Electronic Supporting Information

Inducing ring distortions in unsubstituted metallophthalocyanines using axial N-heterocyclic carbenes

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UV-Vis Spectra

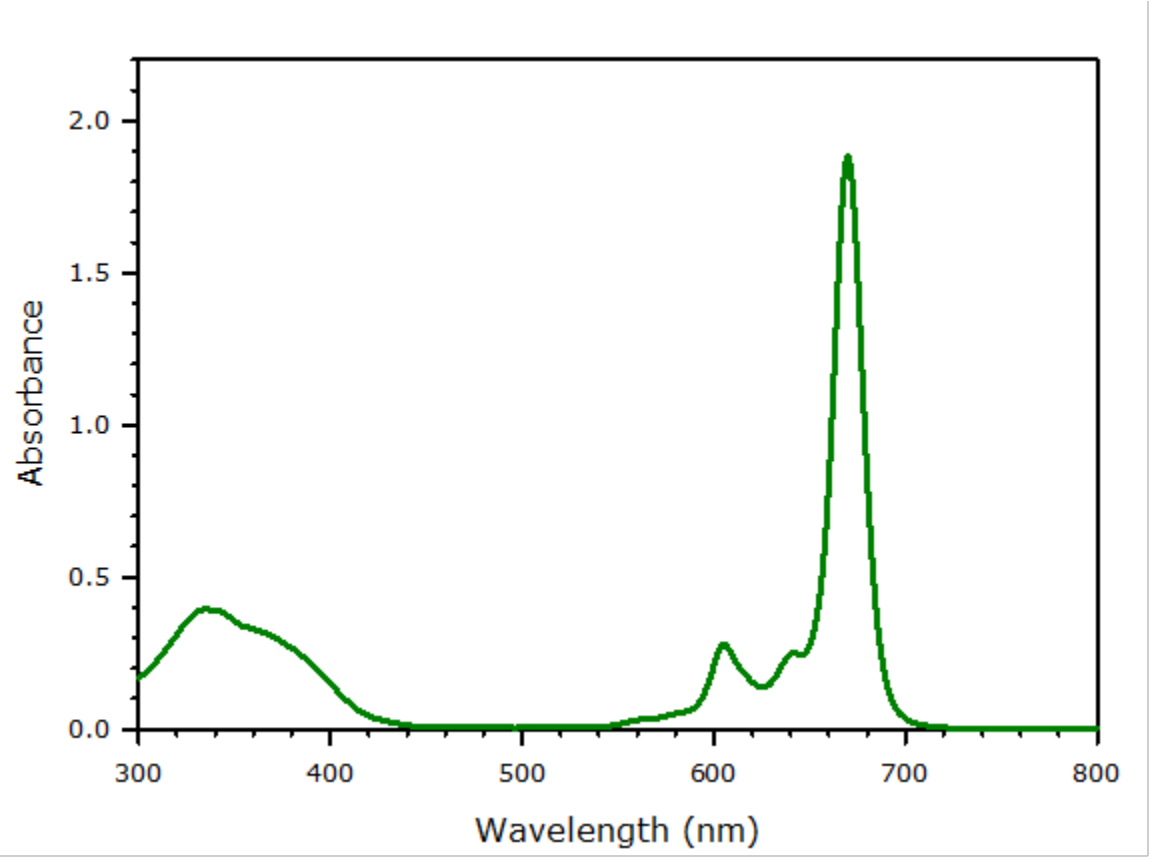

Figure S1 UV-Vis spectrum of $PcZn^{II}$(DIP) in Toluene, acquired under an ambient atmosphere. Q-band (λ max) 670 nm.

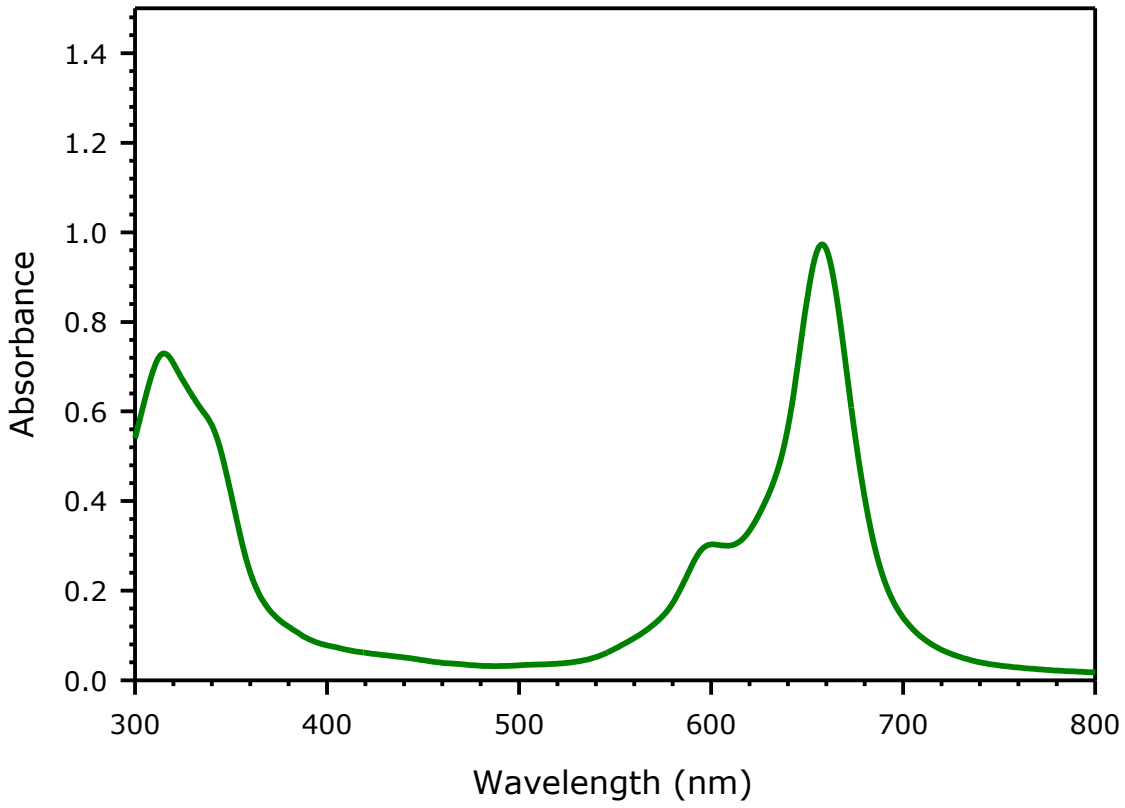

Figure S2 UV-Vis spectrum of $PcCo^{II}$(DIP) in Toluene, acquired in the presence of air. Q-band (λ max) 658 nm.

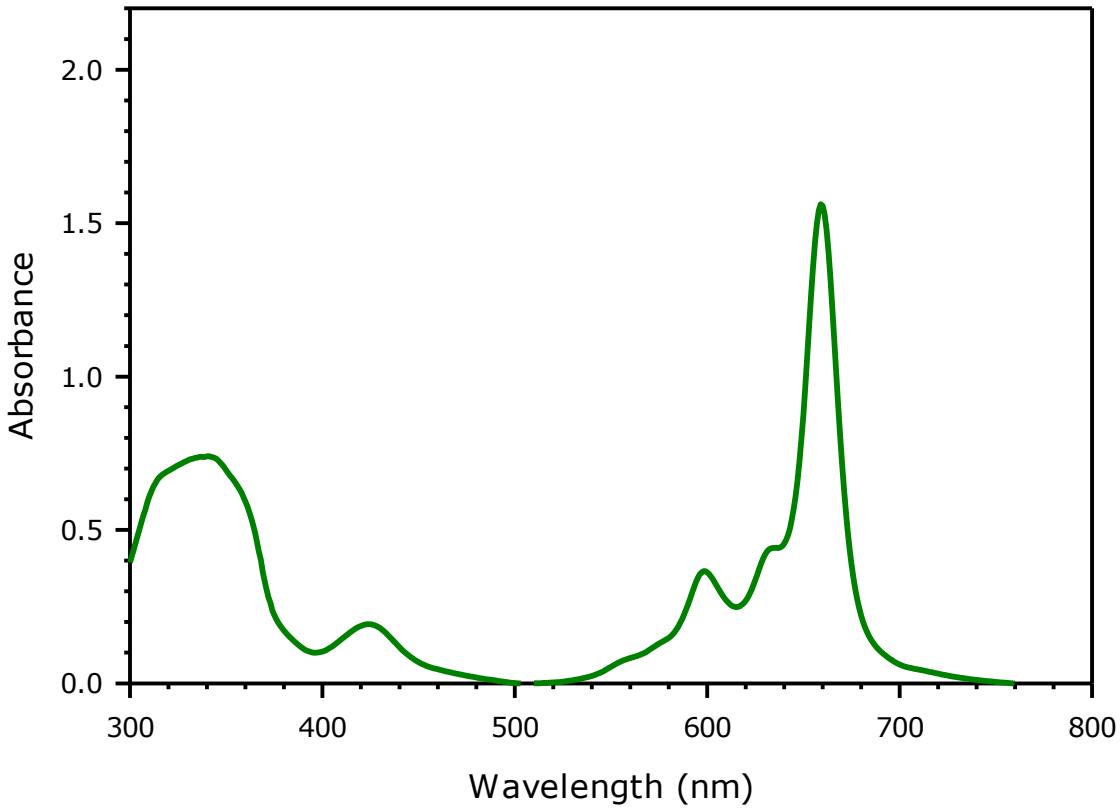

Figure S3 UV-Vis spectrum of $PcFe^{II}(DIP)_2$ in Toluene, acquired under an inert atmosphere. Q-band (λ max) 659 nm.

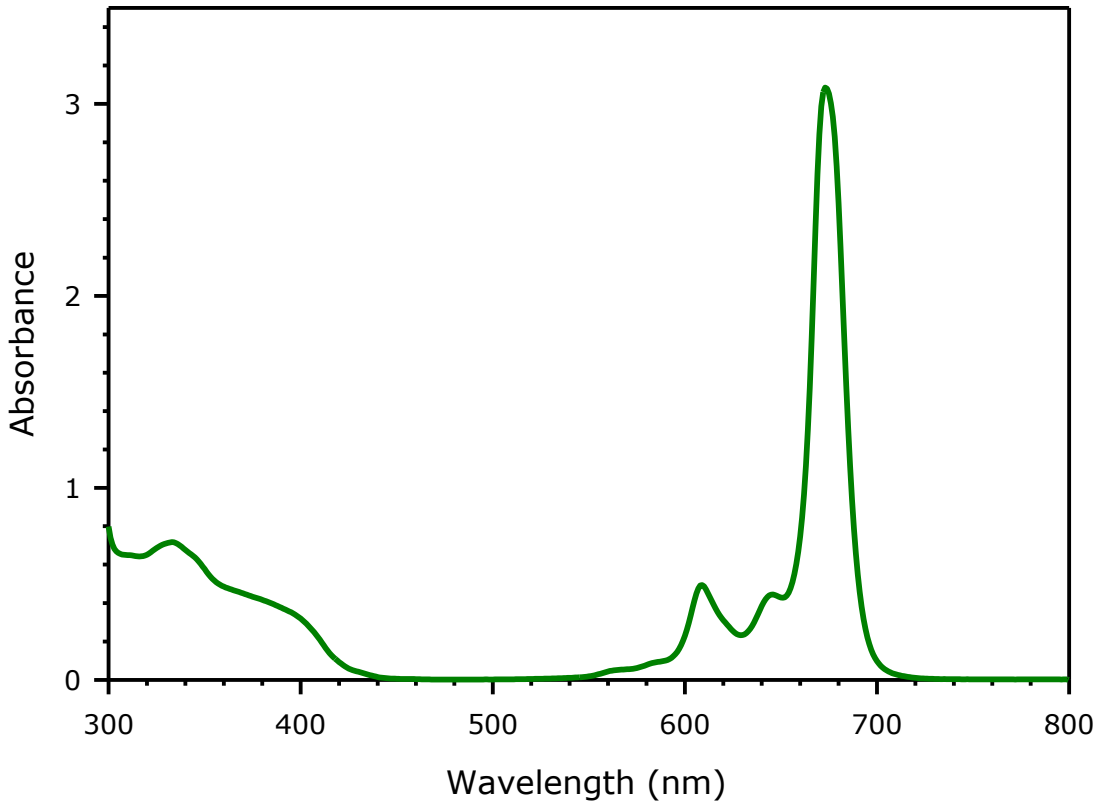

Figure S4 UV-Vis spectrum of $PcZn^{II}$(DMB) in Toluene, acquired in the presence of air. Q-band (λ max) 673 nm.

NMR Spectra

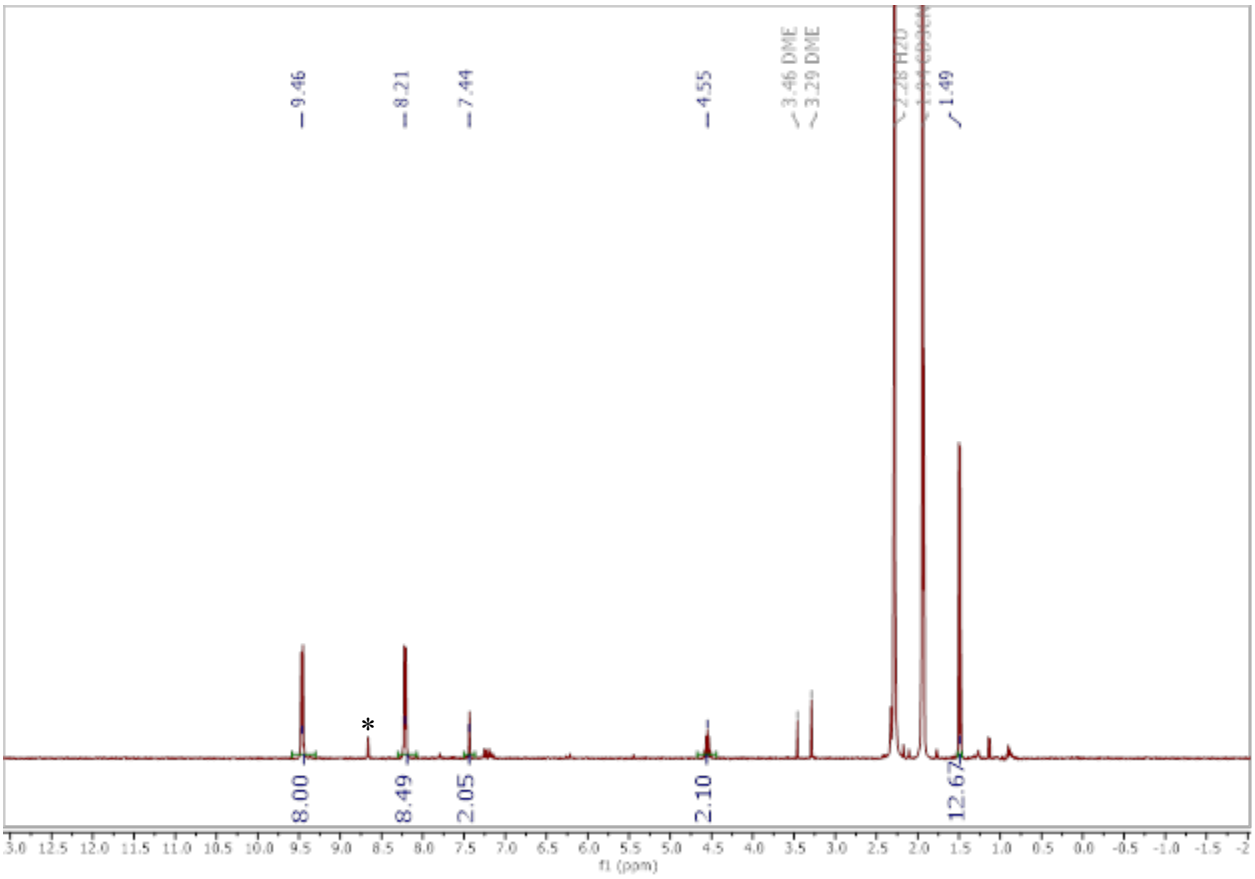

Figure S5 ^{1}H NMR spectrum of $PcZn^{II}$(DIP) (CD_3CN, 400 MHz spectrometer).* Impurity from DIP-based reagent.

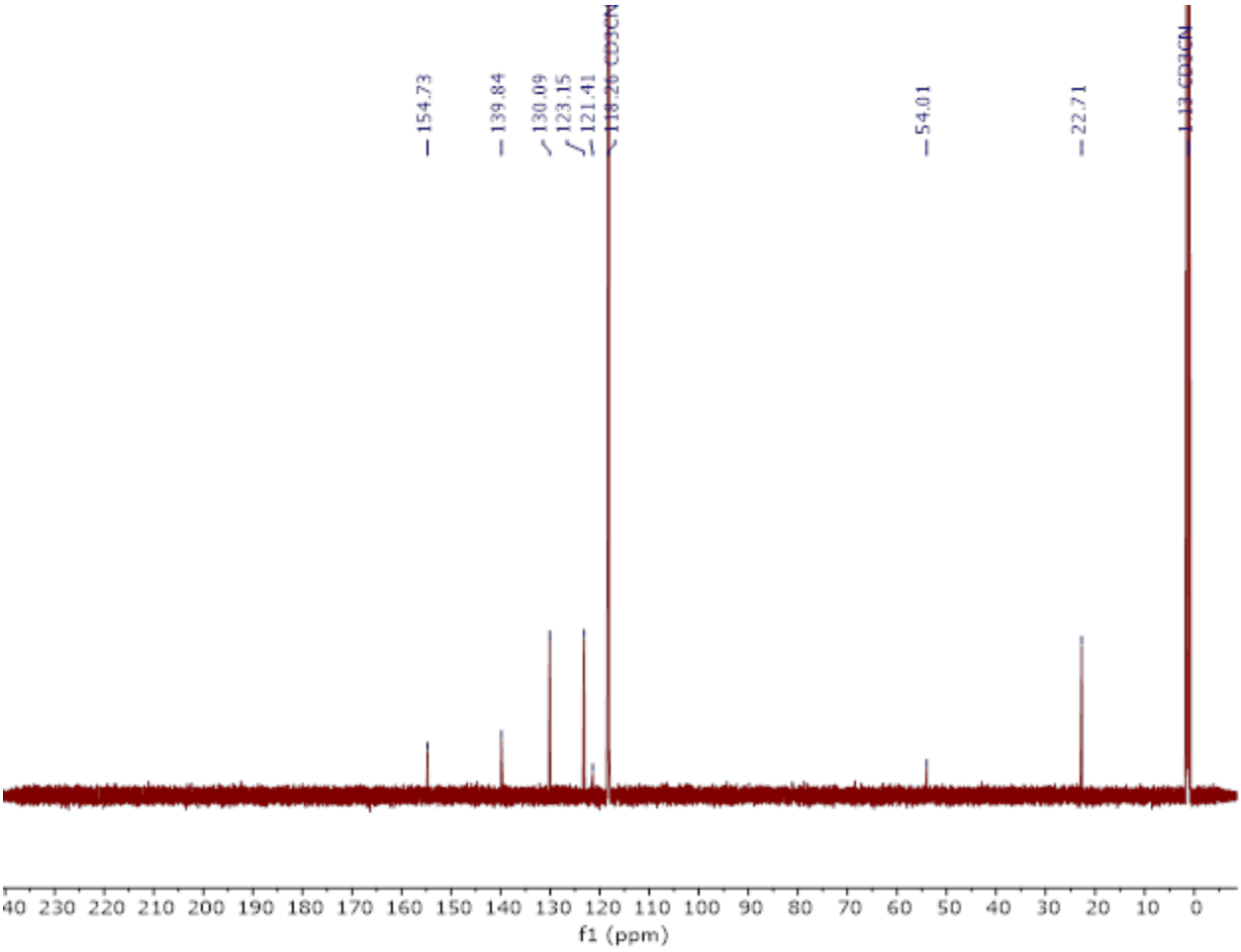

Figure S6 ^{13}C NMR spectrum of $PcZn^{II}$(DIP) (CD_3CN, 125 MHz spectrometer).

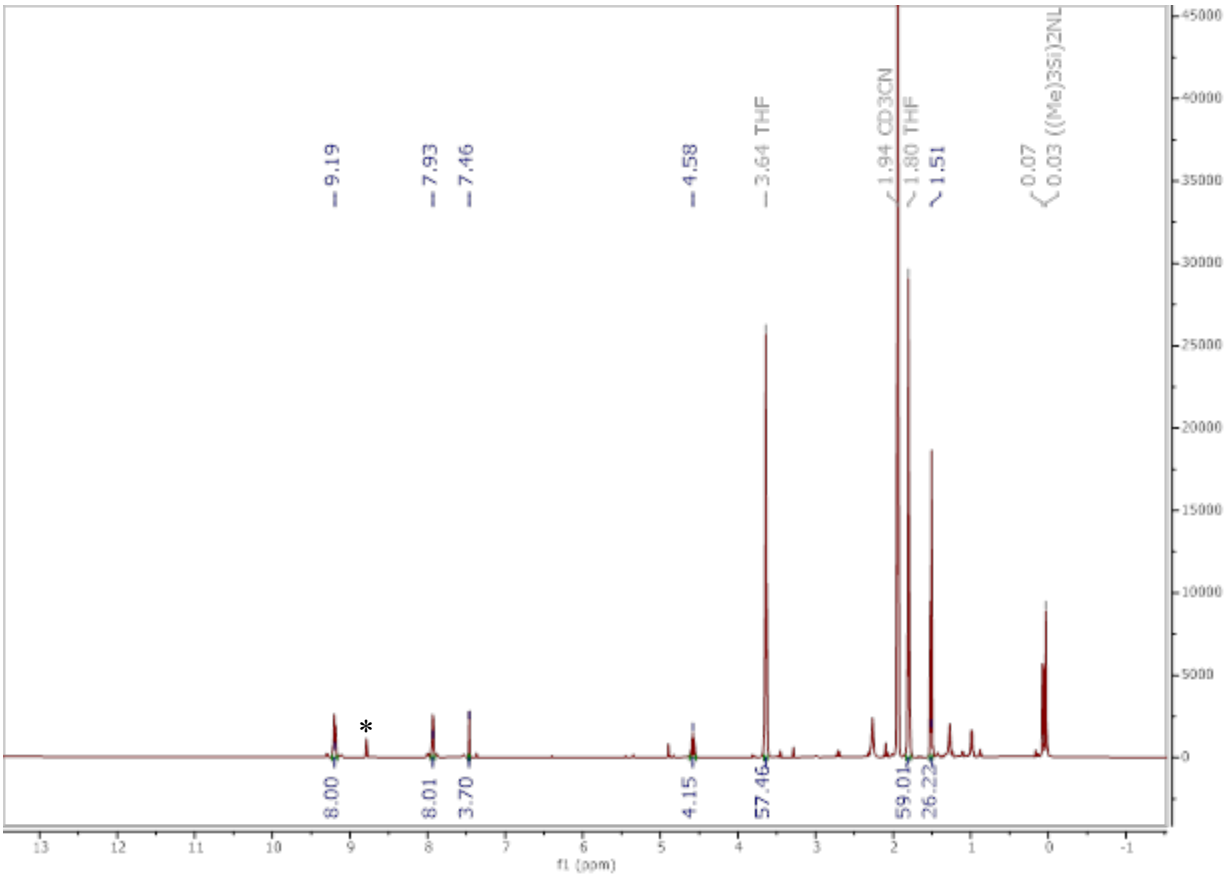

Figure S7 ^{1}H NMR spectrum of $PcFe^{II}(DIP)_2$ (CD_3CN, 500 MHz spectrometer).* Impurity from DIP-based reagent.

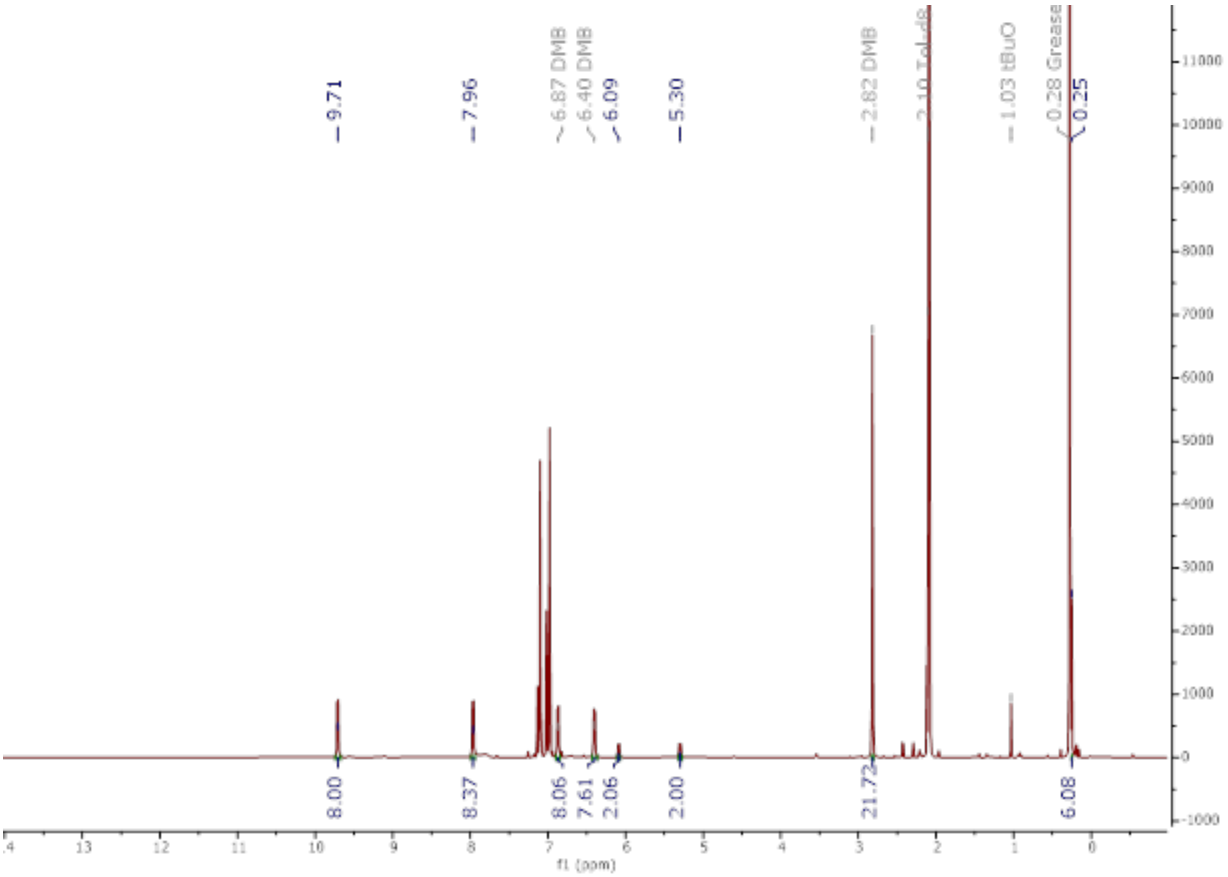

Figure S8 ^{1}H NMR spectrum of PcZn^{II}(DMB) (C_7D_8, 500 MHz spectrometer).

Crystallographic Data

Table S1 Summary of X-Ray crystal structures for $PcM(NHC)_x$ complexes.

Parameter	$PcZn^{II}(DIP)$	$PcCo^{II}(DIP)$	$PcFe^{II}(DIP)_2$	$PcZn^{II}(DMB)$
Chemical Formula	$C_{41}H_{32}N_{10}Zn$	$C_{41}H_{32}N_{10}Co$	$C_{50}H_{48}N_{12}Fe$	$C_{41}H_{26}N_{10}Zn$
Formal Weight (g mol^{-1})	1643.53	1610.57	1149.25	908.35
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	C 2/c	C 2/c	P 2_1/c	P 2_1/c
a (Å)	30.9681(19)	30.898(3)	16.3865(15)	12.0211(4)
b (Å)	14.0317(8)	13.5615(12)	19.1511(16)	15.8643(6)
c (Å)	20.7176(13)	21.2563(19)	19.3050(17)	23.5955(9)
α (°)	90	90	90	90
β (°)	118.052(3)	117.385(4)	90.504(5)	91.751(2)
γ (°)	90	90	90	90
V ($Å^3$)	7944.9(9)	7908.8(12)	6058.0(9)	4497.7(3)
Z	4	4	4	4
T (K)	189.98	189.99	190.00	189.99
ρ (g cm^{-1})	1.374	1.353	1.260	1.341
μ (mm^{-1})	1.245	3.786	2.410	1.155
Reflections	50962	40369	99114	74613
R [I > = 2σ (I)]	0.0551	0.0495	0.0723	0.0447
R_w [I > = 2σ (I)]	0.1239	0.1221	0.1824	0.1083
Goodness of Fit	1.037	1.061	1.050	1.058

Table S2 Selected bond lengths and torsion angles for $PcM^{II}(NHC)_x$ complexes. The torsion angles are defined as follows: The isoindole angle is the dihedral angle between two adjacent isoindole subunits, the N-isoindole angle is the angle between the intersection of the PcN_4 plane and the isoindole plane, and the N_{meso} angle is the dihedral angle between two pairs of N_{meso} atoms.

Bond	$PcFe^{II}(DIP)_2$	$PcCo^{II}(DIP)$	$PcZn^{II}(DIP)$	$PcZn^{II}(DMB)$
M-C (Å)	2.164(3)	2.265(3)	2.094(4)	2.093(3)
M-N (Å)	1.910(3)	1.935(2)	2.081(3)	2.080(2)
M-N (Å)	1.914(3)	1.936(2)	2.089(3)	2.087(2)
M-N (Å)	1.902(3)	1.925(3)	2.082(3)	2.089(2)
M-N (Å)	1.906(2)	1.924(3)	2.084(4)	2.083(2)
N_M-N_M (Å)	3.824(4)	3.838(3)	3.939(4)	3.951(3)
N_M-N_M (Å)	3.807(3)	3.826(4)	3.950(4)	3.961(3)
C_{NHC}-N_{meso} (Å)	3.362(4)	3.340(4)	3.340(4)	3.480(4)
C_{NHC}-N_{meso} (Å)	3.305(4)	3.346(5)	3.346(5)	3.601(4)
C_{NHC}-N_{meso} (Å)	3.323(4)	-	-	-
C_{NHC}-N_{meso} (Å)	3.330(4)	-	-	-
Isoindole (°)	5.2(4)	-3.1(4)	-6.3(4)	3.0(3)
Isoindole (°)	-7.2(4)	-1.3(4)	-3.9(4)	-1.6(3)
Isoindole (°)	-5.8(4)	4.3(4)	5.6(5)	-4.5(3)
Isoindole (°)	9.1(4)	3.1(4)	7.2(4)	2.4(3)
N-Isoindole (°)	13.6(2)	2.4(2)	-0.7(7)	-1.3(1)
N-Isoindole (°)	9.5(1)	1.7(2)	6.0(3)	-3.6(2)
N-Isoindole (°)	12.2(1)	3.6(3)	-0.1(3)	0.5(2)
N-Isoindole (°)	15.8(2)	-8.7(2)	-5.8(3)	-2.7(2)
N_{meso} (°)	23.77(6)	6.55(6)	0.41(7)	-3.74(5)

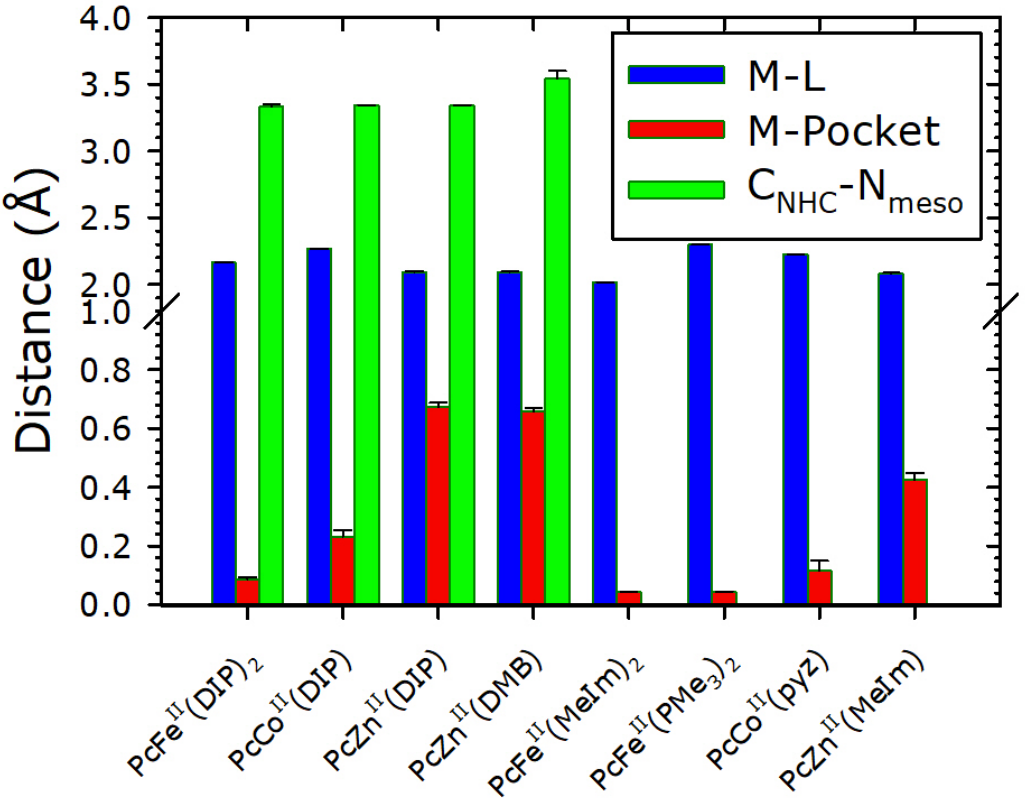

Figure S9 Summary of the crystallographic distances of interest for the PcM(NHC)$_x$ complexes as well as selected literature complexes for reference.

Solubility

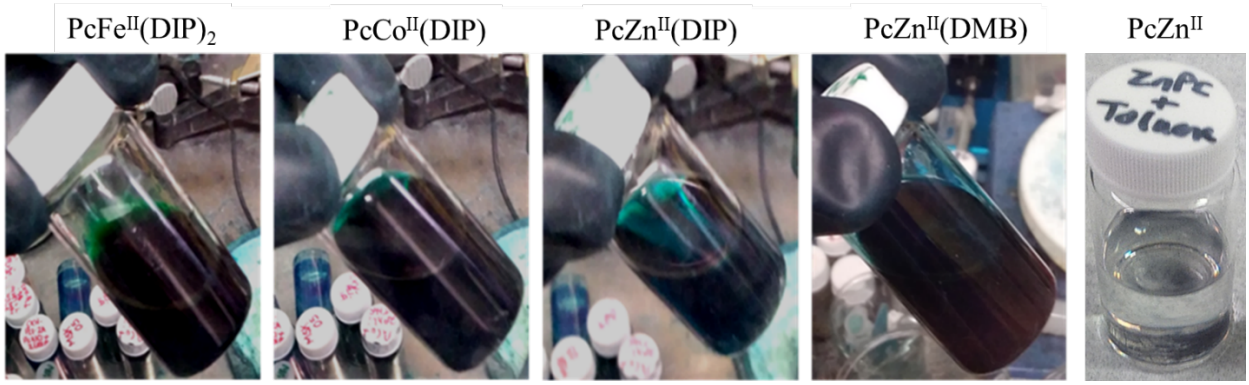

Figure S10 PcM^{II}(DIP/DMB) reaction photos after filtering through Celite in toluene and the insoluble PcZn^{II} starting material in toluene (far right).

Computations

Bond dissociation energies were calculated by subtracting the single point energy (E) of the products from the reactants, after taking into account the zero point energy (E_Z), thermal energy (E_T), and entropic energy (S) corrections of the product from the reactants.

$$BDE = (E + E_Z + E_T - S)_{Prod} - (E + E_Z + E_T - S)_{React} \qquad (\textbf{\textit{Eq. S1}})$$

Table S3 Correlation between BDE and organometallic CBC model for PcM^{II}(NHC)$_x$ complexes.

Complex	M-C BDE (kcal/mol)	CBC/ e$^-$ #
PcFe^{II}(DIP)$_2$	6.5	ML_4X_2 18 e–
PcCo^{II}(DIP)	4.1	ML_3X_2 17 e$^-$
PcZn^{II}(DIP)	-1.4	ML_3X_2 20 e$^-$
PcZn^{II}(DMB)	0.2	ML_3X_2 20 e$^-$