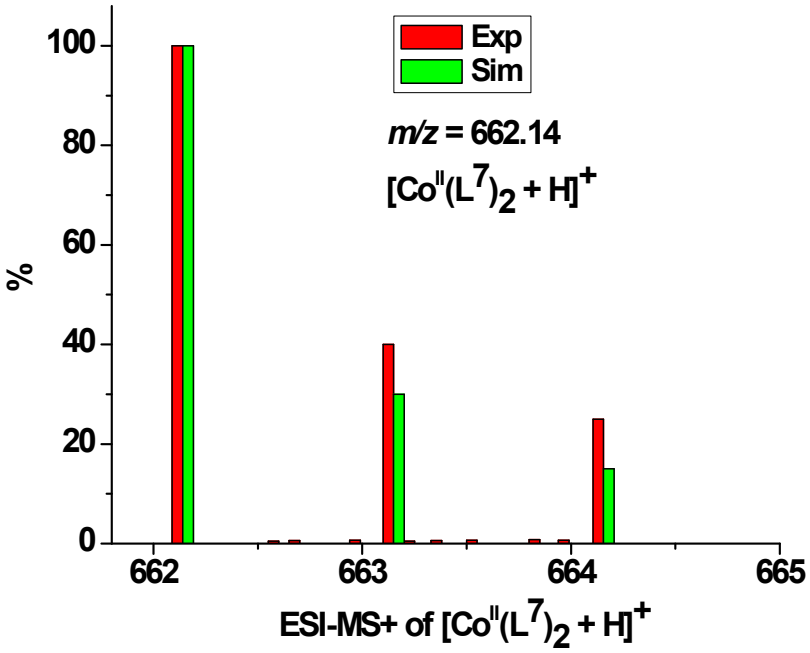


Fig. S5 Positive-Ion ESI-MS spectrum of $[Co^{II}(L^7)_2]$ (3).

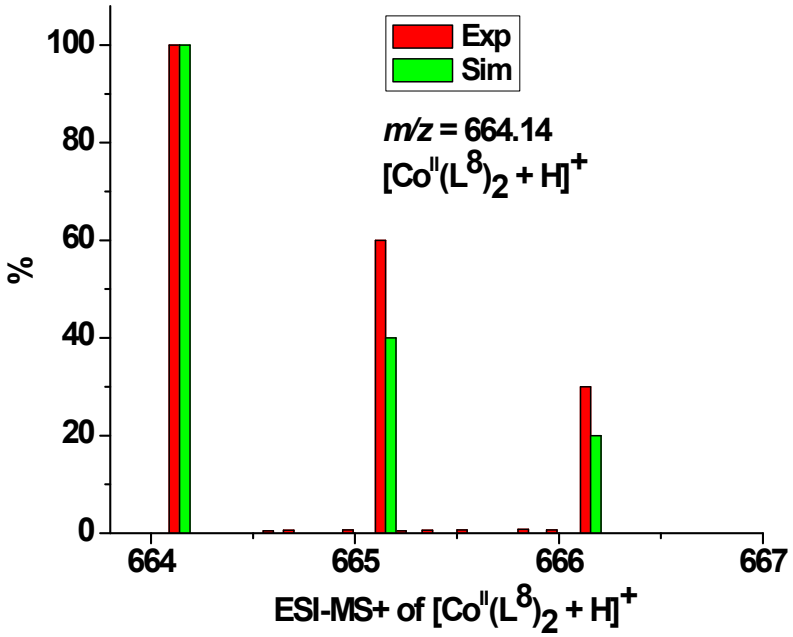


Fig. S6 Positive-Ion ESI-MS spectrum of $[Co^{II}(L^{8})_2]$ (4).

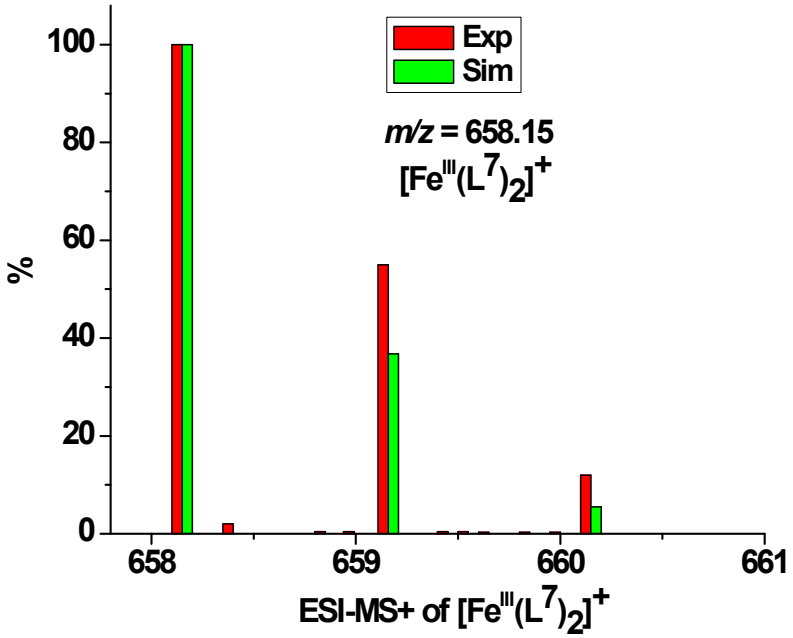


Fig. S7 Positive-Ion ESI-MS spectrum of $[Fe^{III}(L^{7})_2][BF_4]\cdot CH_2Cl_2\cdot H_2O$ (5).

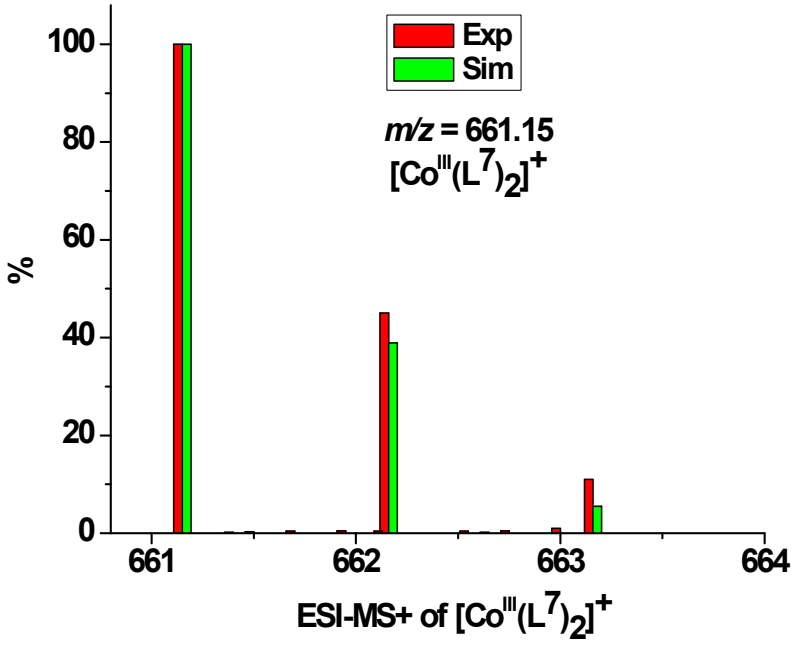


Fig. S8 Positive-Ion ESI-MS spectrum of $[Co^{III}(L^7)_2][ClO_4]$ (6).

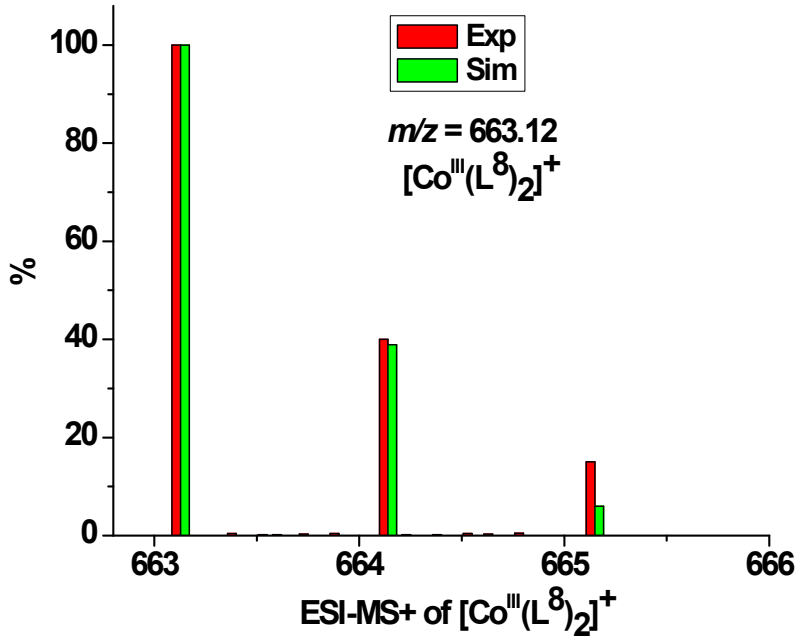


Fig. S9 Positive-Ion ESI-MS spectrum of $[Co^{III}(L^8)_2][PF_6]$ (7).

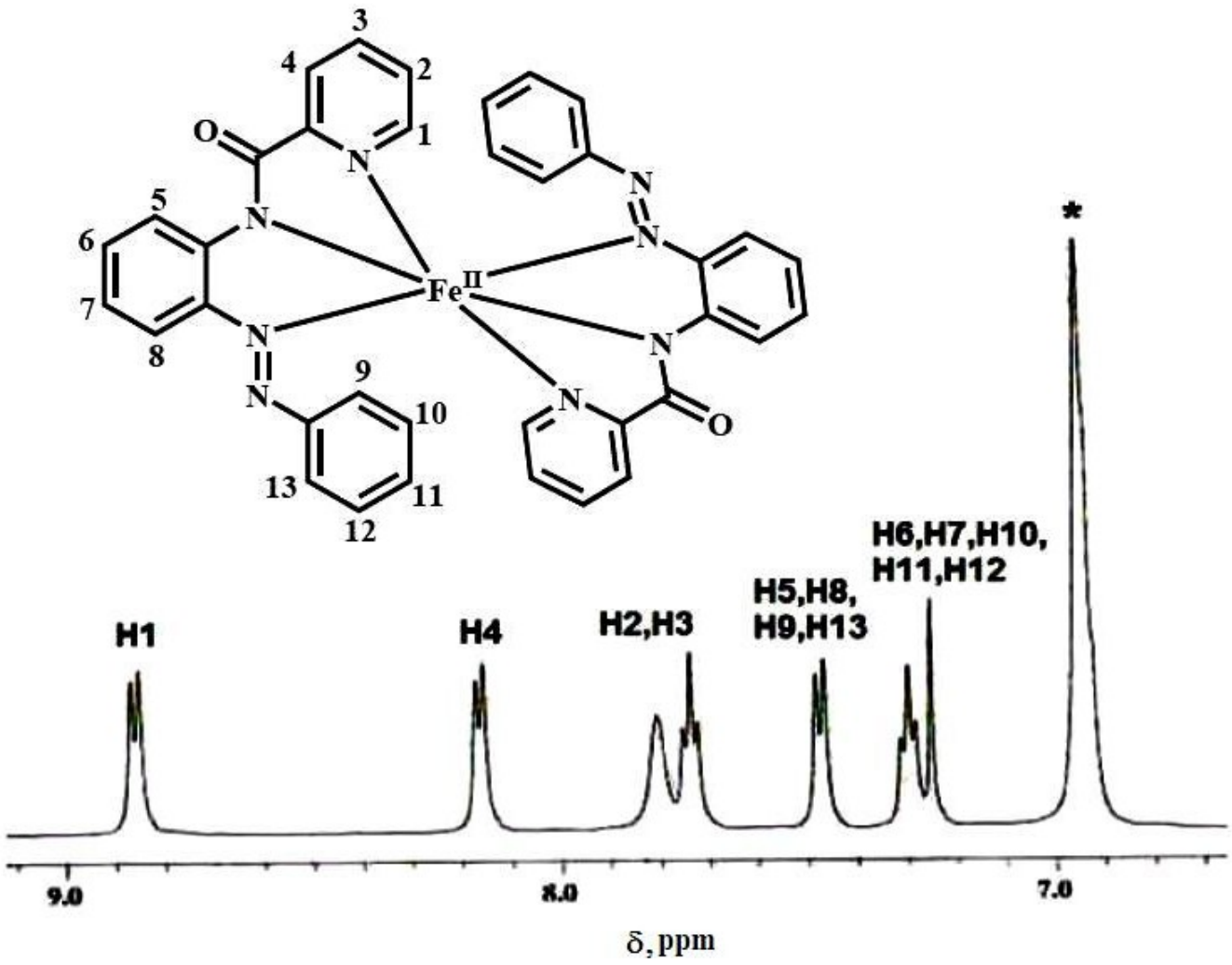


Fig. S10 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1). Peak denoted by * is due to $CHCl_3$.

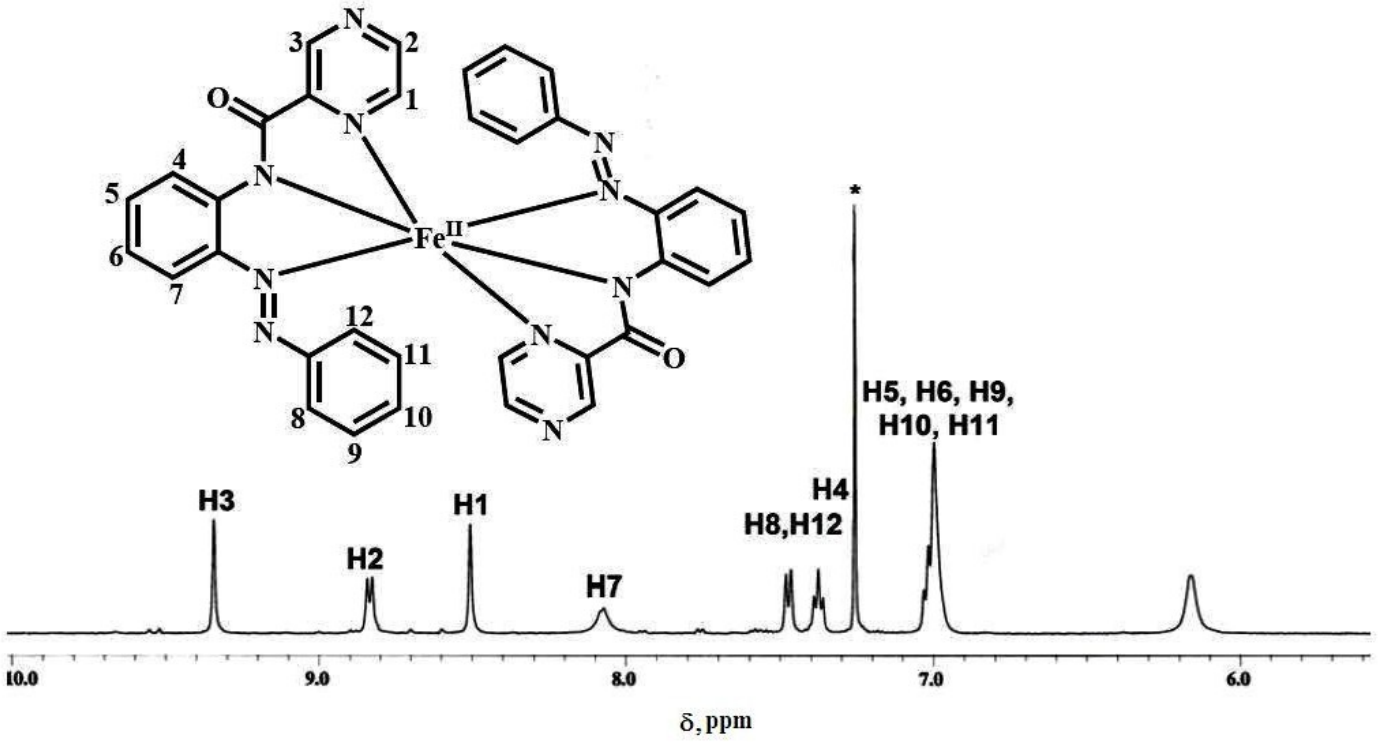


Fig. S11 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $[Fe^{II}(L^8)_2]$ (2). Peak denoted by * is due to $CHCl_3$.

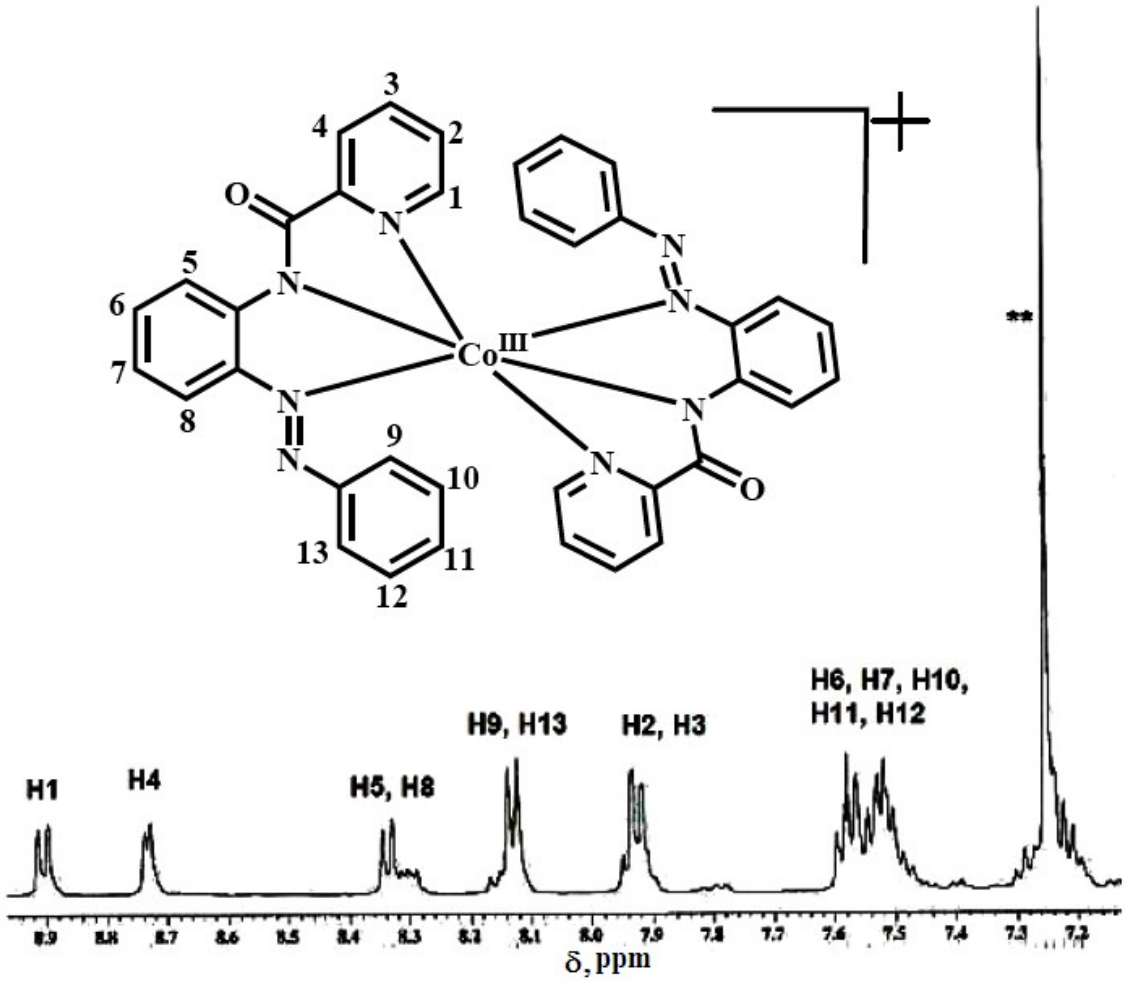


Fig. S12 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $[Co^{III}(L^7)_2][ClO_4]$ (6). Peak denoted by * is due to $CHCl_3$.

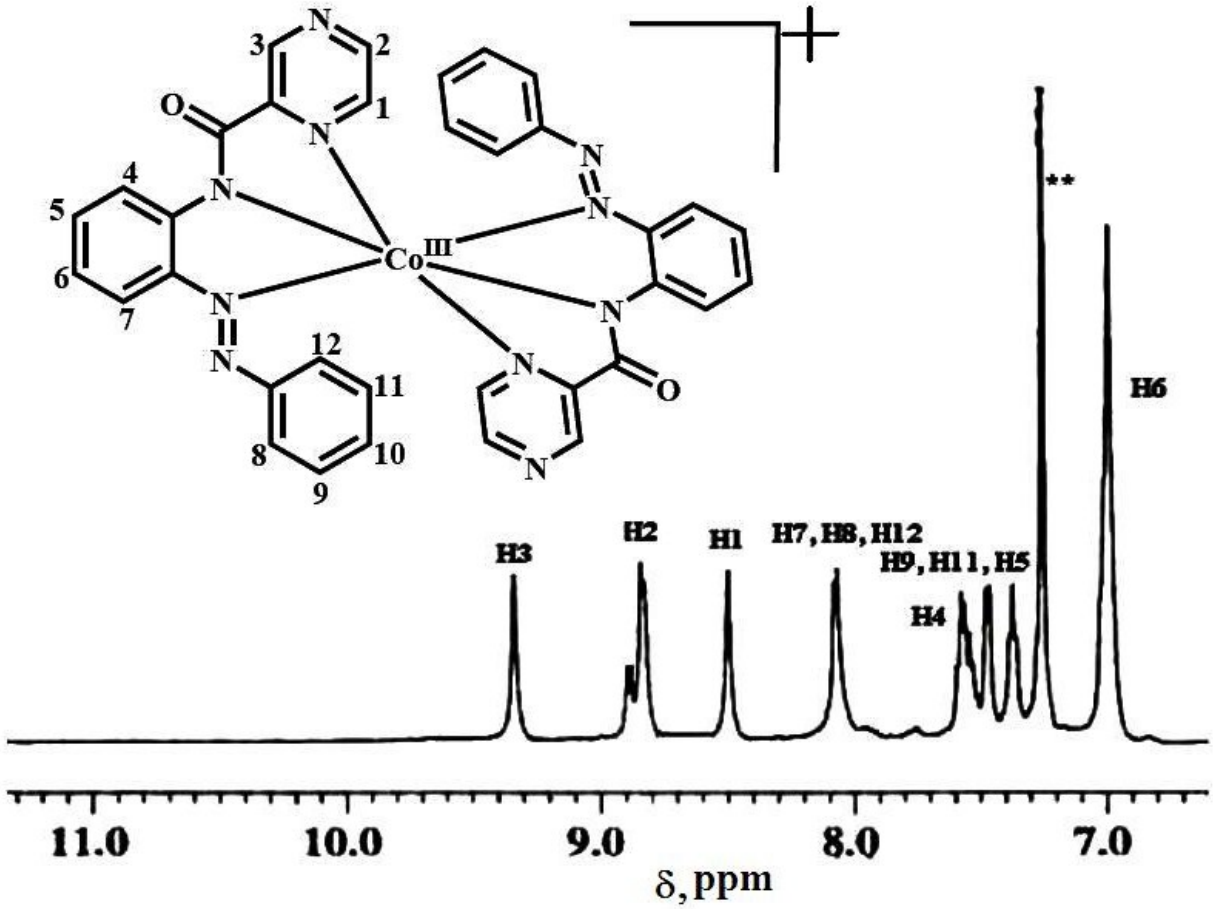


Fig. S13 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of $[Co^{III}(L^8)_2][PF_6]$ (7). Peak denoted by * is due to $CHCl_3$.

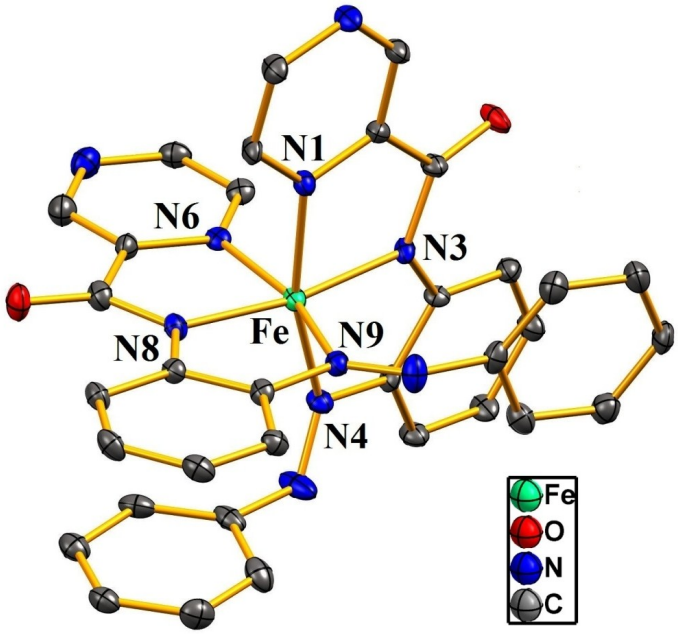


Fig. S14 Perspective view of the metal coordination environment in $[Fe^{II}(L^{8})_2]$ (2).

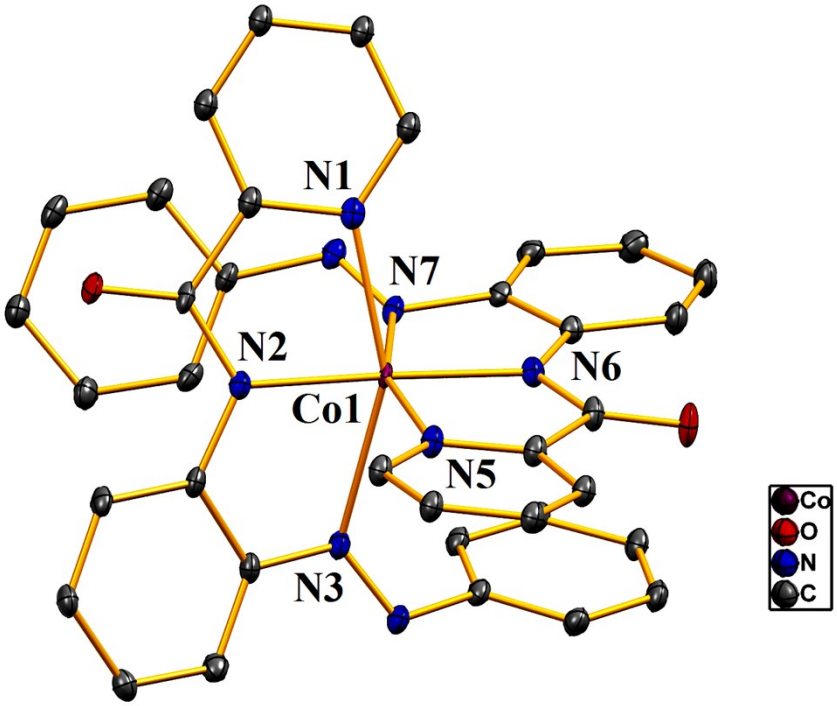
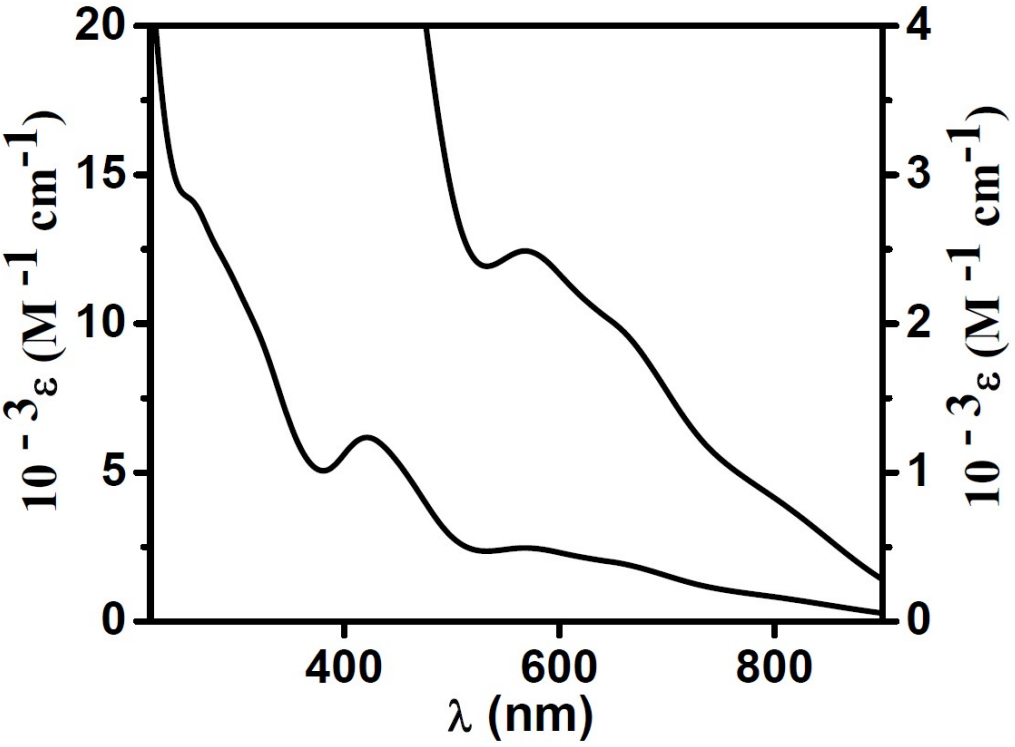
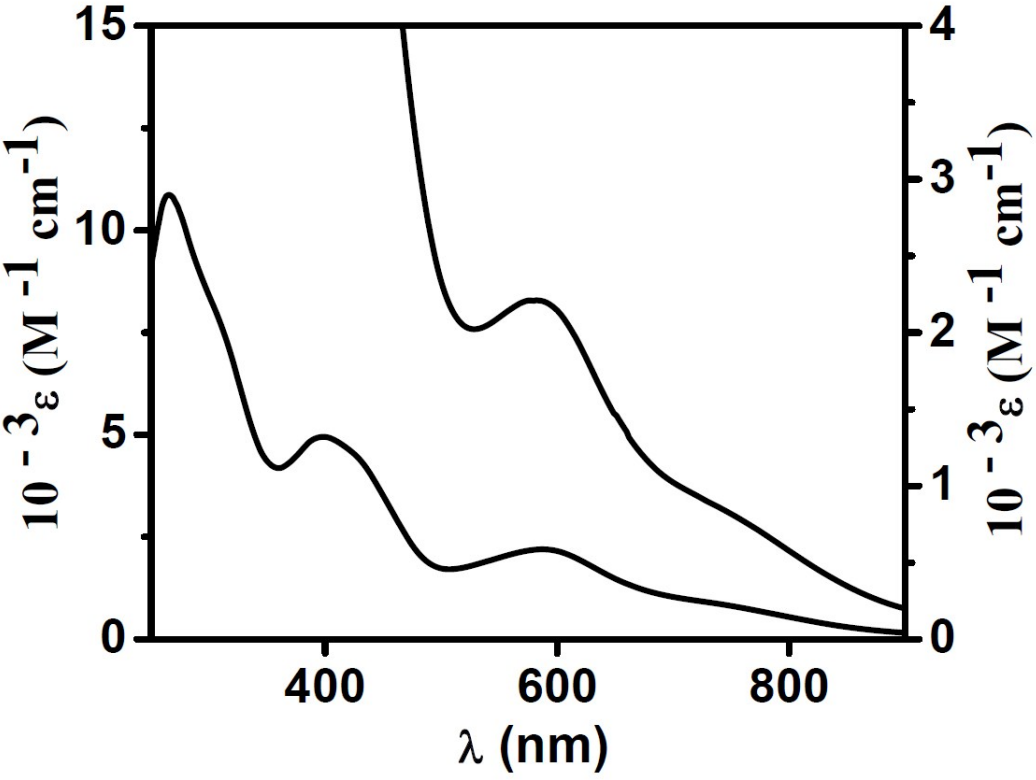


Fig. S15 Perspective view of the metal coordination environment in $[Co^{II}(L^{7})_2]$ (3).

(*a*)


20
15
10
5
0
4
3
2
1
0
400
600
800
λ (nm)
10 - 3ε (M -1 cm-1)
10 - 3ε (M -1 cm-1)

(*b*)


15
10
5
0
4
3
2
1
0
400
600
800
λ (nm)
10 - 3ε (M -1 cm-1)
10 - 3ε (M -1 cm-1)

(*c*)

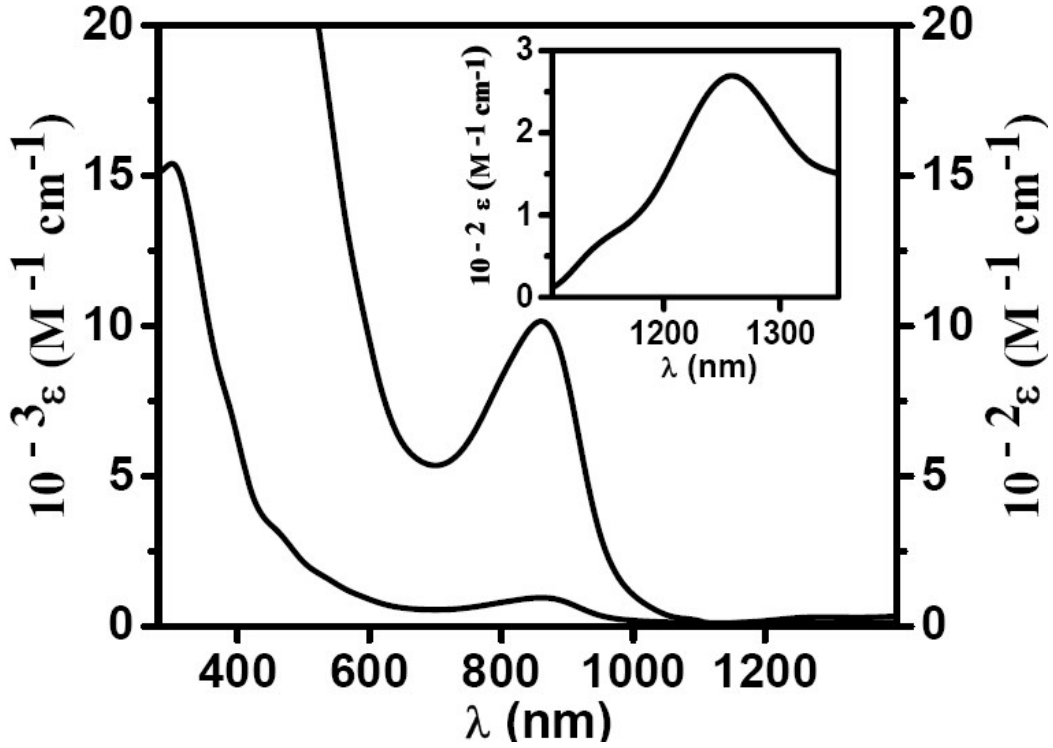
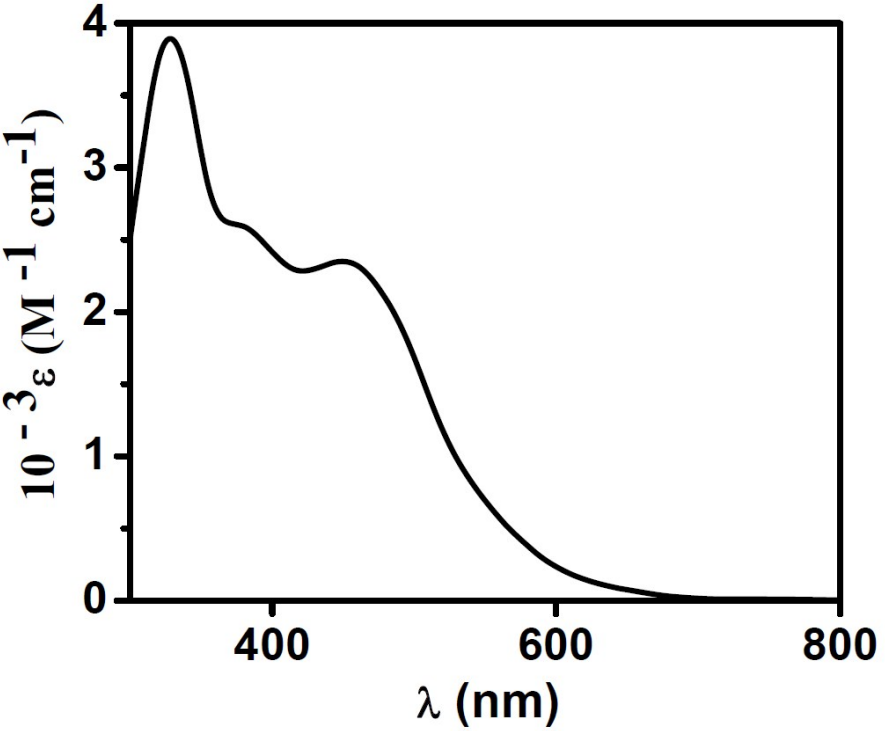
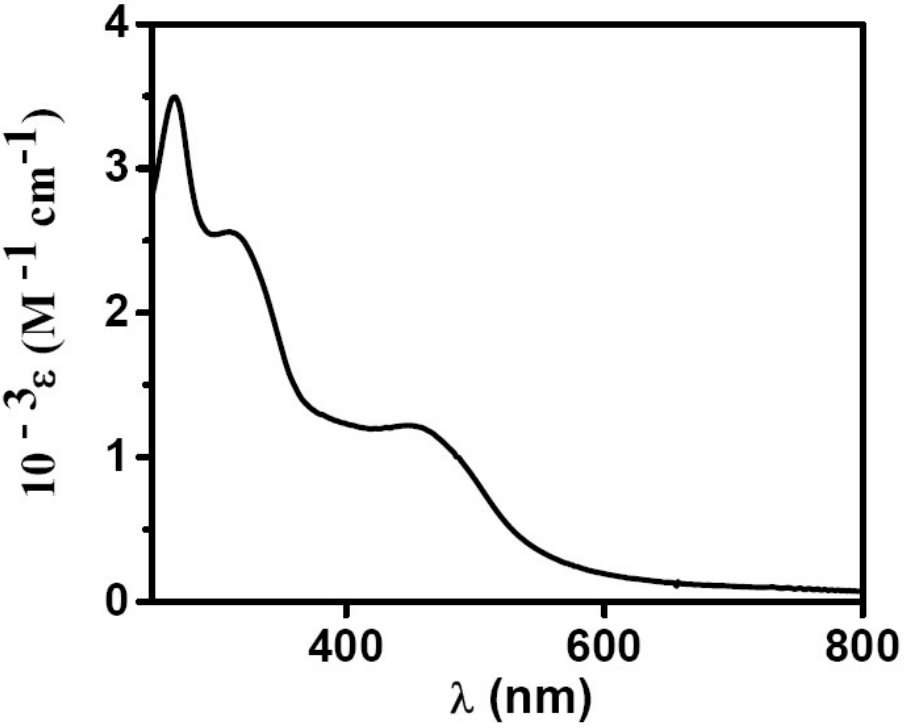


Fig. S16 Absorption spectra (CH_2Cl_2) of (*a*) $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1), (*b*) $[Fe^{II}(L^8)_2]$ (2) and (*c*) $[Fe^{III}(L^7)_2][BF_4]$ (5). Inset displays low-energy absorption of $[Fe^{III}(L^7)_2][BF_4]$ (5).

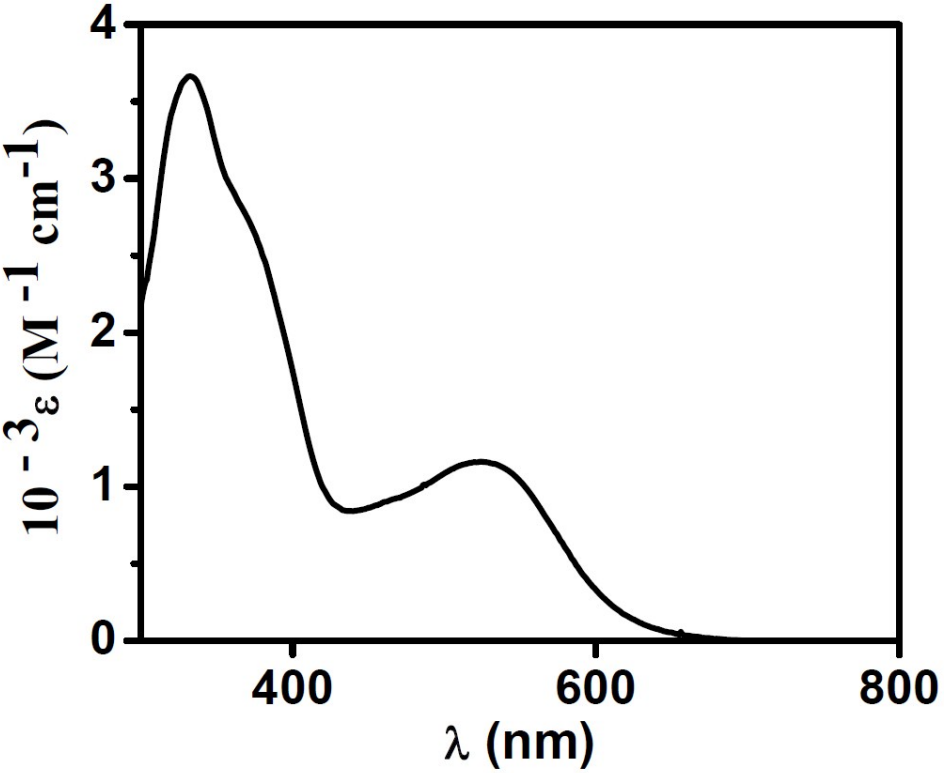
(*a*)


4
3
2
1
0
10 - 3ε (M -1 cm-1)
400
600
800
λ (nm)

(*b*)


4
3
2
1
0
10 - 3ε (M -1 cm-1)
400
600
800
λ (nm)

(*c*)



(*d*)

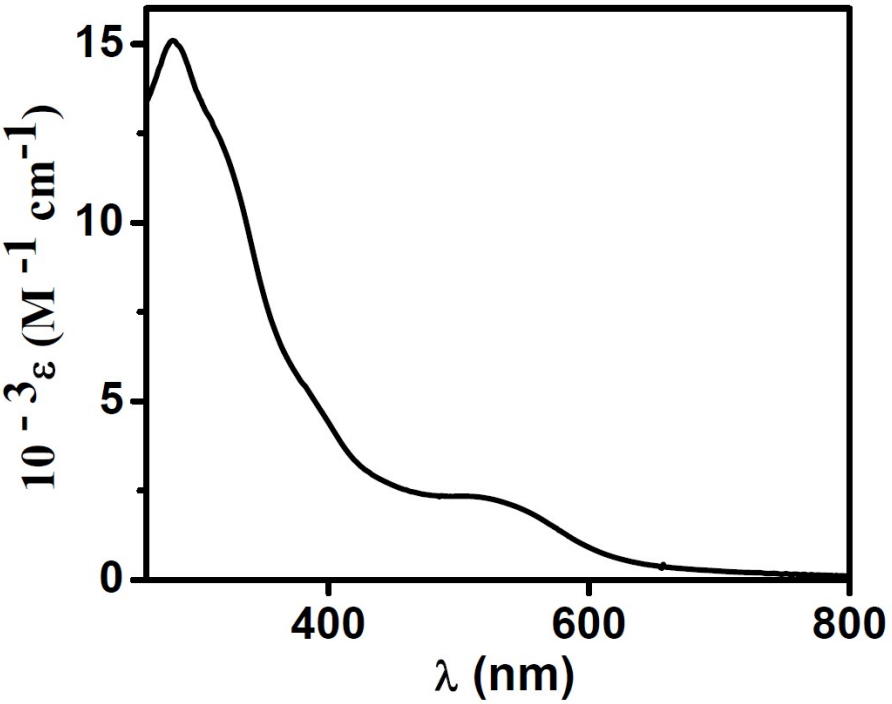


Fig. S17 Absorption spectra (CH_2Cl_2) of (*a*) $[Co^{II}(L^7)_2]$ (3), (*b*) $[Co^{II}(L^8)_2]$ (4), (*c*) $[Co^{III}(L^7)_2][ClO_4]$ (6) and *(d)* $[Co^{III}(L^8)_2][PF_6]$ (7).

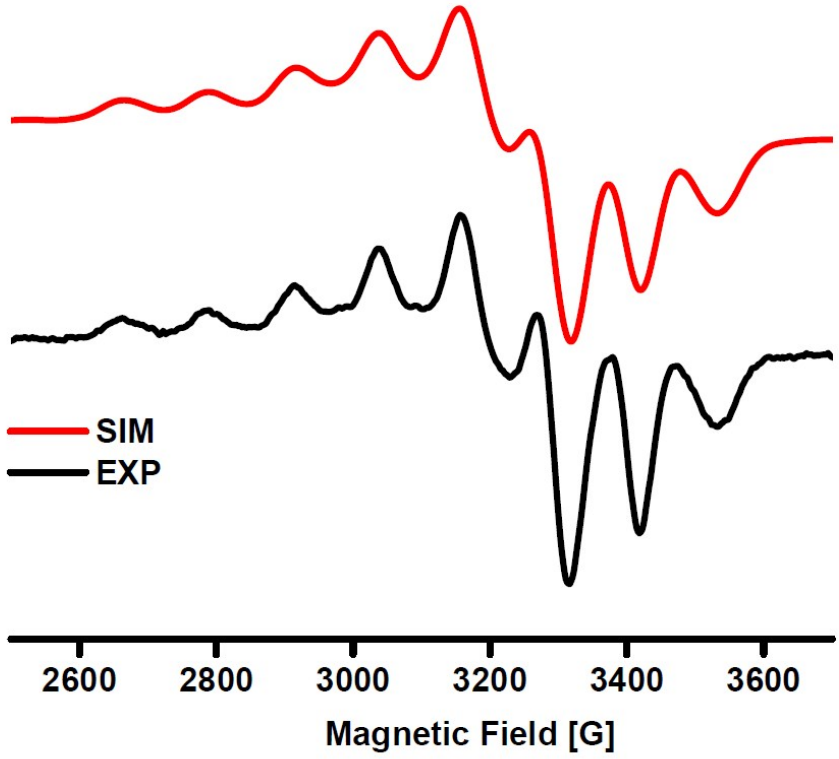


Fig. S18 Lower trace: X-band EPR spectra recorded for $[Co^{II}(L^8)_2]$ (4) as solid (120 K). Upper trace: simulated EPR spectrum with parameters: $g_x = 2.100$, $g_y = 2.341$, $g_z = 1.925$, $A_{yy} = 70 \times 10^{-4}$ cm^{-1}, $A_{zz} = 30 \times 10^{-4}$ cm^{-1}, $Wx = 40$ G, $Wy = 42$ G, $Wz = 30$ G.

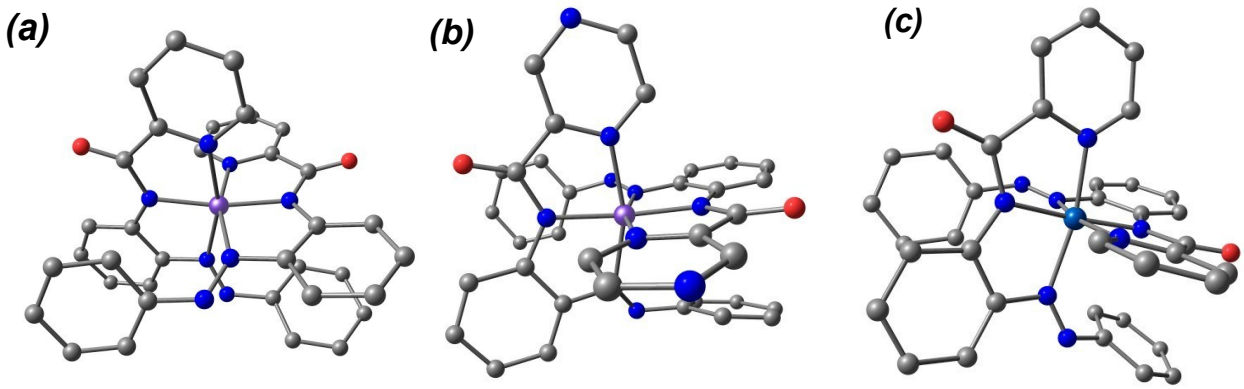


Fig. S19 Spin-density plots for (*a*) $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1), (*b*) $[Fe^{II}(L^8)_2]$ (2) and (*c*) $[Co^{III}(L^7)_2][ClO_4]$ (6).

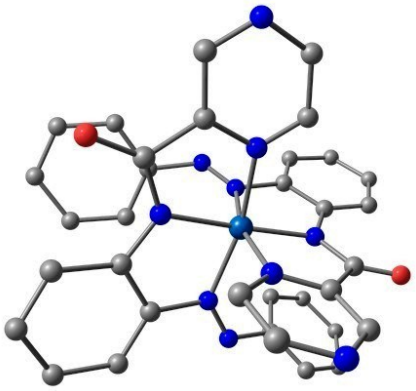


Fig. S20 Spin-density plot for $[Co^{III}(L^8)_2]^+$ (4^+).

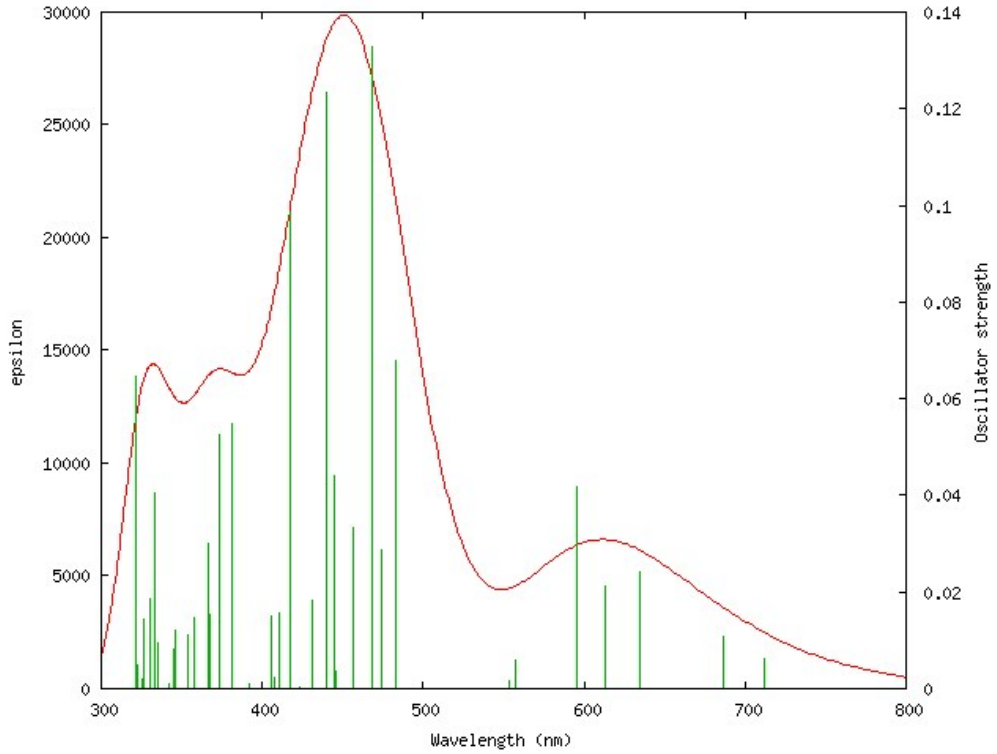
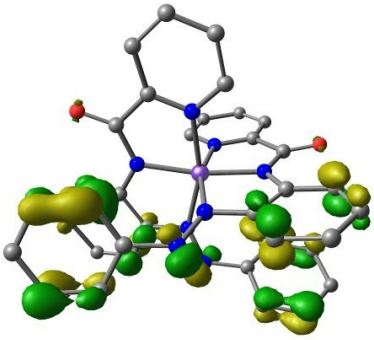
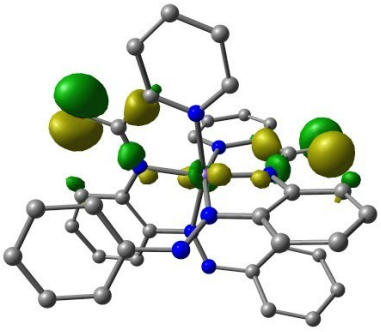


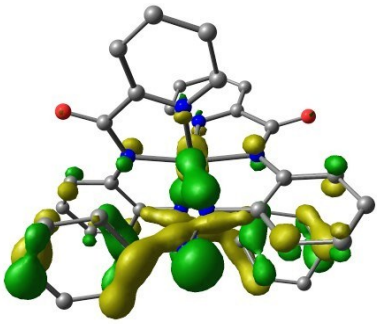
Fig. S21 TD-DFT calculated electronic spectra for $[Fe^{II}(L^7)_2]$ (1).



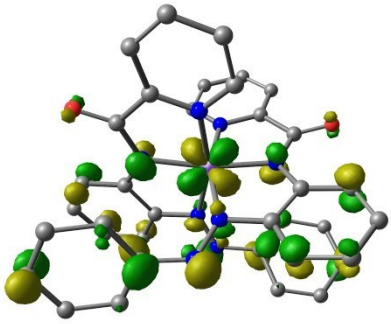
Homo-10 (α/β)



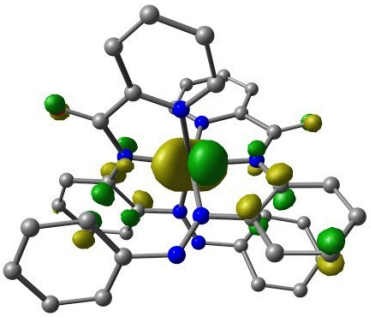
Homo-8 (α/β)



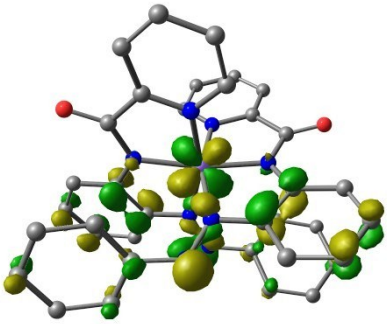
Homo-6 (α/β)



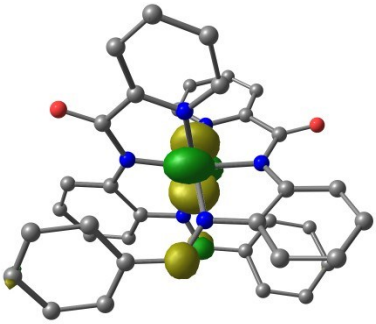
Homo-5 (α/β)



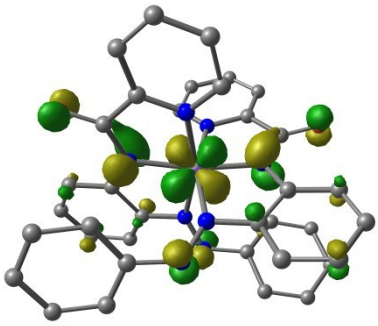
Homo-4 (α/β)



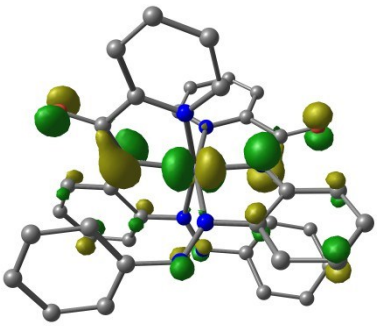
Homo-3 (α/β)



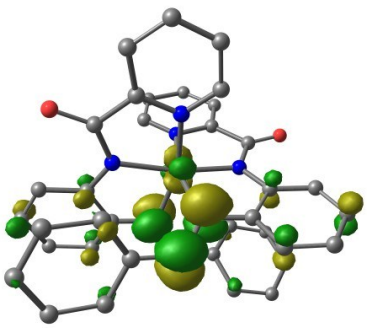
Homo-2 (α/β)



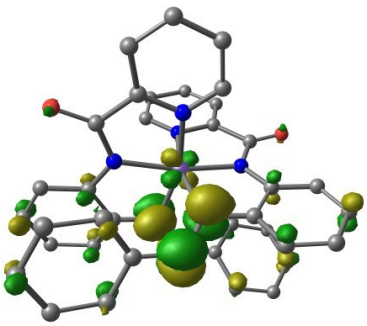
Homo-1 (α/β)



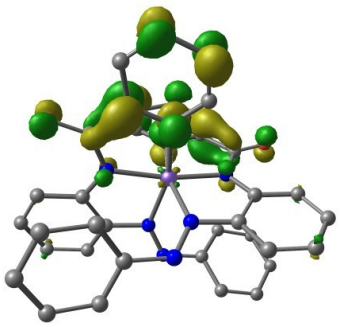
Homo (α/β)



Lumo (α/β)



Lumo+1 (α/β)



Lumo+2 (α/β)

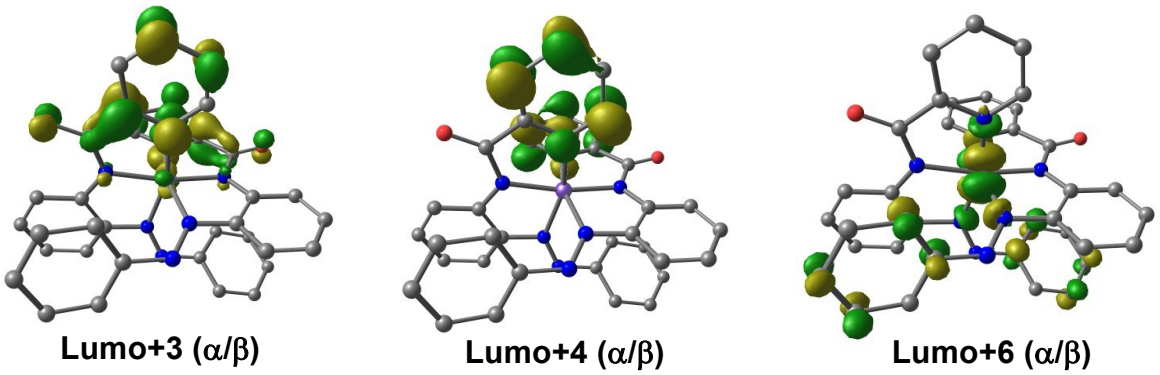


Fig. S22 Representative molecular-orbitals involved in TD-DFT transitions of $[Fe^{II}(L^7)_2]$ (1).

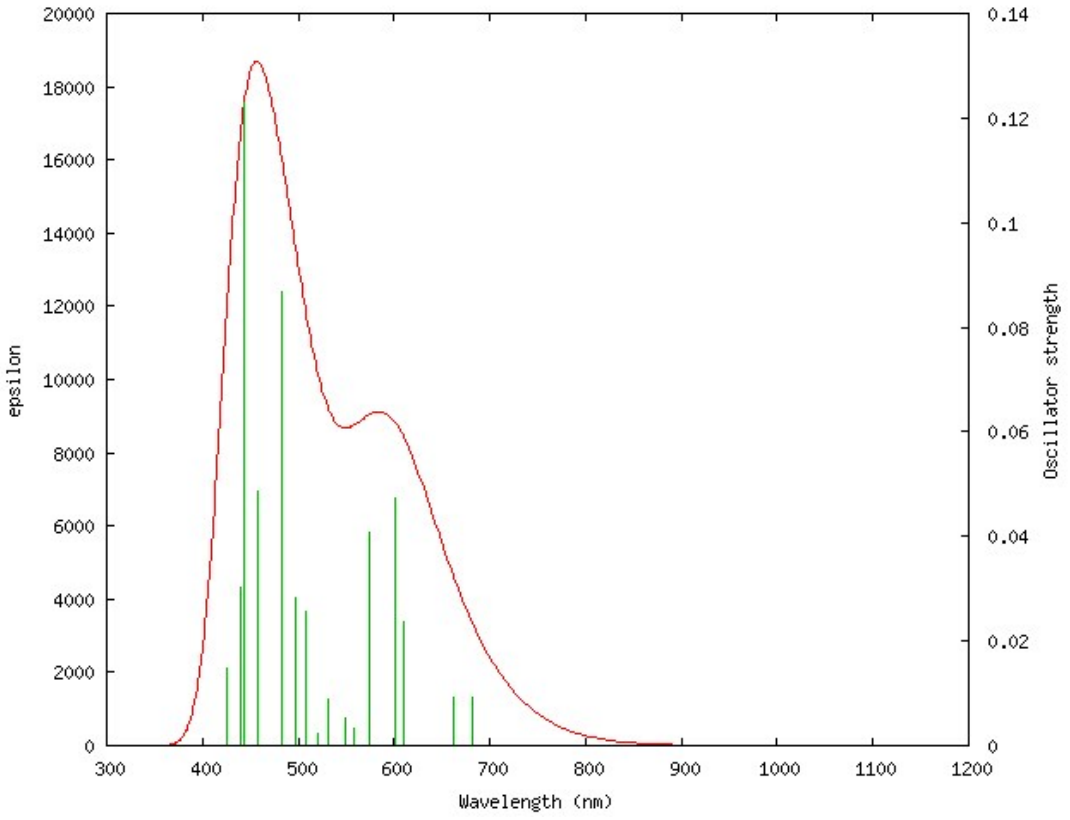


Fig. S23 TD-DFT calculated electronic spectra for $[Fe^{II}(L^8)_2]$ (2).

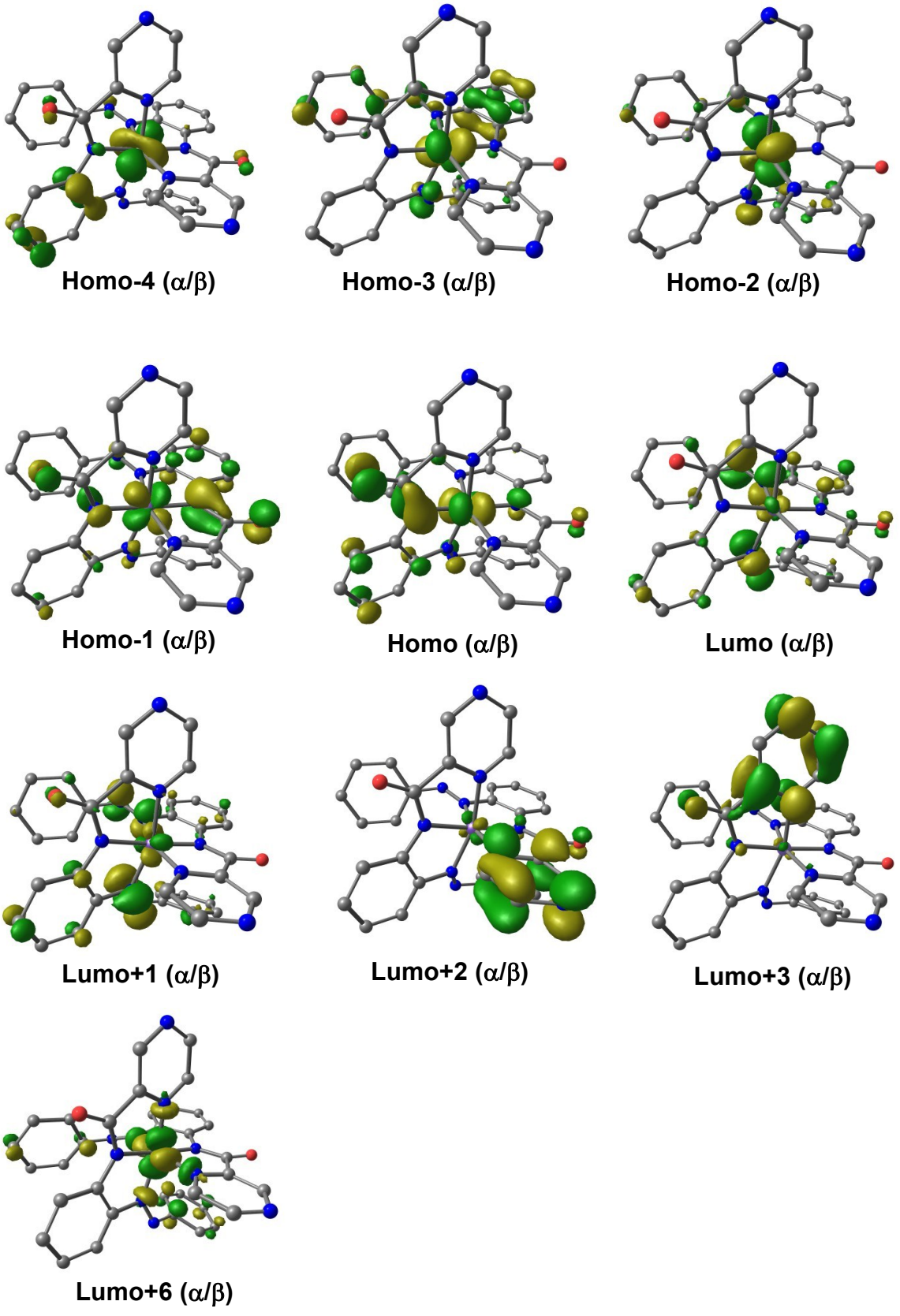


Fig. S24 Representative molecular-orbitals involved in TD-DFT transitions of $[Fe^{II}(L^8)_2]$ (2).

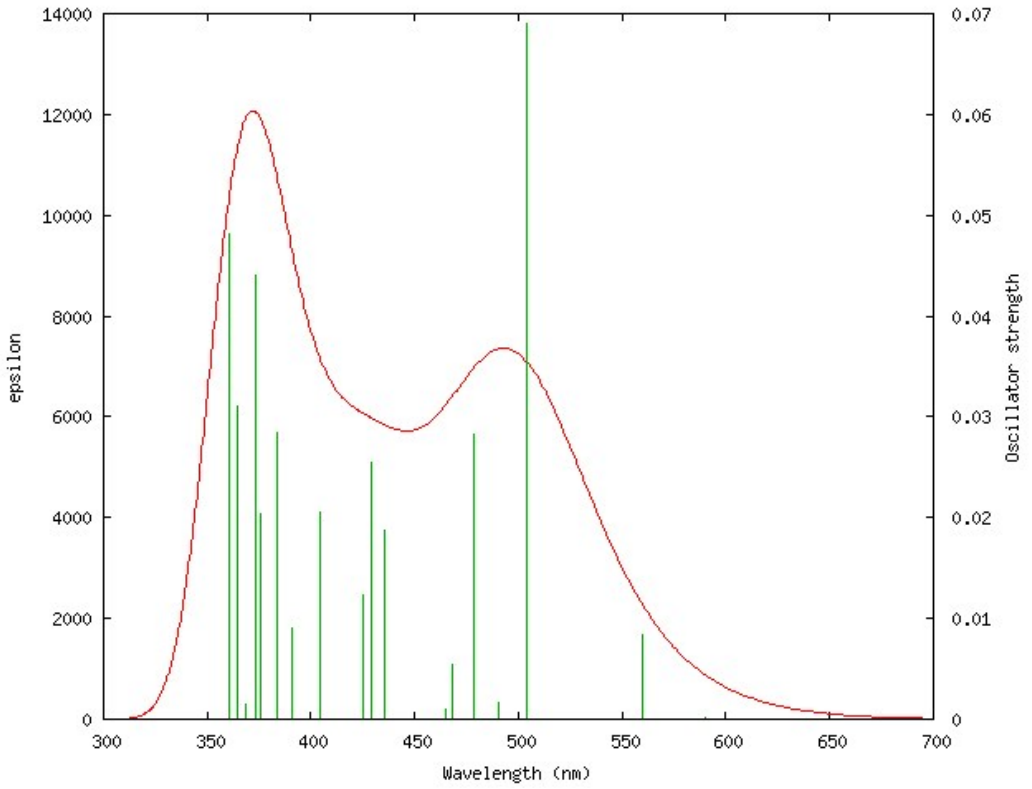
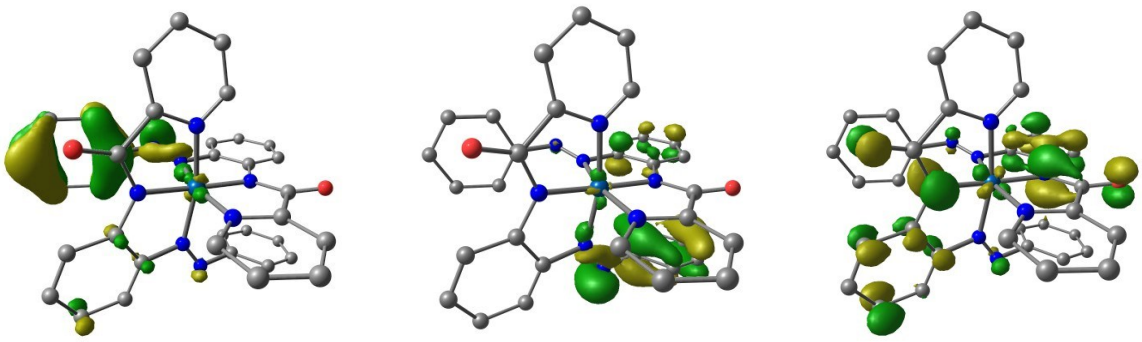


Fig. S25 TD-DFT calculated electronic spectra for $[Co^{III}(L^7)][ClO_4]$ (6).



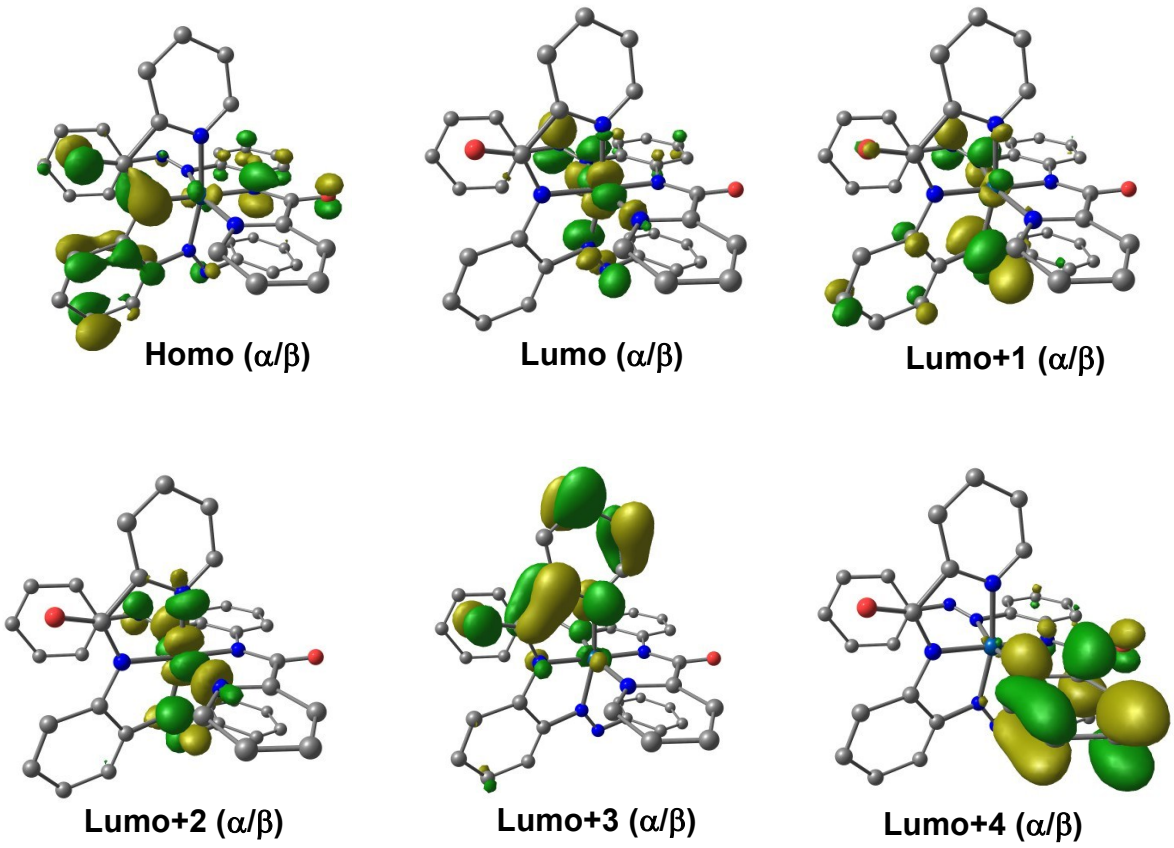


Fig. S26 Representative molecular-orbitals involved in TD-DFT transitions of $[Co^{III}(L^7)][ClO_4]$ (6).

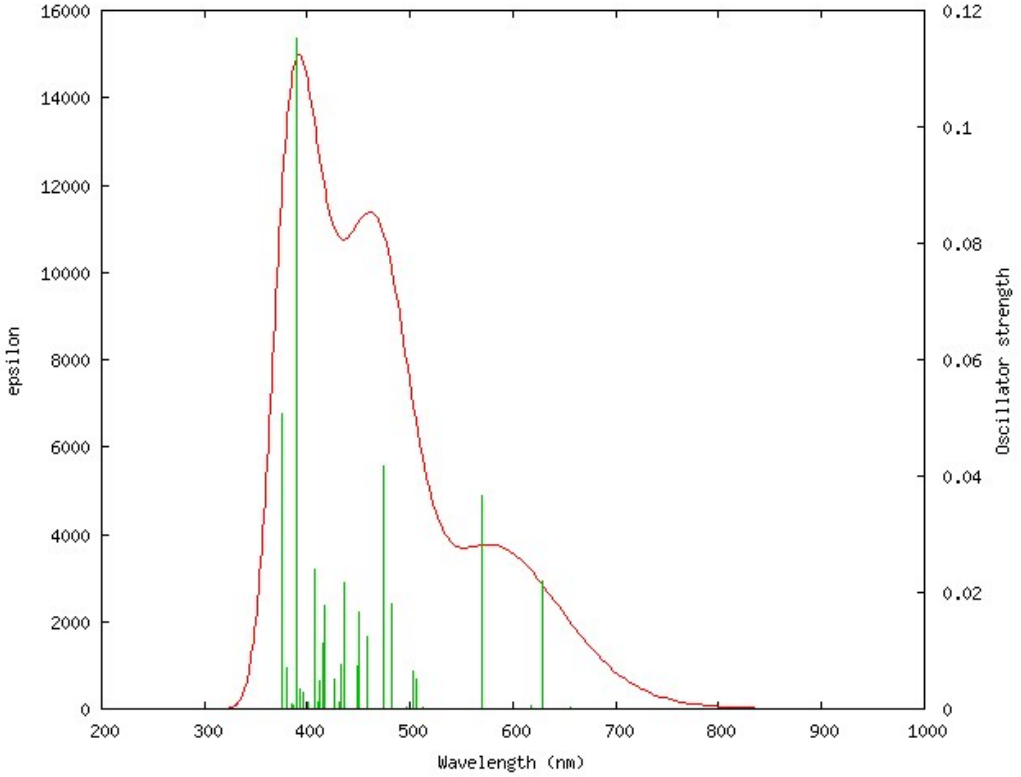
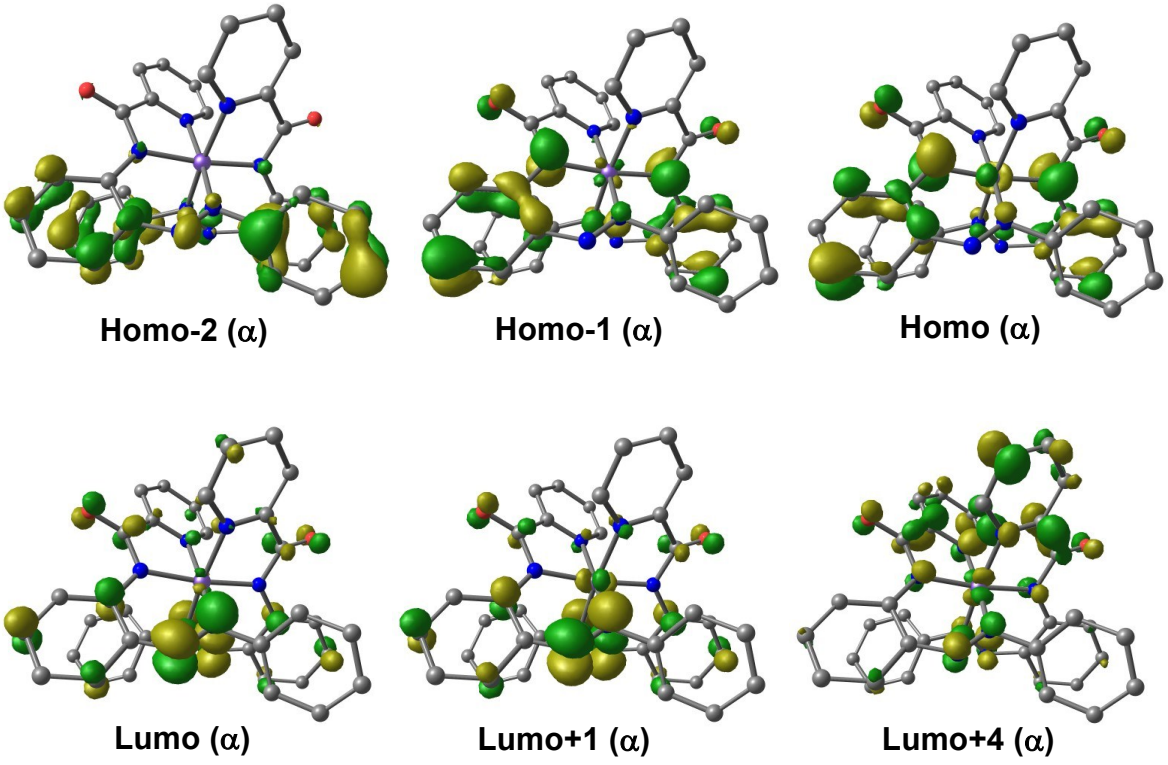


Fig. S27 TD-DFT calculated electronic spectra for $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ ($5\cdot CH_2Cl_2\cdot 3H_2O$).



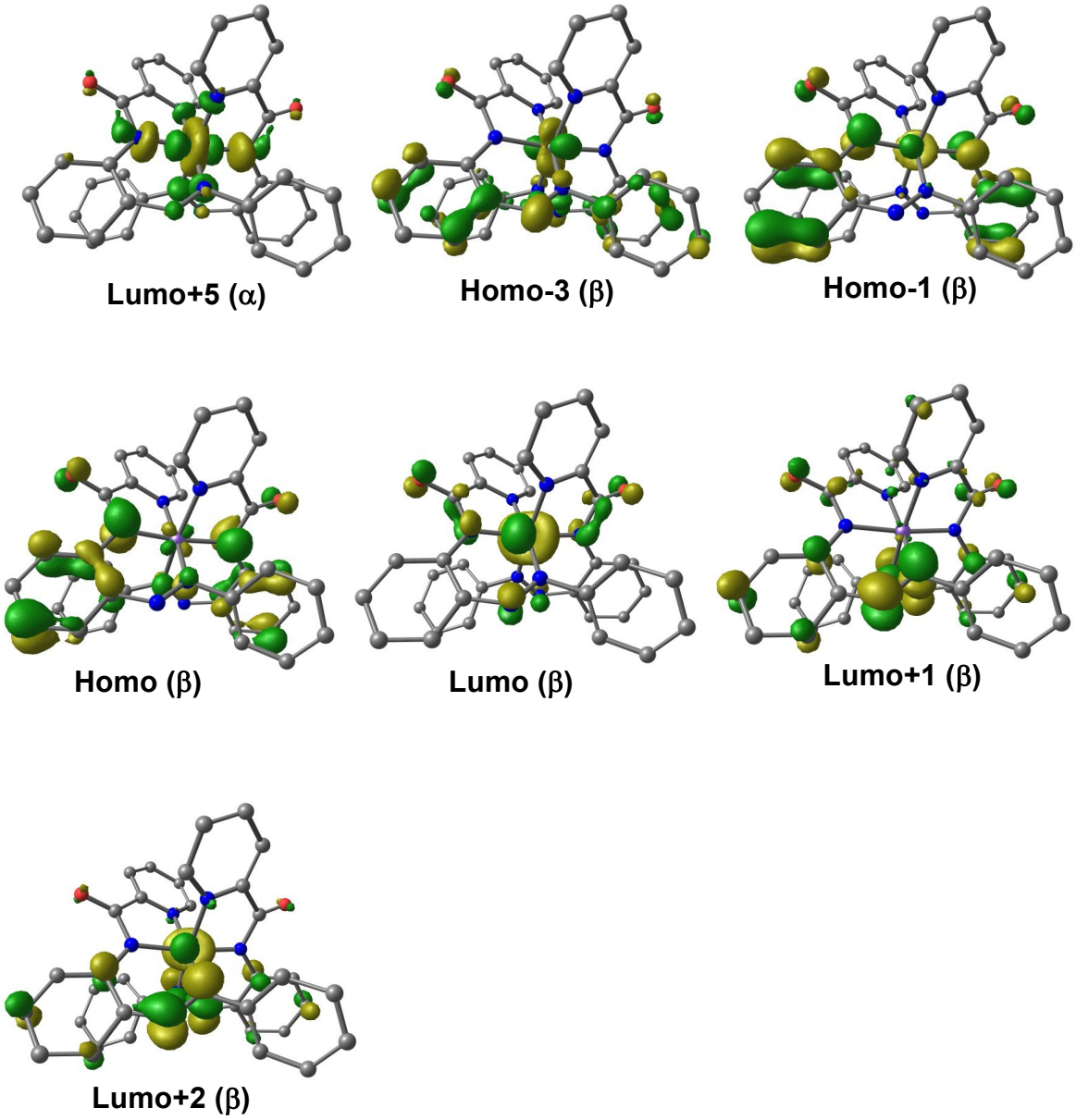


Fig. S28 Representative molecular-orbitals involved in TD-DFT transitions of $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ ($5\cdot CH_2Cl_2\cdot 3H_2O$).

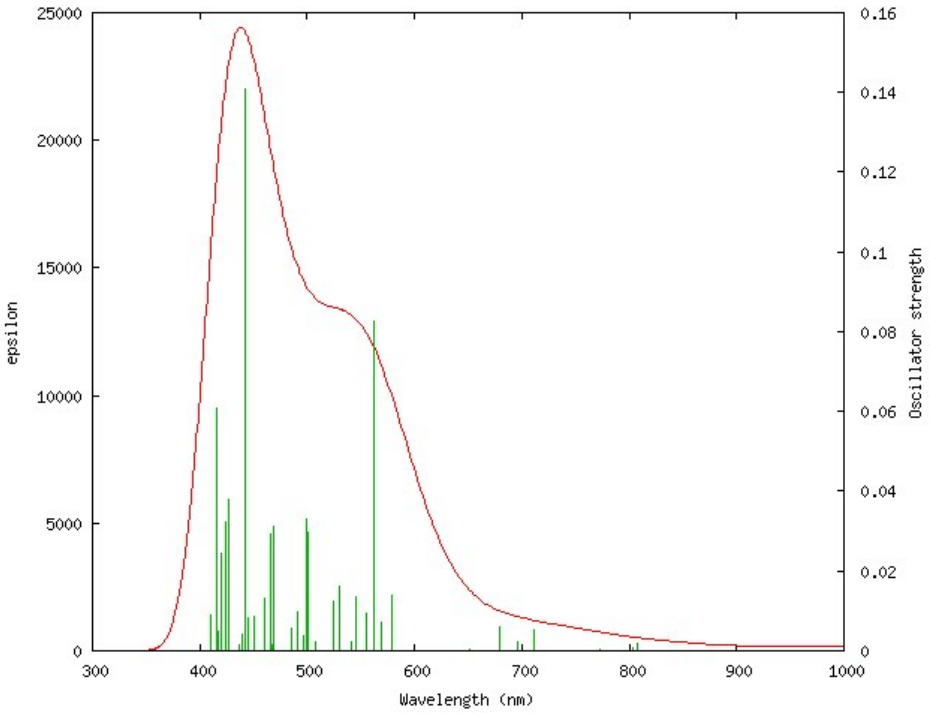
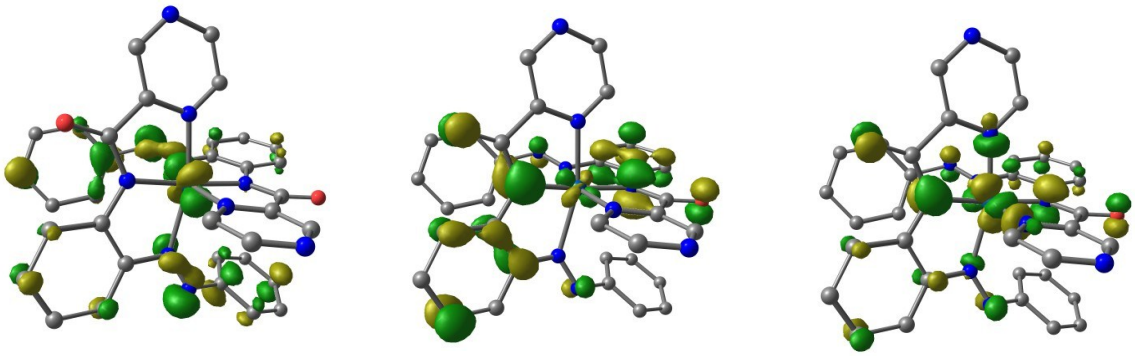
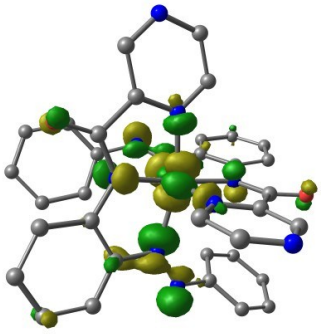
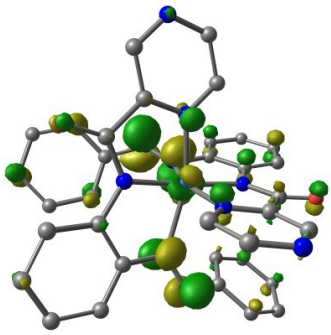


Fig. S29 TD-DFT calculated electronic spectra for $[Co^{II}(L^8)_2]$ (4).

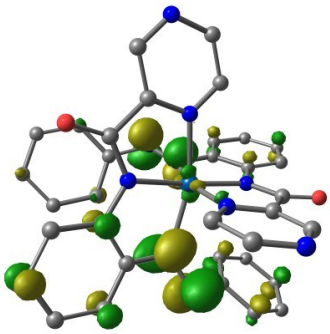




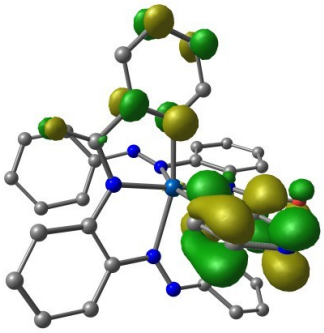
Homo (α)



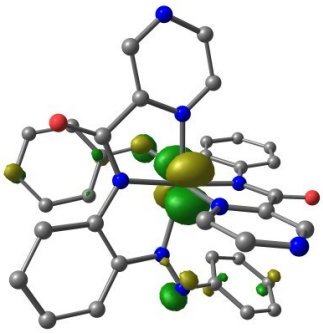
Lumo (α)



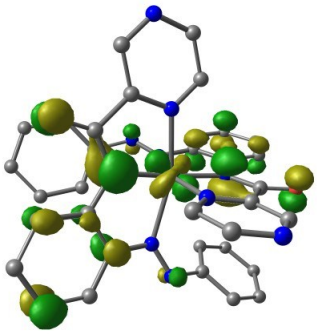
Lumo+1 (α)



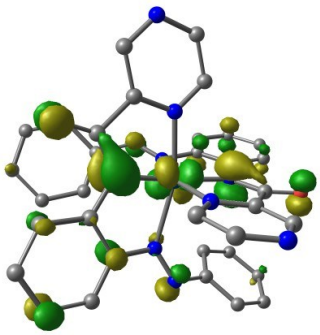
Lumo+2 (α)



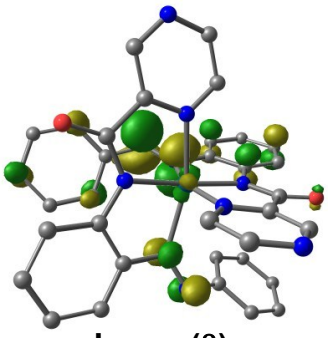
Homo-2 (β)



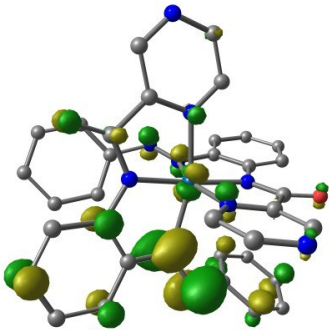
Homo-1 (β)



Homo (β)



Lumo (β)



Lumo+1 (β)

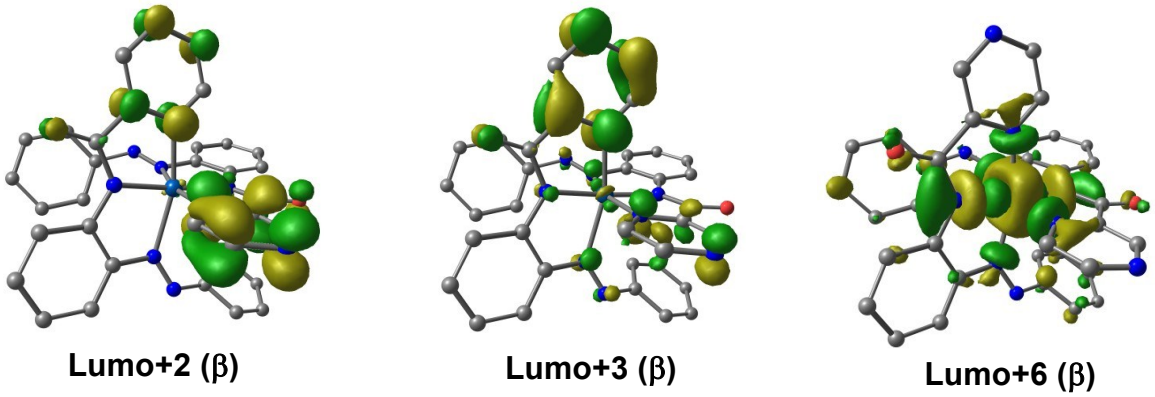


Fig. S30 Representative molecular-orbitals involved in TD-DFT transitions of $[Co^{II}(L^8)_2]$ (4).

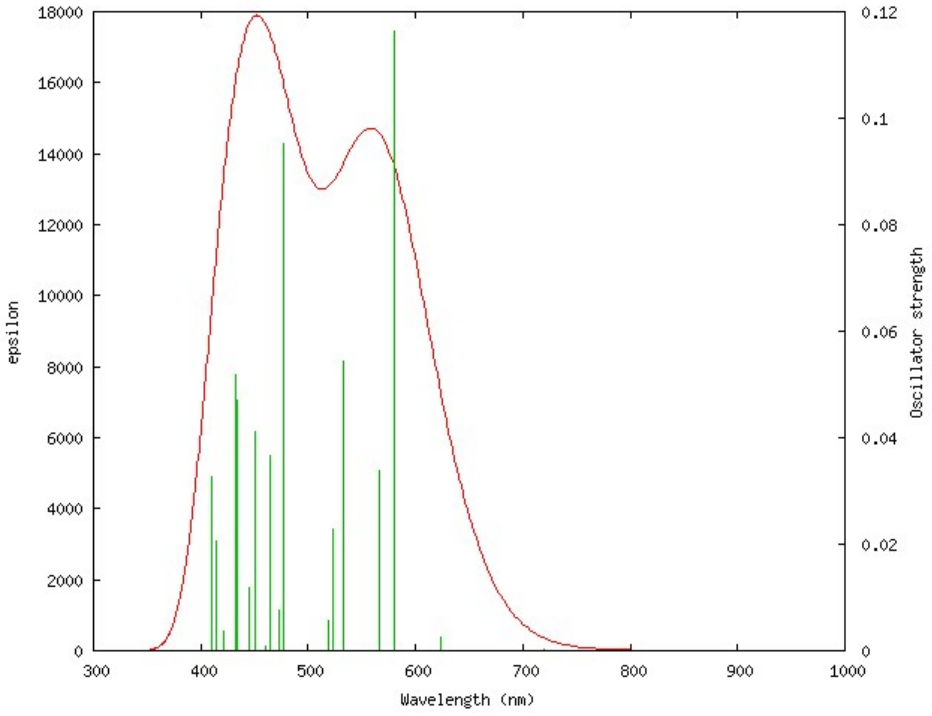
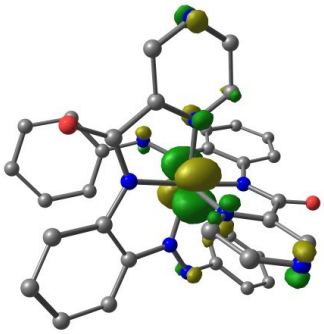
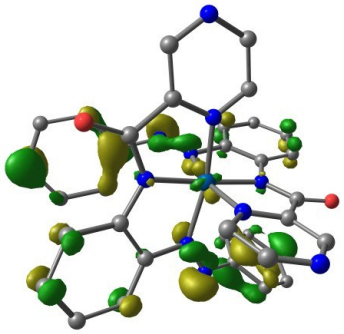


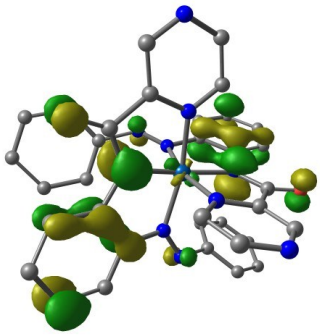
Fig. S31 TD-DFT calculated electronic spectra for $[Co^{III}(L^8)_2]^+$ (4^+).



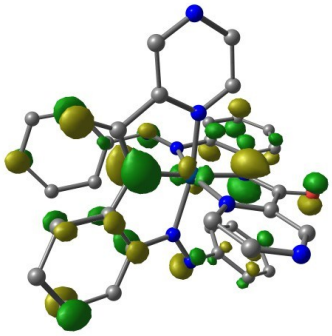
Homo-18 (α/β)



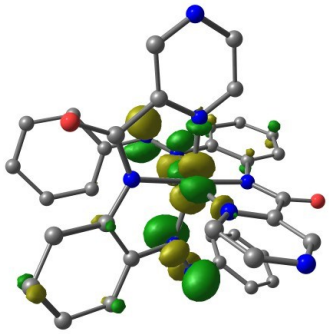
Homo-2 (α/β)



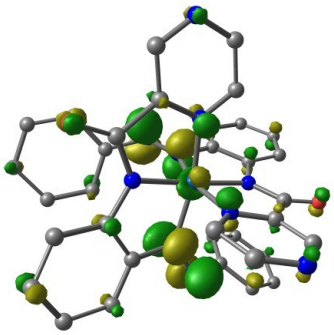
Homo-1 (α/β)



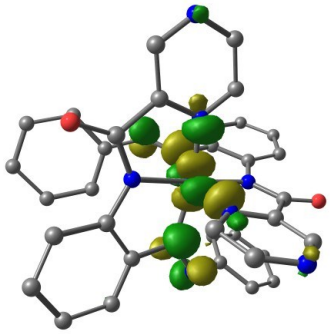
Homo (α/β)



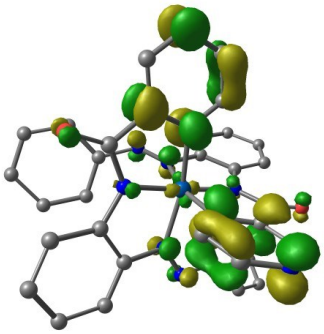
Lumo (α/β)



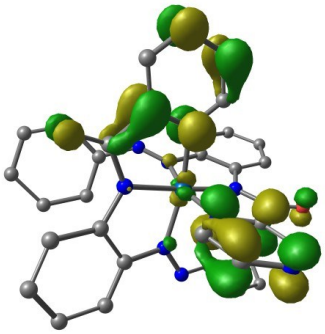
Lumo+1 (α/β)



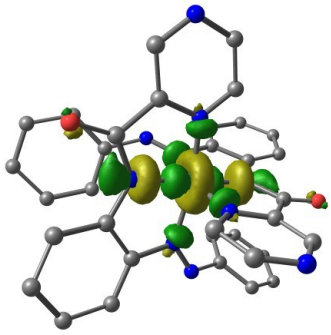
Lumo+2 (α/β)



Lumo+3 (α/β)



Lumo+4 (α/β)



Lumo+5 (α/β)

Fig. S32 Representative molecular-orbitals involved in TD-DFT transitions of $[Co^{III}(L^8)_2]^+$ (4^+).

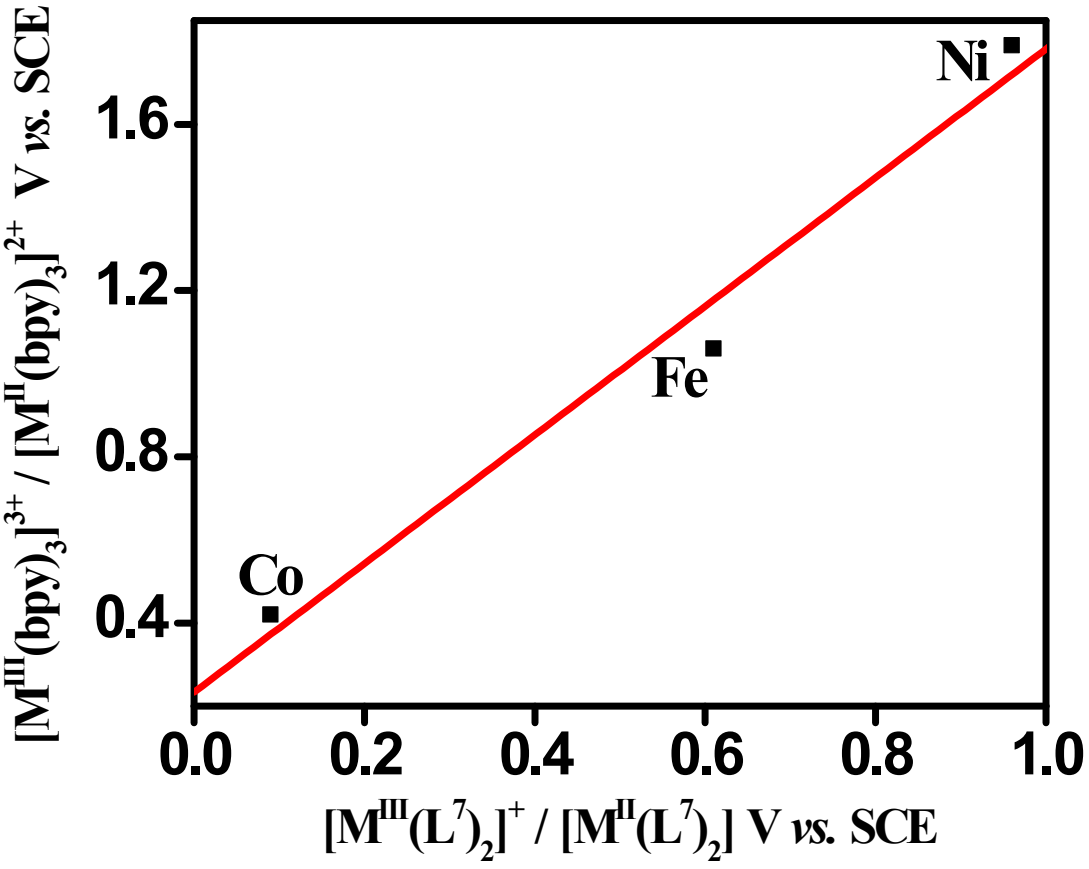


Fig. S33 Least-squares plot of $E_{1/2}$s between $[M^{III}(L^7)_2]^+$ / $M^{II}(L^7)_2]$ and $[M^{III}(bpy)_3]^{3+}$ / $M^{II}(bpy)_3]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line (y = 1.54827x + 0.23329) is ±0.08. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(bpy)_3]^{2+}$ (1.06 V), $[Co(bpy)_3]^{2+}$ (0.42 V) and $[Ni(bpy)_3]^{2+}$ (1.79 V). $E_{1/2}$ (CH_2Cl_2; V *vs.* SCE): $E_{1/2}$ (*vs.* SCE, CH_2Cl_2): $[Fe(L^7)_2]$ (0.61 V), $[Co(L^7)_2]^{2+}$ (0.10 V) and $[Ni(L^7)_2]^{2+}$ (0.94 V).

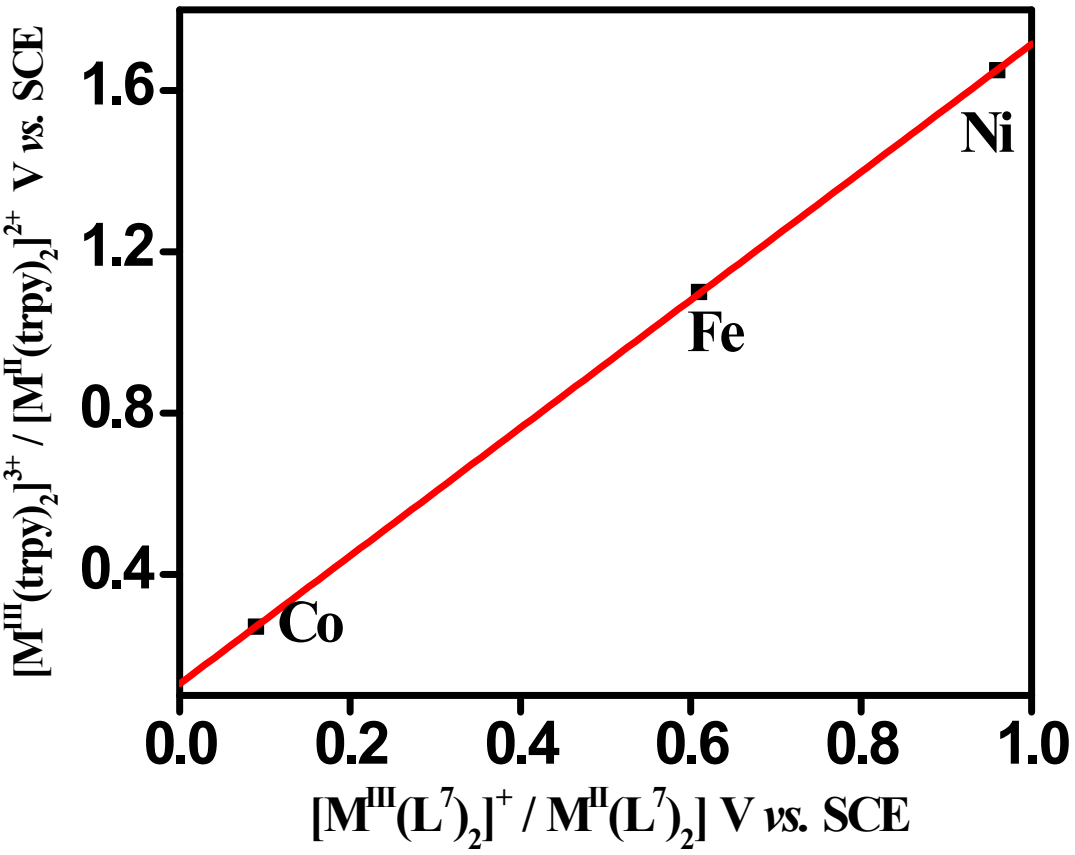


Fig. S34 Least-squares plot of $E_{1/2}$s between $[M^{III}(L^7)_2]^+$ / $[M^{II}(L^7)_2]$ and $[M^{III}(trpy)_2]^{3+}$ / $[M^{II}(trpy)_2]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line (y = 1.58697x + 0.12854) is ±0.004. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(trpy)_2]^{2+}$ (1.10 V), $[Co(trpy)_2]^{2+}$ (0.27 V) and $[Ni(trpy)_2]^{2+}$ (1.65 V). $E_{1/2}$ (*vs.* SCE, CH_2Cl_2): $[Fe(L^7)_2]$ (0.61 V), $[Co(L^7)_2]^{2+}$ (0.10 V) and $[Ni(L^7)_2]^{2+}$ (0.94 V).

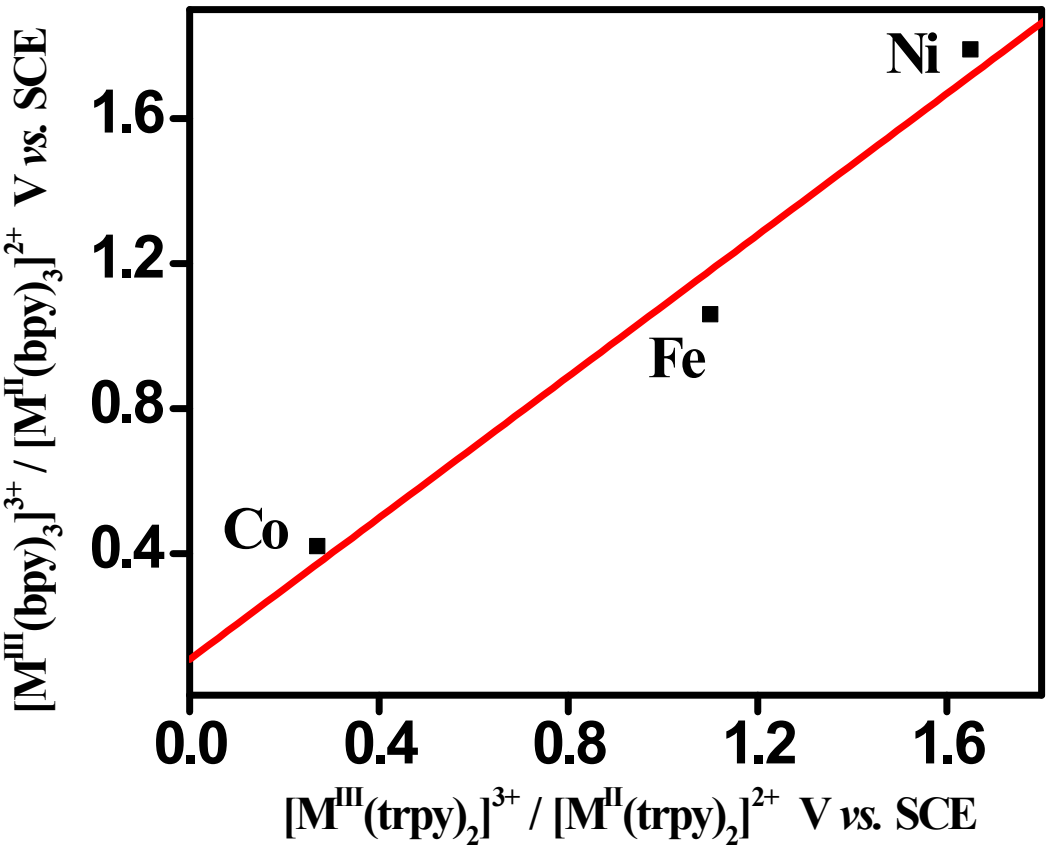


Fig. S35 Least-squares plot of $E_{1/2}$s between $[M^{III}(trpy)_2]^{3+}$ / $M^{II}(trpy)_2]^{2+}$ and $[M^{III}(bpy)_3]^{3+}$ / $M^{II}(bpy)_3]^{2+}$ redox couples. The root-mean-square deviation of the three data points from the least square line (y = 0.97496x + 0.10854) is ±0.08. $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(bpy)_3]^{2+}$ (1.06 V), $[Co(bpy)_3]^{2+}$ (0.42 V) and $[Ni(bpy)_3]^{2+}$ (1.79 V). $E_{1/2}$ (*vs.* SCE, MeCN): $[Fe(trpy)_2]^{2+}$ (1.10 V), $[Co(trpy)_2]^{2+}$ (0.27 V) and $[Ni(trpy)_2]^{2+}$ (1.65 V).

Table S1 Data collection and structure refinement parameters for $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1), $[Fe^{II}(L^8)_2]$ (2) and $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ ($5\cdot CH_2Cl_2\cdot 3H_2O$)

	$1\cdot CH_2Cl_2$	2	$5\cdot CH_2Cl_2\cdot 3H_2O$
Formula	$C_{37}H_{28}Cl_2FeN_8O_2$	$C_{34}H_{24}FeN_{10}O_2$	$C_{37}H_{34}BCl_2F_4FeN_8O_5$
Formula weight	743.42	660.48	871.25
Crystal colour, habit	green, block	green, block	red, block
T / K	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*bca (no. 61)	$P2_1/n$ (no. 14)	*C*2/m (no. 12)
a/Å	20.7434(15)	11.1427(16)	14.714(2)
b/Å	12.0390(9)	12.3508(19)	24.385(2)
c/Å	25.9875(18)	21.115(3)	11.8024(13)
α/°	90.0	90.0	90.0
β/°	90.0	97.055(7)	115.882(4)
γ/°	90.0	90.0	90.0
V/Å^3	6489.9(8)	2883.9(7)	3810.0(8)
Z	8	4	4
D_c/g cm^{-3}	1.52	1.521	1.299
μ/mm^{-1}	0.679	0.660	0.457
Reflections measured	32404	15376	19224
Unique reflections/R_{int}	5724/0.1085	5364/0.1000	3443/0.0927
Reflections used $I > 2\sigma(I)$]	3685	2942	2235
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	$R_1 = 0.0549$[a] $wR_2 = 0.1184$[b]	$R_1 = 0.0545$[a] $wR_2 = 0.1230$[b]	$R_1 = 0.0915$[a] $wR_2 = 0.2485$[b]
R_1[a], wR_2[b](all data)	R_1=0.0977[a] wR_2= 0.1396[b]	R_1=0.0960[a] wR_2= 0.1273[b]	R_1= 0.1339[a] wR_2= 0.2773[b]
GOF on F^2	1.014	0.971	1.046

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w\ (|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

Table S2 Data collection and structure refinement parameters for $[Co^{II}(L^7)_2]$ (3), $[Co^{II}(L^8)_2]$ (4) and $[Co^{III}(L^8)_2][ClO_4]$ (6)

	3	**4**	**6**
Formula	$C_{36}H_{26}N_8CoO_2$	$C_{34}H2_4CoN_{10}O_2$	$C_{36}H_{26}ClCoN_8O_6$
Formula weight	661.58	663.56	761.03
Crystal colour, habit	brown, block	brown,prism	brown, prism
T / K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	12.9608(16)	12.589(5)	12.648(5)
b/Å	11.8152(14)	12.286(5)	12.329(5)
c/Å	19.486(2)	19.148(5)	21.462(8)
α/°	90	90.00	90
β/°	92.100(2)	91.131	97.918(7)
γ/°	90.00	90.00	90
V/Å^3	2982.0(6)	2959.9(16)	3315(2)
Z	4	4	4
D_c/g cm^{-3}	1.474	1.489	1.525
μ/mm^{-1}	0.625	0.632	0.660
Reflections measured	14950	15051	16289
Unique reflections/R_{int}	5238/0.0682	5199/0.0620	5814/0.0554
Reflections used $I > 2\sigma(I)$]	3548	3566	4288
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	$R_1 = 0.0620$[a] $wR_2 = 0.1500$[b]	$R_1 = 0.0482$[a] $wR_2 = 0.0963$[b]	$R_1 = 0.0695$[a] $wR_2 = 0.1741$[b]
R_1[a], wR_2[b](all data)	R_1=0.0985[a] wR_2=0.1722[b]	$R_1 = 0.0812$[a] $wR_2 = 0.1112$[b]	R_1=0.0937[a] wR_2=0.1954[b]
GOF on F^2	1.033	0.995	1.087

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w\,(|F_o|^2 - |F_c|^2)^2]/\,\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

Table S3 Selected bond Lengths (Å) and bond Angles (deg) in for $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1), $[Fe^{II}(L^8)_2]$ (2) and $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ (5)

1·CH_2Cl_2		**2**		**5·CH_2Cl_2·$3H_2O$**	
Fe–N1	1.996(3)	Fe–N1	1.992(3)	Fe1–N1	1.980(5)
Fe–N2	1.935(3)	Fe–N3	1.928(3)	Fe1–N2	1.899(5)
Fe–N3	1.953(3)	Fe–N4	1.960(3)	Fe1–N4	1.968(6)
Fe–N5	1.996(3)	Fe–N6	1.972(3)		
Fe–N6	1.933(3)	Fe–N8	1.928(3)		
Fe–N7	1.950(3)	Fe–N9	1.957(3)		
N1–Fe–N3	163.66(14)	N1–Fe–N4	163.18(14)	N1–Fe1–N4	172.4(2)
N1–Fe–N7	95.39(13)	N1–Fe–N9	87.57(13)	N2–Fe1–N4	90.5(2)
N2–Fe–N1	80.64(13)	N3–Fe–N1	81.07(13)	N2–Fe1–N1	83.1(2)
N2–Fe–N3	83.24(15)	N3–Fe–N4	82.19(14)	N2-Fe1-N1#[a]	95.3(2)
N2–Fe–N5	91.18(13)	N3–Fe–N6	91.10(14)	N2–Fe1–N2#	177.8(3)
N2–Fe–N7	106.00(14)	N3–Fe–N9	104.86(14)	N2–Fe1–N4#	91.0(2)
N5–Fe–N1	90.25(13)	N6–Fe–N1	91.08(13)	N1–Fe1–N4#	93.8(2)
N5–Fe–N3	92.22(13)	N6–Fe–N4	90.95(13)	N1–Fe1–N1#	82.8(3)
N5–Fe–N7	162.56(13)	N6–Fe–N9	163.55(14)	N4–Fe1–N4#	90.3(3)
N6–Fe–N1	91.87(13)	N8–Fe–N1	92.47(14)		
N6–Fe–N2	168.82(13)	N8–Fe–N3	169.92(14)		
N6–Fe–N3	104.47(13)	N8–Fe–N4	104.35(14)		
N6–Fe–N5	80.50(13)	N8–Fe–N6	81.24(14)		
N7–Fe–N3	87.00(13)	N9–Fe–N4	95.08(14)		
N6–Fe–N7	82.83(14)	N8–Fe–N9	82.44(14)		

[a] Atom marked # is generated by symmetry. Symmetry operator: N1#, N2# and N4#, 1–x, y, 1–z.

Table S4 Selected bond lengths (Å) and bond angles (deg) in for $[Co^{II}(L^7)_2]$ (3), $[Co^{II}(L^8)_2]$ (4) and $[Co^{III}(L^7)_2][ClO_4]$ (6)

3		4		6	
Co–N1	2.185(4)	Co–N1	2.062(3)	Co–N1	1.943(4)
Co–N2	1.945(4)	Co–N3	1.915(2)	Co–N2	1.895(4)
Co–N3	2.380(4)	Co–N4	2.125(3)	Co–N3	1.977(4)
Co–N5	2.105(4)	Co–N6	2.018(3)	Co–N5	1.968(4)
Co–N6	1.942(4)	Co–N8	1.916(2)	Co–N6	1.894(4)
Co–N7	2.281(4)	Co–N9	2.096(3)	Co–N7	1.996(4)
N1–Co–N3	153.06(13)	N1–Co–N4	162.27(10)	N1–Co–N3	166.46(16)
N1–Co–N7	78.59(14)	N1–Co–N9	84.05(10)	N1–Co–N5	92.42(16)
N2–Co–N1	80.49(14)	N3–Co–N1	81.43(10)	N1–Co–N7	86.64(16)
N2–Co–N3	76.09(14)	N3–Co–N4	80.85(10)	N2–Co–N1	82.66(17)
N2–Co–N5	93.61(15)	N3–Co–N6	91.73(10)	N2–Co–N3	83.86(18)
N2–Co–N7	105.85(14)	N3–Co–N9	104.95(11)	N2–Co–N5	91.48(16)
N5–Co–N1	107.82(14)	N3–Co–N8	172.42(11)	N2–Co–N6	172.54(17)
N5–Co–N3	86.93(14)	N6–Co–N1	93.76(10)	N2–Co–N7	101.35(17)
N5–Co–N7	160.37(14)	N6–Co–N4	87.45(10)	N3–Co–N7	94.85(16)
N6-Co-N1	101.06(15)	N6–Co–N9	162.61(10)	N5–Co–N3	89.12(16)
N6–Co–N2	175.15(16)	N8–Co–N1	95.25(10)	N5–Co–N7	166.90(17)
N6–Co–N3	103.39(14)	N8–Co–N4	102.42(10)	N6–Co–N1	92.85(16)
N6–Co–N5	81.54(15)	N8–Co–N6	81.66(11)	N6–Co–N3	100.69(17)
N6-Co-N7	78.99(14)	N8–Co–N9	81.37(10)	N6–Co–N5	82.74(17)
N7–Co–N3	95.09(14)	N9–Co–N4	99.88(10)	N6–Co–N7	84.26(18)

Table S5 DFT-optimized cartesian coordinates of $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1)

Fe	9.428766000	2.852475000	2.588435000
O	6.084188000	2.672417000	4.929400000
N	10.512634000	3.718005000	1.189211000
O	10.511244000	4.284477000	-1.082916000
N	10.983988000	3.474072000	3.769023000
N	8.347213000	4.536854000	2.907402000
N	10.177012000	0.953533000	2.759038000
N	8.081909000	2.133276000	3.833280000
N	8.291263000	2.404571000	0.972213000
N	11.306811000	0.420305000	2.586950000
N	11.457480000	3.121731000	4.883130000
C	7.072120000	2.939375000	4.233373000
C	9.282723000	0.133573000	3.518844000
C	11.886721000	4.289017000	3.013026000

C	11.617938000	4.411474000	1.623728000
C	8.117356000	2.767537000	-1.401076000
H	8.561292000	3.231479000	-2.282844000
C	8.569124000	-1.993614000	4.417768000
H	8.715061000	-3.069469000	4.539156000
C	7.158031000	1.685853000	0.927063000
H	6.806904000	1.274770000	1.872692000
C	6.385920000	5.363840000	4.031074000
H	5.539928000	5.122469000	4.676003000
C	8.566326000	5.769030000	2.421314000
H	9.440886000	5.889490000	1.783378000
C	8.154599000	0.783396000	4.086757000
C	13.556755000	5.864404000	1.439376000
H	14.212851000	6.485003000	0.822807000
C	10.043009000	3.732524000	-0.079089000
C	13.568287000	1.069143000	2.086493000
H	13.818123000	0.852555000	3.126958000
C	13.809506000	5.740696000	2.816795000
H	14.650421000	6.268451000	3.272690000
C	12.975629000	4.953290000	3.600739000
H	13.140165000	4.846505000	4.672783000
C	11.898994000	1.176859000	0.322038000
H	10.873905000	1.015804000	-0.011725000
C	6.455473000	1.468857000	-0.257673000
H	5.539623000	0.875540000	-0.236743000
C	6.941721000	2.020261000	-1.445448000
H	6.411682000	1.868998000	-2.388883000
C	10.460135000	0.820306000	7.582768000
H	10.848563000	-0.077803000	8.069360000
C	8.766987000	2.937367000	-0.177312000
C	6.615885000	6.642252000	3.525801000
H	5.940095000	7.466839000	3.765076000
C	9.467716000	3.121268000	6.334053000
H	9.113331000	4.041847000	5.870596000
C	12.890897000	1.554794000	-0.583861000
H	12.624630000	1.730644000	-1.628569000
C	10.648206000	2.521177000	5.864428000
C	8.787719000	2.562982000	7.417422000
H	7.868737000	3.033638000	7.774133000
C	9.483266000	-1.246282000	3.685770000
H	10.353626000	-1.710598000	3.222470000
C	7.450653000	-1.360566000	4.987611000
H	6.730397000	-1.949545000	5.562153000
C	7.235195000	0.004535000	4.831266000
H	6.373207000	0.498797000	5.272719000
C	12.229721000	0.952786000	1.669163000
C	7.272605000	4.336165000	3.705072000
C	14.212582000	1.716807000	-0.157346000
H	14.983969000	2.020463000	-0.869081000
C	11.160350000	1.385712000	6.518817000
H	12.100266000	0.953595000	6.169975000
C	12.481344000	5.216561000	0.841017000
H	12.283880000	5.308266000	-0.224257000
C	14.546953000	1.473403000	1.180407000
H	15.580290000	1.589032000	1.516709000
C	9.272238000	1.406558000	8.036250000
H	8.731628000	0.969607000	8.879246000

C	7.729062000	6.846837000	2.707113000
H	7.955307000	7.827931000	2.285802000

Table S6 DFT-optimized cartesian coordinates of $[Fe^{II}(L^8)_2]$ (2)

Fe	3.685792000	2.783402000	18.091604000
O	2.020496000	3.106381000	14.367212000
O	3.051851000	4.012632000	21.934650000
N	3.201943000	4.606052000	17.370401000
N	4.067731000	3.483227000	19.889034000
N	3.043766000	2.260639000	16.298943000
N	1.855840000	2.575757000	18.903811000
N	-0.530924000	2.456123000	20.365228000
N	2.453347000	6.950428000	16.036579000
C	2.938777000	0.907957000	16.078132000
N	4.099327000	0.790327000	18.203245000
N	5.644999000	3.312375000	17.777213000
N	4.944975000	0.087769000	18.823134000
C	3.504193000	0.100232000	17.100392000
C	2.707218000	4.570687000	16.114807000
C	2.942117000	6.968929000	17.280060000
H	3.041537000	7.943733000	17.767210000
C	3.317794000	5.806708000	17.955837000
H	3.713259000	5.834857000	18.970668000
C	1.792983000	3.004652000	20.183491000
C	3.467275000	-1.301370000	17.021715000
H	3.900048000	-1.886502000	17.833340000
C	5.331583000	3.989673000	20.086448000
C	2.304160000	-1.124166000	14.909983000
H	1.829545000	-1.607453000	14.051661000
C	7.506166000	4.405829000	19.016264000
H	8.140238000	4.317036000	18.134676000
C	6.054359000	0.711957000	14.284813000
H	6.060989000	-0.380252000	14.256024000
N	6.364681000	3.470238000	16.758025000
C	6.498673000	0.956675000	22.628010000
H	6.911949000	1.145661000	23.621578000
C	3.054810000	3.560306000	20.784544000
C	6.115786000	1.363919000	15.517988000
H	6.204069000	0.792746000	16.442194000
C	6.823278000	0.374581000	20.299170000
H	7.471894000	0.094332000	19.466664000
C	6.189480000	3.918462000	18.955939000
C	0.729574000	2.092629000	18.359886000
H	0.775982000	1.748171000	17.327597000
C	5.437826000	0.483721000	20.078711000
C	7.976796000	4.980004000	20.189244000
H	9.001706000	5.354347000	20.241189000
C	2.335646000	5.752383000	15.462786000
H	1.934489000	5.693583000	14.447717000
C	4.583352000	0.784265000	21.153442000
H	3.504784000	0.791415000	20.995442000
C	5.829677000	4.583739000	21.272104000
H	5.174859000	4.646313000	22.137771000

C	5.116973000	1.015865000	22.421827000
H	4.446042000	1.249326000	23.251590000
C	2.334405000	0.265401000	14.970931000
H	1.911004000	0.878549000	14.178575000
C	0.591851000	2.939894000	20.898829000
H	0.569521000	3.299421000	21.930815000
C	6.093597000	3.506246000	14.365201000
H	6.144319000	4.596073000	14.411864000
C	7.131710000	5.068620000	21.309987000
H	7.504337000	5.518910000	22.234007000
C	6.116996000	2.768007000	15.562507000
C	5.979845000	1.445032000	13.097467000
H	5.920789000	0.928668000	12.136531000
C	-0.453375000	2.035739000	19.099584000
H	-1.365211000	1.636101000	18.645413000
C	7.349091000	0.636164000	21.562754000
H	8.428496000	0.576595000	21.722175000
C	2.553802000	3.218015000	15.475429000
C	2.865359000	-1.914307000	15.929196000
H	2.818216000	-3.004055000	15.870976000
C	5.995367000	2.844521000	13.142971000
H	5.944689000	3.423269000	12.217565000

Table S7 DFT-optimized cartesian coordinates of $[Co^{III}(L^7)][ClO_4]$ (6)

C	-0.467439000	-0.016483000	0.102054000
C	-0.456229000	-0.080956000	1.497434000
C	3.901122000	0.494741000	5.259272000
C	5.630439000	-1.532552000	-1.883855000
C	4.980285000	-1.060316000	-0.746720000
C	0.303606000	-0.928899000	-0.618209000
C	4.149685000	-0.060065000	4.012893000
C	2.965645000	-0.110352000	6.121032000
C	0.329281000	-1.045351000	2.128078000
C	6.336944000	-2.741541000	-1.841696000
C	4.974598000	-1.839386000	0.425737000
C	3.450631000	-1.216680000	3.620887000
C	1.063117000	-1.864426000	0.080709000
C	2.278939000	-1.261965000	5.753736000
C	2.514615000	-1.839551000	4.484563000
C	6.380722000	-3.484025000	-0.657851000
C	5.694763000	-3.046131000	0.475484000
C	1.866054000	-2.915894000	-0.635508000
C	0.890735000	-3.652307000	4.573196000
C	5.123311000	-3.636983000	6.179070000
C	4.826215000	-4.000128000	4.865286000
C	4.614502000	-4.378038000	7.250028000
C	0.267650000	-4.620324000	3.604463000
C	3.138709000	-4.903979000	-0.036138000
C	3.288428000	-5.473521000	-1.321761000
C	4.027135000	-5.131762000	4.622872000
C	3.830454000	-5.513110000	7.005898000
C	0.199465000	-5.400259000	1.416020000
C	-0.791262000	-5.443888000	3.979866000

C	3.645916000	-5.613182000	1.081706000
C	3.565012000	-5.913569000	5.699129000
C	3.927701000	-6.700474000	-1.457752000
C	-0.863321000	-6.251125000	1.718036000
C	-1.366107000	-6.278167000	3.021073000
C	4.305111000	-6.846622000	0.926523000
C	4.439572000	-7.390881000	-0.341881000
H	-1.073333000	0.731168000	-0.414822000
H	-1.047251000	0.606649000	2.104523000
H	4.434642000	1.394514000	5.572093000
H	4.463047000	-0.098968000	-0.752441000
H	5.607256000	-0.943955000	-2.803577000
H	4.875530000	0.381510000	3.330810000
H	0.336979000	-0.955554000	-1.708526000
H	2.778520000	0.326425000	7.105248000
H	0.364158000	-1.124051000	3.213280000
H	6.871103000	-3.093011000	-2.727174000
H	1.569016000	-1.739510000	6.424513000
H	6.957199000	-4.410633000	-0.612049000
H	5.762486000	-3.601145000	1.411372000
H	5.762349000	-2.771076000	6.365818000
H	5.256442000	-3.448627000	4.029280000
H	4.846481000	-4.085166000	8.276364000
H	2.907919000	-4.931790000	-2.184146000
H	-1.135231000	-5.394440000	5.014219000
H	0.619084000	-5.353754000	0.412593000
H	3.444875000	-6.102066000	7.840959000
H	4.041351000	-7.130450000	-2.456091000
H	2.994234000	-6.821211000	5.493657000
H	-1.283001000	-6.881005000	0.932054000
H	-2.197313000	-6.937044000	3.282295000
H	4.699921000	-7.354426000	1.805854000
H	4.945712000	-8.349338000	-0.473366000
N	4.432300000	-1.260981000	1.583991000
N	1.076648000	-1.913489000	1.430247000
N	3.663870000	-1.861339000	2.365087000
N	1.893126000	-2.954316000	3.964764000
N	2.505662000	-3.717594000	0.264659000
N	0.753480000	-4.606332000	2.344385000
N	3.482249000	-4.977639000	2.349738000
N	3.857377000	-5.653139000	3.332019000
O	1.856243000	-2.998291000	-1.854642000
O	0.467659000	-3.537421000	5.713780000
Co	2.289114000	-3.343190000	2.130910000

Table S8 DFT-optimized cartesian coordinates of $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ ($5\cdot CH_2Cl_2\cdot 3H_2O$)

Fe	6.033770000	5.522456000	6.913276000
N	4.206193000	5.390729000	7.604189000
C	8.628227000	7.486526000	7.273658000
N	7.613292000	7.624850000	8.188839000

O	2.842771000	3.721731000	8.526342000
N	6.581967000	6.906840000	8.240085000
N	4.444718000	7.657725000	5.705771000
C	10.003591000	6.460726000	5.559602000
H	10.203524000	5.664245000	4.849815000
N	6.346520000	3.996282000	8.218645000
C	6.320359000	7.376849000	4.522335000
C	3.240674000	6.380500000	7.514416000
C	6.569139000	6.521081000	3.445594000
H	6.129713000	5.524938000	3.420166000
C	6.888096000	3.514343000	5.126280000
C	6.830316000	8.680020000	4.525719000
H	6.612286000	9.343286000	5.364369000
N	7.861334000	5.421353000	6.218362000
C	2.460268000	8.520031000	6.528075000
H	2.651595000	9.315851000	5.806510000
C	3.936120000	4.190156000	8.245875000
N	5.727339000	4.038660000	5.557850000
C	5.492082000	6.405048000	10.411003000
H	5.933598000	5.409528000	10.404069000
C	10.911849000	7.505928000	5.676950000
H	11.797455000	7.502397000	5.036427000
N	5.479619000	6.946876000	5.632492000
C	4.713940000	6.817831000	11.496138000
H	4.533865000	6.126680000	12.322805000
C	1.331571000	8.516010000	7.321761000
H	0.597002000	9.320365000	7.254461000
C	4.567371000	3.501783000	5.154310000
H	3.653766000	3.968247000	5.522239000
C	7.552537000	2.319437000	9.419428000
H	8.519024000	1.911561000	9.720001000
C	5.188147000	3.452661000	8.632195000
C	10.720361000	8.550299000	6.598060000
H	11.450928000	9.355812000	6.690499000
C	6.934215000	2.399473000	4.291232000
H	7.908503000	2.016609000	3.984192000
C	8.136851000	4.243613000	5.537811000
C	3.429836000	7.485039000	6.615198000
C	5.730350000	1.830278000	3.870614000
H	5.728577000	0.960014000	3.210450000
C	5.226964000	8.598501000	9.403970000
H	5.444254000	9.290253000	8.588455000
C	4.528777000	2.398442000	4.300251000
H	3.564077000	1.996902000	3.985720000
C	4.442662000	8.999214000	10.487406000
H	4.038637000	10.013772000	10.514274000
C	5.739810000	7.297042000	9.363700000
C	1.144353000	7.441453000	8.208354000
H	0.258003000	7.412740000	8.847219000
C	7.345787000	6.971647000	2.374436000
H	7.526714000	6.309035000	1.524910000
C	5.147085000	2.309699000	9.428673000
H	4.174534000	1.912452000	9.722651000
C	9.592735000	8.523075000	7.392832000
H	9.398493000	9.294291000	8.139888000
C	4.181950000	8.110199000	11.534339000
H	3.573043000	8.426798000	12.384075000

C	8.821832000	6.412699000	6.338914000
C	6.353501000	1.731609000	9.829349000
H	6.359233000	0.839385000	10.459496000
C	7.875143000	8.265632000	2.379588000
H	8.482913000	8.611966000	1.540707000
C	7.613157000	9.118486000	3.455934000
H	8.015056000	10.134215000	3.462831000
C	7.508973000	3.451209000	8.603747000
H	8.420389000	3.934080000	8.251956000
C	2.057575000	6.397413000	8.293089000
H	1.860639000	5.577300000	8.976264000
O	9.232384000	3.789081000	5.243432000

Table S9 DFT-optimized cartesian coordinates of $[Co^{II}(L^8)_2]$ (4)

C	0.031920000	0.302768000	0.097400000
C	0.276795000	-0.242108000	6.383200000
C	2.304071000	0.275711000	0.151318000
C	-0.054318000	-0.901098000	5.196430000
C	-0.010233000	-0.731800000	1.041486000
C	2.284388000	-0.756770000	1.092516000
C	2.369145000	-1.126371000	6.321484000
C	-1.317600000	-1.265680000	1.568348000
C	2.059516000	-1.795054000	5.130671000
C	-3.523939000	-2.459285000	3.125672000
C	-4.471725000	-3.059452000	3.946179000
C	-2.158387000	-2.837427000	3.202698000
C	-2.662002000	-4.088686000	-1.499253000
C	3.078131000	-2.632826000	4.403594000
C	-1.291883000	-3.959360000	-1.283733000
C	-4.112943000	-4.058989000	4.866731000
C	-3.466080000	-4.725543000	-0.545923000
C	-1.806125000	-3.848939000	4.143780000
C	-2.785227000	-4.449169000	4.958871000
C	-0.721487000	-4.421416000	-0.082159000
C	-2.893004000	-5.225851000	0.628272000
C	3.302684000	-3.868632000	2.335562000
C	-1.528113000	-5.071373000	0.868523000
C	4.698566000	-4.109519000	2.412435000
C	2.611914000	-4.333690000	1.179674000
C	5.355428000	-4.773858000	1.383359000
C	3.296110000	-5.012200000	0.153164000
C	1.688105000	-5.761174000	6.498886000
C	1.108080000	-5.591283000	5.227092000
C	4.662655000	-5.230602000	0.248344000
C	2.886202000	-6.459560000	6.631610000
C	1.709317000	-6.182335000	4.101803000
C	3.489998000	-7.036461000	5.507746000
C	2.891898000	-6.906018000	4.249261000
H	-0.458711000	0.392344000	6.887388000
H	-0.905704000	0.714316000	-0.284238000
H	3.255316000	0.682411000	-0.205861000
H	-1.041695000	-0.812116000	4.740649000
H	3.368525000	-1.237390000	6.749598000

H	-3.807560000	-1.695434000	2.407663000
H	3.201427000	-1.191053000	1.494836000
H	-5.516912000	-2.749609000	3.860542000
H	-3.105315000	-3.704704000	-2.421167000
H	-0.643455000	-3.493471000	-2.028710000
H	-4.537537000	-4.843426000	-0.724636000
H	-4.870474000	-4.532335000	5.495624000
H	5.233664000	-3.767420000	3.293748000
H	-3.514736000	-5.738881000	1.365719000
H	-2.472225000	-5.231360000	5.650399000
H	-1.072705000	-5.476689000	1.771842000
H	1.185242000	-5.328621000	7.366443000
H	6.431162000	-4.950203000	1.469563000
H	2.724366000	-5.366372000	-0.704488000
H	5.190792000	-5.762676000	-0.546217000
H	3.345931000	-6.567922000	7.616917000
H	1.229094000	-6.094080000	3.127579000
H	4.420074000	-7.599830000	5.614853000
H	3.351763000	-7.370913000	3.374064000
O	-2.366180000	-0.749279000	1.187274000
O	4.221904000	-2.709102000	4.846318000
Co	0.692135000	-2.832914000	2.856347000
N	1.183751000	0.804932000	-0.349783000
N	1.482183000	-0.353199000	6.949564000
N	1.124275000	-1.255543000	1.529708000
N	0.841316000	-1.677040000	4.577615000
N	-1.129349000	-2.277578000	2.464000000
N	2.550698000	-3.186809000	3.274482000
N	-0.445998000	-4.257234000	4.181135000
N	1.205150000	-4.129180000	1.146032000
N	0.677563000	-4.343558000	0.023269000
N	-0.138420000	-4.942908000	5.191302000

Table S10 DFT-optimized cartesian coordinates of $[Co^{III}(L^{8})_2]^+$ (4^+)

C	0.295672000	0.312171000	0.160784000
C	0.043514000	-0.058970000	6.114125000
C	2.549213000	0.210811000	0.444734000
C	-0.202529000	-0.797322000	4.950852000
C	0.125707000	-0.742560000	1.064299000
C	2.410284000	-0.844084000	1.353984000
C	2.126599000	-0.953376000	6.285934000
C	-1.228379000	-1.248420000	1.474304000
C	1.908899000	-1.705046000	5.126109000
C	-3.480335000	-2.446884000	3.064264000
C	-4.388914000	-3.060728000	3.919541000
C	-2.114410000	-2.804763000	3.126968000
C	-2.777802000	-4.093352000	-1.296586000
C	2.966601000	-2.583245000	4.520049000
C	-1.415447000	-3.931903000	-1.059877000
C	-3.980778000	-4.040985000	4.844726000
C	-3.570359000	-4.810486000	-0.390701000
C	-1.712075000	-3.785204000	4.068640000
C	-2.645631000	-4.409882000	4.916152000

C	-0.851716000	-4.428468000	0.131869000
C	-2.995943000	-5.357278000	0.761250000
C	3.247652000	-3.859238000	2.462737000
C	-1.642483000	-5.161718000	1.035275000
C	4.636071000	-4.112427000	2.541245000
C	2.540321000	-4.304977000	1.317764000
C	5.268125000	-4.789947000	1.504228000
C	3.190327000	-5.004363000	0.284183000
C	1.918549000	-5.700093000	6.211540000
C	1.268504000	-5.584625000	4.967120000
C	4.554224000	-5.239054000	0.376389000
C	3.082241000	-6.457434000	6.312780000
C	1.741831000	-6.302650000	3.853663000
C	3.563622000	-7.161865000	5.201425000
C	2.881410000	-7.096539000	3.982399000
H	-0.724550000	0.612114000	6.510031000
H	-0.585869000	0.767499000	-0.299015000
H	3.543675000	0.594684000	0.198343000
H	-1.148594000	-0.729437000	4.415799000
H	3.088923000	-1.032400000	6.799304000
H	-3.797393000	-1.702896000	2.337477000
H	3.271062000	-1.307456000	1.833803000
H	-5.443357000	-2.779425000	3.862190000
H	-3.221783000	-3.680193000	-2.204841000
H	-0.776669000	-3.415690000	-1.779117000
H	-4.632239000	-4.962420000	-0.596316000
H	-4.712871000	-4.515050000	5.501471000
H	5.183957000	-3.781387000	3.420189000
H	-3.604286000	-5.947085000	1.450460000
H	-2.306030000	-5.173048000	5.615661000
H	-1.183622000	-5.623011000	1.909533000
H	1.505745000	-5.184199000	7.080595000
H	6.341235000	-4.984060000	1.575186000
H	2.612874000	-5.350620000	-0.572383000
H	5.070011000	-5.776146000	-0.422063000
H	3.604533000	-6.521212000	7.269791000
H	1.184517000	-6.285466000	2.917289000
H	4.458636000	-7.781009000	5.293896000
H	3.234428000	-7.673344000	3.124703000
O	-2.251455000	-0.734499000	1.050158000
O	4.082525000	-2.659345000	5.009492000
Co	0.675589000	-2.821639000	2.866952000
N	1.502371000	0.783201000	-0.151460000
N	1.196375000	-0.137510000	6.780311000
N	1.193684000	-1.314541000	1.651028000
N	0.736523000	-1.619973000	4.470061000
N	-1.092078000	-2.266081000	2.374168000
N	2.486252000	-3.177049000	3.388626000
N	-0.323704000	-4.120372000	4.065267000
N	1.137328000	-4.038012000	1.307959000
N	0.542259000	-4.359171000	0.256879000
N	0.030644000	-4.927743000	4.950821000

Table S11 TD-DFT-calculated electronic transitions of $[Fe^{II}(L^7)_2]\cdot CH_2Cl_2$ (1)

Excitation energy (eV)	λ (nm)	*f*	Transition	Character
1.8073	686	0.0108	*α/β*-H-1[~65%L]→ *α/β* -L[~93%L] (31%) *α/β*-H[~71%L]→ *α/β* –L+1[~97%L] (37%)	CT(amide → azo) and MLCT (metal → azo) CT (amide → azo) and MLCT (metal → azo)
1.9534	635	0.0242	*α/β*-H-1[~65%L]→ *α/β* -L[~93%L] (38%) *α/β*-H[~71%L]→ *α/β* –L+1[~97%L] (19%) *α/β*-H-2[~38%L]→ *α/β* –L+1[~97%L] (18%)	CT (amide → azo) and MLCT (metal → azo) CT (amide → azo) and MLCT (metal → azo) MLCT (metal → azo)
2.0237	613	0.0211	*α/β*-H-1[~65%L]→ *α/β* –L+1[~97%L] (44%) *α/β*-H-1[~65%L]→ *α/β* –L+6[~76%L] (15%)	CT (amide → azo) and MLCT (metal → azo) CT (amide → phenyl ring appended to azo) and MLCT(metal → phenyl ring appended to azo)
2.0812	596	0.0418	*α/β*-H [~71%L]→ *α/β* –L+1[~97%L] (23%) *α/β*-H-1[~65%L]→ *α/β* –L[~93%L] (12%) *α/β*-H-2[~38%L]→ *α/β* –L+6[~76%L] (35%)	CT (amide → azo) and MLCT (metal → azo) CT (amide → azo) and MLCT (metal → azo) MLCT (metal → phenyl ring appended to azo)

2.566	483	0.068	*α/β*-H-2[~38%L]→ *α/β* –L+1[~97%L] (62%) *α/β*-H-2[~38%L]→ *α/β* –L+6[~76%L] (10%)	MLCT (metal → azo) MLCT (metal → phenyl ring appended to azo)
2.6463	468	0.1329	*α/β* -H-2[~38%L]→ *α/β* -L[~93%L] (46%) *α/β* -H-1[~65%L]→ *α/β* –L+1[~97%L] (18%) *α/β* -H-4[~52%L]→ *α/β* -L[~93%L] (11%)	MLCT (metal → azo) CT (amide → azo) and MLCT (metal → azo) CT (N-phenyl amide → azo) and MLCT (metal → azo)
2.8163	440	0.1234	*α/β*-H-3[~78%L]→ *α/β*–L[~93%L] (57%) *α/β*-H-1[~65%L]→ *α/β*–L+3[~97%L] (27%)	CT (phenyl ring between azo and amide → azo) and minor MLCT (metal → azo) CT (amide → pyridine) and MLCT (metal → pyridine)
2.9674	418	0.0986	*α/β*-H-4[~52%L]→ *α/β*–L+1[~97%L] (81%)	CT (N-phenyl amide → azo) and MLCT (metal → azo)
3.2520	381	0.0547	*α/β*-H-2[~38%L]→ *α/β*–L+2[~99%L] (90%)	MLCT (metal → pyridine)
3.3201	373	0.0527	*α/β*-H-6[~94%L]→ *α/β*–L[~93%L] (54%) *α/β*-H-2[~38%L]→ *α/β*–L+3[~97%L] (19%)	CT (phenyl ring appended to azo → azo) MLCT (metal → pyridine)
3.3792	367	0.0299	*α/β*-H-2[~38%L]→ *α/β*–L+3[~97%L] (53%) *α/β*-H-5[~83%L]→ *α/β*–L+1[~97%L] (18%)	MLCT (metal → pyridine) CT (phenyl amide → azo)
3.7211	333	0.0406	*α/β*-H-3[~78%L]→ *α/β*–L+3[~97%L] (59%)	CT (phenyl ring between azo and amide → pyridine)
3.7211	321	0.0406	*α/β*-H-10[~99%L]→ *α/β*–L [~93%L] (54%) *α/β*-H-8[~97%L]→ *α/β*–L+1 [~97%L] (22%)	CT (phenyl rings appended to both side of azo → azo) CT (amide → azo)

Table S12 TD-DFT-calculated electronic transitions of $[Fe^{II}(L^8)_2]$ (2)

Excitation energy (eV)	λ (nm)	*f*	Transition	Character
2.0295	611	0.0237	*α/β*-H[~73%L]→ *α/β* -L[~97%L] (46%)	CT (amide → azo), along with minor MLCT (metal → azo)
2.0638	601	0.0473	*α/β*-H-1[~74%L]→ *α/β* -L[~97%L] (56%)	CT (amide → azo), along with minor MLCT (metal → azo)
2.1559	575	0.0408	*α/β*-H-2[~48%L]→ *α/β* L+6[~71%L](32%)	MLCT (metal → phenyl ring appended to azo)
2.5660	483	0.0868	*α/β*-H-2[~48%L]→ *α/β* -L[~97%L] (74%)	MLCT (metal → azo)
2.7091	458	0.0485	*α/β*-H-2[~48%L]→ *α/β* L+1[~94%L](32%)	MLCT (metal → azo)
2.7986	443	0.1228	*α* -H-4[~51%M]→ *α* -L[~97%L] (6%)	MLCT (metal → azo)
			α -H-4[~51%M]→ *α* –L+1[~94%L] (8%)	MLCT (metal → azo)
			α -H-3[~28%M]→ *α* –L+1[~94%L] (5%)	CT (phenyl ring between azo and amide → azo)
			α -H-2[~52%M]→ *α* –L+3[~98%L] (4%)	MLCT (metal → pyrazine)
			β -H-4[~51%M]→ *β* –L[~97%L] (6%)	MLCT (metal → azo)
			β -H-4[~51%M]→ *β* –L+1[~94%L] (8%)	MLCT (metal → azo)
			β -H-3[~27%M]→ *β* –L+1[~94%L] (5%)	CT (phenyl ring between azo and amide → azo)
2.8235	439	0.0302	*α* -H-3[~28%M]→ *α* –L+1[~94%L](10%)	CT (phenyl ring between azo and amide → azo)
			α -H-2[~52%M]→ *α* –L+1[~94%L] (10%)	MLCT (metal → azo)
			α -H-2[~52%M]→ *α* –L+2[~97%L] (7%)	MLCT (metal → pyrazine) CT (phenyl ring between azo and amide → azo)
			β -H-3[~28%M]→ *β* –L+1[~94%L] (10%) *β* -H-2[~52%M]→ *β* –L+1[~94%L] (10%)	MLCT (metal → azo)

Table S13 TD-DFT-calculated electronic transitions of $[Co^{III}(L^7)][ClO_4]$ (6)

Excitation energy(eV)	λ (nm)	*f*	Transition	Character
2.4598	504	0.069	*α*-H [~96%L]→ *α* –L+1[~96%L](37%) *β*-H[~96%L]→ *β* –L+1[~96%L](37%)	CT (phenyl amide → azo) CT (phenyl amide → azo)
2.5932	478	0.0283	*α*-H-1[~97%L]→ *α* –L+1[~96%L](40%) *β*-H-1[~97%L]→ *β* –L+1[~96%L](40%)	CT (phenyl amide → azo) CT (phenyl amide → azo)
2.8904	429	0.0254	*α*-H-1[~97%L]→ *α* –L+2[~77%L](19%) *β*-H-1[~97%L]→ *β* –L+2[~77%L](19%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal) CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
2.9147	425	0.0124	*α*-H-2[~96%L]→ *α* –L [~83%L] (12%) *α*-H-2[~96%L]→ *α* –L+1[~96%L](19%) *β*-H-2[~96%L]→ *β* –L [~83%L] (12%) *β*-H-2[~96%L]→ *β* –L+1[~96%L](19%)	CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo)
3.0632	405	0.0206	*α* –H-3[~97%L]→ *α* –L[~83%L] (16%) *α* –H-2[~96%L]→ *α* –L [~83%L] (13%) *β*-H-3[~97%L]→ *β* –L[~83%L] (16%) *β*-H-2[~96%L]→ *β* –L [~83%L] (13%)	CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo) CT (phenyl ring appended to azo → azo)
3.2299	384	0.0285	*α* –H [~96%L]→ *α* –L+3[~97%L](41%) *β*-H [~96%L]→ *β* –L+3[~97%L](41%)	CT (phenyl amide → pyridine) CT (phenyl amide → pyridine)
3.3034	375	0.0203	*α* -H [~96%L]→ *α* –L+4[~99%L](45%) *β* -H [~96%L]→ *β* –L+4[~99%L](45%)	CT (phenyl amide → pyridine) CT (phenyl amide → pyridine)

3.3228	373	0.044	α –H-1 [~97%L]→ α –L+3[~97%L](36%)	CT (phenyl amide → pyridine)
			β –H-1 [~97%L]→ β –L+3[~97%L](36%)	CT (phenyl amide → pyridine)
3.4027	364	0.0311	α –H-1 [~97%L]→ α –L+4[~99%L]	CT (phenyl amide → pyridine)
			β –H-1 [~97%L]→ β –L+4[~99%L] (42%)	CT (phenyl amide → pyridine)
3.4373	361	0.0481	α –H-3 [~97%L]→ α –L [~83%L] (13%)	CT (phenyl ring appended to azo → azo)
			α –H-3 [~97%L]→ α –L+1[~96%L](23%)	CT (phenyl ring appended to azo → azo)
			β –H-3 [~97%L]→ β –L [~83%L] (13%)	CT (phenyl ring appended to azo → azo)
			β –H-3 [~97%L]→ β –L+1 [~96%L](23%)	CT (phenyl ring appended to azo → azo)

Table S14 TD-DFT-calculated electronic transitions of $[Fe^{III}(L^7)_2][BF_4]\cdot CH_2Cl_2\cdot 3H_2O$ (5)

Excitation energy (eV)	λ (nm)	*f*	Transition	Character
1.9738	628	0.022	α-H[~95%L]→ α -L[~98%L] (13%)	CT (amide → azo)
			β-H[~97%L]→ β -L[~62%L] (55%)	CT (amide → metal and azo)
2.1736	570	0.0366	α-H[~95%L]→ α -L[~98%L] (16%)	CT (amide → azo)
			α-H-1[~98%L]→ α –L+1[~97%L] (10%)	CT (amide → azo)
			β-H[~97%L]→ β -L[~62%L] (26%)	CT (amide → metal and azo)
			β-H[~97%L]→ β –L+2[~86%L](16%)	CT (amide → azo)

2.6130	475	0.0418	α-H-1[~95%L]→ α -L[~98%L] (38%)	CT (amide → azo)
			β-H[~97%L]→ β –L+1[~99%L](36%)	CT (amide → azo)
2.6165	474	0.0415	α-H[~95%L]→ α -L[~98%L] (38%)	CT (amide → azo)
			β-H[~97%L]→ β –L+2[~86%L](40%)	CT (amide → azo)
2.8404	437	0.0218	β-H-1[~91%L]→ β –L+1[~99%L](28%)	CT (amide → azo)
3.0430	407	0.024	α -H[~95%L]→ α –L+5[~58%L] (21%)	CT (amide → metal and azo)
			α -H-1[~98%L]→ α –L+4[~96%L] (11%)	CT (phenyl amide → pyridine and azo)
			β -H-1[~91%L]→ β –L+2[~86%L](12%) (12%)	CT (amide → azo)
2.8235	389	0.01151	α -H-2[~99%L]→ α –L+1[~97%L] (21%)	CT (phenyl ring → azo)
			β -H-3[~77% L]→ β –L+1[~99%L] (38%)	CT (phenyl ring → azo) and minor MLCT (metal → azo)

Table S15 TD-DFT-calculated electronic transitions of $[Co^{II}(L^8)_2]$ (4)

Excitation energy (eV)	λ (nm)	*f*	Transition	Character
2.2062	562	0.0827	*α*-H-1[~78%L]→ *α* -L[~96%L] (22%)	CT (phenyl amide → azo)
			β-H[~84%L]→ *β* –L+1[~96%L](26%)	CT (phenyl amide → azo)
2.4724	502	0.0296	*α*-H-2[~94%L]→ *α* -L[~96%L] (39%)	CT (phenyl amide → azo)
2.4846	499	0.0332	*β*-H-2[~48%L]→ *β* –L+6[~56%L] (11%)	Meta-based transition
			β-H-1[~85%L]→ *β* –L+1[~96%L] (10%)	CT (phenyl amide → azo)
			β-H [~84%L]→ *β* –L+3[~98%L] (12%)	CT (phenyl amide → pyrazine)
2.6439	469	0.031	*β*-H-2[~48%L]→ *β* –L[~98%L] (17%)	MLCT (metal → azo)
			β-H-1[~85%L]→ *β* –L[~98%L] (11%)	CT (phenyl amide → azo)
2.8056	442	0.141	*α* –H-3[~81%L]→ *α* –L+1[~97%L] (16%)	CT in azo-phenyl moiety
			β-H-2[~48%L]→ *β* –L[~98%L] (25%)	MLCT (metal → azo)
2.9244	424	0.0324	*α* –H-2[~94%L]→ *α* –L+2[~99%L] (28%)	CT (phenyl amide → pyrazine)
			β-H-2[~48%L]→ *β* –L+2[~99%L] (19%)	MLCT (metal → pyrazine)
			β -H-1[~85%L]→ *β* –L+2[~99%L] (16%)	CT (phenyl amide → pyrazine)
2.9805	416	0.0608	*α* -H-3[~81%L]→ *α* –L+1[~97%L] (11%)	CT in azo-phenyl moiety
			β -H-2[~48%L]→ *β* –L+2[~99%L] (38%)	MLCT (metal → pyrazine)

Table S16 TD-DFT-calculated electronic transitions of $[Co^{III}(L^8)_2]^+$ (4^+)

Excitation energy(eV)	λ (nm)	*f*	Transition	Character
2.1356	581	0.1163	*α*-H-1[~97%L]→ *α* -L[~78%L] (10%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			α-H[~95%L]→ *α* –L+1[~96%L](23%)	CT (phenyl amide → azo)
			β-H[~95%L]→ *β* –L+1[~96%L](23%)	CT (phenyl amide → azo)
			β-H-1[~97%L]→ *β* –L[~78%L] (10%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
2.1871	567	0.0338	*α*-H[~95%L]→ *α* –L+1[~96%L](14%)	CT (phenyl amide → azo)
			β-H[~95%L]→ *β* –L+1[~96%L] (14%)	CT (phenyl amide → azo)
			α-H-18[~28%L]→ *α* -L[~78%L] (12%)	MLCT (metal → azo)
			β-H-18[~28%L]→ *β* –L[~78%L] (12%)	MLCT (metal → azo)
			α-H-18[~28%L]→ *α* –L+2[~78%L](12%)	MLCT (metal → azo)
			β-H-18[~28%L]→ *β* –L+2[~78%L](12%)	
2.3241	534	0.0545	*α*-H[~95%L]→ *α* –L+2[~78%L](19%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			β-H[~95%L]→ *β* –L+2[~78%L](19%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
2.3681	524	0.0228	*α*-H[~95%L]→ *α* –L+5[~58%L](17%)	LMCT (phenyl amide → metal)
			β-H[~95%L]→ *β* –L+5[~58%L] (17%)	LMCT (phenyl amide → metal)

2.5959	478	0.0952	α –H-1[~97%L]→ α –L+2[~78%L](13%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			α –H-2[~95%L]→ α –L [~78%L] (15%)	CT in phenyl-azo moiety
			β-H-2[~95%L]→ β –L[~78%L] (15%)	CT in phenyl-azo moiety
			β-H-1[~97%L]→ β –L+2[~78%L] (13%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
2.6711	464	0.0366	α –H-1[~97%L]→ α –L+2[~78%L](15%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			α –H-2[~95%L]→ α –L [~78%L] (16%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			β-H-2[~95%L]→ β –L [~78%L] (16%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
			β -H-1[~97%L]→ β –L+2[~78%L] (15%)	CT (phenyl amide → azo) and minor LMCT (phenyl amide → metal)
2.7514	451	0.0412	α -H [~95%L]→ α –L+3[~97%L] (40%) β -H [~95%L]→ β –L+3[~97%L] (40%)	CT (phenyl amide → pyrazine) CT (phenyl amide → pyrazine)
3.0180	411	0.0326	α –H-1 [~97%L]→ α –L+4[~98%L] (32%) β –H-1 [~97%L]→ β –L+4[~98%L] (32%)	CT (phenyl amide → pyrazine) CT (phenyl amide → pyrazine)