Supporting Information

A prodigiosin analog designed for metal coordination: Stable zinc and copper pyrrolyldipyrrins

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NMR Analysis

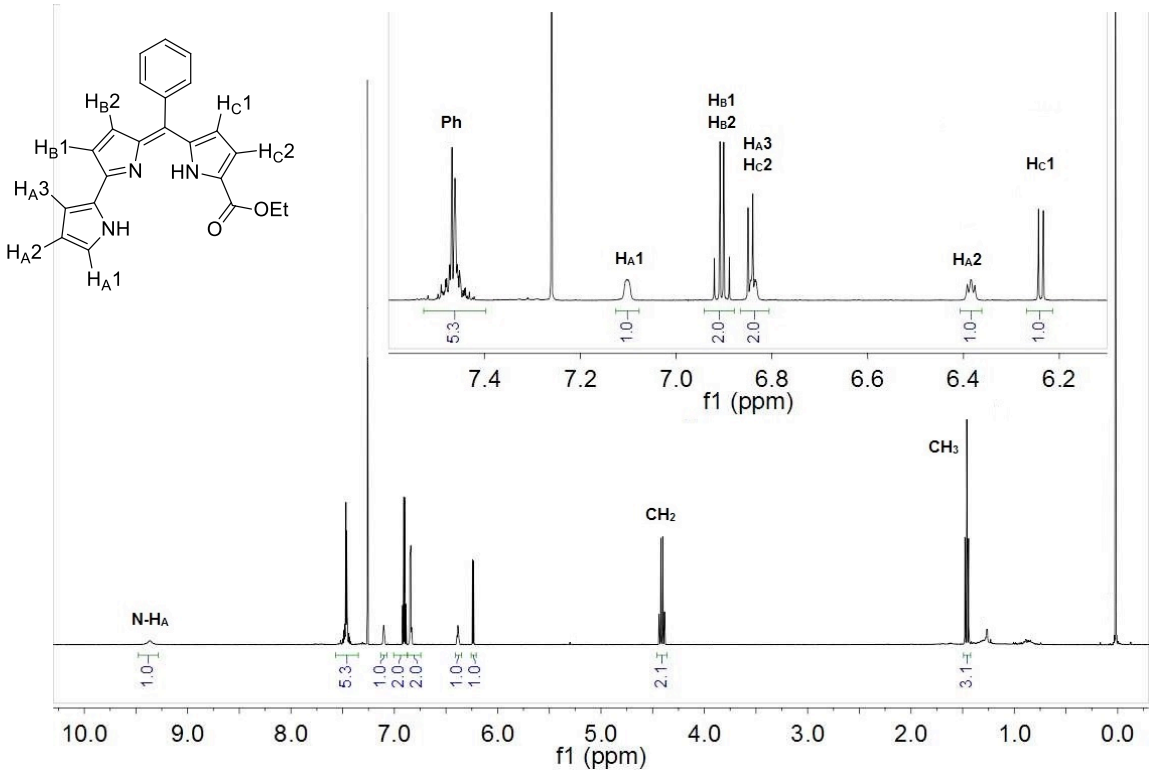


Figure S1. ^{1}H NMR spectrum of free base ligand H_2PD1 (400 MHz, $CDCl_3$, 27 ºC). Resonances were assigned based on COSY and NOESY correlation data (see below).

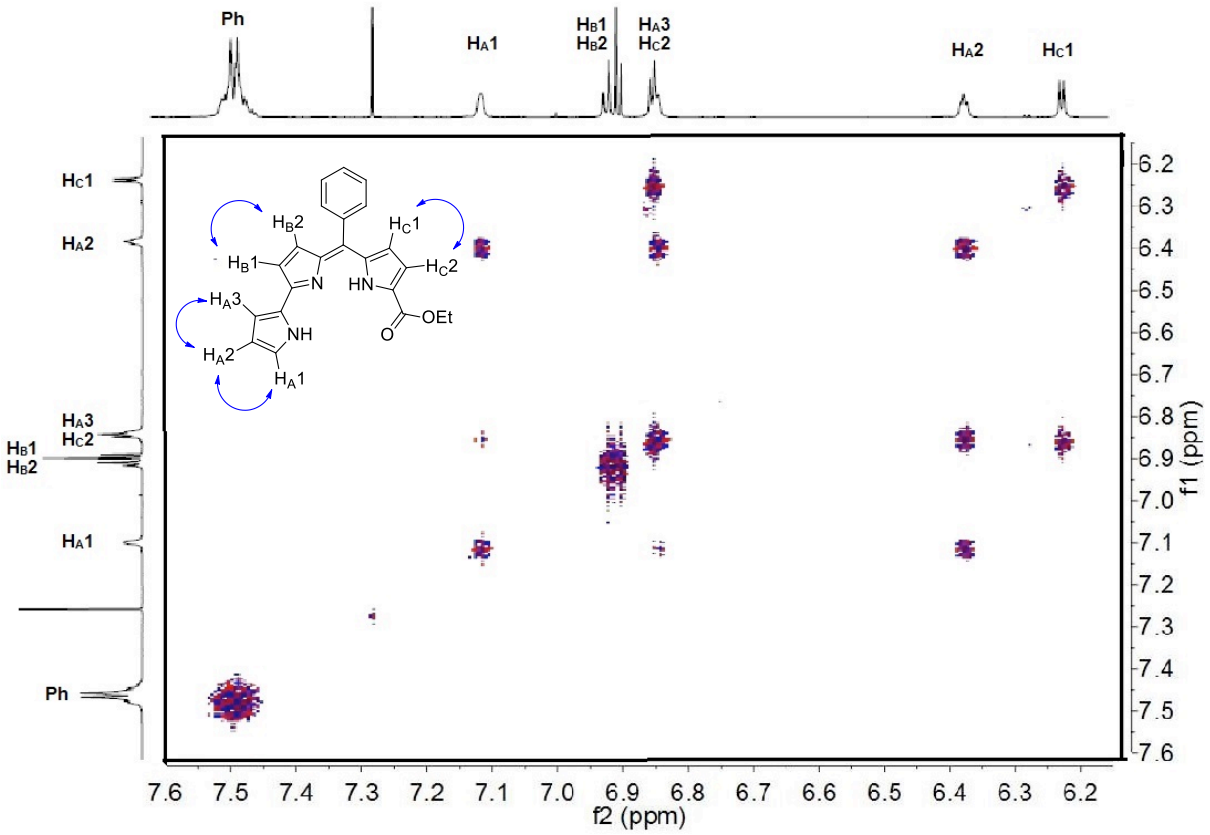


Figure S2. 2D COSY NMR plot of H_2PD1 (600 MHz, $CDCl_3$, 27 ºC, 40 mM) showing the assignment of observed cross-peaks.

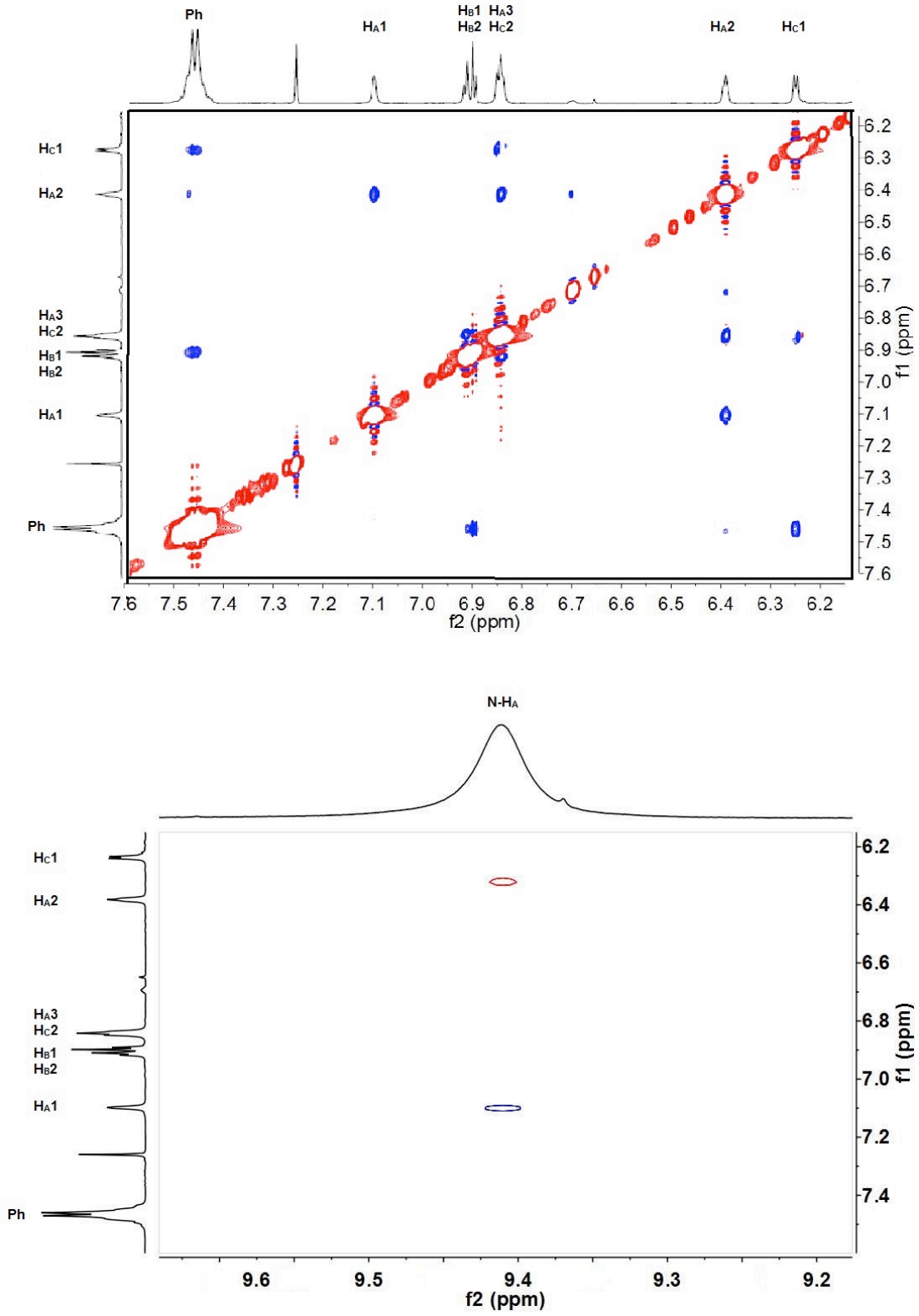
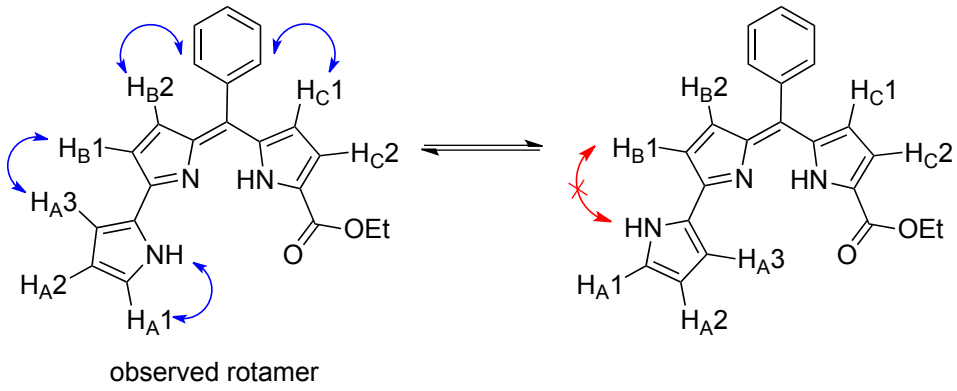


Figure S3. Portions of 2D NOESY NMR plot of H_2PD1 (600 MHz, $CDCl_3$, 27 ºC, 40 mM) showing relevant crosspeaks for the assignment illustrated in Scheme S1.



Scheme S1. Assignment of rotameric structure for H_2PD1 based on observed NOESY crosspeaks.

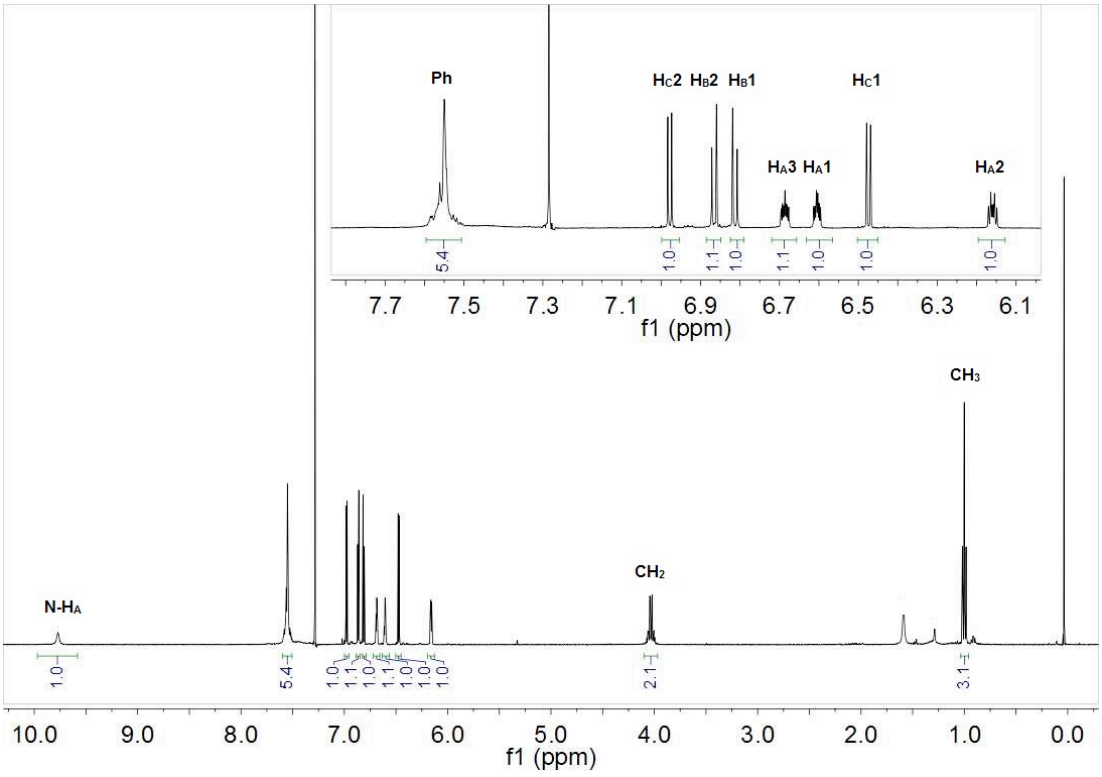


Figure S4. ^{1}H NMR spectrum of Zn(HPD1)$_2$ (400 MHz, $CDCl_3$, 27 °C). Resonances were assigned based on COSY and NOESY correlation data (see below).

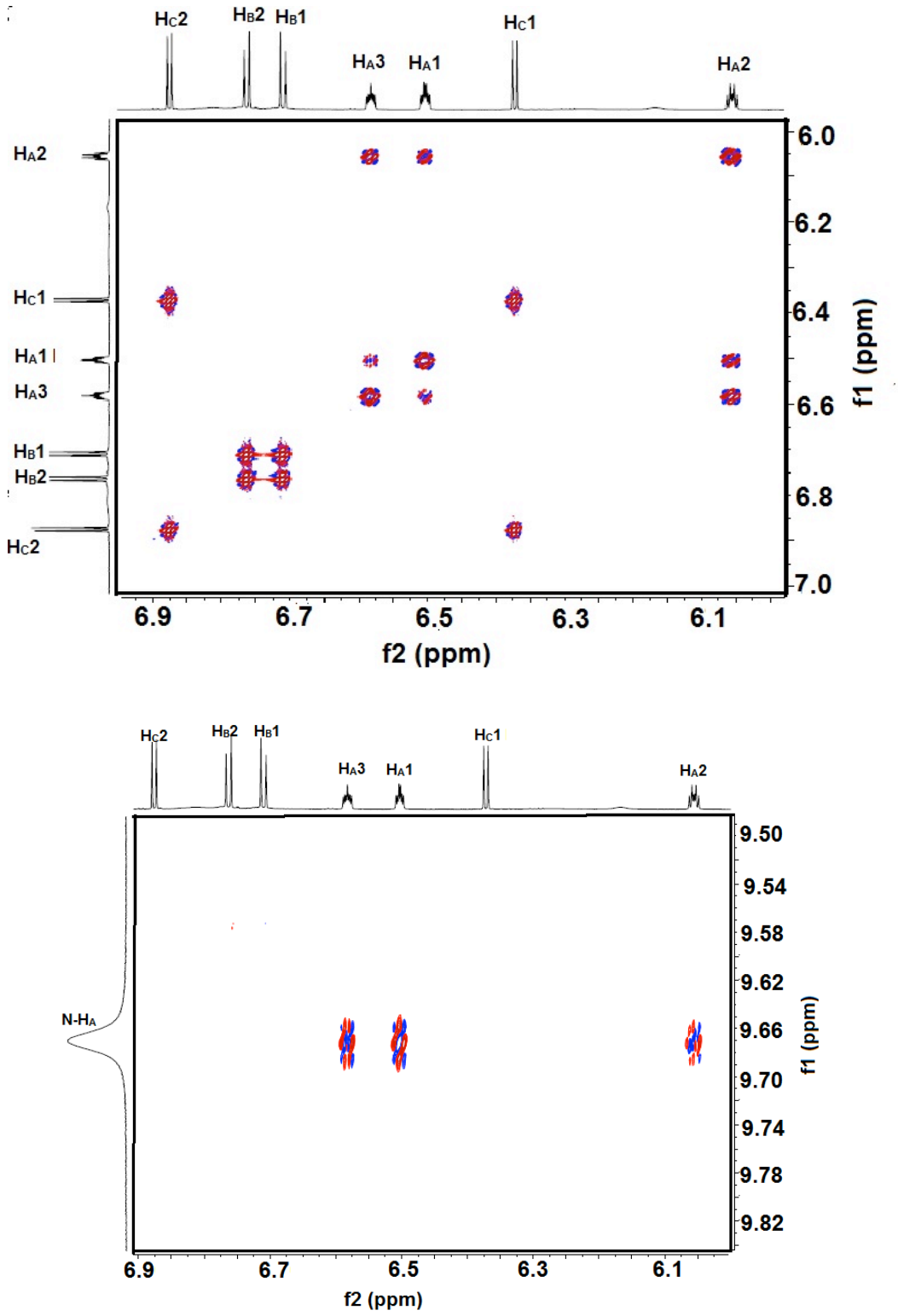


Figure S5. 2D COSY NMR plots for $Zn(HPD1)_2$ (600 MHz, $CDCl_3$, 27 °C, 11 mM).

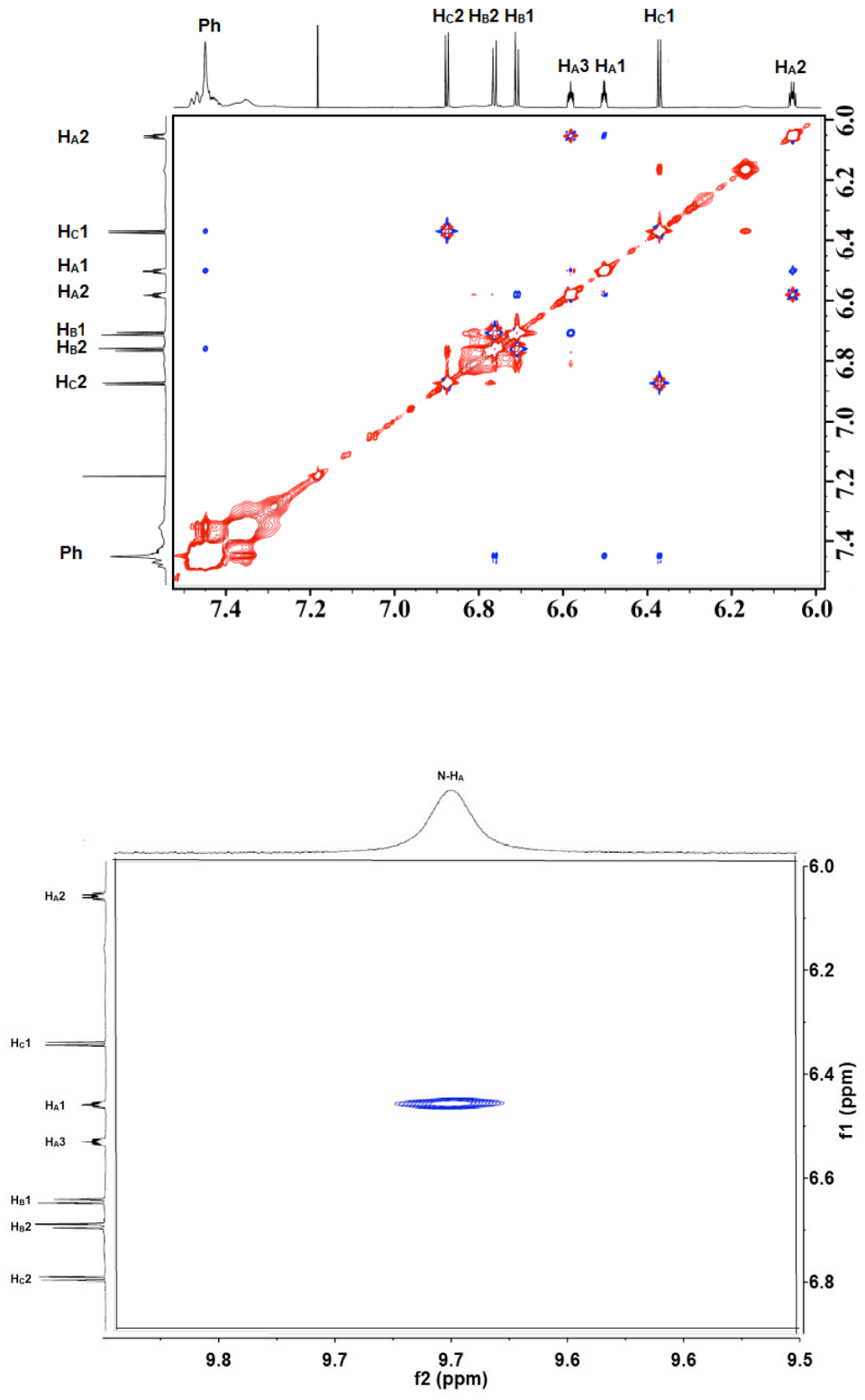
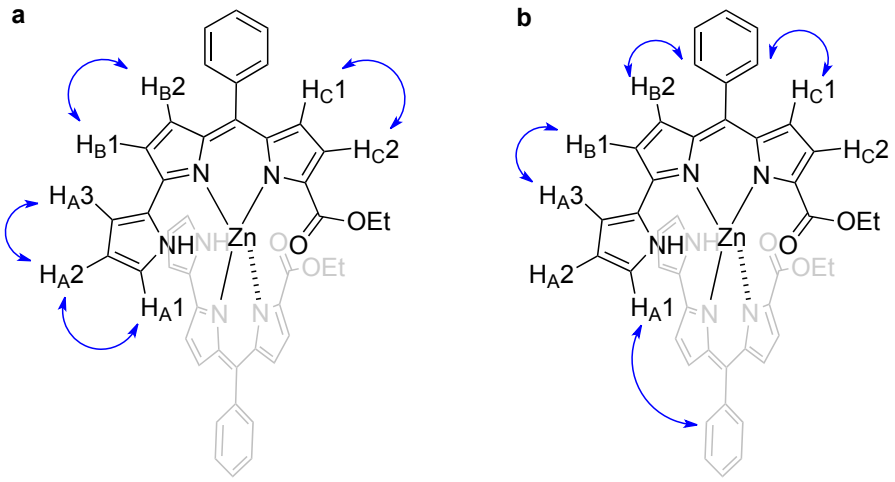


Figure S6. 2D NOESY NMR plots for $Zn(HPD1)_2$ (600 MHz, $CDCl_3$, 27 °C, 11 mM).



Scheme S2. Structure of complex $Zn(HPD1)_2$ based on correlations observed in COSY (a) and NOESY (b) 2D NMR data.

X-Ray Diffraction Analysis

Crystal data for $C_{44}H_{36}N_6O_4Zn$. M_r = 778.18, 0.05 × 0.04 × 0.01 mm, triclinic, space group *P*-1 (No. 2), a = 9.7497(6), b = 13.8451(9), c = 13.8646(9) Å, α = 84.270(2), β = 76.557(2), γ = 81.568(2)°, V = 1796.4(2) Å^3, Z = 2, ρ_{calc} = 1.439 g/cm^3, F_{000} = 808, Mo-Kα radiation, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 50.1º, 23528 reflections collected, 6371 unique (R_{int} = 0.1018). Final *GooF* = 1.006, R_1 = 0.0592, wR_2 = 0.1051, R indices based on 3866 reflections with $I > 2\sigma[I]$ (refinement on F^2), 498 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.739 mm^{-1}.

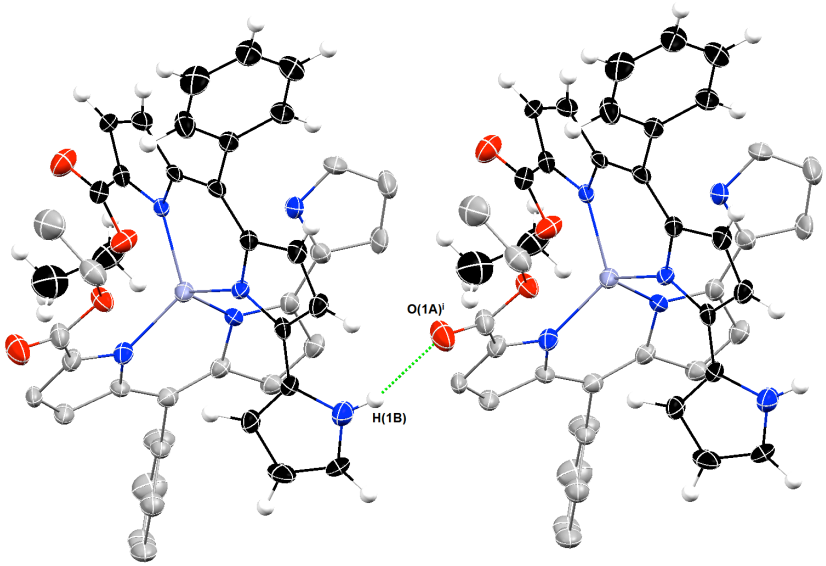


Figure S7. Intermolecular hydrogen bond between two Zn(HPD1)$_2$ complexes (i = x-1, y, z).

Crystal data for $C_{22}H_{20.60}CuN_3O_{3.8}$. M_r = 450.45, 0.20 × 0.02 × 0.01 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 16.847(4), b = 16.690(4), c = 7.3211(18) Å, β = 100.475(7)°, V = 2024.2(8) Å^3, Z = 4, D_c = 1.481 g/cm^3, F_{000} = 932, Mo-K α radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 39.6º, 13467 reflections collected, 1822 unique (R_{int} = 0.1239). Final *GooF* = 1.080, R_1 = 0.0569, wR_2 = 0.2189, R indices based on 1267 reflections $I > 2\sigma[I]$ (refinement on F^2), 266 parameters, 7 restraints. Lp and absorption corrections applied, μ = 1.112 mm^{-1}.

Table S1. Crystal data collection parameters for complexes Cu(PD1) and $Zn(HPD1)_2$

	Cu(PD1)	**$Zn(HPD1)_2$**
Molecular formula	$C_{22}H_{20.60}CuN_3O_{3.8}$	$C_{44}H_{36}N_6O_4Zn$
Formula weight [g.mol^{-1}]	450.45	778.16
Temperature [K]	120(2)	120.15
Crystal class	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a [Å]	16.847(4)	9.7497(6)
b [Å]	16.690(4)	13.8451(9)
c [Å]	7.3211(18)	13.8646(9)
α [°]	90.00	84.270(2)
β [°]	100.475(7)	76.557(2)
γ [°]	90.00	81.568(2)
Volume [Å^3]	2024.2(8)	1796.4(2)
Z	4	2
ϱ_{calc} [g/cm^3]	1.481	1.439
μ [mm^{-1}]	1.112	0.739
F(000)	932.0	808.0
Crystal size [mm]	0.2 × 0.02 × 0.01	0.05 × 0.04 × 0.01
Measured reflections	13467	23528
Independent reflections	1822	6371
Independent reflections, $I > 2\sigma[I]$	1267	3866
R_{int}	0.1239	0.1018
R_σ	0.0823	0.1248
Goodness-of-fit on F^2	1.080	1.005
R_1, $I > 2\sigma[I]$[a]	0.0569	0.0592
wR_2, all data[b]	0.2186	0.1251
peak/hole [e Å^{-3}]	0.86/-0.53	0.68/-0.45

[a] $R = \Sigma[|F_o| - |F_c|] / \Sigma |F_o|$ [b] $wR = [\Sigma w(F_o^2 - F_c^2) / \Sigma wF_o^4|]^{½}$

EPR and Pulsed ENDOR Analysis of Cu(PD1) in Solution

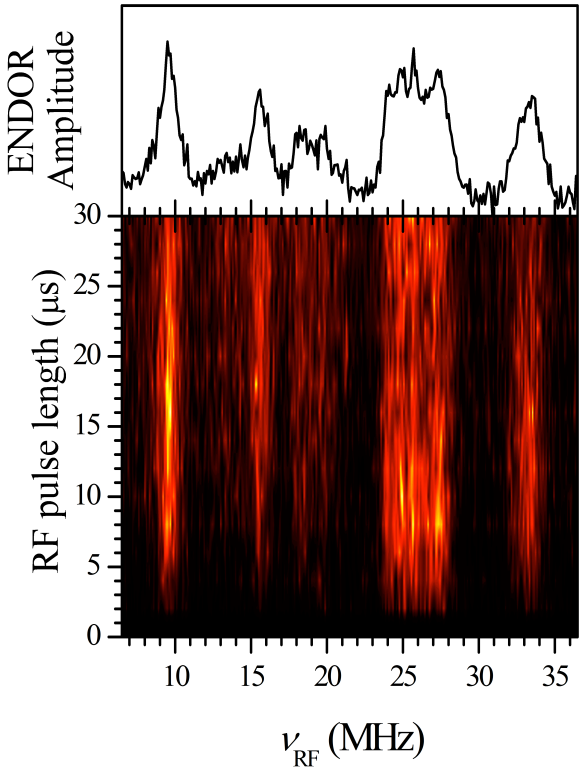


Figure S8. ^{14}N Davies ENDOR spectrum of Cu(PD1) solution in toluene. The experiment was performed in a 2D fashion, ν_{RF} *vs*. the RF pulse length, t_{RF}, and the obtained 2D spectrum is shown in the bottom panel. This 2D spectrum was integrated over t_{RF} to obtain the 1D spectrum shown in the top panel. Experimental conditions: mw frequency, 30.360 GHz; magnetic field, B_o = 970 mT (marked by an asterisk in Fig. 4b of the manuscript); mw pulses, 160, 80, and 160 ns; time interval between the 1st and 2nd mw pulses, 36 μs; time interval between the 2nd and 3rd mw pulses, 400 ns; t_{RF} variation range, 2 – 32 μs; temperature, 15 K.