

ELECTROSYNTHESIS OF IRON AND COBALT MOLECULAR MATERIALS

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ABSTRACT

Molecular materials are formed by the condensation and rearrangement of molecular units. Their microstructure is of special interest because they are generally formed by a regular molecular pattern that can generate preferential ways for electrical conduction, which is why they are sometimes called quasi-one-dimensional solids or low-dimensional linear chains. This work reports the synthesis and characterization of iron and cobalt molecular materials that were formed through an oxidation-reduction reaction in an electrosynthesis cell from electronic acceptor and donor species. Material characterization was made through infrared (IR) spectroscopy, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). These materials have a structure of polymeric chains formed from the coordination of the metallic ion to the phthalocyanine with the organic compound 1,8-dihydroxyanthraquinone. The synthesized materials show large chemical and thermal stabilities which may lead to their application in thin-film technology. Their room-temperature thermal conductivity in pellet form is of the order of $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$.

Key words: Electrosynthesis, Molecular Materials, Chemical Characterization.

ELECTROSÍNTESIS DE MATERIALES MOLECULARES DE FIERRO Y COBALTO

RESUMEN

Los materiales moleculares son aquellos formados por condensación y organización de unidades moleculares. La microestructura de estos materiales resulta fundamental, dado que están formados generalmente por apilamientos regulares de moléculas que pueden generar direcciones preferenciales para la conductividad; por esta situación, a menudo estos materiales son llamados sólidos *casi unidimensionales* o materiales de cadenas lineales de baja dimensión. El presente trabajo se refiere a la síntesis y caracterización de materiales de hierro y cobalto, formados mediante una reacción de oxido-reducción en una celda de electrosíntesis y a partir de especiesceptoras y donadoras electrónicas. La caracterización de los materiales se llevó a cabo por técnicas de análisis como Espectroscopía Infrarroja (IR), Microscopía Electrónica de Barrido (MEB) y Análisis de Energía Dispersiva (EDS). Estos materiales se encuentran en la forma de cadenas tipo poliméricas, formadas por la coordinación del ion metálico de la ftalocianina, con el compuesto orgánico 1,8-dihidroxi-antraquinona. Los materiales sintetizados presentan una alta estabilidad química y térmica, lo que los hace susceptibles a ser utilizados en la preparación de películas delgadas con propiedades eléctricas, ya que adicionalmente, presentan una conductividad eléctrica a temperatura ambiente del orden de $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$.

Palabras claves: Electrosíntesis, Materiales Moleculares, Caracterización Química.

INTRODUCTION

For the last 25 years, there has been a considerable research effort directed towards finding new materials for electronics. When these studies began, the field of inorganic materials was the only one that had been significantly explored. Organic, metal-organic and organometallic derivatives had been essentially neglected. Nevertheless, the potential of these materials in this regard became evident when it was reported that the tetrathiofulvalene-chloride salt (TTF) was a conductor at relatively low temperatures [1]. Later on, Cowan and collaborators [2] introduced the tetrathiofulvalene tetracyano- π -quinodimethane compound (TTF-TCNQ) as the first organic metal, with a conductivity approaching that of copper at room temperature.

Molecular materials are formed by the condensation and organization of molecular units that may be organic, organometallic, or metal-organic species and that can be individually characterized from their properties, such as redox potential, highest occupied orbitals and lowest unoccupied orbitals, chemical nature and polarizability, among others. Molecular materials' properties can be derived from the characteristics of those molecular units that integrate them. These materials exhibit varying electrical properties and may behave as insulators, semiconductors, conductors or superconductors [3]. Furthermore, they can be used in the production of diodes, transistors, solar cells and electronic switches, among other applications [4].

MATERIALS AND METHODS

For this work, raw materials were obtained from commercial sources without purification prior to their use. The molecular-material electro-synthesis cells were composed by two anodic and cathodic compartments separated by a porous plaque. These cells used two Pt electrodes (anode and cathode), connected to a current source of 0 to 15 μ A with variations of 0.1 μ A (Fig. 1).

The electric flow through the electrodes generates an oxidation-reduction reaction between donor and acceptor species leading to molecular-material deposition on the anodic electrode. The characterization of molecular materials was performed with IR spectroscopy, using KBr pellets in a Bruker spectrophotometer, model Tensor 27. The X-ray energy-dispersive spectrometry study was carried out with a Leica Cambridge scanning electron microscope, model Stereoscan 440, coupled to an X-ray EDS working at 20 keV. For the electro-synthesis of molecular materials, several variables, such as temperature, type of solvent, concentration of the solutions of donor and acceptor species and electric current applied, were modified according to the desired material characteristics.



Fig. 1. Electro-synthesis cell

Molecular materials were prepared from iron and cobalt phthalocyanines [5] as well as 1,8-dihydroxyanthraquinone. For the molecular material's electro-synthesis, an absolute-ethanol solution of 1×10^{-3} M of 1,8-dihydroxyanthraquinone and 1×10^{-2} M of the phthalocyanine was introduced in the anodic and cathodic compartments, respectively. An electric current of 0.9 μ A at 25°C was applied to ensure the process would be as slow as possible, thus favoring a slow crystal growth as well as the coexistence of neutral and charged molecules throughout the whole crystallization process.

NaPcCo(CN)₂ preparation. In 60 ml of absolute ethanol, dissolve 0.57 g (1 mmol) of cobalt (II) phthalocyanine and 0.98 g (20 mmol) of sodium cyanide. The mixture is kept in reflux during 72 hours in an oxygen atmosphere. After three days, the deep-blue solid is filtered and washed in distilled water and separated from the unsolved cobalt phthalocyanine by Soxhlet extraction with acetone. The product is vacuum dried with CaCl₂. The reaction yields 82%. Calculated analysis for C₃₄H₂₆N₁₀O₅CoNa: C, 56.20; H, 2.20; N, 19.28; O, 11.02. Obtained analysis: C, 56.36; H, 2.78; N, 19.89; O, 11.76. IR (KBr): $\nu(\text{C}\equiv\text{N}) = 2070 \text{ cm}^{-1}$, $\nu(\text{C-H}) = 1616 \text{ cm}^{-1}$, $\nu(\text{C-C}) = 1508 \text{ cm}^{-1}$, $\nu(\text{C-N}) = 1118 \text{ cm}^{-1}$.

Preparation of KPcFe(CN)₂. Weigh and dissolve 1.28 g of iron (III) phthalocyanine chloride and 1.47 g of potassium cyanide with 70 ml of ethanol. Keep in reflux during 72 hours. Filter, wash and dry in vacuum. Recrystallize with ethanol. 0.728 g of product was obtained with 56% yield. Calculated analysis for C₃₄H₂₆N₁₀O₅FeK: C, 55.20; H, 3.20; N, 19.28; O, 10.82. Obtained analysis: C, 55.36; H, 3.78; N, 19.89; O, 11.76. IR(KBr): $\nu(\text{C}\equiv\text{N}) = 2155 \text{ cm}^{-1}$, $\nu(\text{C-H}) = 1611 \text{ cm}^{-1}$, $\nu(\text{C-C}) = 1513 \text{ cm}^{-1}$, $\nu(\text{C-N}) = 1120 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Separate studies of the redox behavior of the phthalocyanines and the 1,8-dihydroxyanthraquinone compounds were first performed in order to find whether the corresponding radical ions would form in the molecular solid derived from both species. The most immediate information was available from cyclic voltammetry, from which one could find the potentials at which the radical ions are formed. Thus, cyclic voltammetry provided a means to test whether the acceptor electroaffinity was large enough and the donor ionization energy was small enough to allow a significant production of radical ions suitable for crystallization.

The voltametric characterization was performed with three electrodes: working electrode (platinum), reference electrode (silver/silver chloride), counter-electrode (platinum) and a solution of the initial compound with a concentration of 0.1 M in tetrabutylammonium tetrafluoroborate as supporting electrolyte. Although the oxidation and reduction potentials could not be obtained from the electrochemical studies for the different electronic acceptor and donor species that participated in the electro synthesis reaction, it was nonetheless carried out in order to synthesize iron and cobalt molecular materials as derivatives from the starting compounds.

The molecular materials obtained were the result of an electro synthesis process in which a controlled electric current in the range of μA passed through an electrochemical cell at a constant temperature (25°C). The molecular material is generated within the electrochemical cell and deposited on the anode of the cell. Table 1 shows all the operating parameters for each molecular-material synthesis.

Table 1. Operating parameters of the electrosynthesis cells

Material	Anode	Cathode	I (μA)
1	NaPcCo(CN) ₂	1,8 Dihydroxy- anthraquinone	1.2
2	KPcFe(CN) ₂	1,8 Dihydroxy- anthraquinone	1.8

IR spectroscopy was used for the characterization of the synthesized materials in order to identify their main functional groups: C \equiv N, C=O, C-O and O-H. The wavelengths corresponding to these groups were evaluated for each of the prepared molecular materials. Figure 2 shows the IR spectrum for material 1.

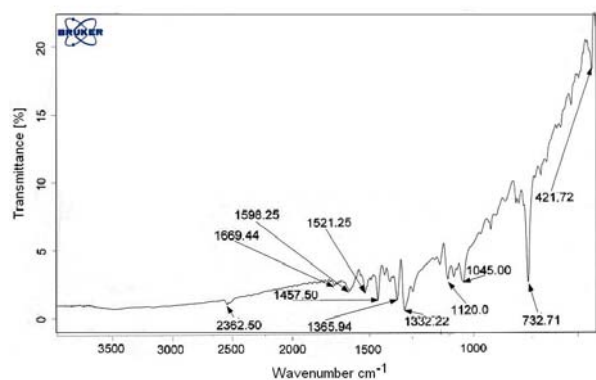


Fig. 2. IR spectrum for material 1 in KBr pellet

In order to decide whether a new material or merely a mixture of the raw materials has been formed, it is necessary to analyze the IR spectra of each of the raw materials involved, as well as the spectrum obtained for the molecular material. The presence and/or absence of certain bands corresponding to functional characteristic groups are shown in Table 2. The formation of a new molecular material can be deduced in these results, as the signs of functional groups C=O and C-O appear at the 1605 cm^{-1} and 1088 cm^{-1} wavelengths, respectively. In the IR spectrum, these signs correspond to the characteristic bands of the 1,8-dihydroxyanthraquinone raw material. On the other hand, the absence of the 2158 cm^{-1} wavelength related to the C-N group of the cobalt phthalocyanine supports the hypothesis of new molecular material formation, where 1,8-dihydroxyanthraquinone is located at the fifth and sixth position on the coordination sphere of the cobalt atom.

The results for material 2 are shown in Table 3. The presence of C=O and C-O functional groups, with wavelengths at 1600 cm^{-1} and 1328 cm^{-1} , respectively, corresponds to characteristic signs of 1,8-dihydroxyanthraquinone.

Table 2. IR characteristic bands for material 1 (cm^{-1})

IR Bands	CN ⁻	C=O	C-O	OH
NaPcCo(CN) ₂	2158	---	---	---
1,8-dihydroxy-anthraquinone	---	1600	1084	3359
Compound 1	---	1605	1088	---

Accordingly, molecular-material formation is assumed, which is corroborated by the absence of the 2158 cm^{-1} wavelength corresponding to the characteristic C-N group of iron phthalocyanate. Once again, the anthraquinone group is located at the fifth and sixth positions of the iron coordination sphere.

Table 3. IR characteristic bands for material 2 (cm^{-1}).

IR Bands	CN ⁻	C=O	C-O	OH
KFtFe(CN) ₂	2158	---	---	---
1,8-dihydroxy-anthraquinone	----	1600	1328	3359
Compound 2	---	1609	1320	---

SEM and EDS were performed in order to determine the morphology and composition of the synthesized materials in such a way that it could be possible to discard the production of a mixture of non-reacting reagents. SEM also provided further information on the morphology of such materials. Figure 3 shows the microphotographs of the synthesized materials. For material 1 (Figure 3a), and material 2 (Figure 3b), a structure formed by piled-up elements of varying sizes may be observed, with some regular edges of cubic morphology.

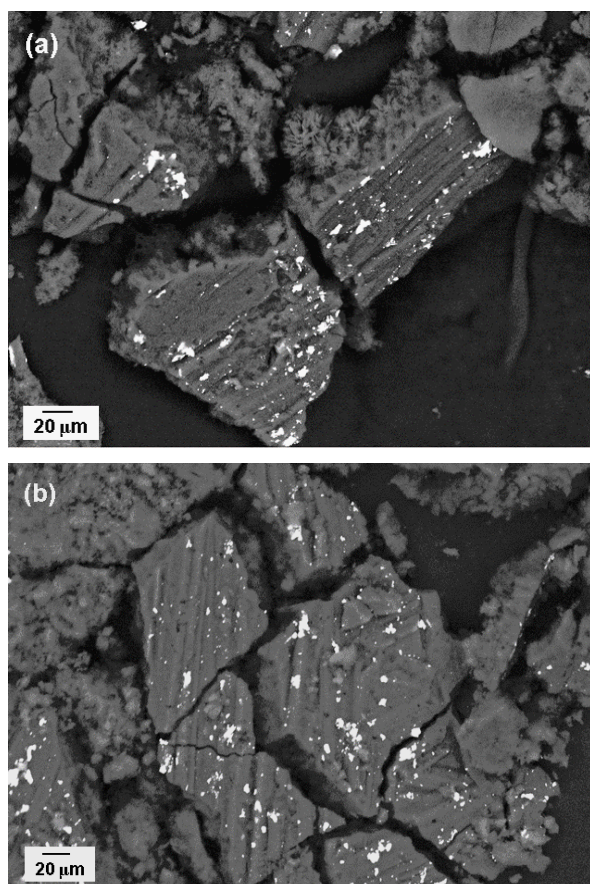


Fig. 3. Microphotographs of materials formed from (a) NaPcCo(CN)_2 and (b) KPcFe(CN)_2 at 500x.

Elemental analysis of pellets made from these compounds was performed by EDS. The pellets were placed in the specimen holder with a thin film of adhesive graphite. Figure 4 shows the EDS of material 1. Similar results were obtained for material 2. From the EDS analysis, the presence of cobalt and nitrogen atoms corresponding to the phthalocyanine derivative, as well as oxygen from 1,8-dihydroxyanthraquinone, was verified. This was just as expected and complemented the results from IR spectroscopy. The absence of sodium suggests the formation of a new molecular material in polymeric-type chains where the molecules of phthalocyanine bind to each other from the 1,8-dihydroxyanthraquinone, which is coordinated to the metallic atom. This is corroborated by the absence of the $\text{C}\equiv\text{N}$ band in the IR spectrum.

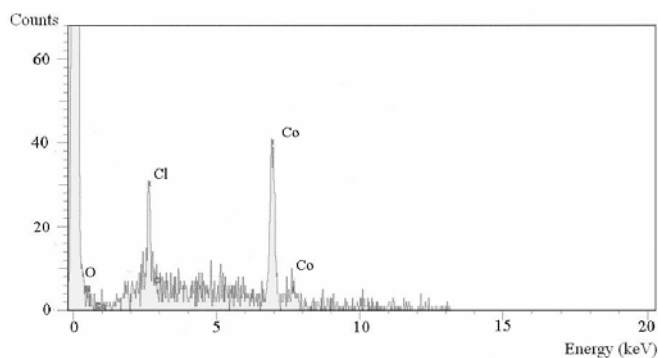


Fig. 4. EDS analysis of the electrodeposited material from the combined species NaPcCo(CN)_2 and 1,8-dihydroxyanthraquinone. The presence of reference elements is observed.

From the EDS analysis shown in Figure 5, the presence of iron and nitrogen corresponding to the phthalocyanine and the oxygen sign of 1,8-dihydroxyanthraquinone can be established. The absence of potassium suggests the formation of molecular materials in chains, where the metallic atom of the phthalocyanine coordinates to 1,8-dihydroxyanthraquinone.

The electrical conductivity of the materials in pellet form was found using the two-point method. The conductivity for both materials used was in the order of $1 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$. It is usually more accurate to evaluate the electrical conductivity from a thin film or a single crystal; nevertheless, the fact that these materials have conductivities of this order suggests that they clearly belong to the molecular-conductor category.

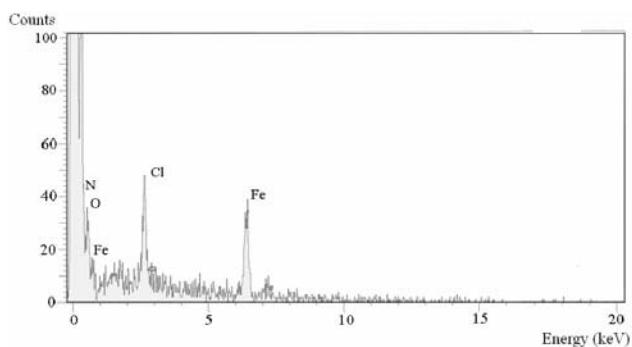


Fig. 5. EDS analysis of the electrodeposited material from the combined species KPcFe(CN)_2 and 1,8-dihydroxyanthraquinone. The presence of reference elements is observed.

CONCLUSIONS

Two new molecular materials were synthesized by electrosynthesis from phthalocyanines of iron and cobalt and 1,8-dihydroxyanthraquinone derivatives. These materials, characterized via IR spectroscopy and EDS, are in the form of polymeric chains formed from the coordination of the metallic ion to the phthalocyanine with the organic compound 1,8-dihydroxyanthraquinone. Room-temperature electrical conductivity for these materials is of the order of $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$.

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