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Synthesis of novel tetra (4-tritylphenoxy) substituted metallophthalocyanines and investigation of their aggregation, photovoltaic, solar cell properties

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ABSTRACT

4-(4-tritylphenoxy) phthalonitrile was synthesized and characterized. Copper, zinc and cobalt phthalocyanines were obtained by reaction of 4-(4-tritylphenoxy)phthalonitrile with CuCl₂, ZnCl₂, CoCl₂ metal salts. New compounds were characterized by using electronic absorption, nuclear magnetic resonance spectroscopy, infrared. The aggregation investigation for phthalocyanine complexes carried out in different concentrations tetrahydrofuran. Copper, cobalt and zinc phthalocyanines were used as sensitizers in dye-sensitized solar cell structures (DSSC) by growing on TiO₂ coated on FTO (Fluorine doped Tin Oxide) conductive glass substrates. Current density (J) versus voltage (V) measurements were applied to investigate the photovoltaic properties of the synthesized complexes. The calculated power conversion efficiencies (η %) of the complexes using the obtained current density (J) versus voltage (V) curves show that these devices can be used as promising sensitizers in solar cell applications.

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Introduction

Today, there is an effort to load new functions into chemical compounds at the expense of research. Some of the chemicals which have been extensively studied for their new properties are compounds of phthalocyanine. While phthalocyanine compounds are used as paint in the early days,^[1] today they have application potential in different areas such as solar cell,^[2] chemical sensor,^[3] semiconductors,^[4] electro-chromic displaying systems,^[5] non-linear optics,^[6] laser dyes,^[7] optical storage devices,^[8] photodynamic therapeutic agents (PDT)^[9] and liquid crystal.^[10] The use of these compounds for dye sensitized solar cell (DSSC) applications is of interest to researchers. This can contribute to renewable energy production. Sensitizers that convert incoming energy to electricity by absorpting the light from the solar energy used as a source have an effective role in the structure of a DSSC.^[11,12] Ruthenium complexes have been used as promising sensitizers in DSSCs because of their photoelectron chemical properties and high stability in the oxidized state.^[13] As an alternative to silicon-based solar cells, DSSCs have a great interest in photovoltaic applications, with advantages such as low-cost production and wide application areas. Despite these advantages, because the efficiency of DSSCs is lower than that of silicon-based solar cells, they have been used on a limited basis in the commercial field.^[14,15] This is why the DSSCs, which have high productivity in parallel with low-cost, need to be fabricated. In this case, it is possible to obtain DSSCs with high efficiency by

changing the sensitizers having an important relative value such as absorbing light in DSSCs.^[16]

In the literature, the synthesis of different phthalocyanines such as polymeric, oligomeric, ball type, dimeric, crown ethers has been studied due to their chemical structure.^[17-21] As a natural consequence of this diversity, new phthalocyanine compounds are synthesized and contribute to the improvement of the properties of the technological products they use.^[22] It appears that the solubility problems of the synthesized phthalocyanine compounds are not completely solved.^[23] Existing studies are based on the use of DSSC of phthalocyanines with electron-withdrawing groups.^[24] Here, it shows that there is a potential for use in different phthalocyanines. Currently, phthalocyanine compounds with high solubility are needed. Here, the effect of improving the solubility of the selected substituent group is present.^[25] We have described the synthesis, characterization, aggregation, DSSC of phthalocyanines bearing 4-tritylphenoxy substituents on the peripheral positions. In this study designed combination for the synthesis may prevent the formation of aggregation in organic solvents such as CHCl₃, CH₂Cl₂, THF, DMF, DMSO, and add interesting properties to phthalocyanines such as highly solubility. Moreover, phthalocyanines were used as a sensitizer in DSSC by growing on TiO₂ coated on FTO conductive glass substrate. Current density (J) versus voltage (V) measurements were applied to investigate the photovoltaic properties of the synthesized metal phthalocyanines. The calculated power conversion efficiency $(\eta\%)$ of the complexes using the

CONTACT Mehmet Salih Ağırtaş a salihagirtas@hotmail.com Department of Chemistry Faculty of Science, Van Yüzüncü Yıl University, Van, 65080, Turkey. Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lsrt. © 2019 Taylor & Francis Group, LLC obtained current density (J) versus voltage (V) curve shows that this product can be used as a promising sensitizer in solar cell application.

Experimental

General

Copper (II) chloride (CuCl₂), zinc (II) chloride (ZnCl₂), Cobalt (II) chloride (CoCl₂), Potassium carbonate (K₂CO₃), 4-tritylphenol, dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform (CHCl₃), 1,2-dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($C_2H_4Cl_2$) were purchased from Merck, Sigma and used without further purification. All reactions were carried out under a dry nitrogen atmosphere. Melting points were measured on an electrothermal apparatus. Electronic spectra were recorded on a Hitachi U-2900 Spectrophotometer (Van YYU, Central Laboratory, Turkey). Routine FT-IR spectra were recorded on a Thermo Scientific FT-IR (ATR sampling accessory) spectrophotometer (Van YYU, Central Laboratory, Turkey). ¹H NMR spectra were recorded on an Agilent 400 MHz spectrometer (Van YYU, Central Laboratory, Turkey) with tetramethylsilane as internal standard. Current density (J) versus voltage (V) measurement was performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator.

4 -(4-tritylphenoxy) phthalonitrile (3)

A mixture of 4-nitrophthalonitrile (1) (0.2573 g, 1.486 mmol) and 4-tritylphenol (2) (0.500 g, 1.486 mmol) in 20 mL dimethylformamide (DMF) was stirred at room temperature under nitrogen atmosphere. After stirring for 15 min, K₂CO₃ (2g, 14.5 mmol) was added into the mixture over a period of 2 h. After stirring the reaction mixture for a further 24 h, the reaction mixture was poured into water (200 mL) and stirred. The precipitate was filtered off, washed with water to neutralize it, then dried under vacuum oven. Yield; 0.640 g (93.12%). The compound is soluble in DMSO, DMF, THF, CH₂Cl₂, CHCl₃, acetone, acetonitrile. Mp: 224-227 °C. $C_{33}H_{22}ON_2$:462.54 g/mol. ¹H NMR (400 MHz, DMSO-d₆): (δ: ppm) 8.11, 8.08, 7.85, 7.43, 7.41, 7.25, 7.21, 7.19, 7.17, 7.16, 7.13, 7.08, 3.34, 2.49. 13C NMR (400 MHz, DMSO-d₆): (δ: ppm) 161.16, 152.19, 146.67, 144.17, 136.79, 132.99, 130.89, 128.25, 126.57, 123.40, 122.65, 119.68, 117.17, 115.87(C \equiv N), 108.76, 64.54, 40.16. FT-IR spectrum (cm⁻¹): 3051(C-H aromatic), 2231(C≡N), 1593(C=C), 1566, 1487, 1442, 1288, 1253 (Ar-O-Ar), 1213, 1174, 1082, 1014, 956,885, 825, 750, 700, 632.

[Tetrakis -(4-tritylphenoxy) phthalocyaninato] Copper (II) (4)

A mixture of 4-((4-tritylphenoxy)phthalonitrile **3** (0.059 g, 0.128 mmol) and CuCl₂ (0.014 g, 0.105 mmol) was powdered in a quartz crucible and heated in a sealed glass tube for 7 min 270 °C. After cooling to room temperature, the

product was multiply washed successively with water, methanol and ethanol. This compound is soluble CH_2Cl_2 , CHCl₃, THF, toluene, DMF, DMSO. Yield: 0.020 g (32.78%). UV-Vis) (THF) λ max, nm (log ε): 674 (5.21), 608(4.61), 346 (4.93). IR spectrum (cm⁻¹): 3053(C–H aromatic), 1598(C=C), 1490, 1447, 1442, 1230(Ar–O–Ar), 1085, 1050, 1033, 893, 825, 746, 700, 669.

[Tetrakis -(4-tritylphenoxy) phthalocyaninato] Zinc (II) (5)

A mixture of 4-((4-tritylphenoxy)phthalonitrile **3** (0.059 g, 0.128 mmol) and ZnCl₂ (0.014 g, 0.103 mmol) was powdered in a quartz crucible and heated in a sealed glass tube for 7 min 270 °C. After cooling to room temperature, the product was multiply washed successively with water, methanol and ethanol. This compound is soluble CH₂Cl₂, CHCl₃, THF, toluene, DMF, DMSO. Yield: 0.023 g (37.70%). UV-Vis) (THF) λ max, nm (log ϵ): 674 (5.17), 608 (4.51), 350 (4.82). ¹H NMR (400 MHz, DMSO-d₆): (δ : ppm) 8.09, 8.08, 7.82, 7.32, 7.29, 7.21, 7.17, 7.14, 7.11, 3.32, 2.50. IR spectrum (cm⁻¹): 3053(C-H aromatic) 1593(C=C), 1483, 1442, 1230(Ar-O-Ar), 1215, 1172, 1083, 1035, 1014, 829, 746, 700, 628.

[Tetrakis -(4-tritylphenoxy) phthalocyaninato] Cobalt (II) (6)

A mixture of 4-((4-tritylphenoxy)phthalonitrile **3** (0.059 g, 0.128 mmol) and CoCl₂ (0.014 g, 0.108 mmol) was powdered in a quartz crucible and heated in a sealed glass tube for 7 min 270 °C. After cooling to room temperature, the product was multiply washed successively with water, methanol and ethanol. This compound is soluble CH₂Cl₂, CHCl₃, THF, toluene, DMF, DMSO. Yield: 0.024 g (39.34%). UV-Vis) (THF) λ max, nm (log ϵ): 662 (5.24), 600 (4.72), 328 (5.14). IR spectrum (cm⁻¹): 3055(C–H aromatic), 1598(C=C), 1490, 1467, 1232(Ar–O–Ar), 1166, 1093, 1056, 956, 893, 746, 700.

The current density (J) – voltage (V)

For J–V measurement, fluorine-doped tin oxide (FTO, 13Ω sq⁻²) conductive glass substrates were used as the photoelectrodes. The TiO₂ paste was coated on the FTO substrates using the doctor blade method, then sintered at 450 °C for 45 minutes. A certain amount of copper phthalocyanine suspension was dropped on TiO₂ coated on FTO conductive glass substrate. The substrate was dried with N₂ gas and secured against Cu₂S counter electrodes containing polysulfide electrolytes.

Results and discussion

Synthesis and characterization

The synthetic route and the structures of the 4-(4-tritylphenoxy)phthalonitrile (3) and metallophthalocyanines (4-6)



Scheme 1. The route for the synthesis of compound 3-6.

are shown in Scheme 1. The 4-(4-tritylphenoxy)phthalonitrile (3) was accomplished by a base-catalyzed nucleophilic aromatic nitro displacement reaction between 4-tritylphenol 1 and 4-nitrophthalonitrile 2 in the presence of dry K_2CO_3 in dry DMF under a nitrogen atmosphere for 24 h at room temperature. The phthalocyanine (4) was synthesized by the reaction of 4-(4-tritylphenoxy)phthalonitrile (3) with CuCl₂. Similar to the synthesis of compound 4, the zinc and cobalt salts were changed and phthalocyanine compounds 5–6 were obtained. The complexes were washed with different solvents and their purity was checked by TLC. The characterization of the new compounds was achieved by the combination of several spectroscopic methods, including FT-IR, ¹H NMR, and UV-vis spectra.

In the IR spectrum of **3**, the characteristic "C \equiv N" vibration was observed at 2231 cm⁻¹, the aromatic and aliphatic "C-H" peaks was observed at 3051 cm⁻¹, "C = C" vibration peaks were observed at 1593 and 1566 cm⁻¹, "Ar-O-Ar" vibration was observed at 1253 cm^{-1} After the formation of metallophthalocyanines, the "C \equiv N" stretching frequency peak disappeared in the IR spectra. The vibration peaks for phthalocyanine 4 observed at 3053 cm^{-1} , "C = C" vibration at 1598 cm^{-1} , and "Ar-O-Ar" vibration 1230 cm^{-1} . The vibration peaks for phthalocyanine 5 observed at 3053 cm^{-1} , "C = C" vibration 1230 cm^{-1} . The vibration peaks for phthalocyanine 5 observed at 3053 cm^{-1} , "C = C" vibration at 1593 cm^{-1} , and "Ar-O-Ar" vibration 1230 cm^{-1} . For this compound, a shift is observed in the "C = C" IR peaks while the other peaks show the same value. The vibration peaks for phthalocyanine 6 observed at 3055 cm^{-1} , "C = C" vibration at 1598 cm^{-1} , and "Ar-O-Ar" vibration 1232 cm^{-1} .

The structure of compound **3** is confirmed by ¹H NMR for the 4-(4-tritylphenoxy)phthalonitrile through aromatic ring protons in its respective regions. In the ¹H NMR spectrum of compound **3** in DMSO-d₆, aromatic protons appear at 8.11, 8.08, 7.85, 7.43, 7.41, 7.25, 7.21, 7.19, 7.17, 7.16, 7.13, 7.08 (Ar–H), 3.34, 2.49. In the ¹³C NMR spectrum of



Figure 1. ¹H NMR spectrum of compound 3.

compound **3** in DMSO-d₆, aromatic protons appear at 161.09, 152.25, 146.25,144.03, 136.79, 133.06, 131.02, 128.45, 126.57, 123.50,122.79, 119.82, 117.46, 116.30, 108.51,64.51, 40.16. Figures 1 and 2 show the proton and carbon NMR spectra of compound **3**. ¹H NMR measurements of compounds **4** and **6** were excluded due to their paramagnetic property. The ¹H NMR protons of the zinc phthalocyanine compound **5** are observed in the range of 8.09–7.11. DMSO-d₆ solvent peaks were observed at 3.32–2.5.

Some information obtained from the aggregation studies of phthalocyanine compounds reveals the properties of the structure. It gives information about the structure form and the interaction with the solvent in the environment. These features are also necessary for applications. Especially in the investigation of phthalocyanine complexes, this parameter is mostly given in the literature. The phthalocyanine compounds can be monitored in UV spectral data for the severity of the characteristic Q band.^[26,27] Electronic absorptions spectroscopy has been extensively used to determine the formation of Pc aggregation. In this study, the aggregation behaviors of 4 were also investigated at different concentrations in THF (Figure 3). Synthesized copper phthalocyanine compound 4 exhibited a quite good solubility in THF. Phthalocyanine compound 4 did not show aggregation behavior at studied concentration ranges in THF. The concentration-dependent aggregation study shows that the Q band is not affected. The aggregation behavior for compounds **5-6** shows that these compounds act as monomers in the THF solution. Concentration-dependent changes of these two compounds are shown in Figures 4 and 5. Therefore, these complexes can be used potentially for many applications.

In our current study, compound **4**, compound **5** and compound **6** were used as the sensitizer in DSSC structures. The current density (J) – voltage (V) measurements were applied to investigate the photovoltaic properties of complexes. The power conversion efficiencies of the complexes were calculated using the recorded J–V curves. Power conversion efficiencies (η) are calculated using the following Equation (1).

$$\eta = \frac{P_m}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}} \tag{1}$$

Where P_m : maximum output power density, P_{in} : power density of incoming light, J_{SC} : short circuit current density, V_{OC} : open circuit voltage, *FF*: fill factor. The FF can be obtained from the relation is given in Equation (2).

$$FF = \frac{P_m}{J_{SC}V_{OC}} = \frac{J_{mp}V_{mp}}{J_{SC}V_{OC}}$$
(2)

Where J_{mp} : the current corresponding to the maximum power point and V_{mp} : the voltage corresponding to the maximum power point. The recorded J–V curves for compound **4**, compound **5** and compound **6** are revealed in Figure 6.



Figure 2. ¹³C NMR spectrum of compound 3.



Figure 3. Aggregation studies of compound 4 in THF.



Figure 4. Aggregation study of compound 5 in THF.

Table 1 indicates the obtained J_{SC} , V_{OC} and $\eta(\%)$ values for compound **4**, compound **5** and compound **6**, respectively. The observed high $\eta\%$ values for each complex can be assigned with the high a number of electrons which are injected into a conduction band of TiO₂ from the excited dye of compound **4**, compound **5** and compound **6**. Because it is known well that an increase in number of injected electrons into TiO₂ causes an improvement in the electron injection efficiency and an increase in V_{OC} . Moreover, the complexes have a wide absorption spectral responses which lead to producing more photogenerated excitons in free charge carriers. Hence, this situation results in an increase in J_{SC} value. Thus, it can be said that J_{SC} and V_{OC} values play an important role to improve the efficiency of compound **4**, compound **5** and compound **6** based DSSC structure. Furthermore, our result suggests that that these complexes can be used as a promising sensitizer in dye-sensitized solar cell technology.



Figure 5. Aggregation study of compound 6 in THF.



Figure 6. The recorded J–V curve for compounds 4–6.

Table 1. The obtained J_{SC} , V_{OC} and $\eta(\%)$ values for compound **4**, compound **5** and compound **6**, respectively.

Samples (Complexes)	J_{SC} (mA/cm ²)	V_{OC} (V)	η (%)
Compound 4	5.99	0.56	1.77
Compound 5	4.96	0.58	1.51
Compound 6	5.48	0.49	1.43

Conclusions

As a result, (4-tritylphenoxy) substituted copper, zinc and cobalt phthalocyanines and its starting material were obtained with high yield by an economical method. These novel compounds were characterized by spectroscopic data such as IR, UV-Vis and NMR. Aggregation and J-V measurements of the phthalocyanine compounds were performed. The measurement results show that the copper, zinc and cobalt phthalocyanines compound can be used in dye-sensitized solar cell technology.

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