Electronic Supplementary Information (ESI)

Hetero-bimetallic complexes of pyridine-/pyrazine-2-carboxamide ligands: synthesis, structure, redox properties and magnetism

Sharmila Pandey, Narottam Mukhopadhyay, Francesc Lloret and Rabindranath Mukherjee*

Figures:

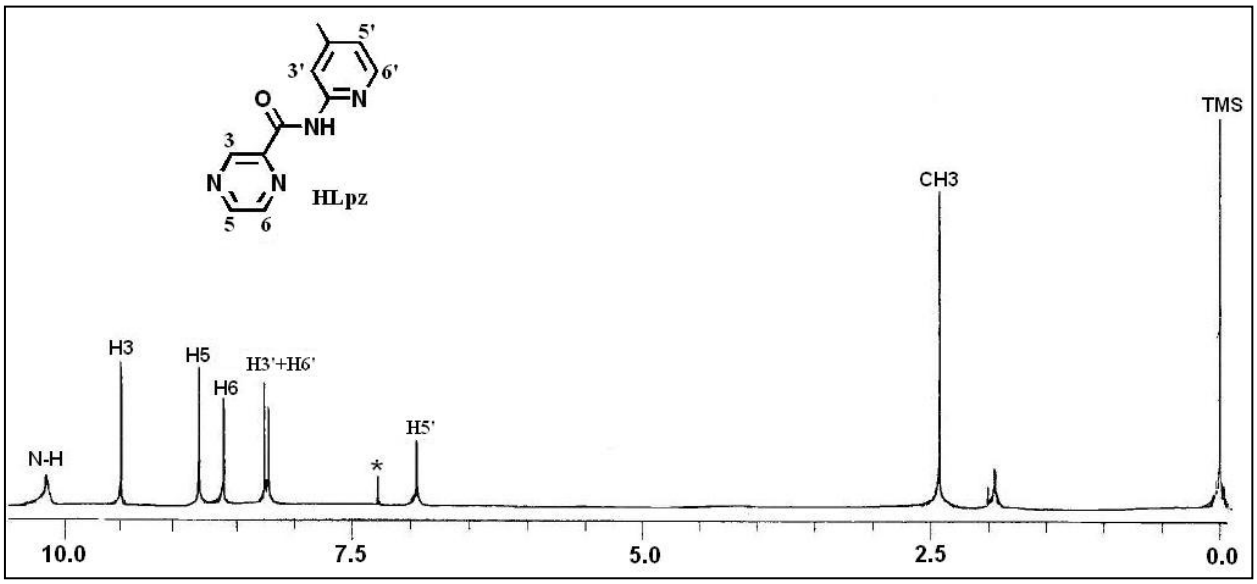


Fig. S1 ^{1}H NMR spectrum (400 MHz) of HLpz in CD_3Cl_3 at 298 K (water peak is marked by *).

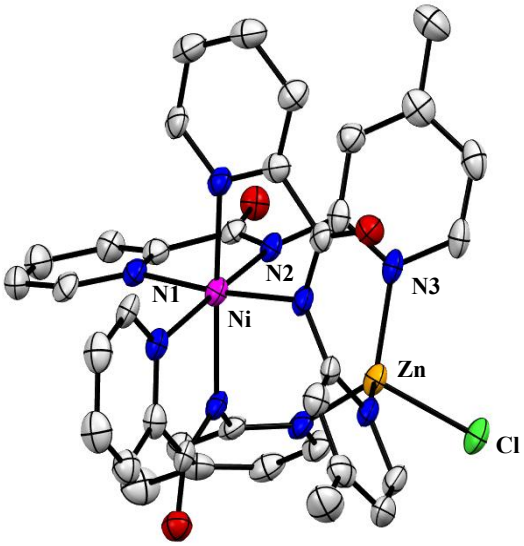


Fig. S2 Perspective view of $[Ni^{II}(Lpy)_3Zn^{II}Cl]\bullet xH_2O$ (**2**). Only donor atoms are labeled. All the hydrogen atoms are omitted for clarity.

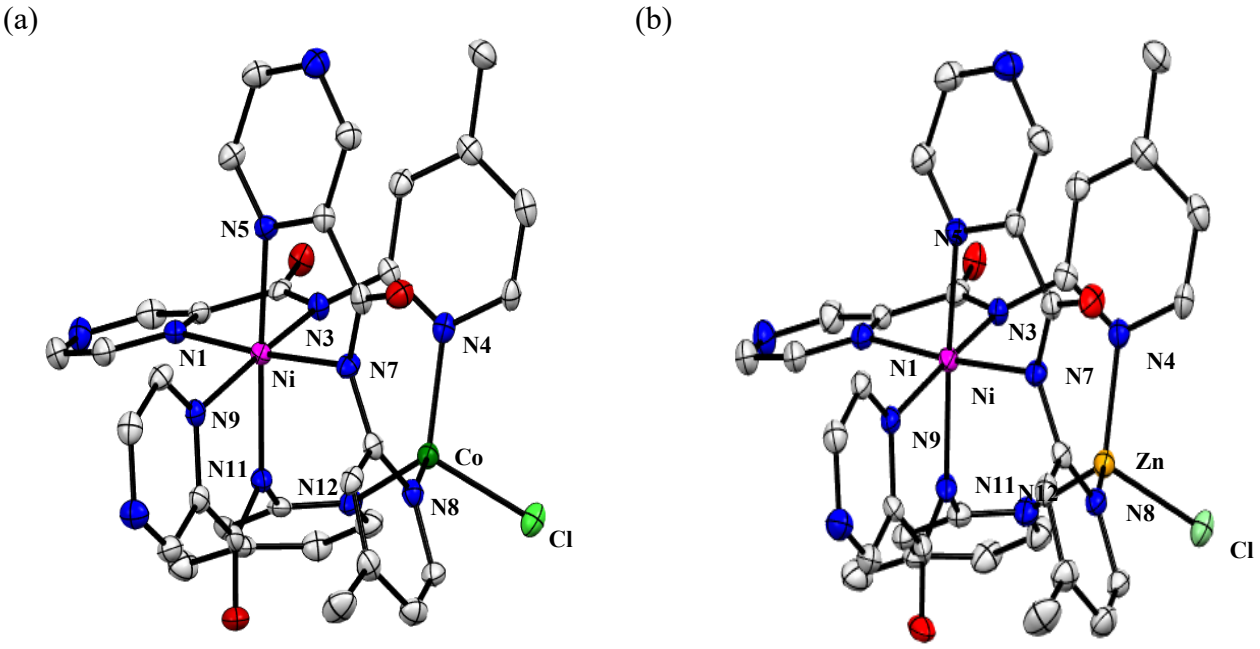


Fig. S3 Perspective views of $[Ni^{II}(Lpz)_3Co^{II}Cl]\bullet H_2O$ (**5**) and $[Ni^{II}(Lpz)_3Zn^{II}Cl]\bullet H_2O$ (**6**). Only donor atoms are labeled. All the hydrogen atoms are omitted for clarity.

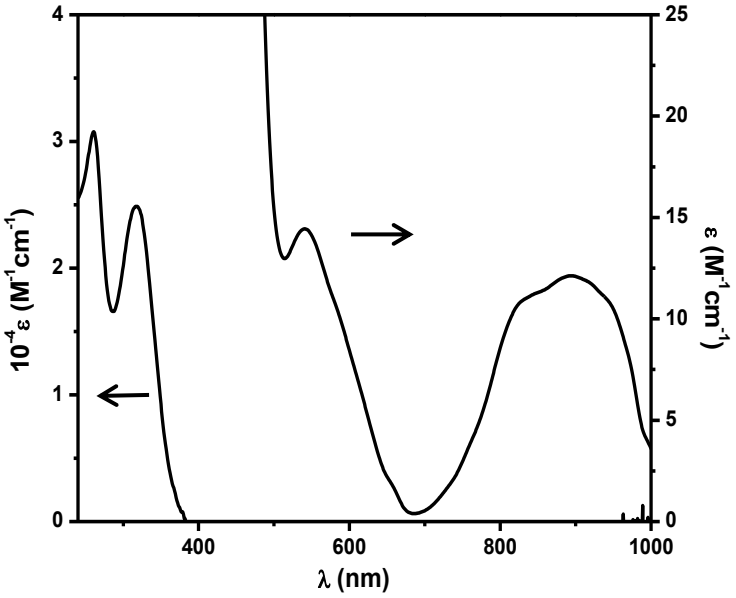
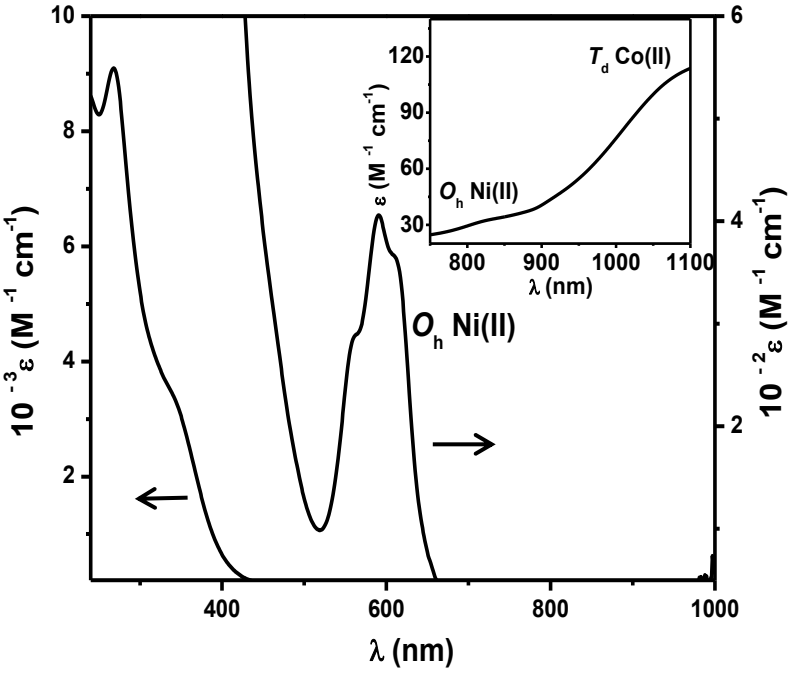


Fig. S4 Absorption spectrum of **2**.

(*a*)



(*b*)

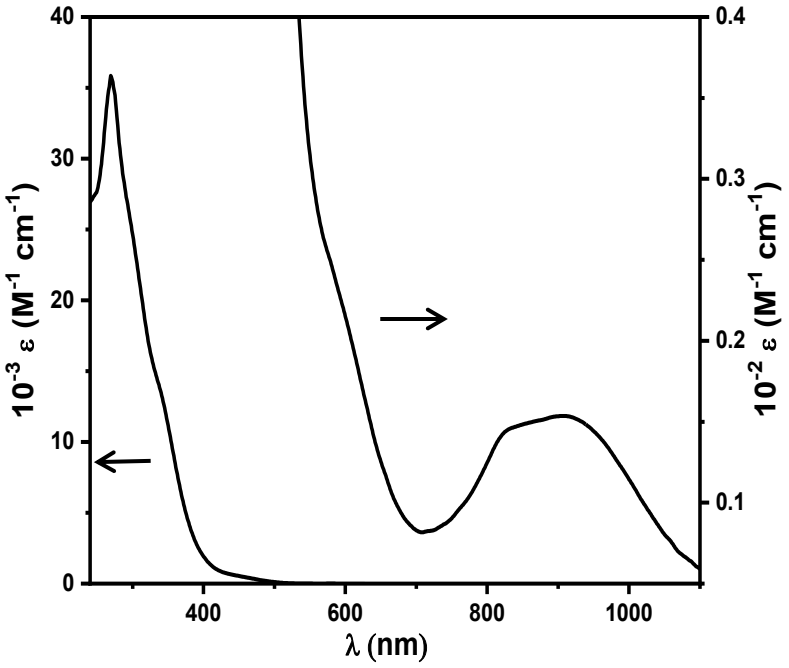


Fig. S5 Absorption spectra of (*a*) **5** and (*b*) **6** in CH_2Cl_2. The enlarged feature (a) between 700–1100 nm is shown as an inset for **5**.

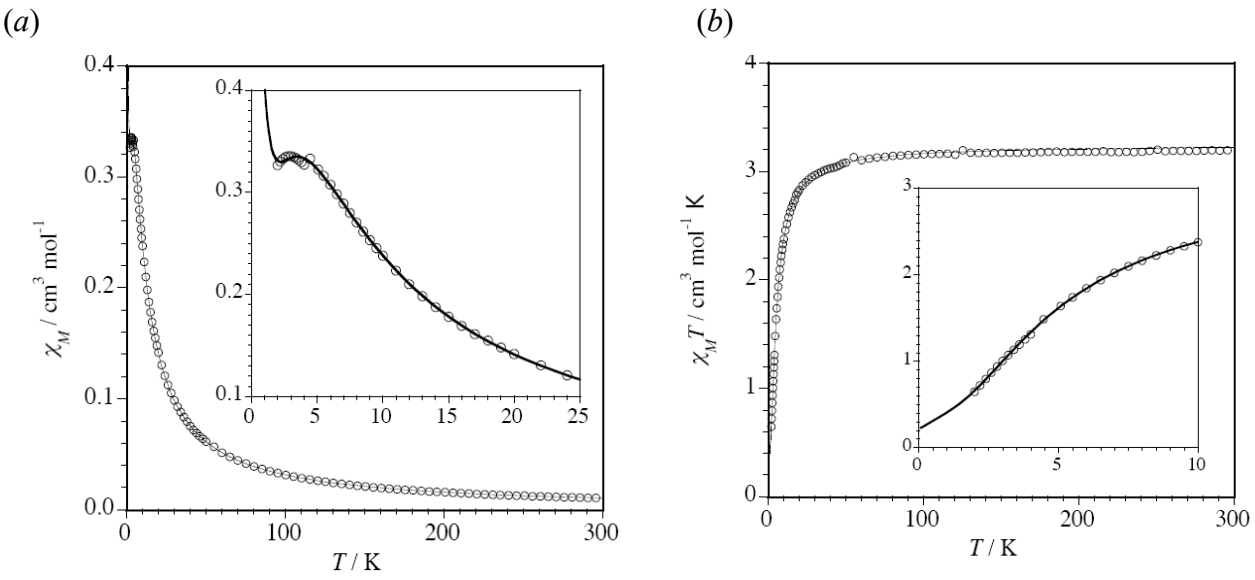


Fig. S6 (*a*) Plot of χ_M *vs. T* for a crystalline sample of **5.** The solid line represents the best theoretical fit, describe in the text. The enlarged feature between 2–10 K is shown as an inset. (*b*) Plot of $\chi_M T$ *vs. T* for a crystalline sample of **5**. The solid line represents the best theoretical fit, describe in the text. The enlarged feature between 2–25 K is shown as an inset.

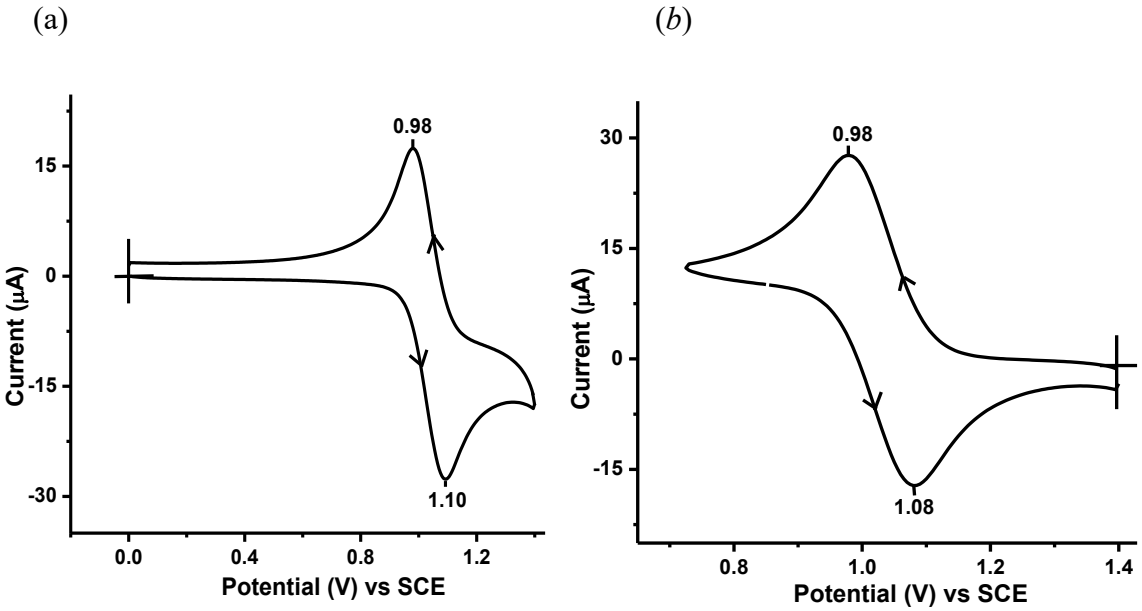
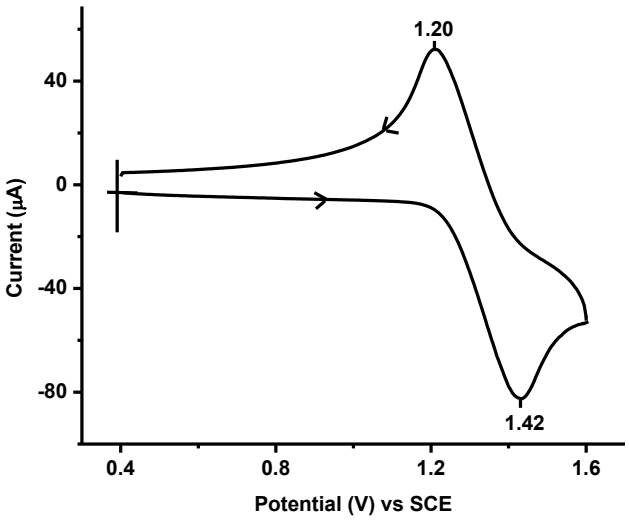


Fig. S7 Cyclic voltammograms (100 mV/s) of (a) **2** and (b) its coulometrically-generated one-electron oxidized species at a platinum electrode in CH_2Cl_2 (0.1 M in TBAP).

(*a*)



(*b*)

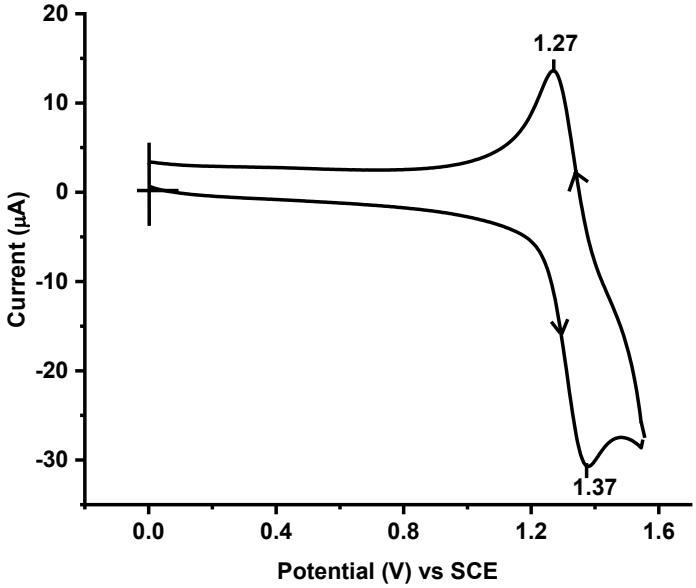


Fig. S8 Cyclic voltammograms (100 mV/s) of solutions of (*a*) **5** and (*b*) **6** at a platinum electrode in CH_2Cl_2 (0.1 M in TBAP).

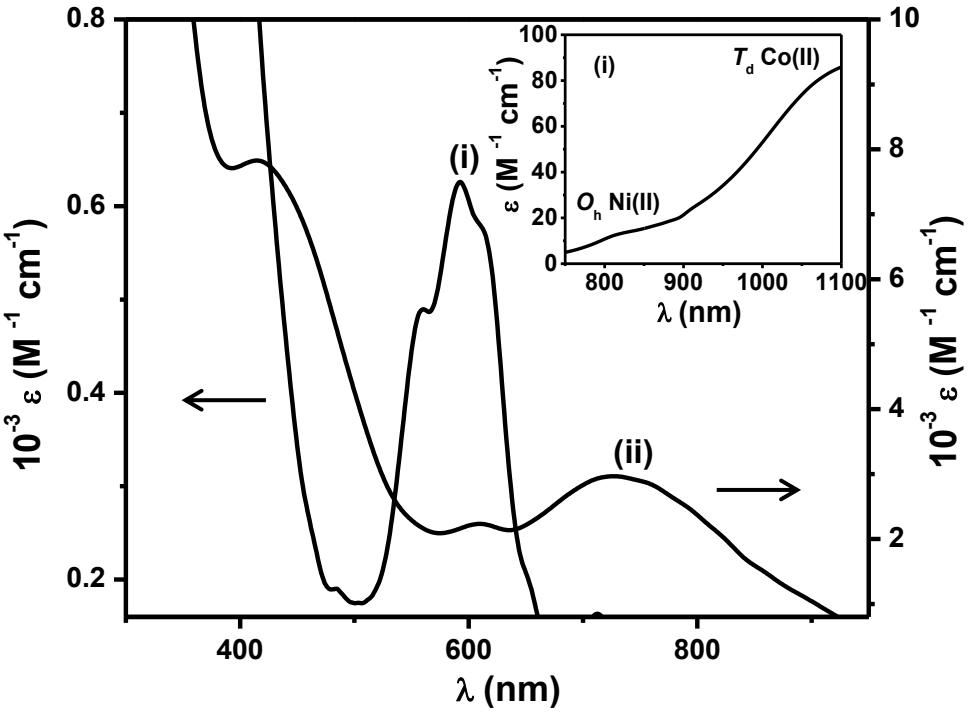


Fig. S9 Absorption spectra (CH_2Cl_2 solution) of (i) **1** and (ii) its coulometrically-generated one-electron oxidized species.

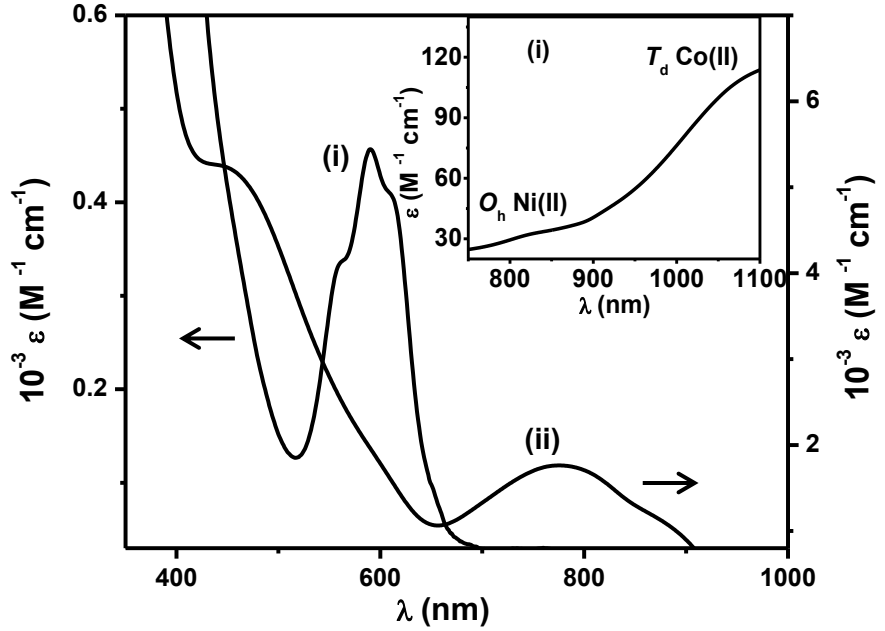


Fig. S10 Absorption spectra (CH_2Cl_2) of (i) **5** and (ii) its coulometrically-generated one-electron oxidized species.

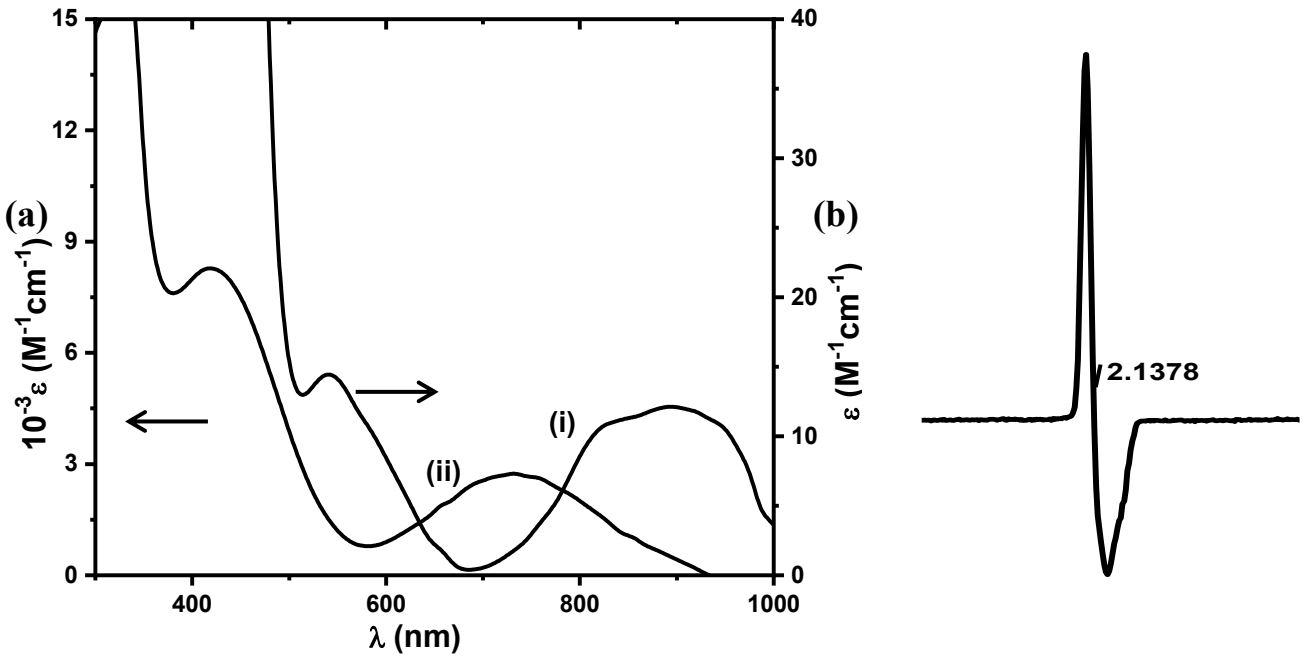


Fig. S11 (a) Absorption spectra (CH_2Cl_2 solution) of (i) **2** and (ii) its coulometrically-generated one-electron oxidized species. (b) X-band EPR spectrum (CH_2Cl_2; 120 K) of coulometrically-generated one-electron oxidized species of **2**.

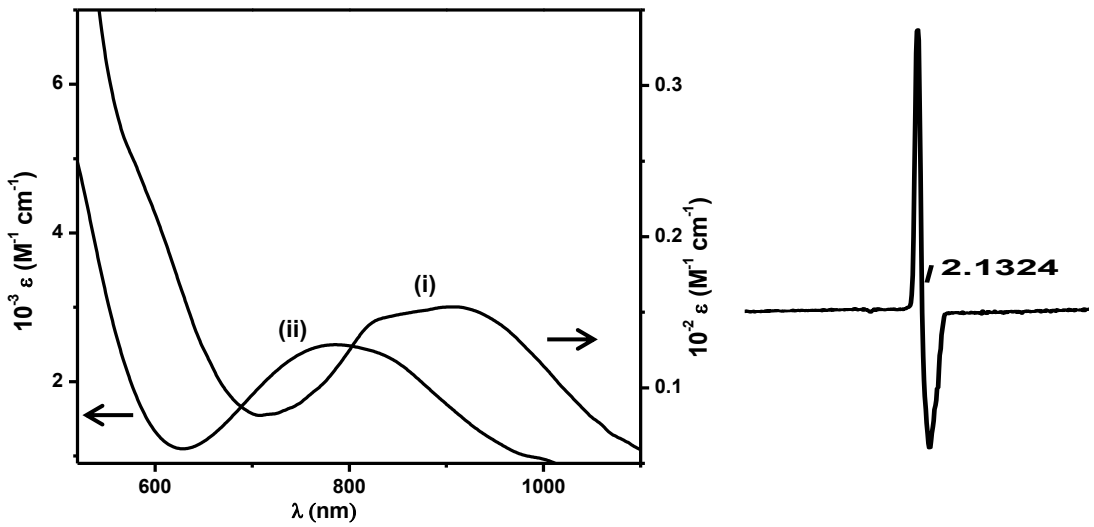


Fig. S12 (a) Absorption spectra (CH_2Cl_2) of (i) **6** and (ii) its coulometrically-generated one-electron oxidized species; (b) X-band EPR spectrum (CH_2Cl_2; 120 K) of coulometrically-generated one- electron oxidized species of **6**.

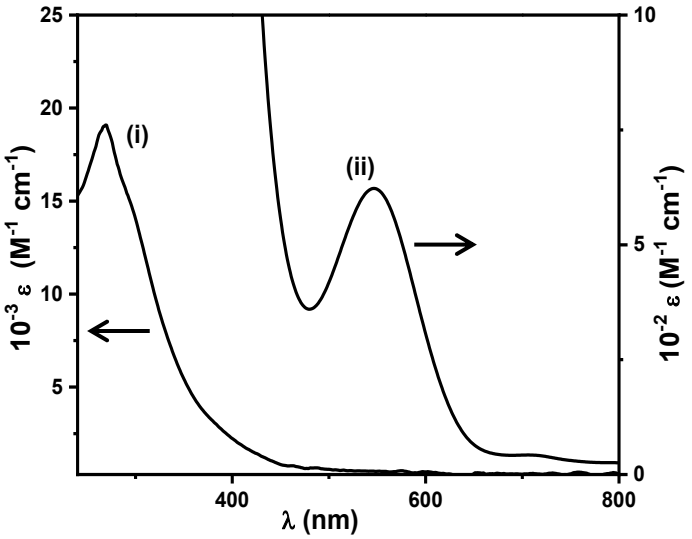


Fig. S13 Absorption spectra (CH_2Cl_2) of (i) **3** and (ii) its coulometrically-generated one-electron oxidized species.

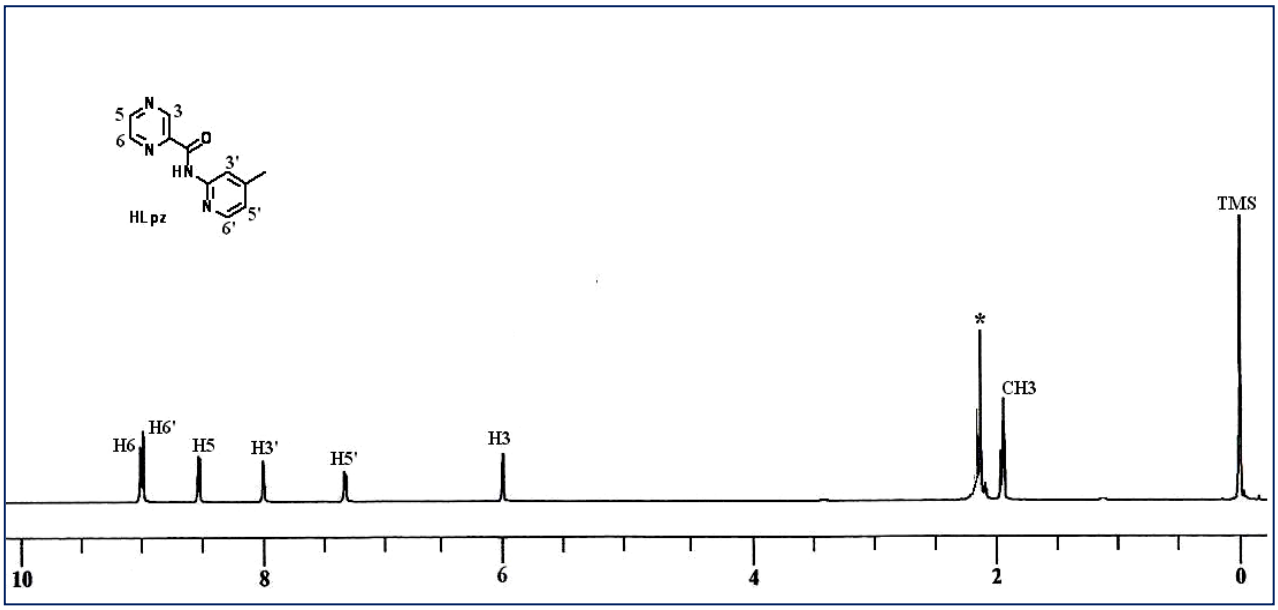


Fig. S14 ^{1}H NMR spectrum (400 MHz) of $[Co^{III}(Lpz)_3Zn^{II}(Cl)](PF_6)$ (**4**) in CD_3CN at 298 K (water peak is marked by *).

Table S1 Data Collection and Structure Refinement Parameters for **1**

	1
chemical formula	$C_{36}H_{42}ClCoN_9NiO_9$
formula weight	897.87
crystal colour, habit	Green, Block
temp / K	100(2)
crystal system	Trigonal
crystal size/(mm × mm × mm)	0.4 × 0.3 × 0.2
space group	*P*-3 (# 2)
a/Å	15.380(5)
b/Å	15.380(5)
c/Å	10.4419(17)
α/°	90
β/°	90
γ/°	120
U/Å^3	2139.1(7)
Z	2
d_{calcd}/g cm^{-3}	1.394
μ/mm^{-1}	0.951
Reflections measured	11101
Unique reflections/R_{int}	2512/0.0700
Reflections used $I > 2\sigma(I)$]	1988
final R indices	R_1 = 0.0435[a] wR_2 = 0.1131[b]
R indices (all data)	R_1 = 0.0576[a] wR_2 = 0.1228[b]
Goodness-of-fit on F^2	1.034

[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 **3**, **4**, **5**, and **6**

	3	**4**	**5**	**6**
chemical formula	$C_{33}H_{29}ClCoN_{12}O_4Zn$	$C_{39}H_{42}ClCoF_6N_{13}O_5PZn$	$C_{33}H_{29}ClCoN_{12}NiO_4$	$C_{33}H_{29}ClN_{12}NiO_4Zn$
formula weight	817.43	1077.57	810.77	817.21
crystal colour, habit	red, block	green, block	green, block	yellow, block
temp/K	100(2)	100(2)	100(2)	100(2)
crystal system	Orthorhombic	Triclinic	Orthorhombic	orthorhombic
crystal size/(mm × mm × mm)	0.2 × 0.1 × 0.1	0.3 × 0.25 × 0.2	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.2
Space group	*P*bca	*P*-1	*P*bca	*P*bca
a/Å	18.578(5)	12.484(4)	18.257(5)	18.385(5)
b/Å	16.484(5)	13.730(4)	16.417(5)	16.393(5)
c/Å	22.217(5)	14.952(4)	22.303(5)	22.388(5)
α/deg	90	85.618(5)	90	90
β/deg	90	68.888(5)	90	90
γ/deg	90	86.867(5)	90	90
V/Å^3	6804(3)	2383.0(12)	6685(3)	6747(3)
Z	8	2	8	8
d_{calcd}/g cm^{-3}	1.596	1.502	1.611	1.609
μ/mm^{-1}	1.330	1.020	1.199	1.407
Reflections measured	33577	12195	32938	33345
Unique reflections/R_{int}	6014/0.0905	8219/0.0410	5904/0.0912	5960/0.0580
Reflections used $I > 2\sigma(I)$]	4164	5793	4256	4638
final R indices	$R_1 = 0.0482^a$ $wR_2 = 0.1064^b$	$R_1 = 0.0624^a$ $wR_2 = 0.1618^b$	$R_1 = 0.0475^a$ $wR_2 = 0.1049^b$	$R_1 = 0.0397^a$ $wR_2 = 0.0923^b$
R indices (all data)	$R_1 = 0.0810^a$ $wR_2 = 0.1213^b$	$R_1 = 0.0847^a$ $wR_2 = 0.1803^b$	$R_1 = 0.0741^a$ $wR_2 = 0.1208^b$	$R_1 = 0.0564^a$ $wR_2 = 0.1023^b$
Goodness-of-fit on on F^2	1.019	0.997	1.037	1.041

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

Table S3 Selected Bond Lengths (Å) and Angles (°) in $[Ni^{II}(Lpy)_3Co^{II}Cl]\bullet 6H_2O$ (**1**)[a]

1	
Ni–N(1)	2.089(2)
Ni–N(2)	2.078(2)
Co–N(3)	2.019(2)
Co–Cl(1)	2.263(14)
N1–Ni–N1′	97.38(8)
N(1) –Ni–N2	78.61(9)
N1–Ni–N2′	87.57(8)
N1–Ni-N2′′	174.04(8)
N2–Ni–N2′	96.71(8)
N3–Co–N3′	114.43(5)
N3–Co–Cl	103.89(7)

[a] Symmetry operators for the generated atoms: ′ –x+y+1, –x+1, z.

Table S4 Selected Bond Lengths (Å) and Angles (°) in $[Co^{II}(Lpz)_3Zn^{II}Cl]\bullet H_2O$ (**3**) and $[Co^{III}(Lpz)_3Zn^{II}Cl](PF_6)\bullet(C_2H_5)_2O\bullet CH_3CN\bullet H_2O$ (**4**)

	3	**4**		**3**	**4**
Co–N1	2.155(3)	1.949(4)	N1–Co–N3	77.75(12)	82.49(16)
Co–N3	2.110(3)	1.936(4)	N1–Co–N5	98.66(12)	96.53(17)
Co–N5	2.137(3)	1.958(4)	N1–Co–N7	87.04(12)	176.54(17)
Co–N7	2.089(3)	1.953(4)	N1–Co–N9	100.69(12)	96.92(16)
Co –N9	2.150(3)	1.948(4)	N1–Co–N11	174.08(13)	86.41(16)
Co–N11	2.084(3)	1.934(4)	N3–Co–N5	175.76(12)	86.42(16)
Zn–N4	2.028(3)	2.015(4)	N3–Co–N7	99.66(12)	94.05(16)
Zn–N8	2.015(3)	2.018(4)	N(3)-Co–N9	86.26(13)	176.89(16)
Zn–N12	2.026(3)	2.009(4)	N3–Co–N11	96.63(13)	94.19(16)
Zn–Cl	2.2656(12)	2.2334(14)	N5–Co–N7	77.77(13)	83.02(16)
			N5–Co–N9	96.69(12)	96.68(16)
			N5–Co–N11	87.02(12)	177.06(17)
			N7–Co–N9	171.17(12)	86.54(15)
			N7–Co–N11	95.82(13)	94.06(16)
			N9–Co–N11	76.88(13)	82.72(16)
			N4–Zn–N8	112.56(13)	110.76(15)
			N4–Zn–N12	112.76(14)	112.71(15)
			N8–Zn–N12	114.58(13)	107.93(15)
			N4–Zn–Cl	107.06(10)	105.92(11)
			N8–Zn–Cl	105.86(9)	108.63(11)
			N12–Zn–Cl	103.00(10)	110.84(11)

Table S5 Selected Bond Lengths (Å) and Angles (°) in $[Ni^{II}(Lpz)_3Co^{II}Cl]\bullet H_2O$ (**5**) and $[Ni^{II}(Lpz)_3Zn^{II}Cl]\bullet H_2O$ (**6**)

5		**6**	
Ni–N1	2.111(3)	Ni–N1	2.115(3)
Ni–N3	2.080(3)	Ni–N3	2.079(3)
Ni–N5	2.093(3)	Ni–N5	2.092(3)
Ni–N7	2.064(3)	Ni–N7	2.064(3)
Ni–N9	2.102(3)	Ni–N9	2.102(3)
Ni–N11	2.065(3)	Ni–N11	2.064(3)
Co–N4	2.017(3)	Zn–N4	2.025(3)
Co–N8	2.011(3)	Zn–N8	2.016(3)
Co–N12	2.025(3)	Zn–N12	2.027(3)
Co–Cl	2.2670(12)	Zn–Cl	2.2677(10)
N1–Ni–N3	78.93(12)	N1–Ni–N3	78.98(10)
N1–Ni–N5	97.73(12)	N1–Ni–N5	97.56(10)
N1–Ni–N7	87.32(12)	N1–Ni–N7	87.41(10)
N1–Ni–N9	99.48(12)	N1–Ni–N9	99.40(10)
N1–Ni–N11	174.73(13)	N1–Ni–N11	174.64(10)
N3–Ni–N5	176.01(12)	N3–Ni–N5	175.86(10)
N3–Ni–N7	98.70(13)	N3–Ni–N7	98.56(10)
N3–Ni–N9	86.76(12)	N3–Ni–N9	86.82(10)
N3–Ni–N11	96.07(12)	N3–Ni–N11	95.06(10)
N5–Ni–N7	78.98(12)	N5–Ni–N7	79.09(10)
N5–Ni–N9	95.98(12)	N5–Ni–N9	95.87(10)
N5–Ni–N11	87.33(13)	N5–Ni–N11	87.57(10)
N7–Ni–N9	172.09(12)	N7–Ni–N9	172.07(10)
N7–Ni–N11	95.14(12)	N7–Ni–N11	95.13(10)
N9–Ni–N11	78.42(12)	N9–Ni–N11	78.43(10)
N4–Co–N8	112.38(13)	N4–Zn–N8	112.22(10)
N4–Co–N12	113.23(13)	N4–Zn–N12	113.11(11)
N8–Co–N12	113.71(13)	N8–Zn–N12	113.95(11)
N4–Co–Cl	107.09(9)	N4–Zn–Cl	107.04(8)
N8–Co–Cl	106.62(9)	N8–Zn–Cl	106.47(8)
N12–Co–Cl	102.89(9)	N12–Zn–Cl	103.16(8)