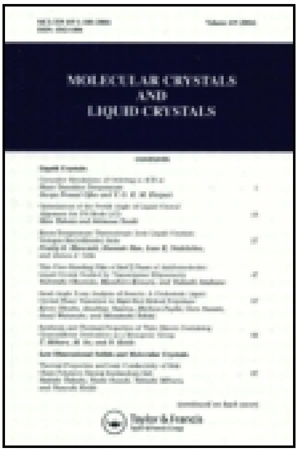

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Jeffrey T. Culp [a], A. NICOLE Morgan [b], Mark W. Meisel [b] & Daniel R. Talham [a]

[a] Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL, 32611-7200

[b] Department of Physics, University of Florida, P.O. Box 118440, Gainesville, FL, 32611-8400

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# Assembly of a Two-dimensional Cobalt-iron Cyanide Grid Network at an Air-water Iinterface

JEFFREY T. CULP[a], A. NICOLE MORGAN[b],
MARK W. MEISEL[b] and DANIEL R. TALHAM[a,*]

[a]*Department of Chemistry, University of Florida, P.O. Box 117200*
*Gainesville, FL, 32611-7200,*
[b]*Department of Physics, University of Florida, P.O. Box 118440,*
*Gainesville, FL, 32611-8400 and*
**Author to whom correspondence should be addressed.*

Reaction of an amphiphillic pentacyanoiron(III) complex with aqueous cobalt(II) ions at the air-water interface yielded a two-dimensional (2D) cobalt(II)-iron(III) cyanide network. The Langmuir monolayers were characterized by pressure vs. area isotherms. The cyanide-bridged networks were transferred to solid supports by the Langmuir-Blodgett technique. Multilayer films were structurally characterized by FT-IR and UV-VIS spectroscopies, X-ray diffraction and SQUID magnetometry.

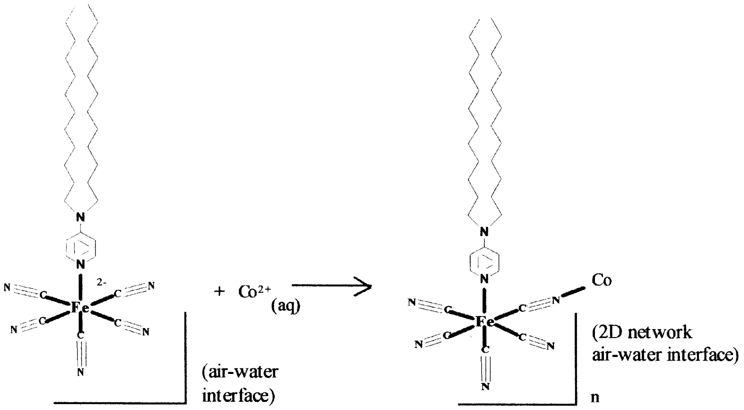
Keywords supramolecular assembly; two-dimensional networks; interface

## INTRODUCTION

There has been a growing interest in the use of supramolecular chemistry to form coordinate covalent network solids[1,2] and supermolecules.[3,4] These materials are being pursued for their potential magnetic, optical, electronic, catalytic, and host/guest properties. To expand the potential application of these materials, new synthetic methods to prepare supermolecular objects at interfaces need to be developed. Recently, the ability to form supermolecular complexes at an interface was demonstrated by the self-assembly of a 3 x 3 silver grid on the water surface.[5] We herein report the successful preparation of an extended 2D metal cyanide grid network at the air-water interface and the transfer of this network to solid supports by the Langmuir-Blodgett technique.

## EXPERIMENTAL

The ligand 4-didodecylaminopyridine (DDAP) was prepared by reaction of 1-bromododecane with N-methyl-4-aminopyridinium iodide in acetonitrile. The ligand was deprotected in molten pyridinium chloride at 190°C. Formation of the amphiphillic complex pentacyano-(4-didodecylaminopyridine)ferrate(III) (FeDDAP) was achieved by reaction of DDAP with a methanolic suspension of $Na_3Fe(CN)_5NH_3$ (Aldrich) in air analogous to a previously reported procedure for the preparation of pentacyano-(4-octadecylamino-pyridine)ferrate(III).[6]



**SCHEME 1.** The assembly strategy used for the formation of a 2D Fe-CN-Co grid network at the air water interface.

## RESULTS

The assembly process used to form the 2D grid network is outlined in scheme 1. Central to the strategy is the use of the amphiphillic complex FeDDAP. The amphiphillic nature of FeDDAP allows for the confinement of the supramolecular building block to the air/water interface. The ensuing reaction with aqueous $Co^{2+}$ ions in the subphase results in the 2D growth of the Fe-CN-Co inorganic network at the water surface. Thus, the water surface works in tandem with the complex geometries to direct the architecture of the final array.

Performing the reaction at the water surface allows one to monitor the assembly process via surface pressure vs. area isotherms. The surface pressure as a function of mean molecular area for FeDDAP spread over $Na^+$ (1mM) and $Co^{2+}$ (0.5mM) subphases was monitored using a Wilhelmy balance. The resulting isotherms are shown in figure 1. Compression over a subphase containing $Co^{2+}$ ions yielded an isotherm with an onset area smaller than the corresponding one over a $Na^+$ subphase. The isotherm over the $Co^{2+}$ subphase also showed a steeper slope and lower mean molecular area at collapse.

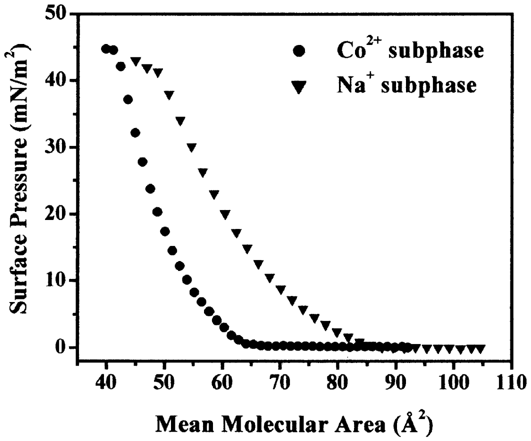


**FIGURE 1.** Surface pressure versus area isotherms for FeDDAP over 1 mM $NaNO_3$ and 0.5 mM $Co(NO_3)_2$ subphases.

This behavior indicates a condensation reaction has occurred between the FeDDAP complex and the aqueous $Co^{2+}$ ions. Furthermore, linear extrapolation of the steepest part of the isotherm over the $Co^{2+}$ subphase intercepts the x-axis at a mean molecular area of approximately 54 $Å^2$/molecule. This mean molecular area is what would be expected if the FeDDAP complex was confined to a 2-D face-centered square-grid with a cell edge of 10.4 Å.

To further characterize the product of the condensation reaction, multilayer films of the Fe-CN-Co networks were deposited by the Langmuir-Blodgett technique onto glass slides made hydrophobic by treatment with octadecyltrichlorosilane. The transfer ratio of the cross-linked films was improved to unity by making the subphase 0.5mM in $Co(NO_3)_2$ and 2 mM in $CsNO_3$ and transferring at a surface pressure of 25 mN/m. The multilayer films were then characterized by UV-Vis and FT-IR spectroscopies and X-ray diffraction.

## Structural characterization

Pentacyano-(4-aminopyridine)ferrate(III) complexes possess a strong ligand to metal charge transfer band in the visible region of the spectrum.[6,7] This band position is solvent dependant, and occurs between 550 and 700 nm. The presence of this band in the absorbance spectrum of a 15 bilayer FeDDAP-Co film, shown in figure 2, indicates the FeDDAP complex remains intact and is not significantly hydrolyzed in the course of the reaction. The intensity of this band increases linearly as a function of total layers transferred showing that similar amounts of film are transferred in each deposition and that the FeDDAP complex is stable on the water surface over the *ca.* two hours of film deposition.

Convincing evidence for a cyanide-bridged network is seen in the FT-IR spectra of the transferred FeDDAP-Co films. The absorbance spectrum of the FeDDAP complex in a KBr pellet shows two strong absorption bands due to CN stretching vibrations at 2056 and 2116 $cm^{-1}$. The absorbance spectrum of a 30 bi-layer FeDDAP-Co film taken in transmission through a glass slide shows these same cyanide stretches at 2105 and 2155 $cm^{-1}$. This shift to higher wave-number in the cyanide stretching vibrations is typical for cyanides in a bridging mode. The same splitting pattern observed for the cyanide vibrations in the FeDDAP-Co films and the FeDDAP KBr pellet also

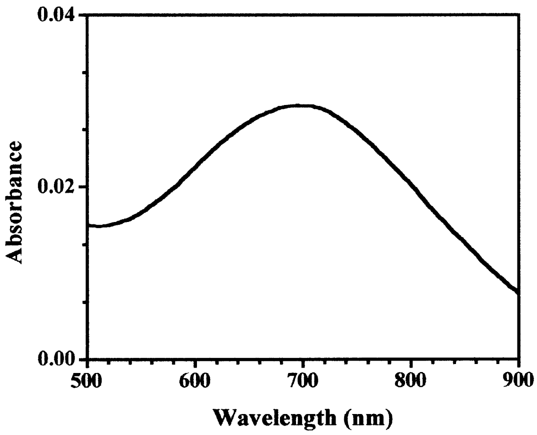


**FIGURE 2.** UV-Vis spectrum of a 15 bilayer sample of FeDDAP-Co showing the ligand-to-metal charge transfer band.

indicates that the site symmetry around the iron is similar in the starting complex and the bridged network in the films, lending further evidence that the iron complex remains intact through the assembly process.

The layered nature of the multilayer assemblies was confirmed by X-ray diffraction. An intense (0 0 1) reflection was observed corresponding to an interlayer spacing of approximately 35 Å.

Further evidence for the formation of a coherent covalent network in these materials was obtained by SQUID magnetometry. Magnetic measurements on a FeDDAP-Co film transferred to Mylar showed an increase in the product of the susceptibility and temperature as the temperature decreased. This behavior is indicative of the development of an exchange-induced magnetic moment at low temperature. The exchange interaction in these materials is expected to be antiferromagnetic as the mismatch in spin values between S=1/2 Fe(III) and S=3/2 Co(II) leads to an S=1 ferrimagnetic state at low temperatures. Similar magnetic behavior has been reported in the three dimensional Fe(III)-Co(II) "Prussian blue" analogues.[8]

## CONCLUSIONS

A 2D grid network has been prepared at the air-water interface by the reaction between an amphiphillic pentacyano-ferrate(III) complex and aqueous $Co^{2+}$ ions. Pressure versus area isotherms of the FeDDAP-Co Langmuir monolayers indicate a 2D condensation reaction occurs on the water surface. The FeDDAP-Co network can be transferred to solid supports by the Langmuir-Blodgett technique. These transferred films were shown to be lamellar by X-ray diffraction. FT-IR spectroscopy of the 2D networks shows the cyanide in a bridging mode. Magnetic measurements on the cyanide bridged assemblies verify the formation of an extended magnetic Fe(III)-CN-Co(II) network coherent over several unit cell lengths. This assembly process demonstrates the potential for using an interface as a structure directing entity in the formation of extended inorganic solids.

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