

Supplementary Information to

Ligand Effects on Gas Adsorption in Nanoporous Phthalocyanine Crystals

Nikolaos-Angelos Stamos,¹ Charles J. McMonagle,² Gemma F. Turner,³ David R. Allan,³ Mark R. Warren,³ Anna J. Warren,^c Neil B. McKeown*¹ and Stephen A. Moggach*³

¹ EastChem School of Chemistry, David Brewster Road, The University of Edinburgh, Edinburgh, EH9 3FJ, United Kingdom

² Swiss–Norwegian Beamlines, European Synchrotron Radiation Facility, Grenoble 38043, France

³ Diamond House, Harwell Science and Innovation Campus, Fermi Ave, Didcot OX11 0DE, United Kingdom

³ School of Molecular Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, Perth, WA, 6009 Australia

Contents

S1. Synthesis of PNCs	1
S2. Single Crystal X-Ray Diffraction	2
S3. Crystallographic and Structural Parameters.....	5
S4. Curvature of Phthalocyanine	6

S1. Synthesis of PNCs

Materials and methods

Molecular components (dipPhO)₈PcCo and (dipPhO)₈PcH₂ were prepared, purified and characterised as previously reported.¹ Commercially available reagents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated all reactions were carried out under an inert atmosphere of dry nitrogen gas. Oven-dried glassware was left in a 100 °C oven for at least 2 hrs and cooled under dry nitrogen flow prior to use. Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected. Infra-red spectra were recorded in the range 4000-600 cm⁻¹ using a Jasco FTIR-660 plus spectrometer. Elemental analysis was carried out with a Carlo Erba EA1101 or a CE 440 elemental analyser. UV/vis absorption spectra were recorded in the range 200-800 nm using a Jasco V-570 UV/vis/NIR spectrophotometer. Volumetric N₂ sorption studies were undertaken at 77 K using a Beckman Coulter 3100 Surface Area Analyzer (Fullerton, California, USA). ¹H NMR spectra were measured in CDCl₃ using an Advance Bruker DPX 400 instrument (400 MHz), with ¹³C NMR spectra recorded at 100 MHz respectively. MALDI-TOF mass spectroscopic analyses were performed with a Waters MALDI Micro MX spectrometer. Thermogravimetric analysis was performed on a TA SDT Q 600 instrument.

Cobalt 2,3,9,10,16,17,23,24-octa(2',6'-di-iso-propylphenoxy)phthalocyanine (PcCo)

A stirred solution of 4,5-bis(2,6-di-iso-propylphenoxy)phthalonitrile (0.50 g, 1.04 mmol) and cobalt(II) acetate (0.18 g, 1.01 mmol) in anhydrous NMP (1 ml) was heated at 165 °C for 20 h under nitrogen. The reaction mixture was cooled to room temperature and poured into water (15 ml). The crude product was collected by filtration. Purification by column chromatography on SiO₂, eluting with hexane-DCM (4:6), gave the title compound as a green solid (0.22 g, 40%). M.p. >300 °C; IR (film)/cm⁻¹ 2961, 1612, 1456, 1462, 1413, 1353, 1269, 1186, 1095, 1050, 904, 864, 799, 777, 755, 729; UV/vis (DCM): λ_{max} 673, 608, 404, 331, 302, 229 nm; MS (MALDI-TOF): cluster centred at m/z 1982.055 (MH⁺); elemental analysis calc (%) for C₁₂₈H₁₄₄N₈O₈Co: C 77.59, H 7.32, N 5.66 found C 77.68, H 7.52, N 5.52.

Crystallisation of PNCs

Single crystals of PNC[Co-cbipy-Co] and PNC[Co-cbpm-Co] were grown as previously reported.¹

S2. Single Crystal X-Ray Diffraction in a Gas Cell

Single crystal X-ray diffraction experiments were carried out using a static quartz capillary gas cell (5 mm outer diameter) on beamline I19-2 at Diamond Light Source, United Kingdom.² A single crystal of PNC[Co-cbipy-Co] and PNC[Co-cbpm-Co] were each glued to a MiTeGen loop to avoid movement of the crystal upon introduction of gas. The goniometer head was connected to a gas rig through stainless-steel capillary tubing (Swagelok SS-T1-S-014-6ME). The crystals were initially treated under high vacuum (10^{-6} mbar) for at least 10 minutes to remove as much residual solvent as possible. After exposing PNC[Co-cbipy-Co] and PNC[Co-cbpm-Co] to CO or NO, the crystal was then evacuated for at least 10 minutes to determine the reversibility of the gas uptake in the pores. Collections were carried out successively on a single crystal of either PNC[Co-cbipy-Co] or PNC[Co-cbpm-Co].

Diffraction data were collected using an X-ray wavelength of 0.6889 Å, an exposure time of 1 s and a step size of 0.5°. Data were integrated and reduced in Xia2,³ and an absorption correction was applied using AIMLESS.³ Crystal structures were solved using ShelXT⁴ and refined against $|F^2|$ using ShelXL⁵ in Olex2.⁶ The aromatic rings in the phthalocyanine units were restrained to hexagonal geometry. All other geometric parameters were refined freely. Thermal similarity restraints were applied to the phenyl rings and isopropyl groups on the phthalocyanine unit, and on the CO or NO ligands, where applicable. The pore volume and electron-count per pore were calculated using the SQUEEZE algorithm in PLATON.⁷

Abridged crystallographic data are given in *Tables S1-2*.

Supplementary Table 1. Experimental crystallographic data for PNC[Co-cbipy-Co] under vacuum, CO and NO environments in the gas cell.

Gas cell conditions	Vacuum (10^{-6} mbar, 10 min)	5 bar CO	2.63 bar NO	Vacuum (10^{-6} mbar, 10 min)
Chemical formula	$\text{Co}_2\text{C}_{266}\text{H}_{288}\text{N}_{18}\text{O}_{16}$	$\text{Co}_2\text{C}_{266.74}\text{H}_{288}\text{N}_{18}\text{O}_{16.74}$	$\text{Co}_2\text{C}_{266}\text{H}_{288}\text{N}_{20}\text{O}_{18}$	$\text{Co}_2\text{C}_{266}\text{H}_{288}\text{N}_{20}\text{O}_{18}$
M_r	4111.11	4131.84	4171.12	4171.12
Crystal system, space group	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$
Temperature (K)	298	180	180	298
a (Å)	37.8156(2)	37.438(2)	37.9704(2)	37.785(2)
V (Å ³)	54077.0(5)	54628.9(5)	54743.9(5)	53946.7(5)
Z	6	6	6	6
Radiation type	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å
μ (mm ⁻¹)	0.13	0.13	0.13	0.14
Crystal size (mm)	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1
Diffractometer	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K
Absorption correction	Empirical correction, CCP4 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, CCP4 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, CCP4 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, CCP4 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.
T_{\min}, T_{\max}	0.976, 1.000	0.977, 1.000	0.974, 1.000	0.984, 1.000
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	213161, 6495, 4049	181240, 4769, 3653	181688, 4792, 3659	179058, 4738, 3237
R_{int}	0.1187	0.1057	0.0940	0.0962
σ_{max} (°)	22.499	20.136	20.143	20.143
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0930, 0.3121, 1.101	0.0920, 0.2601, 1.054	0.0873, 0.2555, 1.092	0.0947, 0.3145, 1.093
No. of reflections	4049	4769	4792	4738
No. of parameters	262	273	280	280
No. of restraints	302	304	315	316
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\rho_{\text{max}}, \rho_{\text{min}}$ (e Å ⁻³)	0.771, -0.622	0.708, -0.627	0.648, -0.609	0.628, -0.421

Table S2. Experimental crystallographic data for PNC[Co-cbpm-Co] under vacuum, CO and NO environments in the gas cell.

Gas cell conditions	Vacuum (10 ⁻⁶ mbar, 10 min)	5 bar CO	Vacuum (10 ⁻⁶ mbar, 38 min)	4-28 bar NO	Vacuum (10 ⁻⁶ mbar, 10 min)
Chemical formula	Co ₂ C ₂₆₄ H ₂₈₆ N ₂₀ O ₁₆	Co ₂ C _{264.62} H ₂₈₆ N ₂₀ O ₁₆	Co ₂ C ₂₆₄ H ₂₈₆ N ₂₀ O ₁₆	Co ₂ C ₂₆₄ H ₂₈₆ N ₂₂ O ₁₈	Co ₂ C ₂₆₄ H ₂₈₆ N ₂₂ O ₁₈
M_r	4113.09	4130.45	4113.09	4173.10	4173.10
Crystal system, space group	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$	Cubic, $Pn\bar{3}n$
Temperature (K)	298	180	298	180	298
a (Å)	37.7457(3)	37.8873(2)	37.7086(3)	37.9112(2)	37.6730(5)
V (Å ³)	53777.7(6)	54385.2(6)	53619.0(7)	54488.2(6)	53467.6(11)
Z	6	6	6	6	6
Radiation type	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å	Synchrotron, $\lambda = 0.6889$ Å
μ (mm ⁻¹)	0.14	0.13	0.14	0.13	0.14
Crystal size (mm)	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1	0.1 x 0.1 x 0.1
Diffractometer	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K	Pilatus 300K
Absorption correction	Empirical correction, <i>CCP4</i> 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, <i>CCP4</i> 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, <i>CCP4</i> 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, <i>CCP4</i> 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.	Empirical correction, <i>CCP4</i> 7.0.027: AIMLESS, version 0.5.31, spherical harmonics.
T_{\min}, T_{\max}	0.986, 1.000	0.985, 1.000	0.986, 1.000	0.985, 1.000	0.991, 1.000
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	175822, 4714, 2771	177785, 4769, 3229	175135, 4693, 2678	178040, 4771, 3280	173529, 4680, 2401
R_{int}	0.1007	0.0897	0.1027	0.0981	0.1295
ϑ_{max} (°)	20.128	20.138	20.134	20.132	20.132
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.1283, 0.3590, 1.278	0.1053, 0.3570, 1.400	0.0864, 0.2927, 1.007	0.1005, 0.3487, 1.391	0.1220, 0.3693, 1.218
No. of reflections	4714	4769	4693	4771	4680
No. of parameters	256	260	317	270	269
No. of restraints	287	323	321	332	332
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\rho_{\text{max}}, \rho_{\text{min}}$ (e Å ⁻³)	0.936, -0.691	0.625, -0.444	0.728, -0.348	0.583, -0.379	0.662, -0.646

S3. Crystallographic and Structural Parameters

Table S3. Unit cell dimensions and structural parameters for ligand binding in PNC[*vA*-Co-*cL*-Co-*vA*], where L is bipy or bpm and A is CO or NO, during gas dosing. Note that the structures are listed in chronological order of analysis.

PNC[<i>vA</i> -Co- <i>cbipy</i> -Co- <i>vA</i>]						
Conditions	<i>a/b/c</i> (Å ³)	<i>V</i> (Å ³)	A % [c]	Co-A (Å)	∠Co-C/N-O (°)	Co-L (Å)
Ambient [a]	37.8533(2)	54238.9(5)	0	n/a	n/a	2.215(8)
Vacuum, 10 min [b]	37.8156(2)	54077.0(5)	0	n/a	n/a	2.205(8)
5.0 bar CO [a]	37.9438(2)	54628.9(5)	37	1.96(4)	180.00(2)	2.230(8)
2.6 bar NO [a],[d]	37.9704(2)	54743.9(5)	100	1.898(11)	120.6(9)	2.393(8)
Vacuum, 10 min [b]	37.7852(2)	53946.7(5)	100	1.914(11)	117.0(7)	2.106(11)
PNC[<i>vA</i> -Co- <i>cbpm</i> -Co- <i>vA</i>]						
Vacuum, 10 min [b]	37.6730(5)	53777.7(6)	0	n/a	n/a	2.302(15)
5.0 bar CO [a]	37.9111(2)	54487.8(5)	31	1.81(3)	180.00(2)	2.335(12)
5.0 bar CO [a],[e]	37.8873(2)	54385.2(6)	31	1.87(4)	180.00(2)	2.313(12)
Vacuum, 24 min	37.7086(3)	53619.3(7)	0	n/a	n/a	2.293(11)
4-28 bar NO	37.9112(2)	54488.2(6)	100	1.888(11)	120.5(12)	2.483(11)
Vacuum 10 min	37.6730(5)	53467.6(1)	100	1.972(19)	112.5(16)	2.413(15)

[a] *T* = 180 K; [b] *T* = 298 K; [c] refined crystallographic occupancy of CO or NO; [d] measurement taken after crystal was treated under high vacuum for at least 10 min; [e] different crystal used in measurement, which was then used for all subsequent measurements.

Table S4. Cavity and void dimensions, and distortion of the Co-phthalocyanine unit (*d*) in PNC[Co-*cL*-Co-*vA*], where L is bipy or bpm and A is CO or NO, during gas dosing. Note that the structures are listed in chronological order of analysis.

PNC[Co- <i>cbipy</i> -Co- <i>vA</i>]							
Conditions	Cavity <i>V</i> (Å ³) ^[e]	Cavity <i>e</i> ^[e]	Void <i>V</i> (Å ³) ^[e]	Void <i>e</i> ^[e]	<i>cCo</i> ...Co (Å) ^[f]	<i>vCo</i> ...Co (Å) ^[g]	<i>d</i> (Å) ^[h]
Ambient [a]	3642	822	18559	2391	11.561(2)	26.292(2)	0.60(3)
Vacuum, 10 min [b]	3336	672	18371	2033	11.566(2)	26.250(1)	0.60(3)
5.0 bar CO [a]	3438	810	18538	2951	11.566(2)	26.358(2)	0.61(4)
2.6 bar NO [a],[c]	3492	882	18461	3087	11.931(2)	26.039(2)	0.79(3)
Vacuum, 10 min [b]	3216	972	17939	1204	11.505(2)	26.280(2)	0.58(4)
PNC[Co- <i>cbpm</i> -Co- <i>vA</i>]							
Vacuum, 10 min [b]	3348	420	18142	3929	11.505(3)	26.106(2)	0.62(4)
5.0 bar CO [a]	3978	1128	18705	2582	11.707(3)	26.204(2)	0.67(3)
5.0 bar CO [a],[d]	3984	1092	18691	2327	11.696(3)	26.191(2)	0.66(4)
Vacuum, 24 min	3426	564	18168	1271	11.653(3)	26.056(2)	0.64(4)
4-28 bar NO	3613	1170	18226	2950	12.040(2)	25.871(2)	0.83(3)
Vacuum 10 min	3108	636	17578	4200	11.904(4)	25.749(2)	0.79(4)

[a] *T* = 180 K; [b] *T* = 298 K; [c] measurement taken after crystal was treated under high vacuum for at least 10 min; [d] different crystal used in measurement, which was then used for all subsequent measurements; [e] Cavity and nanovoid volume per unit cell and total quantity of guest adsorbed in each pore per unit cell from PLATON SQUEEZE,⁸ using a probe radius of 1.2 Å and truncation of 1.2 Å; [f] distance between Co²⁺ centres across the cavity; [g] distance between Co²⁺ centres across the nanovoid; [h] distance between Co²⁺ and a plane defined by the O-atoms in the phthalocyanine unit.

S4. Curvature of Phthalocyanine

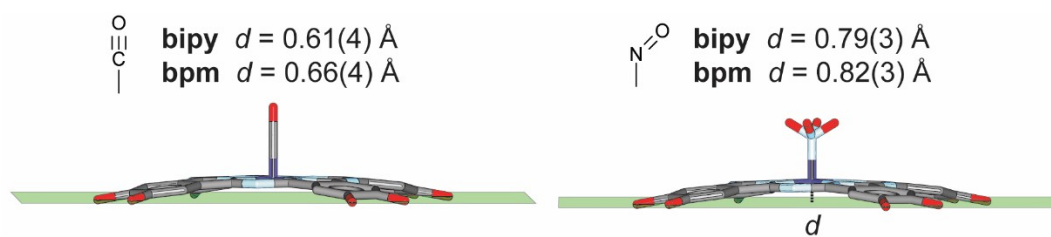


Figure S1. Curvature of phthalocyanine group chemisorption of NO, taken as the distance between the Co^{2+} centre and the plane made by the O-atoms in the phthalocyanine unit.

References

1. C. Grazzia Bezzu, M. Helliwell, J. E. Warren, D. R. Allan and N. B. McKeown, *Science*, 2010, **327**, 1627-1630.
2. H. Nowell, S. A. Barnett, K. E. Christensen, S. J. Teat and D. R. Allan, *J. Synchrotron Radiat.*, 2012, **19**, 435-441.
3. G. Winter, *J Appl Cryst*, 2010, **43**, 186-190.
4. G. M. Sheldrick, *Acta Cryst A*, 2015, **A71**, 3-8.
5. G. M. Sheldrick, *Acta Cryst C*, 2015, **C71**, 3-8.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Cryst*, 2009, **42**, 339-341.
7. A. L. Spek, *Acta Cryst C*, 2015, **C71**, 9-18.
8. A. L. Spek, *Acta Cryst. C*, 2015, **71**, 9-18.