Photovoltaic, thermal, fluorescence and aggregation properties of non-peripherally metallophthalocyanines bearing four 3,4-dimethoxyphenethoxy substituents

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Received: 10 February 2020; Revised: 26 February 2020; Accepted: 27 February 2020

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ABSTRACT

In this study, a non-peripheral phthalonitrile compound was prepared as a starting material. Then this 3,4-dimethoxyphenethoxy substituted non-peripheral phthalonitrile compound was reacted with Co, Zn and Cu salts. Non-peripheral phthalocyanine compounds were prepared using an easy and practical method. The fluorescence spectra of the zinc phthalocyanine compound were measured in tetrahydrofuran. Aggregation studies showed the compliance with the lambert-beer law in the concentration range studied for non-peripheral phthalocyanine compounds. Thermogravimetric (TG) analyses showed that the compounds were stable. The photovoltaic performance of these phthalocyanine compounds was measured as current density-voltage (J-V). The calculated power conversion effects showed that these compounds had the potential to be used for dye-sensitized solar cell (DSSC) structures.

Keywords: Photovoltaic, phthalocyanine, thermal, non-peripheral, fluorescence.

3,4-dimetoksifensentoksi sübstitüenti taşıyan periferik olmayan metaloftalosiyanilerin fotovoltaik, termal, floresans ve agregasyon özellikleri

ÖZ

Bu çalışmada, başlangıç materyali olarak non periferik bir ftalonitril bileşigi hazırlanmıştır. Daha sonra bu 3,4-dimetoksifensentoksi sübstitüenti non periferal ftalonitril bileşiği, Co, Zn ve Cu tuzları ile reaksiyona sokuldu. Kolay ve pratik bir metot kullanılarak non periferal ftalosiyanin bileşikleri hazırlanı. Çinko ftalosiyanin bileşiğinin floresan spektrumları tetrahidrofuran içinde ölçüldü. Agregasyon Çalışmaları, non periferal ftalosiyanin bileşikleri için incelenen konsantrasyon aralığına lambert-beer yasasına uyum göstermiştir. Termogravimetrık (TG) analizler bileşiklerin kararlı olduğunu gösterdi. Bu ftalosiyanin bileşiklerinin fotovoltaik performansı akım yoğunluk voltajı (J-V) olarak ölçüldü. Hesaplanan güç dönüşüm etkileri, bu bileşiklerin, boyaya duyarlı günes pili (DSSC) yapaların için kullanımla potansiyeline sahip olduğunu göstermiştir.

Anahtar Kelimeler: Fotovoltaik, ftalosiyanin, termal, periferik olmayan, floresan.
One of the obstacles in front of the mentioned applications is the low solubility of these compounds. To solve this problem, solubility can be increased by attaching appropriate peripheral or non-peripheral groups to the core of phthalocyanine. Synthesis of soluble phthalocyanines contributes to potential application areas (PDT etc.). This allows the compounds to be used in new technological areas. It contributes to setting new targets for research. Another important issue is the effort to find alternative energy sources for rapidly depleted fossil fuels. The compound is easily dissolved in solvents such as dichloroethane, acetonitrile, acetone, chloroform, dichloromethane, THF, DMF and DMSO. Yield: 0.63 g (71%). Mp: 143°C. 1H NMR (400 MHz, DMSO-d6) δ ppm: 7.84, 7.81, 7.79, 7.63, 7.61, 6.94, 6.91, 6.85, 6.81, 4.37, 3.74, 3.70, 3.39, 3.00, 2.48, 2.07, 1.07. 13C NMR (400 MHz, DMSO-d6) δ ppm: 161.58, 148.85, 147.79, 136.19, 130.54, 125.77, 120.99, 118.72, 115.90, 115.35, 113.95, 113.08, 111.98, 102.98, 70.70, 55.81, 40.60, 39.45, 34.42. FT-IR spectrum (cm⁻¹): 3078, 2905, 2939, 2916, 2881, 2839, 2233, 1585, 1519, 1458, 1423, 1354, 1288, 1265, 1238, 1195, 1157, 1138, 1045, 1022, 864, 794, 763. Anal calculated for C₁₃H₁₄N₂O₂: (308.33 g mol⁻¹) C 70.12; H 5.23; N 9.09 %. Found C 70.19; H 5.18; N 9.06 %.

2.3. 2,10,16,24-tetrakis (3,4-dimethoxyphenethoxy)phthalocyaninato) Cobalt (II) (4)

The substances 3- (3,4-dimethoxyphenethoxy) phthalonitrile 3 (0.050 g, 0.16 mmol) and Co(CH₃COO)₂ (0.021 g) were powdered in a quartz crucible. It was heated in a glass tube for 5 minutes under nitrogen at 280°C and in the presence of DBU. After cooling, the product was washed with cold and hot water, ethanol, methanol, hexane and diethyl ether. The product soluble in THF was collected and the solvent was removed to obtain a green solid. This compound is soluble in acetonitrile, dichloromethane, CHCl₃, THF, DMF, DMSO. Yield: 0.020 g (38.69%). Anal calculated for C₁₃H₁₄N₂O₂: (1292.26 g mol⁻¹) C 66.92; H, 4.99; N, 8.67%. Found: C, 71.05; H, 4.97; N, 8.64 %. UV-Vis (THF) λmax (log ε): 698 (5.07), 630 (4.60). IR spectrum (cm⁻¹): 2958, 2912, 2870, 1600, 1516, 1489, 1465, 1365, 1234, 1141, 1068, 860. MS (MALDI-TOF) m/z: 1292.8[M⁺]⁺.

2.4. 2,10,16,24-tetrakis (3,4-dimethoxyphenethoxy phthalocyaninato) zinc (II) (5)

Preparation of compound 5 was prepared under the same conditions as compound 4, except for metal salt and temperature (Zn(CH₃COO)₂). Yield: 0.033 g (63.52%). Anal calculated for C₁₃H₁₄N₂O₂Zn (1298.70 g mol⁻¹) C 66.59; H 4.97; N 8.63 %. Found C, 66.54; H, 4.93; N, 8.59 %. UV-Vis (THF) λmax (log ε): 698 (5.14), 630 (4.47), 314 (4.73). 1H NMR (400 MHz, DMSO-d6) δ ppm: 8.02, 7.73, 7.58, 7.25, 7.03, 6.91, 6.85, 6.78, 6.56, 4.87, 3.76, 3.64, 3.20, 2.47, 2.05, 1.34. IR spectrum (cm⁻¹): 3066 (Ar), 2931, 2870 (aliphatic), 1589, 1516 (C–C), 1489, 1465, 1265, 1234, 1203, 1141, 1026, 806, 748 cm⁻¹. MS (MALDI-TOF) m/z: 1299.8 [M +1]⁺.
2.5. 2,10,16,24-tetrakis(3,4-dimethoxyphenethoxy phthalocyaninato) Copper (II) (6)

Preparation of compound 6 was prepared under the same conditions as compound 4, except for metal salt (Zn(CH\textsubscript{3}COO)\textsubscript{2}). Yield: 0.015 g (28.95%). Anal calculated for C\textsubscript{52}H\textsubscript{46}CuN\textsubscript{15}O\textsubscript{12} (1296.87 g mol\textsuperscript{-1}) C 66.68; H 4.97; N, 8.64. % Found C, 66.71; H, 4.91; N, 8.61%; UV-Vis (THF) λ\textsubscript{max} (log ε): 706 (5.06), 636(4.57). IR spectrum (cm\textsuperscript{-1}): 2947, 1597, 1512 (C=C), 2912, 2870 (aliphatic), 1589, 1516 (Ar), 1482, 1479, 136.19, 130.54, 125.77, 120.99, 118.72, 115.90, 115.35, 113.95, 113.08, 111.98, 102.98, 70.70, 55.81, 40.60, 39.45, 34.42. One of the techniques used to characterize new compounds is the mass spectrum. It makes an important feature of these compounds is that the absorption range is more suited to the electronic structure. The practical method used in this study gives the same data as the spectral data of the functional groups in the previous studies, but provides the advantage of an easier and more economical preparation.\textsuperscript{20,21}

When the IR spectral data for the evaluation of functional groups are examined, the intermediate peaks are observed at 3078 cm\textsuperscript{-1} (Ar-CH), nitrile 2233 cm\textsuperscript{-1} (CN), carbon carbon peak 1585-1519 cm\textsuperscript{-1} (C = C), aromatic oxygen peak 1265 cm\textsuperscript{-1} (Ar-O-Ar). These peaks confirm the phthalonitrile structure. The most significant change in the IR peaks of phthalonitrile derivatives and phthalocyanine compounds is the change in the nitrile peak. It is the complete disappearance of the sharp nitrile peak in the phthalonitrile derivative. IR vibrations of the resulting phthalocyanine compounds resemble the phthalonitrile peaks with minor shifts, except for nitrile peaks. The IR spectra of compound 4 displayed vibration peaks at 2958, 2912, 2870 cm\textsuperscript{-1} (aliphatic), 1600, 1516 C=C cm\textsuperscript{-1}, and Ar-O-Ar peaks at 1234 cm\textsuperscript{-1}. Vibration peaks compound 5 appeared at 3066 cm\textsuperscript{-1} (Ar-H), 2931, 2870 cm\textsuperscript{-1} (aliphatic), 1589, 1516 C=C cm\textsuperscript{-1}, and Ar-O-Ar peaks at 1234 cm\textsuperscript{-1}. For compound 6, the vibration peaks were also observed at 2947, 1597-1512 C=C cm\textsuperscript{-1}, and Ar-O-Ar peaks at 1265 cm\textsuperscript{-1}. This data confirms the expected structures.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

Similar to our previous method\textsuperscript{20}, 3-(3,4-dimethoxyphenethoxy) phthalonitrile (3) was synthesized as the starting material of non-peripheral phthalocyanines. The temperature and reaction time were slightly altered to give the desired phthalonitrile derivative. Non-peripheral metallophthalocyanines (4-6) were also obtained from the appropriate reaction of the metal salts with this starting material. The reaction route of all these newly synthesized substances is given in Scheme 1. An important feature of these compounds is that the absorption range is more suited to the phototherapeutic window. Elemental analysis, mass spectra, FTIR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and UV-spectrum spectra were used for the characterization of chemical structures. The data obtained with the expected structure was found to be in good agreement. In the \textsuperscript{1}H NMR spectrum of compound 3 in DMSO-d\textsubscript{6}, aromatic protons appear at 7.84, 7.81, 7.79, 7.63, 7.61, 6.94, 6.91, 6.85, 6.81 (Ar-H) and aliphatic protons appear at 3.74, 3.00, 2.07, 1.07. In \textsuperscript{13}C NMR spectrum of compound 3 (400 MHz, DMSO-d\textsubscript{6}) δ ppm: 161.58, 148.85, 147.79, 136.19, 130.54, 125.77, 120.99, 118.72, 115.90, 115.35, 113.95, 113.08, 111.98, 102.98, 70.70, 55.81, 40.60, 39.45, 34.42. In the \textsuperscript{1}H NMR spectrum of compound 5 within DMSO-d\textsubscript{6}, aromatic protons appear at 8.02, 7.73, 7.58, 7.25, 7.03, 6.91, 6.85, 6.78, 6.56, and aliphatic protons appear at 4.87, 3.76, 3.64, 2.05, 1.34 ppm. \textsuperscript{1}H NMR spectra for compounds 4 and 6 were not deemed necessary due to the magnetic state of their electronic structure. The practical method used in this study gives the same data as the spectral data of the functional groups in the previous studies, but provides the advantage of an easier and more economical preparation.\textsuperscript{20,21}

One of the techniques used to characterize new compounds is the mass spectrum. It makes an important contribution to supporting the structure. The mass spectral study by the MALDI-TOF technique on the new compounds (4-6) gave the following results, m/z: 1292.8 [M]+ for 4, m/z: 1299.8 [M+1]+ for 5, m/z: 1297.6 [M+1]+ for 6. The characteristic Q and B bands in THF were observed due to 4, 5 and 6 phthalocyanine compounds in the UV-Vis spectra. The Q band of the phthalocyanine compounds is due to the transitions of π→π* from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. Non-peripheral electron donor groups are known to cause bathochromic shift in the Q band.\textsuperscript{22} It can be said that in the UV-Vis spectra of compounds 4 and 5, the Q bands are observed at 696 and 698 nm due to the non-peripheral shift. The compound 6 give the Q band at 706 nm as expected. These spectral data confirm the bathochromic shift. The Q bands of non-peripheral substituted cobalt (II) phthalocyanines (4) were approximately 36 nm red-shifted according to the related peripheral substituted
Scheme 1. Representation of compounds prepared for DSSC with formula.
counterparts. The Q bands of non-peripheral substituted Zn (II) and Cu (II) phthalocyanines shifted to about 22 and 30 nm red, respectively, relative to their respective peripheral substituted analogs. The substitution group which is non-peripherally bound to phthalocyanines is more affected as it is closer to the phthalocyanine ring conjugation. As a result, it more incapacitates HOMO orbitals and cause bathochromic shifts. The changes in absorbance versus the varying concentration of complex 5 compound is given in Figure 1.

Figure 1. The change of absorption of compound 5 against concentration.

The fluorescence emission, absorption and excitation spectra of zinc phthalocyanine were recorded in THF at 1x10^-5 M and the spectra obtained were given in Figure 2. In this study, the emission and extinction measurements and stokes shift value of diamagnetic zinc phthalocyanine compound were determined. The difference between emission (704 nm) and extinction (698) is given by the Stokes shift value. The stokes shift value of this compound was found to be 6 nm. This value is close to the values in the literature.

The synthesized phthalocyanine compounds are soluble in polar organic solvents such as acetone, dichloromethane, CHCl₃, THF, DMF, DMSO. Resolution is required for many application areas. The absorption spectra of compound (5) in different solvents are given in Figures 3. The choice of solvent for photodynamic therapy and the determination of fluorescence efficacy have become necessary for applications. In addition to the best possible singlet oxygen production, some parameters such as solubility, low dark toxicity, strong absorption in phototherapeutic window should be considered when a photosensitizer is designed for biomedical applications.

Thermogravimetric (TG) analyses of 3-(3,4-dimethoxyphenethoxy) phthalonitrile 3 and phthalocyanine complexes 4-6 were carried out in air and nitrogen atmosphere. After initial loss of moisture, the substance is decomposed in a single step at a temperature ranges of 250°C and 370°C, and the loss of weight at major decomposition temperature was 91% for compound 3 (Figure 4). The thermal decomposition of zinc phthalocyanine 4 in nitrogen atmosphere was observed to be at temperature ranges of 220°C and 800°C, and the loss of weight at major decomposition temperature was 61%. At the same conditions, the weight losses of the compounds 5 and 6 were estimated...
Figure 4. TG/DTG curves of compound 3.

Figure 5. J-V curves of DSSCs based on phthalocyanines complexes (4-6).

to be 54% and 53%, respectively. When 3-(3,4-dimethoxyphenethoxy)phthalonitrile is organic, it is decomposed 90% at low temperature while phthalocyanine compounds give lower weight loss at higher temperatures. This provides an adequate contribution to the literature. The results of TG and DTA show that the compounds of phthalocyanine are thermochromically stable.

Figure 5 shows current density–voltage (J–V) characteristics of devices based on the three metal complexes (4-6). The corresponding open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor (FF) and power conversion efficiency (PCE) for different three samples are listed in Table 1. It can be seen that all $V_{oc}$, $J_{sc}$, FF, and PCE are increased from compound 6 to compound 4. The $J_{sc}$ based on compound 4 reached 3.38 mA/cm$^2$, which is nearly 1.6 times of that of the device based on compound 6 (2.07 mA/cm$^2$); the power conversion efficiency (PCE) based on compound 4 reached 1.15%, which is more than two times of that of the device based on compound 6 (0.56%). The lower $J_{sc}$ of compounds 5 and 6 might be ascribed to the poor charge separation and transportation.

Table 1. The photovoltaic parameters for DSSCs.

| Samples   | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF   | PCE (%) |
|-----------|----------------------|--------------|------|---------|
| Compound 6 | 2.07                 | 0.53         | 0.51 | 0.56    |
| Compound 5 | 2.50                 | 0.55         | 0.55 | 0.76    |
| Compound 4 | 3.38                 | 0.59         | 0.58 | 1.16    |
It suggests that the compound 4 could make better electric contact than the complexes of compounds 5 and compound 6. Poor adsorption to the TiO₂ surface and recombination losses due to short alkyl in the thiophene ring are two main factors limiting the effectiveness of DSSCs. More works are being researched to optimize device performance. Phthalocyanines are able to overcome the disadvantages of porphyrins with their Remarkable light gathering capabilities and thermal stability in the distant and near IR spectral region and show themselves among the dyes accepted in photovoltaic technologies. In particular, Phthalocyanines have an effective role in improving the technology of dye-sensitized solar cells (DSSCs). Therefore they are good candidates for inclusion in such trial programs. Phthalocyanine compounds synthesized in this study show that they are soluble in many different solvents, can be prepared easily and can be used in different applications with their photovoltaic performances. Phthalocyanine compounds are also commercially important with high thermal stability in dye chemistry. Recently, DSSCs have been receiving intense interest as a solution to increasing energy demands. Phthalocyanine dyes are promising for DSSCs. The power conversion effects offer the option of being interchangeable depending on the bound substituent group. Among the renewable energy sources, solar energy is the cleanest and greenest. Investigations for this purpose focus on phthalocyanine compounds with p-type organic semiconductor for DSSCs. The Photovoltaic conversion effect can be significantly enhanced by both composite material and varying substituents. The advantages of metal phthalocyanines are not limited to the rich metal variety, the conjugated system, the organic solar cell, the organic semiconductor material for hybrid solar cells, but also the potential of electronic and optical device application as xerographic application.

4. CONCLUSIONS

The major advantage of these compounds is that they are soluble in organic solvents and non-aggregation in the concentration range studied. Zinc phthalocyanine compound shows fluorescence property. This property indicates that the compounds can potentially be used in medical applications such as PDT. The studied phthalocyanines have thermal stability. Photovoltaic measurement results show that cobalt, zinc and copper phthalocyanine compounds can potentially be used in dye-sensitive solar cell (DSSC) technology. The measurements show that compound 4 provide the best electrical contact.

ACKNOWLEDGEMENTS

We thanks to Van YYU Office of Scientific Research Projects (Project number: FDK-2019-8105).

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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