Co(II) and Co(III) complexes of benziphthalocyanine

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Supporting Information

General Methods: The reagents 1,3-diiminoisoindolene (97%) and *m*-phenylenediamine (99+%) for the ligand synthesis were obtained from Acros Organics and used as received. Solvent pyridine (anhydrous, 99.0%, Acroseal) and hexanes (anhydrous, 99.9%, acroseal) were purchased from Acros Organics. Cobalt acetate tetrahydrate, 98+% was purchased from Aldrich, dicobalt octacarbonyl (stabilized with 1-5% hexane) and manganese carbonyl 98%) were purchased from Strem Chemicals and all used without further purification. Mass spectra were recorded using an LCT electrospray spectrophotometer at the Mass Spectrometry and Proteomics Facility of Ohio State University. Elemental analysis was conducted at the University of Illinois, School of Chemical Sciences Microanalysis Laboratory. Magnetic susceptibility measurements were made on a Johnson Matthey Magnetic Susceptibility Balance using ultra-thin bore sample tubes. All ^{1}H spectra were recorded on Varian VXR spectrometers at 300 MHz in pyridine.

Single crystal X-ray diffraction data was collected with 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 watts power. The detector was placed at a distance of 5.009 cm from the crystal. Integration and refinement of crystal data was done using Bruker SAINT software package and Bruker SHELXTL (version 6.1) software package, respectively. Absorption correction was completed using the SADABS program. Crystals were placed in paratone oil before removal from the glove box and mounted on a plastic loop in the oil.

Preparation of Benziphthalocyanine (H$_3$bzpc): This two-step synthesis is based on the procedure by Linstead *et al.* (Scheme S4.1). Diiminoisoindoline (14.5 g; 0.10 mol) was dissolved in 100 mL of hot ethanol. The solution was cooled down to 0 ºC and 0.5 equivalents of 1,4-diaminobenzene (5.40 g, 0.05 mol) were added to the solution drop wise. The resulting mixture was stirred at 0ºC for 24 h. and a yellow-white precipitate was formed. The resulting precipitate was washed with cold ethanol and diethyl ether. Yield 12.5 g, 63%.

The intermediate compound (12.0 g; 0.03 mol) and diaminobenzene (3.30 g, 0.03 mol) was dissolved in 100 mL n-butanol and heated to reflux for 24 h. The resulting deep purple-red precipitate of H$_3$bzpc was washed with ethanol and diethyl ether. Yield 6.70 g, 51%.
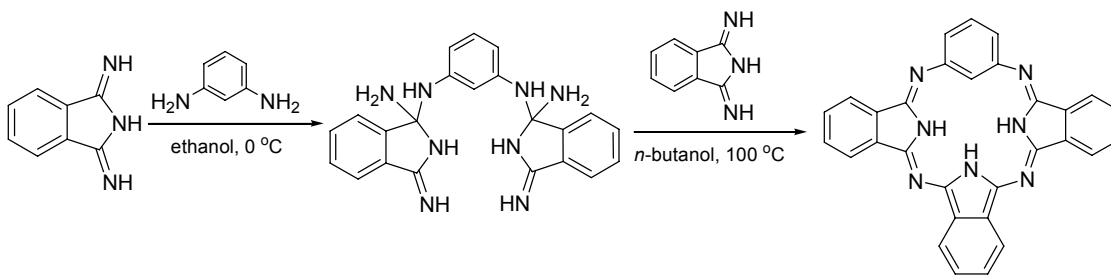
Scheme S4.1 Synthesis of benziphthalocyanine (H_3bzpc).

Preparation of (benziphthalocyanine) (pyridine) Cobalt(II), Co^{II}(bzpc)py: Free base H_3bzpc was weighed into the reaction flask before transporting into glove box. H_3bzpc (125 mg, 0.26 mmol) was dissolved in 10 mL of pyridine. The resultant solution was reddish brown in color. $Co_2(CO)_8$ (50.0 mg, 0.130 mmol) was weighed in the glove box and dissolved in 2 mL of pyridine producing a red colored solution. The $Co_2(CO)_8$ solution was added drop wise over 1 min. and the reaction was refluxed for 3 h. The color changed to a darker brown color. The solution was filtered through a fine frit and the solution was layered with anhydrous hexanes to afford red crystalline blocks within three days.

Co(bzpc)py: Yield: 71 mg (45%) This complex is paramagnetic. (μ_{eff} = 1.80, spin state S = ½) High resolution ESI MS (positive ion) calculated for Co(bzpc): 532.4 *m/z*, found: 532.0 *m/z*. CHN analysis calc. for $C_{35}H_{22}N_8Co$: C, 69.46, H, 3.79, N, 18.23. Found C, 70.06, H, 4.50, N, 18.57. Crystal data and structure refinement parameters are summarized in Table S.1.

Preparation of (benziphthalocyanine) (dipyridine) Cobalt(III), Co^{III}(bzpc)py$_2$: Air exposure of a pyridine solution of Co^{III}(bzpc)py results change in the color of the solution from red to green. Crystallization of this product from pyridine/hexanes resulted in the formation of green block crystals.

Co(bzpc)py$_2$: High res. ESI MS (positive ion) calculated for Co(bzpc): 532.4 *m/z*, found: 532.0 *m/z*. Analysis calc. for $C_{30}H_{17}CoN_7$: C, 67.42, H, 3.21, N, 18.34. Found: C, 67.37, H, 3.36, N, 17.35. ^{1}H NMR (300 MHz, [D_5]pyridine): δ= 9.34 (s, 1H), 8.72 (m,

4H), 8.67 (t, J = 7.9, 1H), 8.59 (d, J = 7.9, 2H), 8.44 (m, 4H), 8.30 (s, 2H), 7,24 (s, 1H).

The axial pyridine peaks are obscured by the solvent resonances. Crystal data and structure refinement parameters are summarized in Table S.2.

Preparation of (benziphthalocyanine hydroxide) (dipyridine) Cobalt(III), Co^{III}(bzpc-OH)py$_2$: Co(OAc)$_2$·4H$_2$O (100 mg, 0.400 mmol) and H$_3$bzpc (190 mg, 0.390 mmol) was dissolved in 10 mL of DMF. The resulting mixture was refluxed for 24 h. and added to about 30 mL of H$_2$O. The deep brown precipitate was collected, washed with ethanol and air dried. The product was dissolved in 1:1 pyridine/*p*-xylene solvent mixture and the solvent was slowly evaporated. Deep red crystals are formed within one week.

Co(bzpc-OH)py$_2$: Yield 56.4 mg (20%) High res. ESI MS (positive ion) calculated for Co(bzpc-OH): 550.4 m/z, found: 550.0 *m/z*. CHN analysis calculated for C$_{30}$H$_{17}$N$_7$CoO$_1$: C, 65.44, H, 3.11, N, 17.82. Found C, 65.19, H, 3.22, N, 17.71. Crystal data and structure refinement parameters are summarized in Table S.3.

Table S 1. Crystal data and structure refinement for **1**.

Identification code	Co(bzpc)py
Empirical formula	$C_{48} H_{39} Co N_{10}$
Formula weight	814.84
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 15.4472(15) Å $\quad \alpha = 90°$.
	b = 18.5201(18) Å $\quad \beta = 116.181(2)°$.
	c = 16.7680(17) Å $\quad \gamma = 90°$.
Volume	4304.9(7) $Å^3$
Z	4
Density (calculated)	1.320 Mg/m^3
Absorption coefficient	0.448 mm^{-1}
F(000)	1596
Crystal size	0.30 x 0.20 x 0.05 mm^3
Theta range for data collection	1.49 to 27.00°.
Index ranges	-19<=h<=19, -23<=k<=23, -21<=l<=21
Reflections collected	35546
Independent reflections	9370 [R(int) = 0.0374]
Completeness to theta = 27.00°	99.7 %
Absorption correction	Empirical SADABS
Max. and min. transmission	0.9783 and 0.8420
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9370 / 0 / 513
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0992
R indices (all data)	R1 = 0.0474, wR2 = 0.1033
Largest diff. peak and hole	0.681 and -0.422 e.$Å^{-3}$

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Table S 2. Crystal data and structure refinement for **2**.

Identification code	Co(bzpc)py$_2$
Empirical formula	C50 H36 Co N11
Formula weight	849.83
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 9.9002(16) Å $\quad$ α= 90°.
	b = 10.0469(16) Å $\quad$ β= 93.700(3)°.
	c = 44.850(7) Å $\quad$ γ = 90°.
Volume	4451.8(12) Å^3
Z	4
Density (calculated)	1.268 Mg/m^3
Absorption coefficient	0.433 mm^{-1}
F(000)	1760
Crystal size	0.18 x 0.05 x 0.01 mm^3
Theta range for data collection	1.82 to 28.36°.
Index ranges	-12<=h<=12, -13<=k<=13, -59<=l<=59
Reflections collected	37698
Independent reflections	10627 [R(int) = 0.0990]
Completeness to theta = 28.36°	95.4 %
Absorption correction	Empirical SADABS
Max. and min. transmission	0.9957 and 0.6374
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10627 / 0 / 563
Goodness-of-fit on F^2	0.978
Final R indices [I>2sigma(I)]	R1 = 0.0760, wR2 = 0.1626
R indices (all data)	R1 = 0.1369, wR2 = 0.1835
Largest diff. peak and hole	0.574 and -1.054 e.Å^{-3}

Table S 3. Crystal data and structure refinement for **3**.

Identification code	Co(bzpcOH)py$_2$
Empirical formula	C56 H46 Co N9 O
Formula weight	919.95
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.5789(11) Å α= 75.7250(10)°.
	b = 13.3090(12) Å β= 76.5220(10)°.
	c = 15.3136(13) Å γ = 69.3530(10)°.
Volume	2294.6(3) Å^3
Z	2
Density (calculated)	1.331 Mg/m^3
Absorption coefficient	0.426 mm^{-1}
F(000)	960
Crystal size	0.28 x 0.18 x 0.08 mm^3
Theta range for data collection	1.66 to 26.00°.
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18
Reflections collected	17911
Independent reflections	8946 [R(int) = 0.0259]
Completeness to theta = 26.00°	99.1 %
Absorption correction	Empirical SADABS
Max. and min. transmission	0.9667 and 0.7065
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8946 / 0 / 608
Goodness-of-fit on F^2	1.110
Final R indices [I>2sigma(I)]	R1 = 0.0946, wR2 = 0.2567
R indices (all data)	R1 = 0.1158, wR2 = 0.2722
Largest diff. peak and hole	4.570 and -0.470 e.Å^{-3}