# Spontaneous Solution-Phase Redox Deposition of a Dense Cobalt(II) Phthalocyanine Monolayer on Gold

**Ursula Mazur, Maya Leonetti, William A. English, and K. W. Hipps***

*Department of Chemistry and Materials Science Program, Washington State University, Pullman, Washington 99164-4630*

A dense monolayer of cobalt(II) phthalocyanine, CoPc, can be formed on a gold surface by spontaneous redox deposition followed by vacuum annealing at about 110 °C. $CsCoPc(CN)_2$ or $KCoPc(CN)_2$ in dilute (~$10^{-6}$ M) ethanol solution rapidly forms a dense adlayer that, when washed with ethanol, can be imaged by scanning tunneling microscopy, STM, in air. This adlayer is converted to a monolayer of CoPc by vacuum annealing as confirmed by STM and X-ray photoelectron spectroscopy (XPS). This spontaneous surface redox adsorption process represents a novel method for depositing metallorganic complexes, which are ultimately only physisorbed on gold.

## Introduction

Phthalocyanine (Pc) and porphyrin-based (P) electrical conductors are used extensively as building blocks for constructing stable 2D supermolecular electronic assemblies. The architectural forms of these structures include simple clusters, wires, arrays, and even designer surfaces.[1–7] Understanding the principles of architecture and the ability to control Pc assembly on surfaces continues to be of critical importance in the rational design and construction of functional optoelectronic nanoscale devices derived from phthalocyanines and porphyrins. The most basic monolayer architectures arise from vapor deposition. Simple complexes deposited on conductive surfaces in vacuum or from solution exhibit a close-packed arrangement that results from van der Waal's interactions between the molecules.[2–4] Hipps and co-workers vapor deposited different 2D metal phthalocyanine and porphyrin assemblies on gold and imaged them by UHV scanning tunneling microscopy (STM) with remarkable submolecular resolution.[2,3,6] Bai demonstrated that monolayer molecular arrays of alkane-derivitized phthalocyanine can be assembled from solution on straight-chain alkane templates deposited on graphite.[4] Recently, Itaya formed both a pure MPc and a mixed CoPc and copper tetraphenylporphyrin (CuTPP) adlayer by immersing a Au single crystal into a benzene solution containing the parent compounds. By imaging the adsorbate system in aqueous solution, he demonstrated a structural dependence of the adlayer on the crystallographic orientation of the gold surface.[5]

The 2D self-assembly of adsorbed Pc and P molecules also can be directed by selectively controlling noncovalent intermolecular interactions such as van der Waals attraction and hydrogen bonding.[6–8] The best-known examples of hydrogen bonding-driven surface assembly include data reported by Hipps, Yokoyama, and Griessl. Hipps and co-workers found the formation of a new well-ordered 2D structure with 1:1 stoichiometry of $F_{16}CoPc$ and NiTPP on gold by vapor-phase deposition in UHV.[6] Yokoyama observed small clusters and chains of CN-substituted porphyrins vacuum deposited on Au(111) in a low-temperature STM environment.[7] Griessl and co-workers

studied the extensive hydrogen bonding networks formed by trimesic acid on graphite.[8]

All of the above methods for monolayer formation share a common failing—they produce monolayers that are not substrate location-selective. Because the final layer is physisorbed rather than chemisorbed, almost any surface the adsorbate hits will support it (snow on a field). Given a complex device structure with exposed surfaces of various metals and semiconductors, all of the surfaces will be coated.

A pathway to the 2D architecture of physisorbed complex molecules that has not been explored is the formation of self-organized molecular monolayers by spontaneous redox processes at the substrate surface. In this report, we present a generalized approach where a soluble species having a redox reaction induced by a metal electrode spontaneously decomposes to a well ordered physisorbed layer of insoluble product upon electrical contact with that metal. The chemistry described here is very different from that of the conventional thiol or thiolate precursor SAM films. In those systems, the final monolayer is chemisorbed to the substrate surface.[9] The procedure presented here does not require complex vacuum technology. Rather, it relies on solubility partitioning between solution and adsorbed phases, and it can create very reproducible well-ordered submonolayers, monolayers, and multilayers. We note that we previously observed the conversion of soluble FePcCl to insoluble FePc by spontaneous reduction on an aluminum surface.[10] In that work, however, we did not determine the surface structure of the adsorbed layer.

Here we demonstrate the formation of a stable 2D assembly of CoPc from solution via spontaneous redox reactions between a biaxially substituted dicyano cobalt phthalocyanine salt, $MCoPc(CN)_2$ (M = K, Cs), and a gold substrate. We selected the $CoPc(CN)_2^{-1}$ ion (shown in Figure 1) because of its chemical stability and solubility in simple organic solvents. Its X-ray structure has been reported.[11]

The process by which the CoPc adlayer is formed on the gold electrode can be elucidated in part from the cyclic voltammetry (CV) studies of $MCoPc(CN)_2$ reported by Hanack and co-workers.[12] On the basis of their voltammetric data, Hanack proposed that in acetone $MCoPc(CN)_2$ is oxidized to a

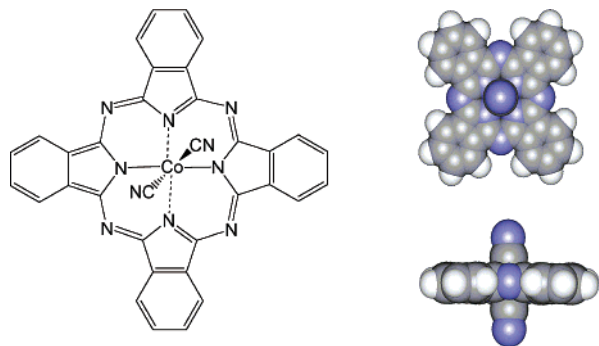* Corresponding author. E-mail: hipps@wsu.edu.

**Figure 1.** Molecular structure of the CoPc(CN)$_2^-$ ion, which measures approximately 1.4 nm across and 0.61 nm along the NC−Co−CN fragment.

neutral radical, CoPc(CN)$_2$. The oxidization potential ($E_{1/2}$) of MCoPc(CN)$_2$ in acetone and 0.1 M Bu$_4$NClO$_4$ was measured at 0.88 V (sce). Applying our orbital-mediated tunneling (OMT) model to this process, we predict that an $E_{1/2(oxd)}$ of 0.88 V (sce) is equivalent to 5.29 V relative to the vacuum state.[10] That value is very close to the measured work function for Au(111), 5.3 V. Thus, we expect CoPc(CN)$_2^{-1}$ in contact with the Au(111) to oxidize spontaneously to the radical. We have found that the CoPc(CN)$_2$ radical then follows a complex redox pathway with the eventual formation of neutral and insoluble CoPc derivative species adsorbed on the gold surface. Upon low temperature (110 °C) annealing in vacuum, this monolayer converts completely to cobalt(II) phthalocyanine. We note here that the isolated MCoPc(CN)$_2$ salt is stable to 300 °C before the first cyanide is cleaved from the cobalt ion.[13]

### Experimental Section

The ionic complex, MCoPc(CN)$_2$ (M = K or Cs), was prepared and purified by published methods.[13] Elemental analysis, ^{1}H NMR, and infrared spectroscopy confirmed the purity. Well-organized phthalocyanine monolayers on Au(111) were formed by exposing freshly annealed Au(111) substrates to a 10$^{-6}$ M ethanolic solution of the MCoPc(CN)$_2$ complex for 10 min, washing with a small amount of ethanol, and drying under a gentle flow of inert gas for 15 min. A high-vacuum multipurpose deposition chamber was used for the preparation of CoPc submonolayers on Au(111)/mica samples by vapor deposition. CoPc was purchased from Strem Chemicals[14] and twice sublimed before it was deposited from a tantalum box source. Both solution- and vacuum-deposited samples were transported in air to the load lock of the XPS where they were analyzed under UHV.

Scanning tunneling microscopy (STM) was performed both in air and in UHV. The ambient STM images were collected using a Digital Instruments stand alone head and a Nanoscope E controller, and the UHV STM data were obtained with an RHK Technology[15] microscope (model UHV300) and control electronics (model SPM100). Images were plane fit and low-pass filtered. STM tips were prepared from 0.25-mm W by electrochemical etching or from Pt$_{0.8}$Ir$_{0.2}$ wire by mechanical cutting. W tips always required additional cleaning once in UHV. XPS analysis was performed on a Kratos Axis-165 electron spectrometer having a base pressure of 5 × 10$^{-10}$ Torr. Monochromatic radiation from an Al Kα X-ray source was used for excitation. Samples could be heated and cooled in place in the XPS system.

### Results and Discussion

Solution-grown specimens were first examined in air by STM and then transferred into the UHV chamber housing either the RHK STM or the XPS system. Parts a and b of Figure 2 show typical large-scale STM images of Pc adlayers formed by exposing Au(111) to KCoPc(CN)$_2$ solution. Samples were washed with ethanol and dried prior to measurement. Similar results were obtained from CsCoPc(CN)$_2$ solution. Image 2a was acquired in air. Micrographs such as 2a were obtained with a high level of reproducibility, and samples were stable for at least 1 day when stored in a desiccator. Images b and c of Figure 2 were obtained in an UHV environment after annealing the solution-grown sample at 110 °C for a few minutes.

Large-scale images show well-ordered 2D assemblies with distinct molecules. Measurements made in air also show random groupings of molecules well separated from islands and high spots associated either with axially substituted phthalocyanines or adsorbates on the Pc layer. These isolated molecules and small clusters are not usually observed at room temperature in CoPc films vapor deposited on Au because the CoPc−Au interaction is too weak and there is rapid diffusion of molecules between islands. We were unable to obtain submolecular resolution images in air. This may be due to the mixed composition of the initially formed layer (vide infra) or to a CoPc−O$_2$ adduct that may form under these conditions.[16]

It is useful to note that the STM image obtained in air from the as-deposited solution is less densely packed than that of the annealed monolayer. Figure 2a shows rows with an internal spacing of about 1.2 nm but a row−row spacing of about 1.7 nm. In contrast, the interatomic spacing in parts b and c of Figure 2 is 1.2 nm in any direction. After annealing, the structure is defined by a much denser square unit cell. The origin of this structural change is still unclear but is probably related to the
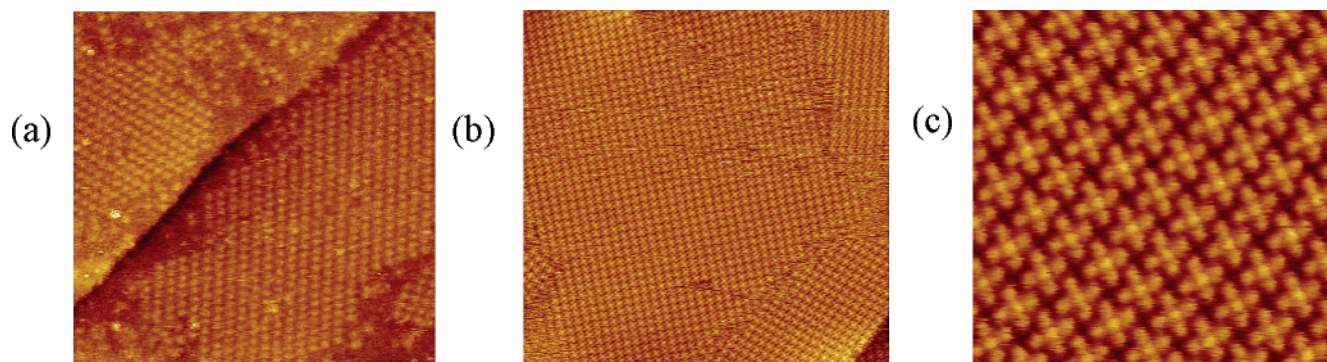


**Figure 2.** STM micrographs of Au(111) exposed to 10$^{-6}$ M ethanolic KCoPc(CN)$_2$ for 10 min and washed with ethanol: (a) 50 × 50 nm$^2$ image acquired in air with 0.8-V bias voltage and 180-pA tunneling current, (b) 50 × 50 nm$^2$ image, and (c) high-resolution 10 × 10 nm$^2$ image. Both b and c were obtained under UHV conditions after annealing at 110 °C. Sample bias and tunneling current were +0.32 and +0.75 V and 100 pA, respectively, for images b and c. A PtIr tip was used for all three images.
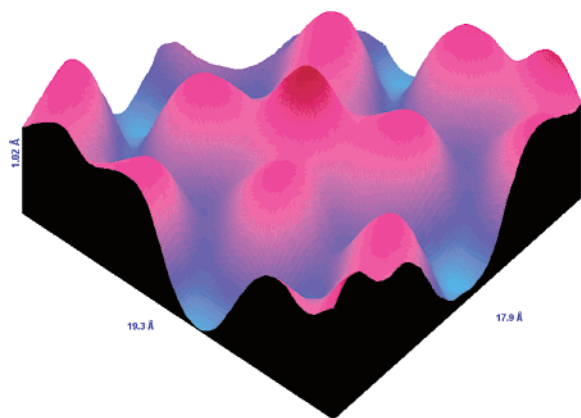
Letters

*J. Phys. Chem. B, Vol. 108, No. 44, 2004* **17005**



**Figure 3.** Correlation-averaged 3D image of a single CoPc molecule on Au formed from redox adsorption from solution.

mixed composition (vide infra) of the as-formed monolayer. Alternatively, the coadsorption of solvent may also influence the as-grown structure.

Details of the internal structure, orientation, and packing of the adsorbed complex are seen in the high-resolution image (Figure 2c) obtained in UHV after sample annealing. Individual phthalocyanine molecules can be recognized by their clover-leaf shapes with a central peak and four additional spots at the corners. To better define the single-molecule constant current contour, we performed a correlation average on the data in Figure 2c, and a highly accurate image results (Figure 3). In this low-noise, high-resolution image, one may observe that the benzene rings of the Pc ring are more effective conductors than the five-membered rings. The large characteristic increase in the tunneling probability at the center of the molecule has been attributed to the half-filled $d_{z^2}$ orbital acting as an atomic wire. The apparent height at the molecular center is lower than expected for the case of cyano substitution, but this is NOT a definitive test. Note that although alkali ions can be observed in STM[17] no features attributable to either potassium or cesium ions have been seen in our STM studies.

XPS analysis of both the unannealed and annealed CsCoPc-(CN)$_2$ ethanolic solution samples (after washing) shows that there is less than 5% of the expected Cs/Co ratio. That is, there was no detectable Cs in the XPS of the adsorbed film. Thus, the surface species is clearly a neutral complex. The Co 2p region of the XPS is also very informative. Initially (lower curve of Figure 4) there are both Co$^{2+}$ and Co$^{3+}$ species present on the surface, with peaks near 778.2 and 780.2 eV assigned to the 2p$_{3/2}$ transition in Co$^{2+}$ and those near 779.7 and 781.1 eV being due to Co$^{3+}$. With annealing at 100 °C for 10 min, most of the surface layer has been converted to Co$^{2+}$. After annealing at 110 °C, the Co 2p XPS becomes identical to that of authentic CoPc (top curve of Figure 4).

Our interpretation of these results is that the initial monolayer is a mixture of CoPc and a monoaxially substituted cobalt(III) phthalocyanine. Upon annealing, the axial ligand is removed with the donation of one electron to form the final CoPc monolayer. This model is supported by the fact that the N 1s peak in the XPS shifts by only 0.2 eV throughout the entire conversion process. Thus, the Pc ring is most likely in the −2 state throughout. That the final (annealed) species is unsubstituted CoPc is born out by the following: (1) the XPS spectral positions and the C/N ratio, which is identical to that of authentic CoPc, (2) the fact that the species is neutral (no alkali metal ions present), and (3) the STM images of both the individual molecules and of the overall lattice are identical to those of vapor-deposited CoPc on Au(111).
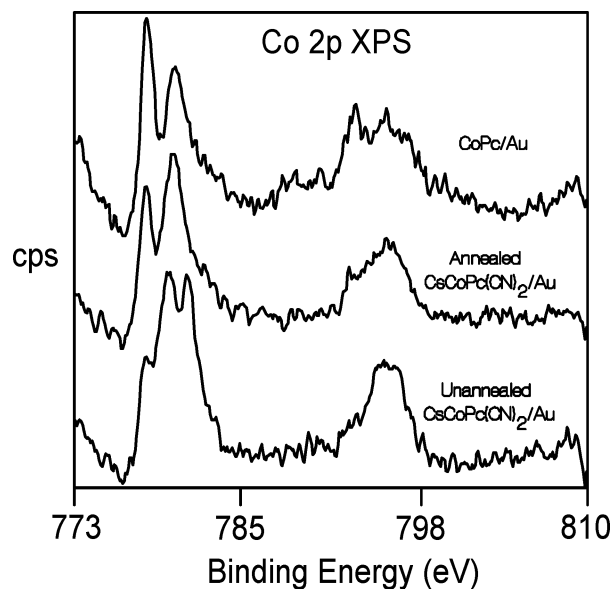


**Figure 4.** XPS of the Co 2p region of phthalocyanine complexes on Au(111).

Our proposed mechanism begins with the spontaneous oxidation of MCoPc(CN)$_2$ by gold, driven essentially by its rather large work function. To test this, we have performed XPS studies of the solution-phase adsorption on both gold and aluminum. (Al has a work function about 1 eV less than that of Au.) We find that, as expected, the initial reaction occurs rapidly with gold metal, but there is no apparent reaction with aluminum. Thus, one may envisage the selective deposition of CoPc upon gold contacts in the presence of a number of other materials (including copper, aluminum, and silicon) that have significantly smaller work functions than does gold. In fact, by tailoring the redox potential of the initial reaction and the relative solubility of the initial and final species, one could tailor the selective deposition of materials where the final product is only physisorbed to the surface. For example, a species that was reduced at about −0.4 V (sce) and became insoluble would be selectively deposited on aluminum but not on gold or silicon. In contrast, either vapor- or solution-phase deposition of the desired material would coat the entire surface.

**References and Notes**

(1) Hecht, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 24.

(2) Scudiero, L.; Barlow, D. E.; Hipps, K. W. *J. Phys. Chem. B* **2000**, *104*, 11899. (b) Scudiero, L.; Barlow, Dan E.; Hipps, K. W. *J. Phys. Chem. B* **2002**, *106*, 996. (c) Hipps, K. W.; Barlow, Dan E.; Mazur, U. *J. Phys. Chem. B* **2000**, *104*, 2444. (d) Hipps, K. W.; Barlow, Dan E.; Mazur, U. *J. Phys. Chem. B* **2000**, *104*, 5993.

(3) Scudiero, L.; Barlow, D. E.; Mazur, U.; Hipps, K. W. *J. Am. Chem. Soc.* **2001**, *123*, 4073.

(4) Lei, S.; Wang, J.; Dong, Y.; Wang, C.; Wan, L.; Bai, C. *Surf. Interface Anal.* **2002**, *34*, 767. (b) Lei, S.; Wang, C.; Yin, S.; Bai, C. *J. Phys. Chem. B* **2001**, *105*, 12272. (c) Lei, S.; Wang, J.; Dong, Y.; Wang, C.; Wan, L.; Bai, C. *Surf. Interface Anal.* **2002**, *34*, 767.

(5) Suto, K.; Yoshimoto, S.; Itaya, K. *J. Am. Chem. Soc.* **2003**, *125*, 14976. Yoshimoto, S.; Tada, A.; Suto, K.; Itaya, K. *J. Phys. Chem. B* **2003**, *107*, 5836−5843.

(6) Hipps, K. W.; Scudiero, L.; Barlow, D. E.; Cooke, M. P., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 2126. (b) Scudiero, L.; Hipps, K. W.; Barlow, D. E. *J. Phys. Chem. B* **2003**, *107*, 2903.

(7) Yokoyama T.; Yokoyama, S.; Kamikado, T.; Okuno, Y.; Mashiko, S. *Nature* **2001**, *413*, 619.

(8) Griessl, S.; Lackinger, M.; Edelwirth, M.; Hietschold, M.; Heckl, W. M. *Single Mol.* **2002**, *3*, 25.

(9) *An Introduction to Ultrathin Organic Films*; Ulman, A., Ed.; Academic Press: San Diego, CA, 1991.

(10) Mazur, U.; Hipps, K. W. *J. Phys. Chem. B* **1999**, *103*, 9721.

(11) Inabe, T.; Maruyama, Y. *Bull. Chem. Soc. Jpn*. **1990**, *63*, 2277.

(12) Leverenz, A.; Speiser, B.; Hanack, M. *J. Electroanal. Chem.* **1992**, *232*, 273. (b) Bchnisch, B.; Leverentz, K.; Hanack, M. *Synth. Met.* **1991**, *41−43*, 267.

(13) Metz J.; Hanack, M. *J. Am. Chem Soc*. **1983**, *105*, 828. (b) Orihashi, Y.; Nishikawa, M.; Ohno, H.; Tsuchida, E.; Matsuda, H.; Nkanishi, H.; Kato, M. *Bull. Chem. Soc. Jpn*. **1987**, *60*, 3731.

(14) Strem Chemicals, Inc. Newburyport, MA.

(15) RHK Technology, Inc. Troy, MI.

(16) Yoshimoto, S.; Tada, A.; Suto, K.; Narita, R.; Itaya, K. *Langmuir* **2003**, *19*, 672.

(17) Kim, Y. G.; Yau, S. L. Itaya, K. *J. Am. Chem. Soc*. **1996**, *118*, 393. (b) Stuhlmann, C.; Villegas, I.; Weaver, M. J. *Chem. Phys. Lett.* **1994**, *219*, 319.