

MORPHOLOGICAL AND MAGNETIC PROPERTIES OF AXIALLY MODIFIED COBALT-PHTHALOCYANINE THIN FILMS ONTO HOPG

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ABSTRACT

In this work, the morphological and magnetic properties of molecular thin films of Co phthalocyanine complexes electrodeposited onto highly oriented pyrolytic graphite surfaces by using cyclic voltammetry techniques were investigated. In order to study the influence of various cyano ligands axially coordinated to the central metal ion, three different PcCo complexes $\text{PcCo}(\text{CN})_2$, $[\text{PcCoCN}]_n$, and $[\text{PcCo}(\text{CN})\text{L}]$ $\text{L}=1,8$ - dihydroxyantraquinone) were studied. From the molecular characteristics, it was observed that the highest conductivity and highest roughness value was found for the $\text{PcCo}(\text{CN})_2$ specie in comparison with the other two compounds. Finally, by using Magnetic Force Microscopy, it was also noticed that the presence of the shorter double-cyano group in the molecule produced larger aggregates with multimagnetic domain states.

Keywords: phthalocyanine; electrodeposition; AFM; MFM.

PROPIEDADES MORFOLÓGICAS Y MAGNÉTICAS DE PELÍCULAS DELGADAS DE FTALOCIANINAS DE COBALTO AXIALMENTE MODIFICADAS SOBRE HOPG

RESUMEN

En el presente trabajo, son estudiadas la morfología y las propiedades magnéticas de películas delgadas de ftalocianinas de cobaltoelectrodepositadas mediante Voltametría Cíclica, sobre sustratos de grafito pirolítico. Con el fin de estudiar la influencia de ligantes coordinados al ion metálico central, se han sintetizado y estudiado $\text{PcCo}(\text{CN})_2$, $[\text{PcCoCN}]_n$, y $[\text{PcCo}(\text{CN})\text{L}]$ $\text{L}=1,8$ -dihidroxiantraquinona. La película delgada electrodepositada que presenta la más alta rugosidad y conductividad es la referente al compuesto $\text{PcCo}(\text{CN})_2$, por otro lado: utilizando Microscopía de Fuerza Magnética se ha encontrado que el ligante ciano en la molécula, produce estados de dominio multimagnético.

Palabras claves: Ftalocianina; Electrodeposición; MFA; MFM.

INTRODUCTION

Nowadays, phthalocyanines complexes have been extensively used to produce novel materials with important conductive characteristics due to their coordination, optical, structural and electronic properties [1,2]. In particular, metallic phthalocyanines (MPcs) have been employed to produce low dimensional conductive

films by changing the degree of oxidation, molecular arrangement and chemical specie of the central ion [3,4]. Moreover, it is well known that molecular characteristics such as size, shape and coordination state, among others, are critical to achieve metallic conductivity characteristics due to large π -conjugated properties and the assembly into cofacially-stacked arrays [5]. Although

the conduction path in these systems has been mainly associated to the π - π overlap of the stacked molecules, it has been noticed that the conductivity can be modified or enhanced by adding organic bridging ligands which allow electron migration from one metal atom to the other [6,7]. It has also been observed, that the introduction of axial coordinated ligands to the central metal atom has a strong influence on the electronic structure of the molecule, since the π -electronic distribution dipole moment of the central metal-axial ligand bond is modified [8]. The axial substitution can also modify the electronic structure of the phthalocyanine, since the spatial relationship between neighboring molecules and the magnitude of the intermolecular interactions change due to steric effects, among others. Additionally, it has been noticed that large axial coordinated ligands are able to change not only the packing arrangement but also their aggregation state. Furthermore, by combining the metal ion of the core in a polymeric chain, special properties such as the electrical conductivity of the compound can be also modified [9, 10]. As a result, a rich variety of molecular conductors have been created by adding or modifying the structure of the ligand, since it changes the physical properties of the assembly [11]. In particular, it has been observed that the presence of cyano groups as bridging ligand improves the conductive properties of materials since they act as mediators in electron transfer processes [12]. In the case of metallic nanoparticles, a better stability and collective magnetic behavior have been observed [13].

On the other hand, recent research work has been oriented to improve the formation of phthalocyanine thin films. For instance, vapour deposition methods have been commonly used to grow thin films of phthalocyanine complexes [14-16]. Nowadays, different techniques such as self-assembly and electrodeposition have also been employed to produce thin molecular films

since phthalocyanines can dissolved in organic or aqueous solutions [17-19]. On the other hand, it has been noticed that the incorporation of solvent molecules into the film lattice tunes the interaction giving rise an increase in the electrical conductivity [20].

Finally, magnetic studies of phthalocyanine thin films have been small although it is well known that they exhibit different magnetic properties when different core transition metal atoms are employed [21]. Nevertheless, magnetic studies of phthalocyanine thin films have been carried out by using Electron Paramagnetic Resonance [22] and superconducting quantum interference devices (SQUID) [23, 24], among others. Unfortunately, little has done to investigate the film magnetic properties locally by using magnetic force microscopy (MFM) [25].

Therefore, in this work, we studied the morphological and magnetic properties of phthalocyanine thin films prepared by electrochemical techniques. The morphology and magnetic properties of each film were investigated by using scanning electron microscopy (SEM), atomic force microscopy (AFM) and magnetic force microscopy (MFM), respectively.

MATERIALS AND METHODS

The complex (cyano)(phthalocyaninate)Co(III) or $[\text{PcCoCN}]_n$ was synthesized from a cobalt(II) phthalocyanine as reported elsewhere [26]. The 1,8-dihydroxyanthraquinone compound was used from a commercial supplier and used without further purification. The synthesis description of the three compounds employed in this work is shown below.

Synthesis of PcCo(CN)_2 . 0.57g of Cobalt (II) phthalocyanine and 0.98g (20 mmol) of sodium cyanide were suspended in 60 mL absolute ethanol. Oxygen was bubbled through the refluxing mixture for 72 h. After

filtration, a deep blue solid residue was washed several times with water. The insoluble PcCo was separated by Soxhlet extraction with dry acetone. Finally, the resulting powder (82%) was dried in vacuum with CaCl_2 . Anal. Calcd for $\text{C}_{34}\text{H}_{16}\text{N}_{10}\text{O}_5\text{CoNa}$: C, 56.20; H, 2.20; N, 19.28; O, 11.02. Found: C, 56.36; H, 2.78; N, 19.89; O, 11.76. IR (KBr, cm^{-1}) ν_{max} : 2131 (C=N).

$[\text{PcCoCN}]_n$ was prepared by extracting $\text{PcCo}(\text{CN})_2$ with water for 72 h in a Soxhlet extractor. Subsequently extraction with acetone separated the unreacted $\text{PcCo}(\text{CN})_2$, yielding a blue product (85%). Anal. Calcd for $\text{C}_{33}\text{H}_{16}\text{N}_9\text{Co}$: C, 66.34; H, 2.70; N, 21.10. Found: C, 66.86; H, 2.68; N, 19.05. IR (KBr, cm^{-1}) ν_{max} : 2158 (C=N).

The $\text{PcCo}(\text{CN})\text{L}$ complex with $\text{L} = 1,8$ -dihydroxyantraquinone was prepared by mixing 2.2 g (1.83 mol) of 1,8-dihydroxyantraquinone in 15 mL pure ethanol with 1.0 g (1.8 mmol) of $[\text{PcCoCN}]_n$ for 7 days at 50°C . In this case, covalent bonds were introduced between the hydroxyl groups and the central metal ion. The green-blue solid residue was filtered and washed several times with pure ethanol. The final product (82%) was then purified with dimethylformamide. Anal. Calcd for $\text{C}_{60}\text{H}_{28}\text{N}_8\text{O}_8\text{Co}$: C, 68.77; H, 2.67; N, 10.70. Found: C, 69.56; H, 3.99; N, 10.31. IR (KBr, cm^{-1}) ν_{max} : 1625 (C-H); 1517 (C-C); 1121 (C=N).

So, at the end of this process 3 different complexes were obtained: $\text{PcCo}(\text{CN})_2$, $[\text{PcCoCN}]_n$, and $[\text{PcCo}(\text{CN})\text{L}]$ where $\text{L} = 1,8$ -dihydroxyantraquinone.

The electrochemical deposition was carried out in a home-made three-electrode cell where highly oriented pyrolytic graphite (HOPG) was used as a working electrode, platinum wire as a counter electrode and silver wire as a reference electrode. The electrochemical experiments were run using cyclic voltammetry between the cathodic (-2.0 V) and anodic ($+2.0$ V) switching

potentials. The film formation was stopped after 40 Potential Scan Cycles (PSC). The potential scan rate was 50 mV s^{-1} in all cases. For the electrochemical deposition, the PcCo complexes were mixed in a 1:1 ratio with 10^{-2} M Tetrabutylammoniumtetrafluoroborate (TBABF) as supporting electrolyte, since it has been successfully used in the formation of conductive polymers [27] and other CoPc studies [28]. The electrochemical process was carried out with a Uniscan Instrument model PG580 in the potentiostatic mode. The surface characteristics and the chemical composition of the electrodeposited films were investigated with a scanning electron microscope (SEM) Jeol JSM5600 LV coupled to a NORAN energy dispersive spectrophotometer (EDS) working at 20 KeV. The AFM and MFM characterization of the electrodeposited films was performed *ex situ* by using the lift mode and CoCr-AFM Mikromash tips in a Jeol JSPM 4210 microscope. For the magnetic measurements a lift height of 40 nm was employed in order to separate the morphological from the magnetic interactions. In order to characterize the morphological properties of the films obtained with AFM and MFM, the WinSpmProcessing software from JEOL was employed.

RESULTS AND DISCUSSION

In Figure 1, the cyclic voltammetry plots of the electrodeposition process for all the compounds is shown. It is clear from the current values that the highest conductivity was found with the $\text{PcCo}(\text{CN})_2$ compound while the lowest conductivity corresponded to the $[\text{PcCo}(\text{CN})\text{L}]$ complex. SEM images of the electrodeposited films onto HOPG are shown. As we can see from the images all the films exhibit a fine granular texture although some small aggregates can be observed in particular for the $\text{PcCo}(\text{CN})_2$ compound. Although the surface coverage seems complete, small uncovered areas can be still observed in particular on images 2a and 2b.

These results are in agreement with the conductivity results from the cyclic voltammetry plots.

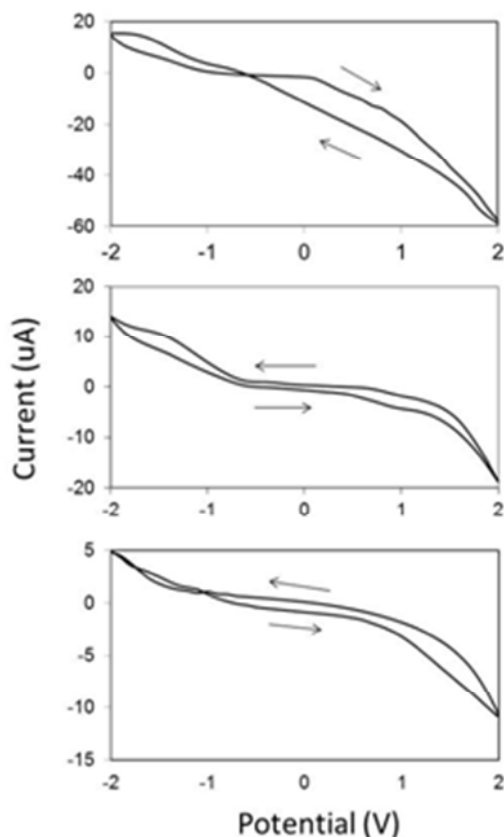


Figure 1. Cyclic voltammetry plots of the electrodeposition process onto HOPG after 40 PSC of deposition for the a) PcCo(CN)_2 , b) $[\text{PcCoCN}]_n$, and c) $[\text{PcCo(CN)L}]$ compounds.

EDS analysis of the films showed a large carbon peak that came from the electrode substrate (HOPG) and a very small cobalt due to the small amount of PcCo material in comparison with the electrode substrate.

In Figure 3, AFM images of the three films produced by the electrochemical method are shown. Here, the difference in the final aspect of the films is clear. Figure 3a shows the HOPG surface covered with small aggregates while Figure 3b shows irregular string-like features possible due to a polymerization process coming from the $[\text{PcCoCN}]_n$ compound. Finally, Figure 3c shows

a very smooth film with very small scattered aggregates which suggests a poor deposition process.

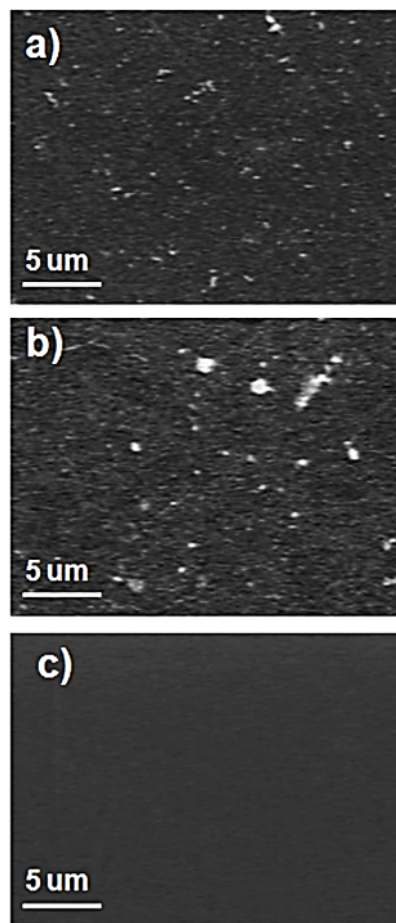


Figure 2. SEM images of the HOPG surface after 40 PSC of deposition for the a) PcCo(CN)_2 , b) $[\text{PcCoCN}]_n$, and c) $[\text{PcCo(CN)L}]$ compounds.

This results agree with the cyclic voltammetry response that showed a decrease in current values starting with the PcCo(CN)_2 , then the $[\text{PcCoCN}]_n$ and finally the $[\text{PcCo(CN)L}]$ compound, in this order. The maximum height of the aggregates was obtained by calculating the Rz value and the roughness was the root mean square (RMS) value both obtained with the processing software.

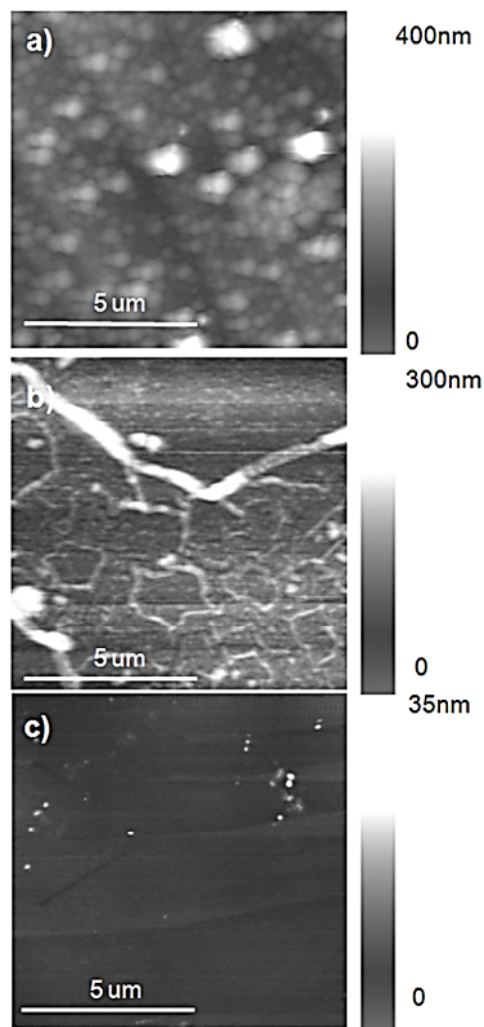


Figure 3. AFM images of the HOPG surface after film formation onto HOPG. a) PcCo(CN)_2 , b) $[\text{PcCoCN}]_n$, and c) $[\text{PcCo(CN)L}]$, respectively. Images sizes are $10 \times 10 \mu\text{m}$.

In table 1, the average height of the aggregates and mean roughness values of the films are shown. Since the average size of the aggregates was smaller than the total height of the image, it means that surface coverage was not homogenous, and therefore, some areas of the substrate were more exposed than others.

Table 1 Roughness and height analysis of the films shown in Figure 2

Compound	Roughness RMS (nm)	Height (nm)
PcCo(CN)_2	63.8	438
$[\text{PcCoCN}]_n$	49.6	327
$[\text{PcCo(CN)L}]$	7.6	57

Finally, in Figure 4, corresponding MFM images of films in Figure 3 are shown. From these images, big differences in the magnetic response are observed. During the AFM scanning, the phase-shift image caused by magnetic force was measured by lifting the cantilever with a constant distance at each point. The contrast observed in the images, suggests that the magnetic interaction depended on the aggregation since the corresponding AFM images correlate with the magnetic features. In particular, it was observed that only the aggregates thicker than 300 nm showed a magnetic interaction with the MFM tip. In Figure 4a, we can see that only large aggregates show a magnetic interaction with the AFM tip, and most of them, exhibit different contrast regions which suggest the presence of multimagnetic domain states (see inset) while the background shows a homogeneous magnetic distribution. In Figure 4b, only the thicker portions of the string-like features showed a magnetic contrast which remained constant for features of similar heights. On the other hand, features with heights lower than 300 nm do not exhibit any kind of magnetic contrast. Finally, the more regular film (Figure 4c) did not exhibit magnetic interactions and this can be attributed either to the small amount of the deposit or the homogeneity of the film. In order to further investigate how the aggregation state

influences the magnetic properties of these films different studies are currently under way.

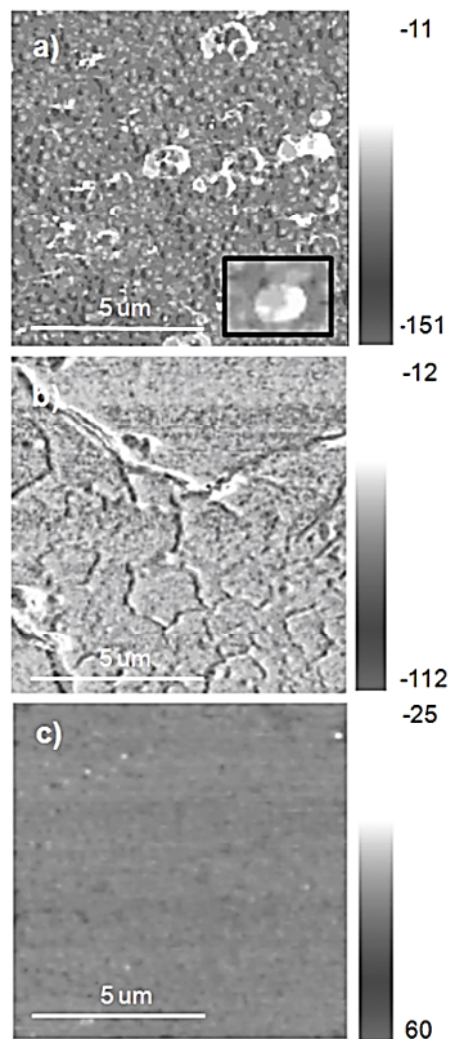


Figure 4. MFM images of the HOPG surface after film formation for the electrodeposited complexes a) NaPcCo(CN)_2 , b) $[\text{PcCoCN}]_n$, and c) $[\text{PcCo(CN)L}]$. Images sizes are 10 x 10 μm . Vertical scale in degrees.

CONCLUSIONS

By using electrodeposition methods molecular thin films from PcCo complexes modified with different cyano-bridge ligands were obtained. In terms of the ligand characteristics, the shorter cyanides axial bridges produced larger conductivities and thicker films in comparison with the polymeric and the modified 1,8-

dihydroxyantraquinone species. In addition, the last two compounds showed small conductivity responses and poor film formations. A possible explanation of these results can be related to the length of the cyano-bridges. For instance, the length of the cyano-bridge in compound PcCo(CN)_2 is shorter in comparison to the other two species, which produces a larger orbital overlap among individual molecules. This effect contributes not only to the increase in the conductivity response and but also to the magnetic properties of the film, which can be important for future technological applications.

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