*Supporting Information:*

# Electrochemical, Spectroscopic, Magnetic and Structural Studies of Complexes Bearing Ferrocenyl Ligands of *N*-(3-Hydroxypicolinoyl)picolinamide

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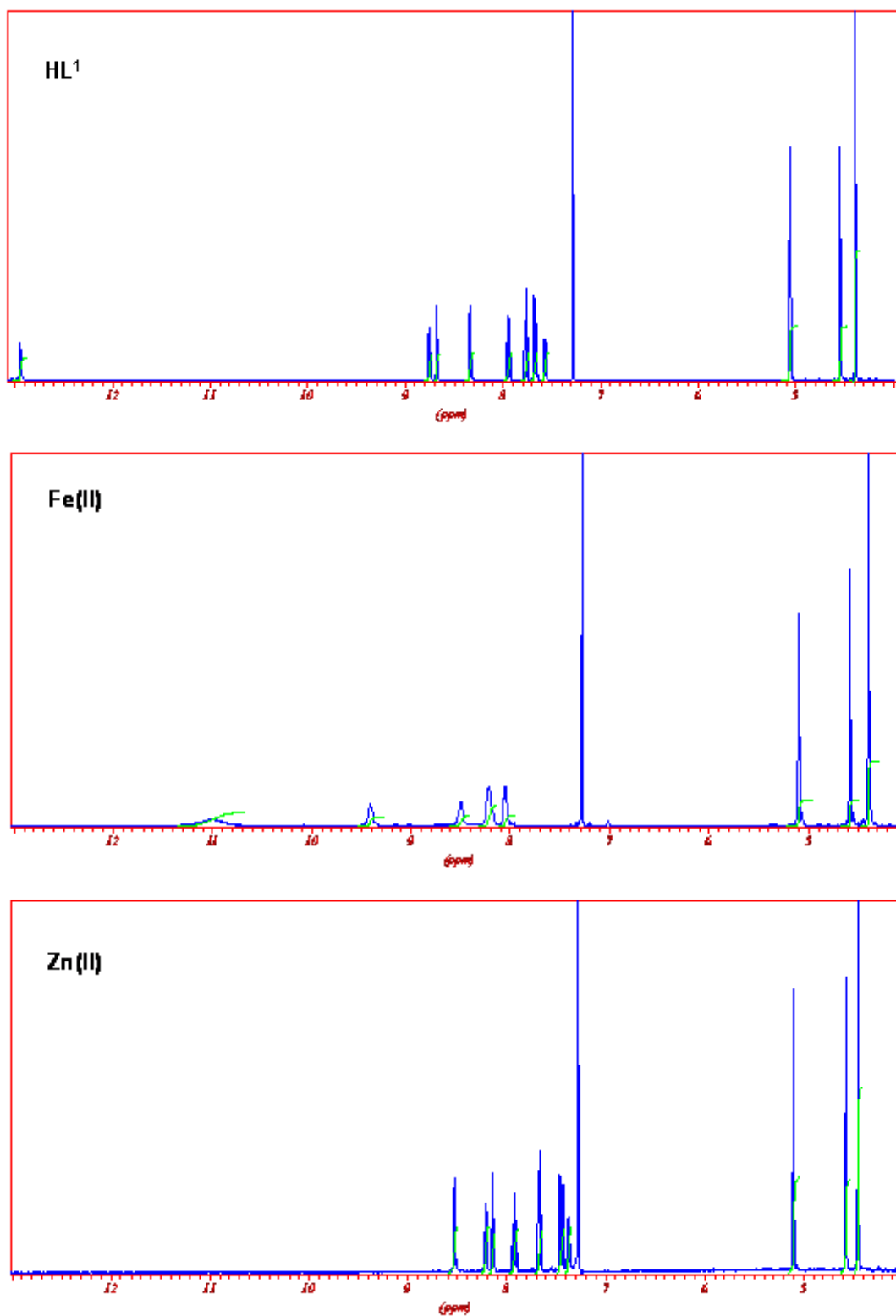
**Figure S1.** Comparison between ^{1}H-NMR spectra of ligand **HL$^1$** and its complexes of Fe(II)

and Zn(II) (stoichiometry 2:1 Ligand:Metal) in CDCl$_3$.

**Figure S2.** Comparison between ${}^1$H-NMR spectra of ligand **HL${}^1$** and its complex of Fe(II) between $\delta = 7$ and 13 ppm (stoichiometry 2:1 Ligand:Metal) in CDCl${}_3$.
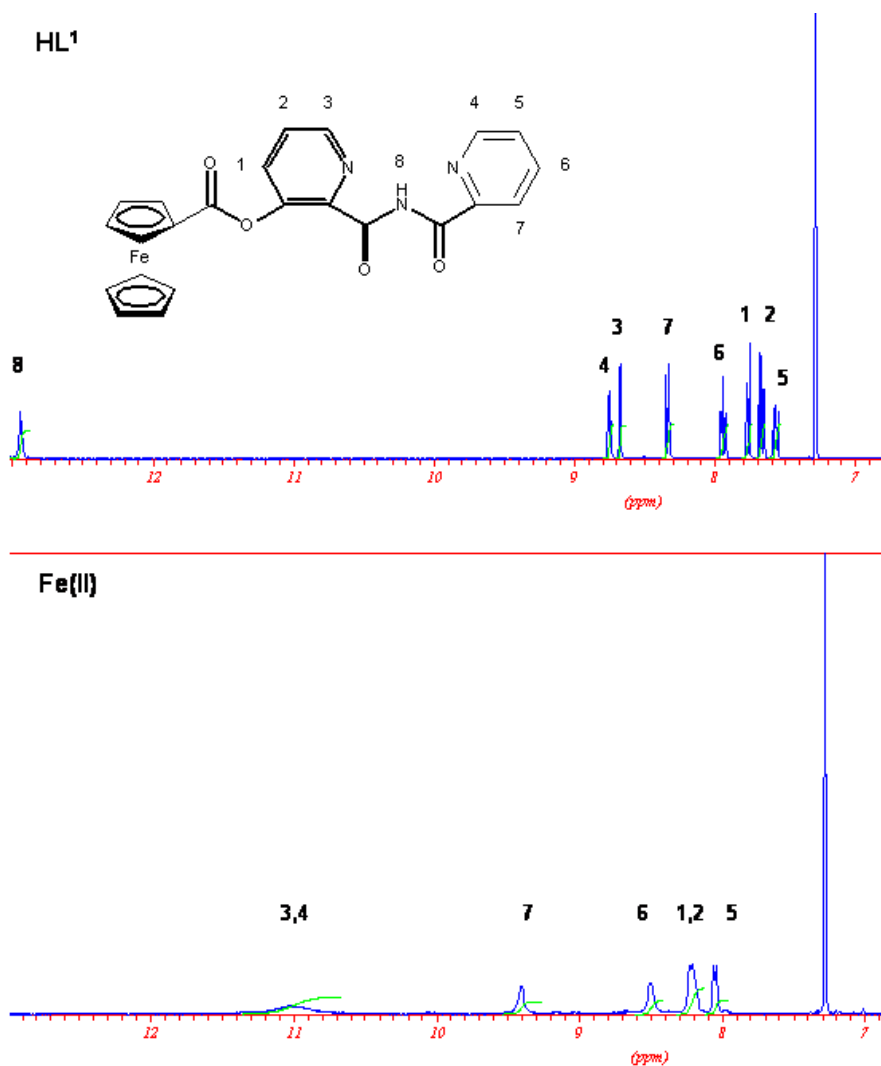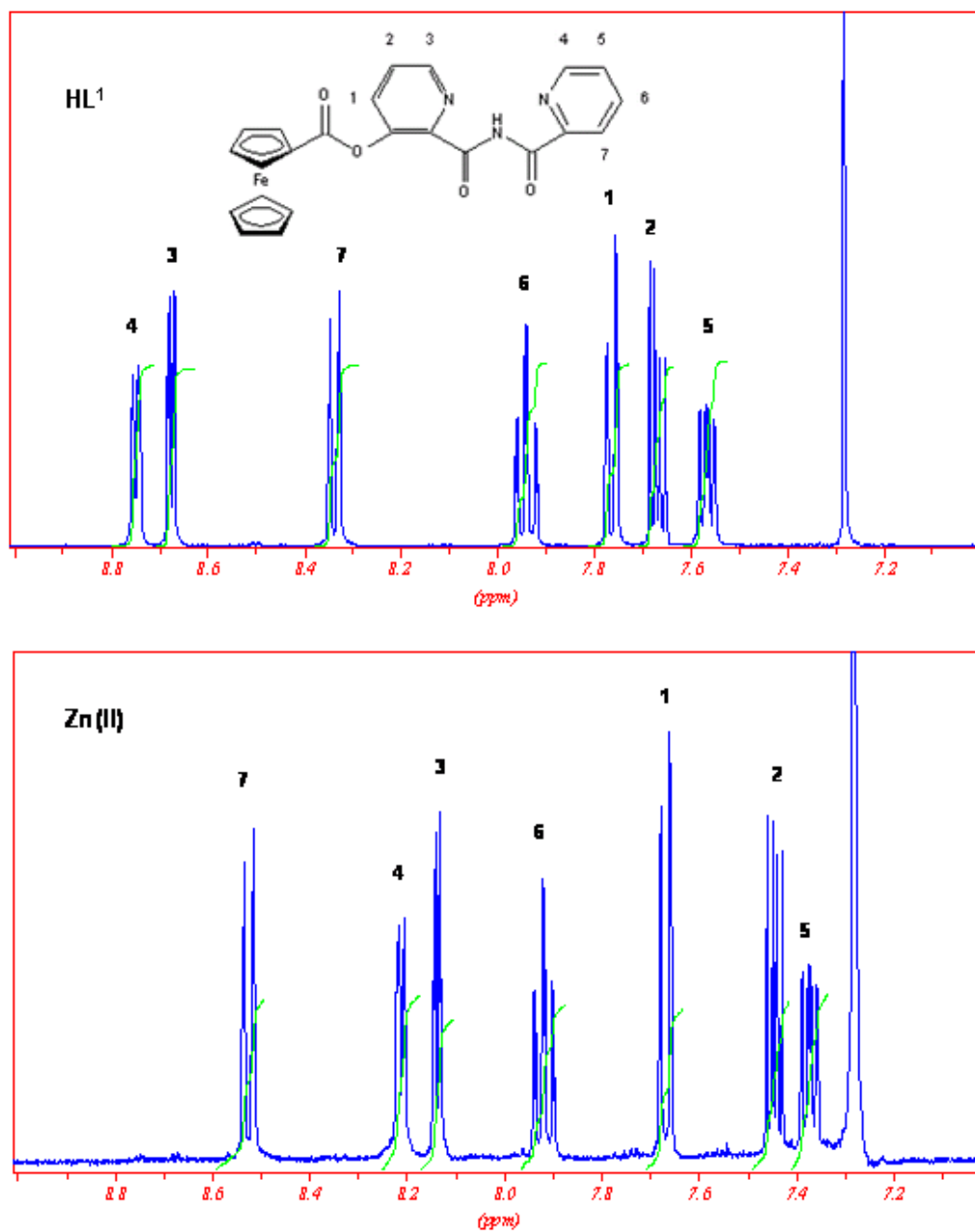
3

**Figure S3.** Comparison between $^1$H-NMR spectra of ligand **HL$^1$** and its complex of Zn(II)

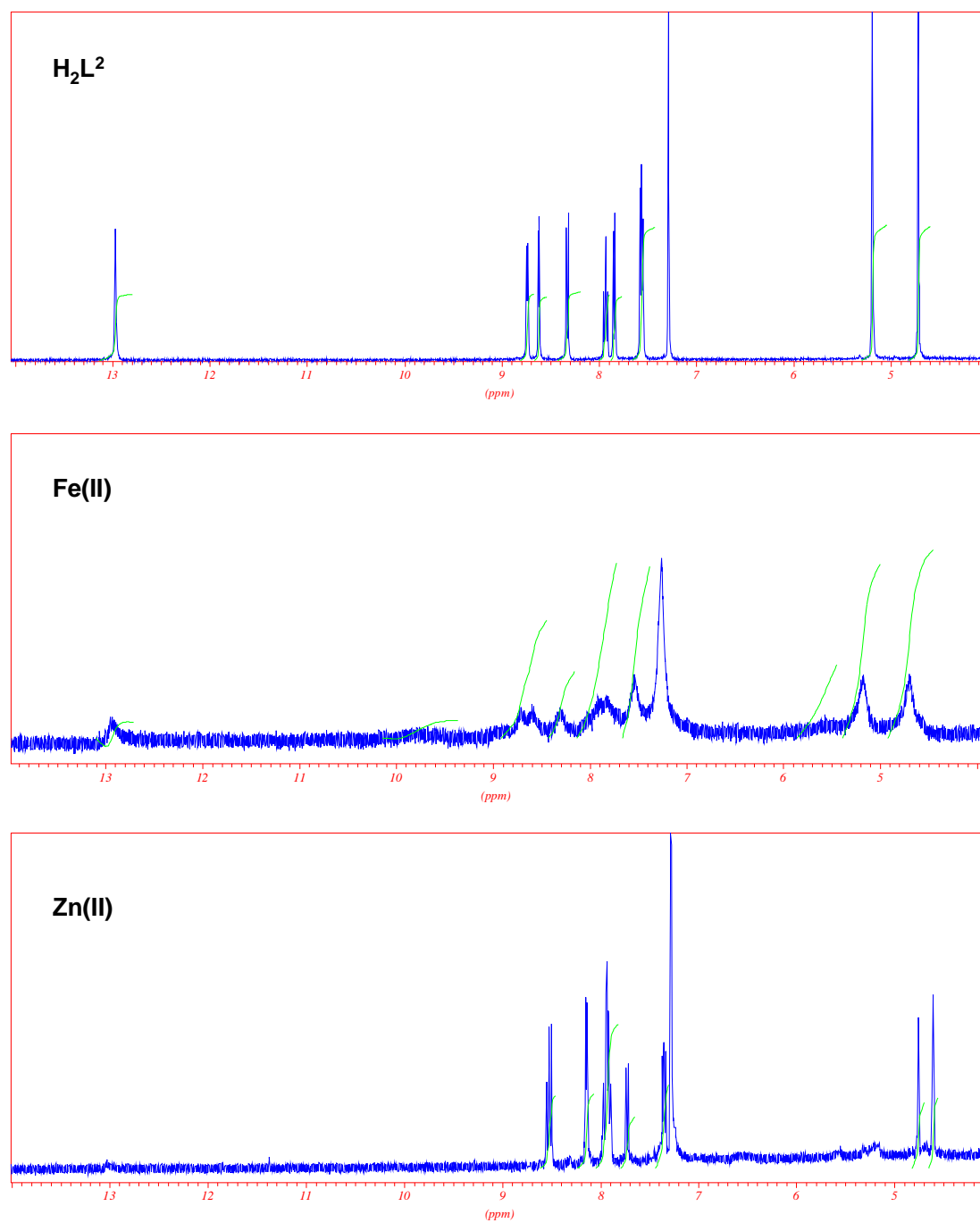between $\delta$ = 7 and 9 ppm (stoichiometry 2:1 Ligand:Metal) in CDCl$_3$.

4

**Figure S4.** Comparison between $^1$H-NMR spectra of ligand **H$_2$L$^2$** and its complexes of Fe(II) and Zn(II) (stoichiometry 1:1 Ligand:Metal) in CDCl$_3$.

**Table S1.** Hydrogen-bond geometry (Å, °) for **HL$^1$**

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H2$N\cdots$N1 | 0.89 (4) | 2.15 (4) | 2.611 (4) | 112 (3) |
| N2—H2$N\cdots$N3 | 0.89 (4) | 2.18 (3) | 2.647 (4) | 112 (3) |
| C9—H9$\cdots$O2$^i$ | 0.95 | 2.58 | 3.448 (4) | 152 |
| C14—H14$\cdots$O3$^{ii}$ | 0.95 | 2.53 | 3.139 (4) | 122 |
| C15—H15$\cdots$O3$^{ii}$ | 0.95 | 2.57 | 3.169 (4) | 121 |
| C15—H15$\cdots$O4$^{ii}$ | 0.95 | 2.33 | 3.247 (4) | 161 |

Symmetry codes: (i) $-x+2$, $-y$, $-z$; (ii) $x$, $y+1$, $z$.

**Table S2.** Hydrogen-bond geometry (Å, °) for **H$_2$L$^2\cdot$2(CHCl$_3$)**,

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H2$N\cdots$N1 | 0.85 (4) | 2.17 (5) | 2.611 (4) | 112 (3) |
| N2—H2$N\cdots$N3 | 0.85 (4) | 2.18 (4) | 2.623 (4) | 113 (4) |
| N5—H5$N\cdots$N4 | 0.83 (4) | 2.17 (5) | 2.599 (4) | 112 (3) |
| N5—H5$N\cdots$N6 | 0.83 (4) | 2.21 (4) | 2.627 (4) | 111 (4) |
| C3—H3$A\cdots$Cl5$^i$ | 0.95 | 2.83 | 3.579 (4) | 137 |
| C8—H8$A\cdots$O8$^{ii}$ | 0.95 | 2.37 | 3.225 (4) | 149 |
| C17—H17$A\cdots$Cl5$^{iii}$ | 0.95 | 2.79 | 3.542 (4) | 136 |
| C18—H18$A\cdots$Cl1$^{ii}$ | 0.95 | 2.82 | 3.749 (4) | 166 |
| C26—H26$A\cdots$O4$^i$ | 0.95 | 2.58 | 3.383 (4) | 143 |
| C35—H35$A\cdots$Cl3$^{iv}$ | 0.95 | 2.82 | 3.701 (4) | 154 |
| C36—H36$A\cdots$Cl6$^{iv}$ | 0.95 | 2.76 | 3.706 (4) | 176 |
| C37—H37$A\cdots$O7$^{ii}$ | 1.00 | 2.57 | 3.314 (5) | 131 |
| C37—H37$A\cdots$O8$^{ii}$ | 1.00 | 2.37 | 3.186 (5) | 138 |
| C38—H38$A\cdots$O3$^v$ | 1.00 | 2.35 | 3.162 (4) | 138 |
| C38—H38$A\cdots$O4$^v$ | 1.00 | 2.40 | 3.150 (5) | 131 |

Symmetry codes: (i) $-x$, $y+1/2$, $-z+1/2$; (ii) $-x+1$, $y-1/2$, $-z+1/2$; (iii) $-x$, $y-1/2$, $-z+1/2$; (iv) $x$, $y+1$, $z$; (v) $x$, $-y+1/2$, $z-1/2$.

**Table S3.** Changes of $\Delta\lambda_{max}$ and $\varepsilon$ upon complexation of ligand **HL$^1$** with metallic cations.

| | $HL^1$ | | $H_2L^2$ |
|---|---|---|---|
| $\lambda$max / nm | 463 | $\lambda_{max}$ / nm | 466 |
| $\varepsilon$ / $dm^3 \cdot mol^{-1}$ | 369 | $\varepsilon$ / $dm^3 \cdot mol^{-1}$ | 420 |
| Shift in $\lambda_{max}$ of $Fe(L^1)_2$ / nm | +25 | Shift of $\lambda_{max}$ of $FeL^2$ / nm | +30 |
| $\varepsilon$ of $Fe(L^1)_2$ / $dm^3 \cdot mol^{-1}$ | 9322 | $\varepsilon$ of $FeL^2$ / $dm^3 \cdot mol^{-1}$ | 3512 |
| Shift in $\lambda_{max}$ of $Ni(L^1)_2$ / nm | -17 | Shift of $\lambda_{max}$ of $NiL^2$ / nm | +18 |
| $\varepsilon$ of $Ni(L^1)_2$ / $dm^3 \cdot mol^{-1}$ | 1437 | $\varepsilon$ of $NiL^2$ / $dm^3 \cdot mol^{-1}$ | 1120 |
| Shift in $\lambda_{max}$ of $Cu(L^1)_2$ / nm | +11 | Shift of $\lambda_{max}$ of $CuL^2$ / nm | +16 |
| $\varepsilon$ of $Cu(L^1)_2$ / $dm^3 \cdot mol^{-1}$ | 2607 | $\varepsilon$ of $CuL^2$ / $dm^3 \cdot mol^{-1}$ | 1239 |
| Shift in $\lambda_{max}$ of $Zn(L^1)_2$ / nm | +18 | Shift of $\lambda_{max}$ of $ZnL^2$ / nm | -15 |
| $\varepsilon$ of $Zn(L^1)_2$ / $dm^3 \cdot mol^{-1}$ | 1448 | $\varepsilon$ of $ZnL^2$ / $dm^3 \cdot mol^{-1}$ | 1400 |

**Table S4.** Change in formal potential,[a] $\Delta E^{\circ'} = E^{\circ'}_{com} - E^{\circ'}_{ligand}$, for the ferrocene-centered redox couple of selected ligand between that of the complexes and that of $HL^1$ or $H_2L^2$ in a mixture of $CH_2Cl_2$:acetonitrile 1:1 v/v at ambient temperature.[a]

| Complexes | $\Delta E^{\circ\prime}$ / mV vs $Fc^{0/+}_{HL1}$ | Complexes | $\Delta E^{\circ\prime}$ / mV vs $Fc^{0/+}_{H2L2}$ |
|---|---|---|---|
| $Fe(L^1)_2$ | +29.0 | $NiL^2$ | +22.0* |
| $Ni(L^1)_2$ | -12.5 | $FeL^2$ | +8.0* |
| $Cu(L^1)_2$ | +13.0 | $CuL^2$ | +24.0* |
| $Zn(L^1)_2$ | -6.5 | $ZnL^2$ | +42.0* |

* obtained by DPV because of the very low complex solubility

[a] Formal potentials, $E^{\circ\prime}$, at ambient temperature, referenced to $E^{\circ\prime}(Fc^{0/+})$ as internal reference, were determined as the midpoint between the anodic and cathodic peak potentials ($E_{pa}$ + $E_{pc}$)/2; the margin of error was ± 5 mV.
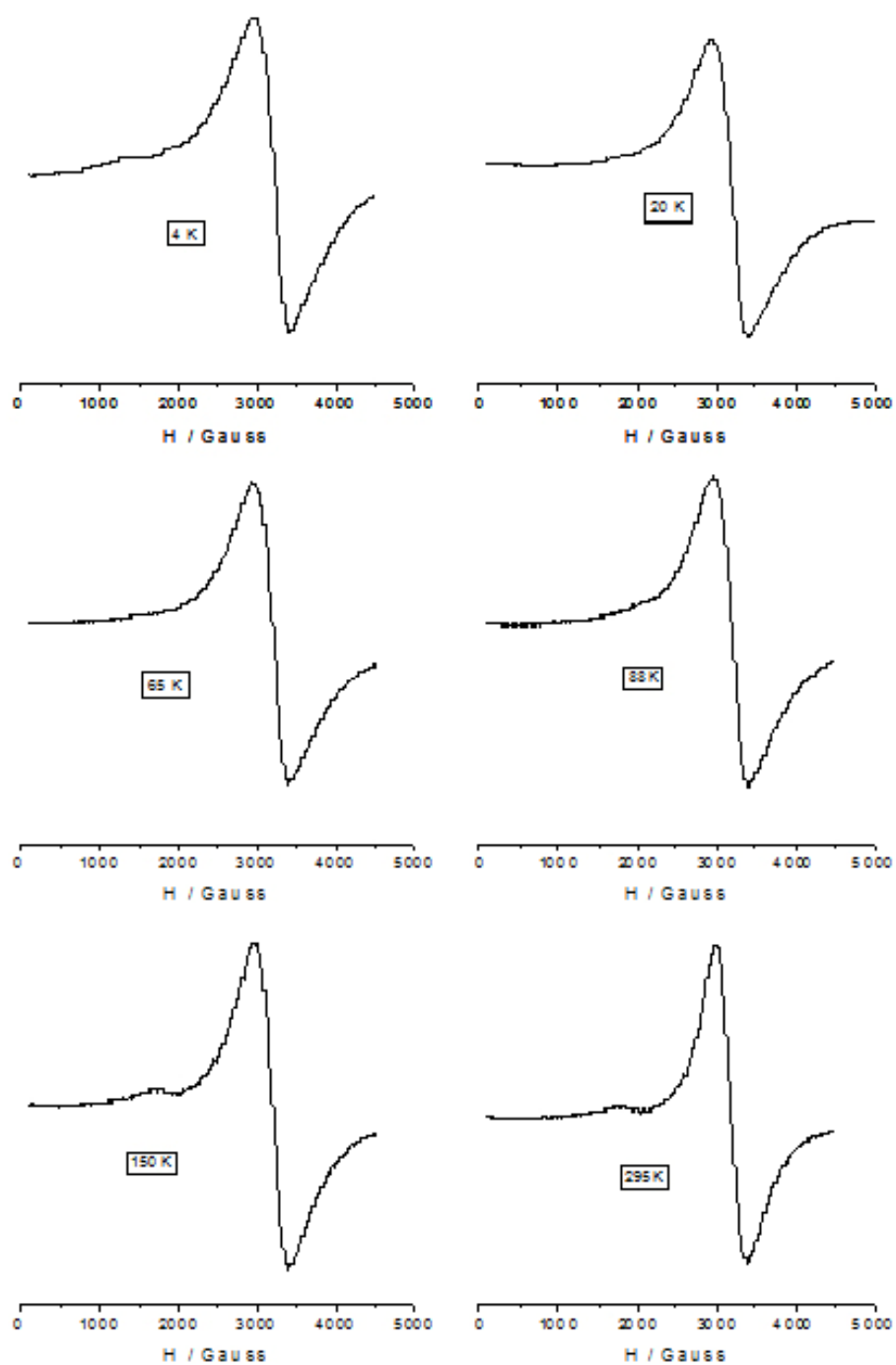
**Figure S5.** EPR spectra of complex $[Cu_2I_2L^2]_n$ at different temperatures.