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A NEW SOLUBLE COPPER PHTHALOCYANINE DERIVATIVE AS A SMART MATERIAL

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Abstract: Copper phthalocyanine (CuPc) and its derivatives are considered as candidate materials in many applications. Particularly, easy and sensitive film-forming ability, commercial availability, chemical stability, and ease in tailoring its molecular structure make CuPc a versatile material. On the other hand, main challenge that Pcs often exhibit is their poor solubility in organic solvents. In this sense, this work involves designing of new CuPc derivatives by introducing suitable substitutions to improve the solubility in organic solvents. Specifically, [2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)] (1) and [2,9,16,23-tetra{(4,5-Diphenyl-1-methyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)] (2) were prepared. The results show that compound 1 is soluble in tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and compound 2 is soluble in chloroform, acetone, methanol, THF, DMF, and DMSO. Optical and spectroscopic properties of the synthesized compounds were also investigated, and it was determined that the energy bang gaps of compounds 1 and 2 are 1.70 eV and 1.56 eV, respectively. Strikingly, we demonstrate that compound 1 is exhibiting a rapid and reversible color change behavior upon altering pH in the entire pH spectrum. As it is known, materials that respond reversibly to chemical and/or physical stimuli in a controllable fashion are regarded as smart materials. Hence, we report that compound 1 is actually a smart material that can be used as a simple yet efficient pH sensor.

Keywords: Phthalocyanine, Copper, pH sensor, Aggregation, Band gap

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1. Introduction

Organic semiconductor materials are receiving a considerable interest for many potential applications. Unlike their inorganic counterparts, the organic semiconductors are lightweight, flexible, cheap, and exhibit improved light absorption over a wide wavelength range. Besides, they also have tunable molecular structures to obtain desired optical and electronic properties (Claessens et al., 2001; Alosabi et al., 2022). Metallophthalocyanines, from the well-known organic semiconductor class, are one of the most promising candidates due to their properties such as favorable band gap and chemical and thermal stability. Stable metallophthalocyanines with 18 delocalized π electrons have a wide range of synthetic variations (Claessens et al., 2001; Afify et al., 2015; Ai et al. 2018). Among the metallophthalocyanines, copper phthalocyanine is widely preferred in organic electronic applications, thanks to its chemical stability, high molecular symmetry, easy and sensitive film-forming ability, commercial availability, and excellent optical and electronic properties (Djurisic et al., 2002; Farag, 2007; Tong et al., 2007; Mali et al., 2012; Sánchez-Vergara et al., 2012; Afify et al., 2015; McAfee et al., 2016; Dakoğlu-Gülmez et al., 2017; Hamam, 2017; Ai et al. 2018).

In fact, copper phthalocyanines have the potential to be used in almost all types of organic electronic devices, including diodes, transistors, photovoltaics, light emitting diodes, photodetectors, rectifiers, temperature sensors, radiation dosimeters, and chemical sensors (Djurisic et al., 2002; Farag, 2007; Tong et al., 2007; Mali et al., 2012; Sánchez-Vergara et al., 2012; Afify et al., 2015; McAfee et al., 2016; Dakoğlu-Gülmez et al., 2017; Hamam, 2017; Ai et al. 2018). Because, copper phthalocyanine is a square planar molecule that forms a stack of different polymorphs with varying molecular arrangements and orientations. Hence, it could be predicted that the diversity in applications might further increase with the modification of the chemical environment of the molecule. For instance, while Raval et al. demonstrated that copper phthalocyanine based organic electronic devices could be used as sensors for ionizing radiation of γ-rays (Raval et al., 2013), Chaure et al. (2011) used 1,4,8,11,15,18,22,25-octakis(hexyl) copper phthalocyanine films in the fabrication of organic field-effect transistors (Chaure et al., 2011). In another work, Wang et al. (2017) showed that tetra-alkyl-substituted copper phthalocyanines could be used as dopant-free hole transport layers in planar perovskite solar cells (Wang et al., 2017). Overall, while copper phthalocyanine is promising in terms of ease in altering its molecular arrangement to adapt it to countless of different applications, the phthalocyanines usually exhibit poor solubility in organic solvents, which hinders them to reach their true potential.

In this context, we aimed at improving the solubility of copper phthalocyanine in organic solvents by designing its new derivatives through selection of suitable substituents. Namely, we prepared [2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)] (1) and [2,9,16,23-tetra{(4,5-Diphenyl-1-methyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)] (2), and demonstrated that the compound 1 was soluble in THF, DMF, and DMSO, and the compound 2 was soluble in chloroform ($CHCl_3$), acetone, methanol (MeOH), THF, DMF, and DMSO. Actually, in designing of any copper phthalocyanine derivatives, examination of the spectroscopic and optical properties is essential to reveal the true potential of the new molecule. Accordingly, we also investigated the optical and spectroscopic properties of the Compounds 1 and 2. Further, we report that while Compound 1 demonstrated colorimetric pH sensor properties, Compound 2 did not exhibit such performance at all.

2. Materials and Methods

2.1 Synthesis

The synthesis reactions were carried out under argon gas and all the solvents used were dried by special methods and on molecular sieves (Armarego et al., 2003). The imidazole-substituted phthalonitrile derivative, which is used as a starting material in the synthesis of imidazole-substituted copper phthalocyanine, was synthesized as a result of the reaction of 4-nitrophthalonitrile and 4,5-diphenyl-2-imidazolethiol according to the literature (Yabaş et al., 2011). The synthesis of the new copper phthalocyanine derivatives are described below and schematized in Figure 1.

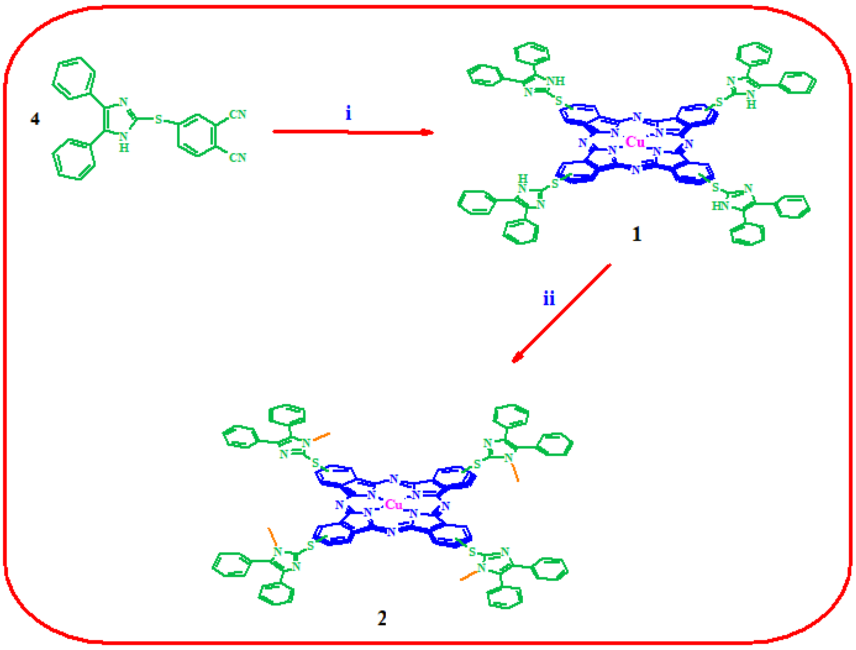

Figure 1. Synthesis of copper phthalocyanine compounds. (**i:** n-pentanol, $CuCl_2$, DBU, 15 hr, 180°C **ii:** DMF, CH_3I, K_2CO_3, 10 hr, RT).

[2,9,16,23-tetra{(4,5-Diphenyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)]

Imidazole substituted phthalonitrile (200.0 mg, 0.52 mmol) was dissolved in 3 mL of pentanol, and copper(II) chloride ($CuCl_2$) (18.0 mg, 0.13 mmol) was added to this solution. This mixture was kept at 180°C for 15 hours in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). After the reaction was complete, the mixture was cooled to room temperature, and was precipitated with ether, filtered and dried. The crude product was washed sequentially with MeOH and acetone until the filtrate lightened in color and dried in vacuum. The resulting green powder was soluble in THF, DMF and DMSO. Yield: 49% (100.0 mg). M.p.: >300°C. UV-Vis (DMSO) λ_{max}/nm: 669, 600, 351. FT-IR (KBr pellet) υ (cm^{-1}): 3433; 3047; 2924; 2851; 1642; 1598; 1523; 1483; 1444; 1403; 1314; 1140; 699. MS (MALDI-TOF) m/z: 1577 $[M]^+$. Anal. Calc. for $C_{92}H_{56}N_{16}S_4Cu$: C, 70.05; H, 3.58; N, 14.21%. Found: C, 70.95; H, 3.71; N, 14.43%.

[2,9,16,23-tetra{(4,5-Diphenyl-1-methyl-1H-imidazole)-2-yl-thio}phthalocyaninato-copper(II)]

CH_3I (78.0 mg, 0.55 mmol) and K_2CO_3 (90.0 mg, 0.65 mmol) were added to a solution of synthesized copper(II) phthalocyanine 1 (200.0 mg, 0.13 mmol) in 4 mL of DMF. This mixture was stirred at room temperature for 10 hours. After the reaction was complete, DMF was evaporated under reduced pressure, and the resulting crude residue was dissolved in $CHCl_3$ and filtered. Next, the organic phase was concentrated, precipitated by the addition of n-hexane, filtered, and the solid was dried in a vacuum. The resulting dark green powder was soluble in $CHCl_3$, acetone, methanol, THF, DMF, and DMSO. Yield: 75% (160.0 mg). M.p.: >300°C. UV-Vis (DMSO) λ_{max}/nm: 683, 613, 353. IR (KBr pellet) υ (cm^{-1}): 3430; 3241; 3052; 3017; 2927; 2859; 2798; 1712; 1642; 1596; 1497; 1445; 1382; 1321; 697. MS (MALDI-TOF) m/z: 1639 [M+H]$^+$. Anal.Calc. for $C_{96}H_{68}N_{16}S_4Cu$: C, 70.41; H, 4.19; N, 13.69%. Found: C, 70.66; H, 4.31; N, 13.94%.

2.2. Characterization

FT-IR and UV-Vis spectra were recorded on a Bruker Tensor II FT-IR spectrophotometer and a Shimadzu UV-1800 UV-Vis spectrophotometer, respectively. The Cary 5000 UV-Vis-NIR spectrophotometer was used for optical characterization, and the optical band gaps were determined by using Tauc plot. The Electrothermal 9100 melting point detector was used to determine the melting points of the synthesized compounds. The pH of the compounds was measured with a glass electrode in an electronic pH meter using perchloric acid ($HClO_4$) and tetrabutylammonium hydroxide (TBAOH) in DMSO solution.

3. Results and Discussions

As summarized in Figure 1, tetrasubstituted copper(II) phthalocyanine 1 was synthesized in high yield as a result of tetramerization reaction of phthalonitrile derivative in the presence of $CuCl_2$. N-methylated copper(II) phthalocyanine 2 was synthesized by N-alkylation reaction of synthesized copper(II) phthalocyanine 1 with CH_3I in basic medium. Compounds were purified by using solubility differences, and then were characterized by FT-IR, UV-Vis, MALDI-TOF MS and elemental analysis.

The FT-IR spectra of compounds 1 and 2 were shown in Figure 2. It can be said that the peaks appearing in the range of 3241-2798 cm^{-1} in the FT-IR spectrum of compound 2 were C-H peaks belonging to the alkyl groups. This indicates that the N-H bonds were converted to N-CH_3. At the same time, it was observed that the sharp C≡N characteristic vibration band of the phthalonitrile derivative, which appeared at 2233 cm^{-1} according to our previous study (Yabaş et al., 2011), disappeared in the FT-IR spectrum of compound 1. This suggests that phthalocyanine compound was formed as a result of the tetramerization reaction. In addition, in the FT-IR spectra of compounds 1 and 2, aromatic C=C stretching bands were observed in the range of 1598-1596 cm^{-1} and the stretching bands of C=N were observed in the range of 1497-1483 cm^{-1}, while vibration bands of the substituted benzene ring were observed in the range of 699-697 cm^{-1}, all of which were in good accordance with previous reports (Yabaş et al., 2018; Yabaş, 2023).

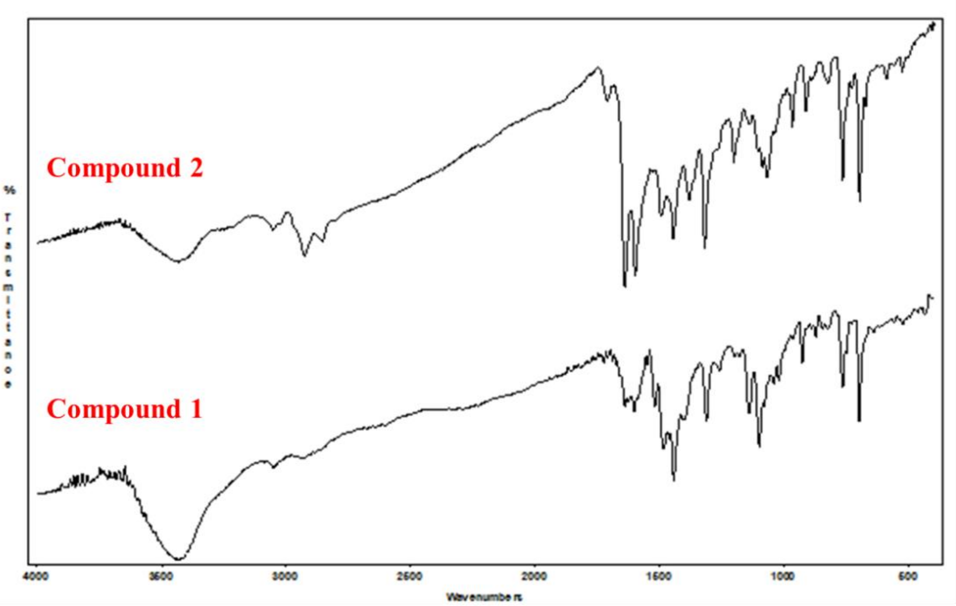

Figure 2. FT-IR Spectra of compounds 1 and 2.

UV-Vis spectroscopy is one of the most basic characterization methods showing the structural formation of phthalocyanines. Two intense bands associated with π–π* transitions dominate the UV-Vis spectra of the phthalocyanine ring, and these characteristic bands prove the formation of phthalocyanine. These two bands are defined as the Q-band, which occurs around 600-700 nm, and the B-band, which occurs at about 300-400 nm. The characteristic Q-band is caused by the transition of the Pc ring from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) π–π*. The characteristic B-band is due to deep π–π* transitions (Nyokong, 2007; Nyokong, 2010; Yabaş et al., 2011; Yabaş et al., 2023). The UV-Vis spectra of the synthesized copper phthalocyanine compounds were shown in Figure 3. The absorption spectra of compounds 1 and 2 exhibited sharp Q-band and B-band in the desired range. Q-bands of compounds 1 and 2 appeared at 669 nm and 683 nm, respectively, while B-bands appeared at 351 nm and 353 nm, respectively. These characteristic peaks suggest that phthalocyanine compounds were successfully formed as a result of the tetramerization reaction. Comparing the UV spectra of compounds 1 and 2, it can be observed that the Q-band position of compound 2 is red-shifted as compared to compound 1. This might be ascribed to the electron donor effect of the methyl groups attached to the structure (van Leeuwen et al., 2014).

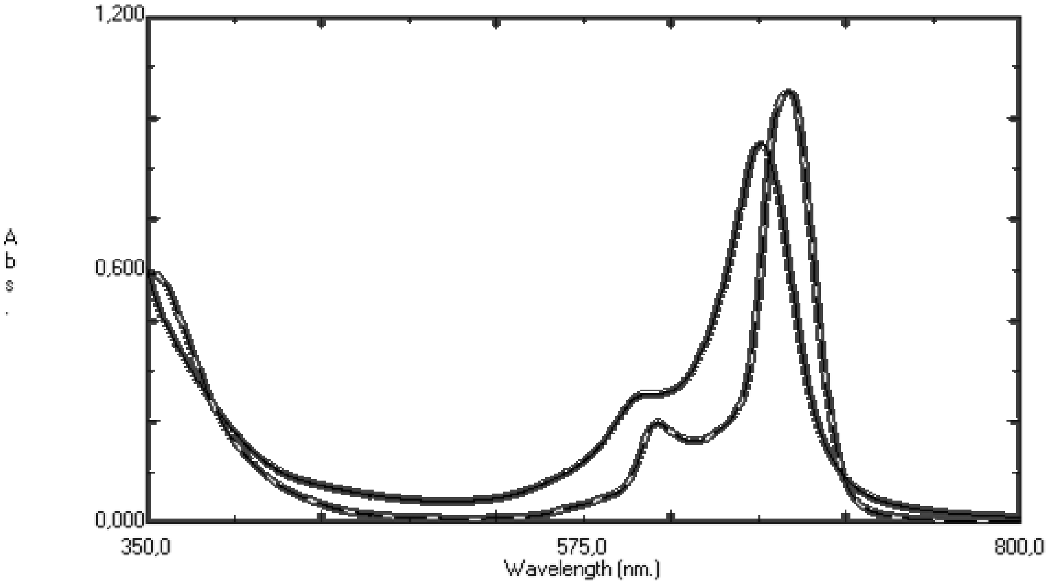

Figure 3. UV-Vis spectra of compounds 1 (-) and 2 (--) in DMSO.

The MALDI-TOF MS results of the synthesized compounds were shown in the experimental part, and were in agreement with the calculated molar masses. In addition, elemental analysis results of the compounds were also consistent with the calculated results. These results further confirm that the compounds were successfully synthesized.

NMR analysis of the synthesized phthalocyanine compounds could not be performed because it is difficult to realize consistent results due to the paramagnetic nature of the copper ion (He et al., 2008).

Phthalocyanines tend to exhibit aggregation behavior as a result of electronic interactions between the rings of two or more molecules. The aggregation behavior of phthalocyanines varies depending on the type of metal ions, the nature of the substituents and the substitution location. Since aggregation in phthalocyanines reduces energy efficiency, it is desirable that the materials to be used in applications do not show aggregation tendency (Yabaş, 2023; Nyokong, 2007; Nyokong, 2010). Aggregation behavior of compounds 1 and 2 in different solvents (THF, DMF, DMSO) and different concentrations in DMF ($10x10^{-6}$, $8x10^{-6}$, $6x10^{-6}$, $4x10^{-6}$, $2x10^{-6}$ M) was easily examined by UV-Vis spectrophotometer. As seen in the concentration-dependent aggregation behavior of compounds 1 and 2 in Figure 4, a proportional decrease in the peaks was observed with the decrease of the concentration, but no shift or new peak formation was detected. Similar results were also observed in different solvents.

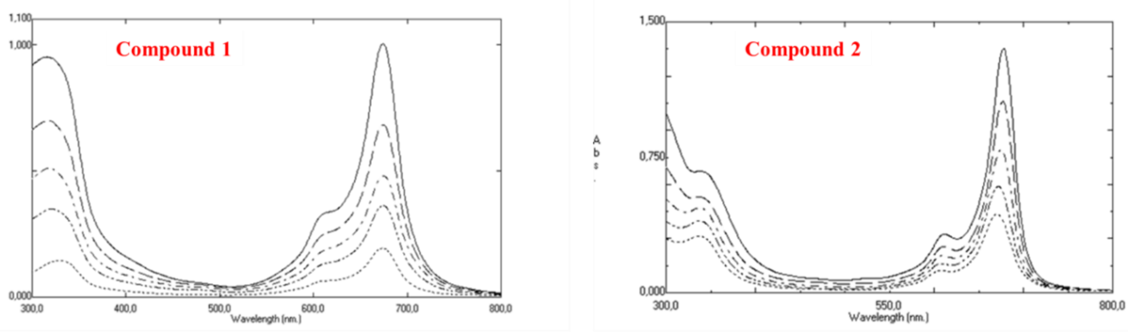

Figure 4. UV-Vis spectra of compounds **1** and **2** at different concentrations in DMF.

According to these results, it can be said that the synthesized copper phthalocyanine compounds did not show a significant aggregation behavior. On the other hand, imidazole substituted copper phthalocyanine 1 showed interesting color changes under acidic and basic conditions. When the color changes of N-alkylated imidazole substituted copper phthalocyanine 2 under acidic and basic conditions were examined, it was observed that the same color change was not observed. According to the literature (Yabaş, 2023), this was thought to be caused by the protonation/deprotonation of the imidazole groups, as schematized in Figure 5. Because no color change was observed after the conversion of the N-H group to N-CH_3 in the substituted imidazole groups on the phthalocyanine ring. In addition, it is thought that the methyl group attached to the imidazole groups changes the electron density of compound 2, thus preventing the color change of the compound in acidic medium.

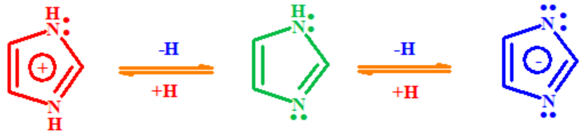

Figure 5. Schematic representation of the protonation/deprotanation of the imidazole group.

Solutions of compounds 1 and 2 at different pHs under acidic and basic conditions were prepared using $HClO_4$ and TBAOH in DMSO with a glass electrode in an electronic pH meter. The spectroscopic changes of the solutions prepared in the pH range of 13.8-3.1 were examined by UV-Vis spectrophotometer, but no significant change was observed in the UV-Vis spectra of both compounds. The color changes at different pHs for compounds 1 and 2 were shown in Figure 6.

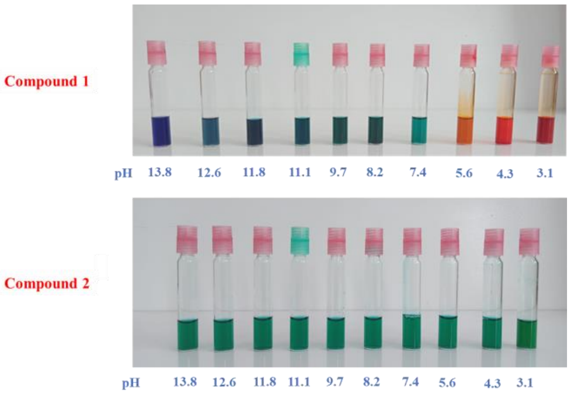

Figure 6. Color changes of compounds 1 and 2 at different pH ranges.

It can be said that compound 1 has colorimetric pH sensor properties in a very wide pH range, with color transformations caused by protonation/deprotonation of imidazole groups (Figure 7), and accordingly electron density changes of the molecule.

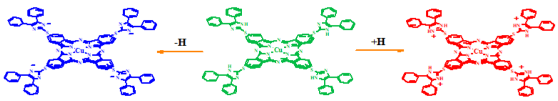

Figure 7. Schematic representation of the protonation/deprotanation of compound 1.

Also, the energy band gaps of compounds 1 and 2 were spectroscopically determined. Because, the optical properties of materials provide information about their electronic structures and optical transition types, and hence, are important in determining their potential for use in optoelectronic applications (Cherian et al., 2008; Yabaş, 2023). Thin films were prepared by dropping solutions of the compounds in THF onto glass substrates and then drying the solvent at room temperature. Then, the energy band gaps were determined by UV-Vis spectrophotometer through Tauc plot by using equation 1 (El Nhass et al., 2001; Hamam et al., 2017):

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \qquad (1)$$

where α is absorption coefficient, hν is the energy of the incident photons and Eg is the value of the optical band gap energy (eV) corresponding to the transitions denoted by the n value. The αo is a constant that depends on the transition probability. The best linear fit for semiconductors was found for n = 0.5, indicating that direct transitions were allowed in the material (Kim et al., 2012; Hamam et al., 2017; Mobtakeri et al., 2021). The corresponding absorbance and transmittance spectra of the thin films were given in Figure 8.

Calculations were made from the obtained data according to equation 1 and a Tauc plot was drawn for each compound as seen in Figure 9. As it is known, extrapolating the Tauc plot to the abscissa gives the value of the energy band gap. As a result of the calculations and measurements, the energy bang gaps for compounds 1 and 2 were determined as 1.70 eV and 1.56 eV, respectively. These values might indicate that particularly the compounds 2 might have a potential to be used in solar cell applications, since an ideal band gap in photovoltaic applications are usually considered to be around 1.4 eV in terms of absorbing more photons from sunlight (Yu et al., 2017; Polat et al., 2020; Yabaş et al., 2023).

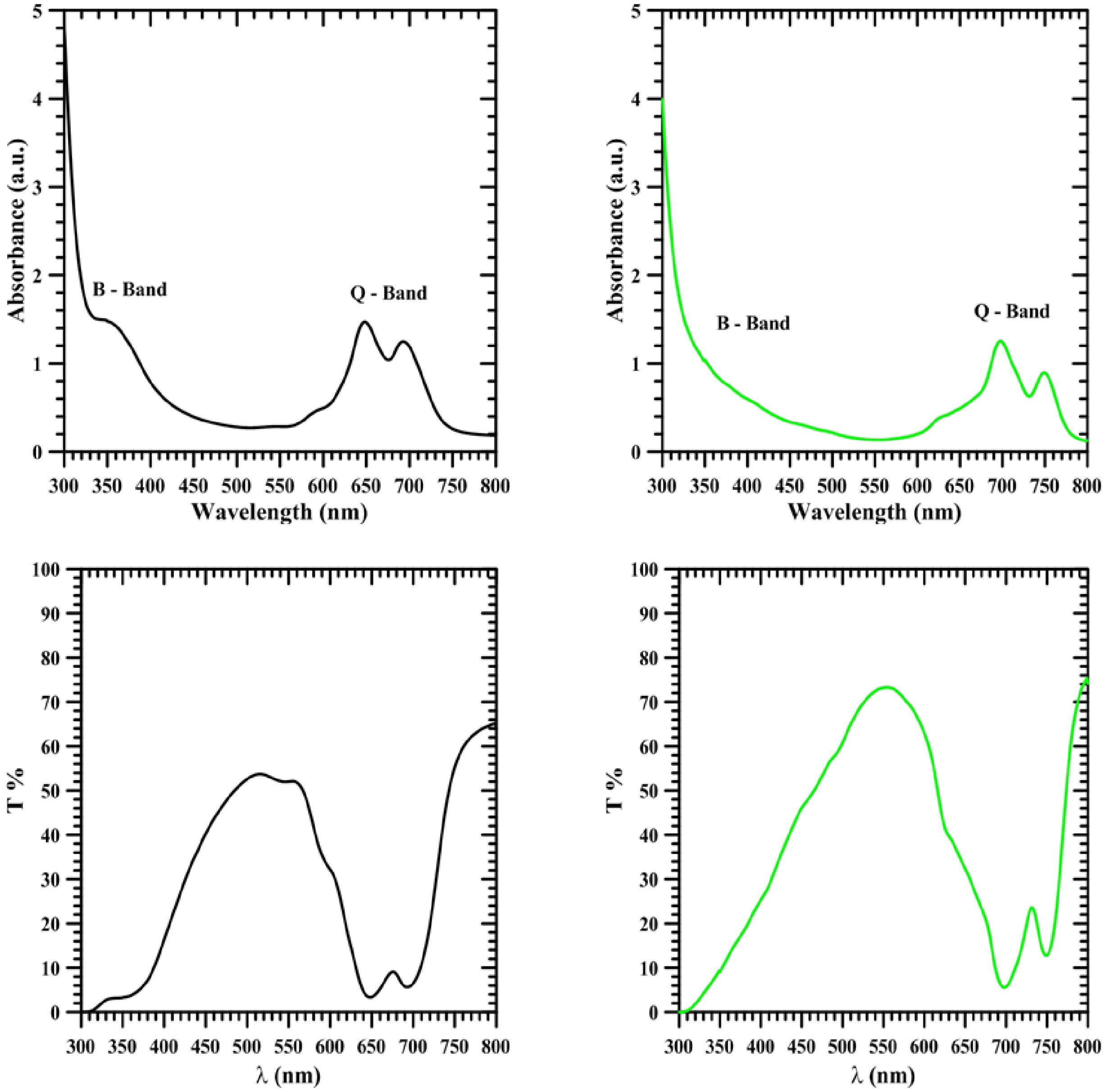

Figure 8. The transmittance and absorption spectrum of compounds 1 (black) and 2 (green) thin film.

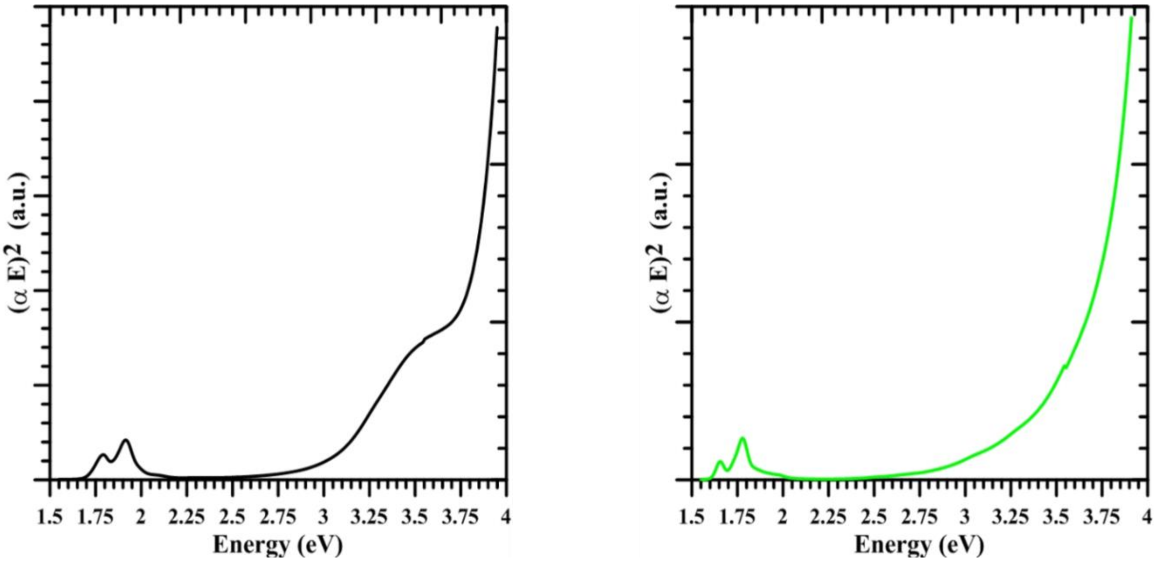

Figure 9. Determination of the band gap of compounds 1 (black) and 2 (green).

4. Conclusions

In this study, new imidazole tetrasubstituted copper phthalocyanine compounds were synthesized as copper phthalocyanine derivatives. These compounds, which were easily purified by washing with different solvents, were characterized by UV-Vis, FTIR, MALDI-TOF MS, and elemental analysis. Also, the bad gaps of compounds 1 and 2 were found to be 1.70 eV and 1.56 eV, respectively. These results suggest that the newly synthesized phthalocyanines might have the potential to be used in optoelectronic applications. In addition, we report that the synthesized compounds did not exhibit a significant aggregation problem, and were actually soluble in organic solvents. This is important, as it is well-known that phthalocyanines usually show aggregation tendencies and aggregation is naturally undesirable in many applications. This situation further increases the potential of the newly synthesized compounds for practical applications. Finally, we showed that compound 1 is actually a smart material that can be used as a simple but effective pH sensor over a wide pH range.

Author Contributions

The percentage of the author(s) contributions is presented below. All authors reviewed and approved the final version of the manuscript.

	F.E.	E.Y.
C	60	40
D	90	10
S	75	25
DCP	60	40
DAI	70	30
L	50	50
W	50	50
CR	50	50
SR	50	50
PM	50	50
FA	50	50

C=Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management, FA= funding acquisition.

Conflict of Interest

There is no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Ethical Consideration

Ethics committee approval was not required for this study because of there was no study on animals or humans. The authors confirm that the ethical policies of the journal, as noted on the journal's author guidelines page, have been adhered to.

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