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## THERMAL AND RAMAN SPECTROSCOPIC ANALYSIS OF COBALT-CONTAINING PHTHALOCYANINE PIGMENT

Annotation

This study presents detailed thermal analysis and Raman spectroscopic data of the synthesized cobalt phthalocyanine pigment. Thermal analysis was used to determine the thermal stability and decomposition temperatures of the pigment, while Raman spectroscopy provided insights into its molecular structure and chemical bonding. In addition, the pigment's optical properties, including its absorption and photoluminescence spectra in various solvents, were investigated to assess its light absorption capacity and emission intensity. The results demonstrate that the pigment is not only promising for use in industrial coatings but also as a high-performance material for optical applications and dye-sensitized solar cells.

**Keywords:** cobalt, phthalocyanine, pigment, thermal analysis, Raman spectrum, optical absorption, photochemical analysis.

## ТЕРМИЧЕСКИЙ И РАМАНОВСКИЙ СПЕКТРОСКОПИЧЕСКИЙ АНАЛИЗ КОБАЛЬТСОДЕРЖАЩЕГО ФТАЛОЦИАНИНОВОГО ПИГМЕНТА

Аннотация

В данной работе подробно представлены данные термического анализа и рамановской спектроскопии синтезированного красителя - кобальтфталоцианина. Термический анализ позволил определить термическую стабильность и температуры разложения пигмента, тогда как рамановская спектроскопия дала информацию о молекулярной структуре и химических связях. Кроме того, изучены оптические свойства пигмента - спектры поглощения и фотолюминесценции в различных растворителях, что позволило оценить его способность к поглощению света и интенсивность эмиссии. Полученные результаты показывают, что данный пигмент является перспективным материалом не только для промышленных красок, но и для высокоэффективных оптических и фоточувствительных солнечных элементов.

**Ключевые слова:** кобальт, фталоцианин, пигмент, термический анализ, спектр комбинационного рассеяния света, оптическое поглощение, фотохимический анализ.

## TARKIBIDA KOBALT SAQLAGAN FTALOSIANIN PIGMENTNING TERMİK VA RAMAN SPEKTROSKOPIK TAHLILI

Annotatsiya

Ushbu ishda sintez qilingan kobolt ftalosianin bo'yoq pigmentning termik analiz va Raman spektroskopik tahlil ma'lumotlari batafsil keltirilgan. Termik tahlil orqali pigmentning issiqlik barqarorligi va parchalanish haroratlari aniqlangan bo'lsa, Raman spektroskopiyasi molekulyar tuzilish va kimyoviy bog'lanishlar haqida ma'lumot beradi. Shuningdek, pigmentning optik xossalari ya'ni turli erituvchilarga nisbatan absorbsiya va fotoluminesensiya spektrlari o'rganilib, uning yorug'lik so'rinish qobiliyati va emissiya intensivligi baholandi. Natijalar pigmentning nafaqat sanoat bo'yoqlari, balki yuqori samarali optik va bo'yoq-sezgir quyosh elementlari uchun istiqbolli material ekanligini ko'rsatadi.

**Kalit so'zlar:** kobalt, ftalosianin, pigment, termik analiz, raman spektr, optik yutulish, fotokimyoviy tahlil.

**Introduction.** In our country, the growing population and the steady increase in industrial production have led to a rising demand for energy resources year by year. Today, one of the most promising and effective solutions to energy challenges is the use of solar energy. This renewable, environmentally friendly, and economically viable source holds particular scientific and practical importance, especially for the development of modern solar cells based on inorganic and organic semiconductor materials. In accordance with the tasks set out in the Resolution of the President of the Republic of Uzbekistan №.PQ-4422 of August 22, 2019, "On measures for the further development of alternative energy sources," effective research and experimental design work are actively being carried out on the synthesis of semiconductor materials intended for solar radiation utilization, as well as on technologies for their photoelectric and thermal processing [1].

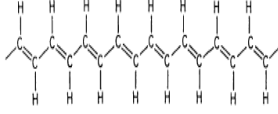
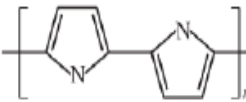
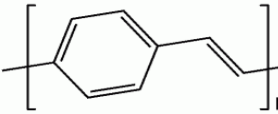
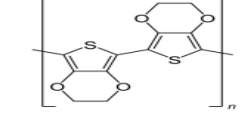
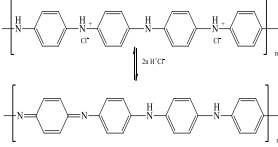
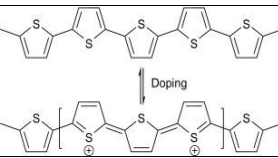
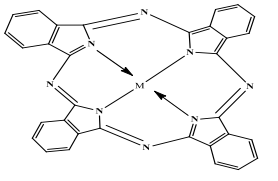
**Literature review.** Phthalocyanine-based molecular semiconductors are currently generating significant scientific interest as promising materials for various fields of organic electronics, including light-emitting elements, solar energy conversion systems, and modern nanoelectronic devices [2]. Charge transport in phthalocyanine molecules involves both electrons and holes. In such materials, under the influence of energy and temperature, the  $\pi$ -electrons in the aromatic system become activated through quantum jumps between energy levels and move in the direction of the applied electric field [3]. The presence of a metal atom at the center of the phthalocyanine structure enables interactions with multi-electron organic components, which significantly enhances overall electrical conductivity. Metal-phthalocyanines exhibit high sensitivity to chemical interactions, making them suitable for use as photoactive layers or coating materials in tandem solar cells, where they efficiently facilitate electron transfer processes. Therefore,

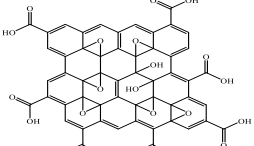
the development of organic semiconductor materials based on such structures represents one of the promising directions for their effective application in solar cells [4].

The key advantages of organic semiconductors based on phthalocyanine include their high optical and electrical activity, the possibility of synthesis using inexpensive and simple technologies, environmental safety, and economic efficiency. These characteristics make these materials an important scientific and practical platform for new research and technological directions. Today, semiconductors based on metal phthalocyanines are being successfully applied in the development of new-generation solar cells, energy storage devices, as well as sensor materials for highly sensitive gas detectors [5]. Phthalocyanine-based complexes exhibit efficient absorption of electromagnetic radiation in the visible and near-infrared regions, and are used to create complex semiconductor structures and tandem solar cells that combine the advantages of both organic and inorganic semiconductors [6]. Furthermore, phthalocyanine and its derivatives are used to fabricate molecularly structured semiconductor films, which serve as nanocomposite bases or active layers for thin-film transistors, sensor devices, photoconverters, and other types of nanoelectronic components. The unique combination of optical, electrical, and chemical properties of phthalocyanines makes them widely applicable in modern materials science and technology. The class of semiconducting polymers includes some of the most important and widely studied representatives: polyaniline (PANI), polypyrrole (PPy), polythiophene, polyacetylene, polyphenylene (PP), poly(p-phenylene vinylene) (PPV), poly(3,4-ethylene dioxythiophene) (PEDOT), polyfuran (PF), graphene and graphene oxide, as well as phthalocyanines and their derivatives containing central metal and nonmetal atoms, among others. These polymers and complex macromolecular structures possess high stability, resistance to aggressive environments, high photo- and electrical conductivity and can be integrated with flexible substrates. Table 1 below provides data on the most important and widely studied semiconducting polymers and phthalocyanine-based materials [7].

Table-1.

General information about organic semiconductor polymers and organometallic materials

№ №	Name of semiconductor materials	Year of discovery	Structural formula	Optical absorption energy band range (eV)	Conductivity S/cm-1
1 1	Polyacetylene	1977		1,5	$10^3 - 1,7 \cdot 10^5$
2	Polypyrrole	1979		3,1	$10^2 - 7,5 \cdot 10^9$
333 3	Poly(phenyl)vinylene	1979		2,5	$3 - 5 \cdot 10^3$
4 4	Poly(3,4-ethylenedioxythiophene) (PEDOT)	1980		1,5	300
5 5	Polyaniline	1980		3,2	30-200
6 6	Polythiophene	1981		2,1	$10 - 10^3$
7 7	Phthalocyanines	1907		1,4	$10^{-6} \text{ Sm}^{-1} \times \text{m}^{-1}$ $10^{-4} \text{ Sm}^{-1} \times \text{m}^{-1}$

88 8	Graphene and graphene oxide	1859		1,4	$2.98 \cdot 10^4 \text{ Sm}^{-1}$ $2 \cdot 10^2 \text{ Sm}^{-1}$
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Phthalocyanines containing metal or non-metal elements as central atoms, as well as phthalic anhydride fragments acting as ligands, form complex organometallic structures through heterocyclic compound formation. The synthesis and study of these new structures represent one of the promising scientific directions in the development of semiconductor and photoanode materials. These compounds exhibit chemical stability, are resistant to strong acids and alkalis, and possess significant optical absorption in the infrared and visible regions [8].

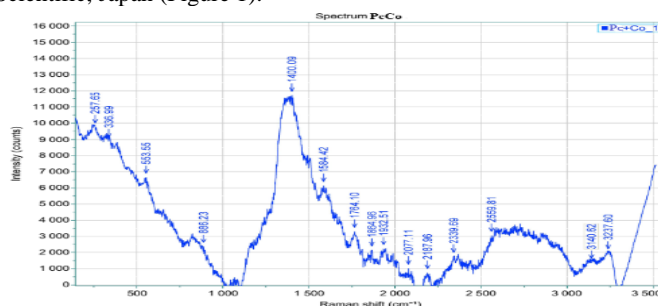
Currently, researchers such as J.B. Fayziyev, Kh.S. Beknazarov, A.T. Djalilov, and A.T. Tillayev are conducting research focused on the synthesis of complex molecular complexes based on phthalocyanine derivatives. They are also exploring methods to increase the number of macrocycles by introducing functional groups into the ligand structure that bonds with the central metal ion, with the aim of studying the electrical and optical properties of these molecules. In addition, active research is being carried out to characterize the photodynamic, optical, and electrophysical processes occurring in these complex organic semiconductors [9].

**Research methodology.** To investigate the thermal properties of the synthesized semiconducting cobalt phthalocyanine pigment, differential thermal analysis and thermogravimetric methods were employed (DTG-60, simultaneous DTA-TG, SHIMADZU). To study the pigment's composition and bonding nature, Raman spectroscopy was performed using a HORIBA instrument. The optical and semiconducting properties of the pigment were examined using a V-5000 spectrophotometer (FORTEK), and the pigment's photochemical characteristics were analyzed using digital multimeters of models III300 and DT 9205A.

### Analysis and results

#### Raman Spectroscopic Analysis of Cobalt-Containing Phthalocyanine Pigment

The Raman spectroscopic analysis of the cobalt-containing phthalocyanine pigment was carried out using an instrument manufactured by HORIBA Scientific, Japan (Figure 1).

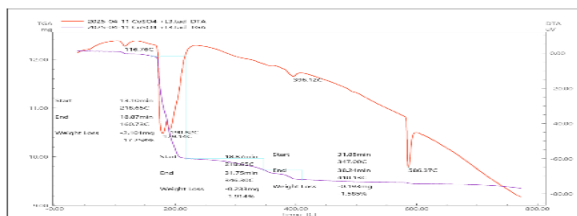


**Figure-1. Raman Spectroscopic Analysis of Cobalt-Containing Phthalocyanine Pigment.**

The following conclusions were drawn from the Raman spectroscopic analysis conducted to study the composition of the pigment. The presence of an aromatic group in the benzene ring was identified by an absorption band at  $3140.62 \text{ cm}^{-1}$ . The bands at  $3237.60 \text{ cm}^{-1}$  correspond to N-H stretching vibrations, while the band at  $2559.81 \text{ cm}^{-1}$  is attributed to  $\text{O-H}$  (hydrogen-bonded) stretching vibrations. The spectra at  $1764.83 \text{ cm}^{-1}$  are related to  $\text{C}=\text{C}$  bonds, showing stretching and intense vibrational spectra. The  $1864.96 \text{ cm}^{-1}$  band corresponds to  $\text{C}=\text{O}$  bonds, and differential vibrational bands of N-H bonds are observed at  $1584.42 \text{ cm}^{-1}$ . The spectra at  $1400.09 \text{ cm}^{-1}$  are assigned to C-H bonds, and the band at  $886.23 \text{ cm}^{-1}$  corresponds to differential bonds of Me-N [10].

#### Thermal Analysis of Cobalt-Containing Phthalocyanine Pigment

The thermal stability of the sorbent obtained by solid-phase synthesis using cobalt sulfate, urea, phthalic anhydride, and sodium borohydride was evaluated through differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a SHIMADZU-DTG-60 instrument (Japan). For the analysis, 5.485 mg of the substance (in powdered form) was placed in a porcelain crucible. The analysis was conducted at a heating rate of  $10^\circ\text{C}$  per minute up to  $800^\circ\text{C}$  under argon atmosphere (argon gas flow rate:  $80 \text{ mL/min}$ ), with T-800, TG-200, and DTA sensitivity of 1/10 galvanometer [11]. The derivatogram was recorded automatically (Figure 2).



**Figure-2. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the Cobalt-containing phthalocyanine pigment.**

A characteristic single exothermic heat release was observed in the differential thermal analysis of the cobalt-containing phthalocyanine pigment. This heat release occurred at 46.75 minutes into the analysis, at a temperature of  $396.12^\circ\text{C}$ , and concluded at 31.85 minutes, when the temperature reached  $586.37^\circ\text{C}$ . The maximum heat absorption point was observed at 38.24 minutes, at

a temperature of 410.13°C. As a result of this exothermic effect, 1.82 J (398.65 J/g), or 409.45 µcal (94.08 cal/g), of heat was released. This heat release is attributed to the decomposition of the organic component of the sample.

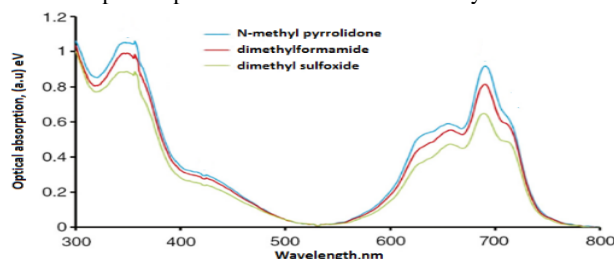
In the thermogravimetric analysis (TGA) of the sample, decomposition of the substance under the influence of temperature occurred in three stages. The first stage of mass loss began at 0.05 minutes of heating, when the temperature reached 36.92°C, and concluded at 18.87 minutes, at 116.76°C. During this stage, 2.101 mg, or 17.258% of the sample mass, was lost. The mass loss within this temperature range is attributed to the evaporation of hygroscopic water and partial decomposition of the organic component of the substance [12].

The second significant mass loss began at a temperature of 190.82°C and concluded at 346.30°C. This process started at 18.87 minutes of heating and ended at 31.75 minutes. During this stage, 1.914% of the sample mass, equivalent to 0.233 mg, decomposed. The third stage of mass loss commenced at 31.85 minutes of heating and continued until 38.24 minutes. This stage started when the temperature reached 410.13°C and continued up to 800°C. In this decomposition stage, 0.193 mg of material, corresponding to 1.585% of the sample mass, decomposed. At this stage, the organic components in the sample completely decomposed at temperatures up to 305°C. Based on the results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the sample, it can be concluded that the synthesized semiconductor pigment is thermally stable, as evidenced by the minimal mass loss during thermal analysis.

#### Optical properties of cobalt-containing phthalocyanine pigment

The absorption spectra of metal phthalocyanines exhibit two main regions with very high intensity. The first is the Soret band, located in the 300–400 nm range, which represents a high-energy strong absorption peak in the ultraviolet (blue) region. The second is the Q band, located in the 650–800 nm range, which represents a lower-energy absorption in the visible red-blue region, characteristic of the pigment's color (Figure-3) [13].

The shape and position of peaks in the absorption spectra can vary depending on the substituent groups present in the central and peripheral parts of the phthalocyanine molecule, the solubility in different solvents, and the specific features of the molecular structure. The  $\pi$ -orbitals of the ligands can act both as  $\pi$ -donors and  $\pi$ -acceptors. The orbitals of the nitrogen atoms in the pyrrole rings define the coordination of the central metal atom and, together with the  $\pi$ -orbitals, form a conjugated electron system. The graph illustrates the shifts in spectral peaks and variations in intensity under the influence of different solvents.



**Figure-3. Optical absorption spectrum analysis of cobalt-containing phthalocyanine pigment.**

This graph illustrates the shifts in spectral peaks and differences in intensity due to the influence of different solvents. In N-methylpyrrolidone, the Soret band - representing the high-energy, strong absorption peak - is observed at approximately 340 nm, while the Q band - representing the low-energy absorption peak - occurs at 675 nm. In dimethylformamide, the Soret band is located at 345 nm and the Q band at approximately 665 nm. In dimethyl sulfoxide, the Soret band appears at 335 nm, and the Q band is near 640 nm. These two optical absorption bands are critical indicators in the study of the photophysical and photochemical processes of phthalocyanines.

Additionally, the spectra of many PcM (metal phthalocyanines) exhibit three additional absorption bands in the ultraviolet (UV) region, designated as follows:

N band – 36,400  $\text{cm}^{-1}$  (275 nm)

L band – 40,800  $\text{cm}^{-1}$  (245 nm)

C band – 47,600  $\text{cm}^{-1}$  (210 nm)

The N band is the most sensitive to changes and strongly responds to variations associated with the substitution of the central metal atom. In the B and Q regions, the highest and lowest absorption bands correspond to the movement of electrons, i.e., the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), sometimes referred to as the frontier orbitals. The energy difference between these frontier orbitals (HOMO-LUMO gap) defines the optical properties of metal phthalocyanines in response to incident light and can be used to estimate the pigments' intensity, stability, and coloration in solution [14].

**Conclusion and Recommendations.** Based on the results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), the obtained pigment was found to be thermally stable. In addition, the pigment's solubility in various solvents and its optical absorption spectra - specifically, its photodynamic properties—were studied. Due to its excellent photon absorption capability in sunlight, this pigment is recommended as a semiconducting photosensitive dye for use in dye-sensitized solar cells. Furthermore, today's increasing industrial and production scales are turning energy supply into one of the most pressing global challenges. Therefore, it is necessary to further expand the use of alternative energy sources and elevate their development to a new level. The ongoing intensive research aims to broaden the application scope of cobalt-containing phthalocyanine pigment in future solar cells, photoanodes, and energy storage applications. This, in turn, will serve to ensure sustainable development, environmental balance and energy security.

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