



Photovoltaic performance properties, DFT studies, and synthesis of (E)-3-(diphenxy) acrylic acid substituted phthalocyanine complexes

Derya Güngördü Solğun¹ · Ümit Yıldık² · Abdullah Özkartal³ · Mehmet Salih Ağırtaş¹

Received: 16 April 2021 / Accepted: 12 July 2021 / Published online: 23 July 2021
© Institute of Chemistry, Slovak Academy of Sciences 2021

Abstract

In this study, firstly, a new phthalonitrile derivative was synthesized from the reaction of caffeic acid with phthalonitrile. Then, metal phthalocyanine complexes were obtained from the reaction of this phthalonitrile derivative with metal salts. Compounds were characterized by UV, NMR, IR and Mass spectroscopy methods. In addition, the fluorescence and electronic properties of the diamagnetic zinc phthalocyanine compound were investigated. The performances of dye-sensitized solar cells of compounds were examined. The calculated power conversion efficiencies (η %) of the complexes using the obtained current density (J)-voltage (V) curves were determined that these compounds can be used as promising sensitizers in solar cell applications. The calculated power conversion efficiencies (% η) of the complexes were found to be at a reasonable level. Molecular orbital properties such as HOMO–LUMO energy gap, Fermi Energies, state density spectrum, and molecular electrostatic potential surfaces were calculated for each phthalocyanine molecule. In addition, the amount of phthalocyanine required for ideal dye sensitivity was investigated.

Keywords Photovoltaic · Synthesis · Fluorescence · Phthalocyanine · DSSCs

Introduction

Alternative options for energy generation are drawing attention today. One of these ways is paint sensitive solar cells. One group of compounds studied for this purpose are phthalocyanines. Phthalocyanines are a class of rare compounds that are not found in nature and are synthesized in a laboratory environment. Due to this type of compound 18 π electrons, dye sensitive solar cells (Amitha et al. 2019; Suzuki et al. 2019; Ağırtaş et al. 2020), liquid crystal (Kong et al. 2019), nonlinear optics (Ou et al. 2021), catalysts (Panwar et al. 2015), laser dye (Lin et al. 2014), coloring for plastics (Ağırtaş 2007), photovoltaic (Güngördü Solğun et al. 2018; Xu et al. 2020), it has been extensively researched for fields such as photodynamic therapy (PDT) (Matshitse et al. 2018;

Cozzolino et al. 2019), DNA Binding Activities (Arslantas and Ağirtas 2018), photosensitizers (PS) for singlet oxygen generation (Janas et al. 2021; Reddy et al. 2021). Many problems are waiting to be solved in the world today. One of the most important of these is the increasing energy demand. The other is the increasing health problems in the world. It is the leading cancer disease. Phthalocyanine compounds are an important alternative to solve or help these two basic problems. Phthalocyanine compounds are being researched extensively for more economical choices for expensive dye-sensitive solar cells. With further improvement of power conversion efficiencies (η %), phthalocyanines can be used instead of expensive compounds such as ruthenium (Urbani et al. 2019; Ghadari et al. 2020). Phthalocyanine compounds with fluorescence properties are also promising in the treatment of new generation cancer with their use as sensor agents for the development of biosensors and photodynamic therapy (Luo et al. 2011; Attia et al. 2019; Ağırtaş 2020).

In this study, (E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid compound was synthesized from the reaction between caffeic acid 4-nitrophthalonitrile. Zinc, cobalt, copper phthalocyanine compounds were synthesized from the reaction of the new phthalonitrile compound with metal salts. Synthesis, fluorescence, electronic, photovoltaic

✉ Mehmet Salih Ağırtaş
salihagirtas@hotmail.com

¹ Department of Chemistry, Faculty of Science, Van Yüzüncü Yıl University, 65080 Van, Turkey

² Architecture and Engineering Faculty, Department of Bioengineering, Kafkas University, Kars, Turkey

³ Department of Physics, Faculty of Science, Van Yüzüncü Yıl University, 65080 Van, Turkey

performance characteristics of phthalocyanine complexes have been reported. Photovoltaic performance shows that the compounds are promising for dye-sensitive solar cells. Quantum calculations were performed with the popular LanL2DZ (Los Alamos National Laboratory 2 Double-Zeta), which is a widely used type basis set of DFT method was used to model the metal atoms.

Experimental

General

(E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid (3)

A mixture of caffeic acid **1** (0.260 g, 1.45 mmol) and 4-nitrophthalonitrile **2** (0.500 g, 2.89 mmol) in 20 mL dimethylformamide (DMF) was stirred at room temperature under nitrogen atmosphere. After stirring for 15 min, K_2CO_3 (1.59 g, 11.56 mmol) was added into the mixture over a period of 2 h. The reaction mixture was further stirred for 42 h at 70 °C temperature. At the end of the reaction, the mixture was cooled to the room temperature and diluted HCl solution (0.1 M) was added to arrange of pH as 2–3. The solid particles were filter. The product was washed until neutral with pure water. It was dried at 80 °C in a vacuum oven. Yield: 0.58 g (47%). MP: 165–170 °C. The final product was soluble in various solvents such as acetonitrile, THF, DMF, DMSO. HRMS (ESI); (M + H) calc. for $C_{25}H_{12}N_4O_4$: 432.09; found: 455.07 [M + Na]⁺. ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 12.45 (–OH), 8.08, 8.02, 7.77, 7.75, 7.63, 7.59, 7.43, 7.41(Ar–H), 6.62–6.58(–CH=COO), 3.31, 2.48, 1.21. ¹³C NMR (400 MHz, DMSO-*d*₆) δ ppm: 167.81, 160.42, 160.28, 146.36, 145.37, 142.46, 136.62, 134.43, 128.07, 123.76, 123.05, 122.56, 122.45, 122.33, 121.18, 117.12, 116.20, 115.67, 115.62, 109.43, 109.28, 40.60, 40.39, 40.18, 39.97, 39.76, 39.56, 39.35. IR spectrum (cm^{–1}): 3523(OH), 3072–3035(Ar–CH), 2887(aliphatic–CH), 2231(–C≡N), 1691(=O), 1641–1587(–C=C), 1577, 1483, 1276, 1242 (Ar–O–Ar), 1199, 1165, 1111, 950, 835.

(E)-3-(diphenyl) acrylic acid substituted Zn (II) phthalocyanine (4)

A mixture of (E)-3-(3,4-bis(3,4-dicyanophenoxy)phenyl) acrylic acid (**3**) (0.050 g, 0.163 mmol) and Zn(CH₃COO)₂ (0.15 g) mixture was powdered in a quartz crucible and heated in a sealed glass tube for 5 min 210 °C in the presence of 2 drops of DBU and under nitrogen. After reaching room temperature, 0.1 M HCl was added and left overnight. The product was filtered. It was washed with pure water until neutral. It was then washed with ethanol, methanol. This compound is soluble in THF, DMF, DMSO. Yield: 0.020 g (37%).

HRMS (ESI); (M + H) calc. for $C_{50}H_{24}N_8O_8Zn$: 928.10; found: 951.09 [M + Na]⁺. UV–Vis (DMF) λ_{max} (log ϵ): 678 (5.14), 612(4.56), 350 (5.20). ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm: 7.93–7.73 (Ar–H), 7.24 (Ar–H), 3.41, 3.36, 3.31, 3.26, 2.87, 2.71, 2.65, 2.53, 2.52, 2.49, 2.48, 2.43, 2.31, 2.07, 1.97, 1.89, 1.51, 1.22, 1.13. IR spectrum (cm^{–1}): 3523 (OH), 3078–3032 (Ar–CH), 2881(aliphatic–CH), 1689(C=O), 1535(–C=C), 1465, 1338, 1288 (Ar–O–Ar), 1085, 1045, 883.

(E)-3-(diphenyl) acrylic acid substituted Co (II) phthalocyanine (5)

A mixture of (E)-3-(3,4-bis(3,4-dicyanophenoxy)phenyl) acrylic acid (**3**) (0.050 g, 0.163 mmol) and Co(CH₃COO)₂ (0.15 g) mixture was powdered in a quartz crucible and heated in a sealed glass tube for 5 min 210 °C in the presence of 2 drops of DBU and under nitrogen. After reaching room temperature, 0.1 M HCl was added and left overnight. The product was filtered. It was washed with pure water until neutral. It was then washed with ethanol, methanol. This compound is soluble in THF, DMF, DMSO. Yield: 0.020 g (37%). HRMS (ESI); (M + H) calc. for $C_{50}H_{24}CoN_8O_8$: 923.10; found: 946.08 [M + Na]⁺. UV–Vis (DMF) λ_{max} (log ϵ): 670 (5.30), 604(4.77). IR spectrum (cm^{–1}): 3523 (OH), 3066–3032 (Ar–CH), 2868 (aliphatic–CH), 1691(C=O), 1641–1535(–C=C), 1409, 1338, 1271 (Ar–O–Ar), 1085, 954, 906, 806.

(E)-3-(diphenyl) acrylic acid substituted Cu (II) phthalocyanine (6)

A mixture of (E)-3-(3,4-bis(3,4-dicyanophenoxy)phenyl) acrylic acid (**3**) (0.050 g, 0.163 mmol) and Cu(CH₃COO)₂ (0.15 g) mixture was powdered in a quartz crucible and heated in a sealed glass tube for 5 min 210 °C in the presence of 2 drops of DBU and under nitrogen. After reaching room temperature, 0.1 M HCl was added and left overnight. The product was filtered. It was washed with pure water until neutral. It was then washed with ethanol, methanol. This compound is soluble in THF, DMF, DMSO. Yield: 0.018 g (33%). HRMS (ESI); (M + H) calc. for $C_{50}H_{24}CuN_8O_8$: 927.10; found: 928.10 [M + H]⁺. UV–Vis (DMF) λ_{max} (log ϵ): 680 (5.09). IR spectrum (cm^{–1}): 3523 (OH), 3072–3032 (Ar–CH), 2883 (aliphatic–CH), 1691(C=O), 1641–1535(–C=C), 1447, 1406, 1340, 1288 (Ar–O–Ar), 1083, 952, 910, 794.

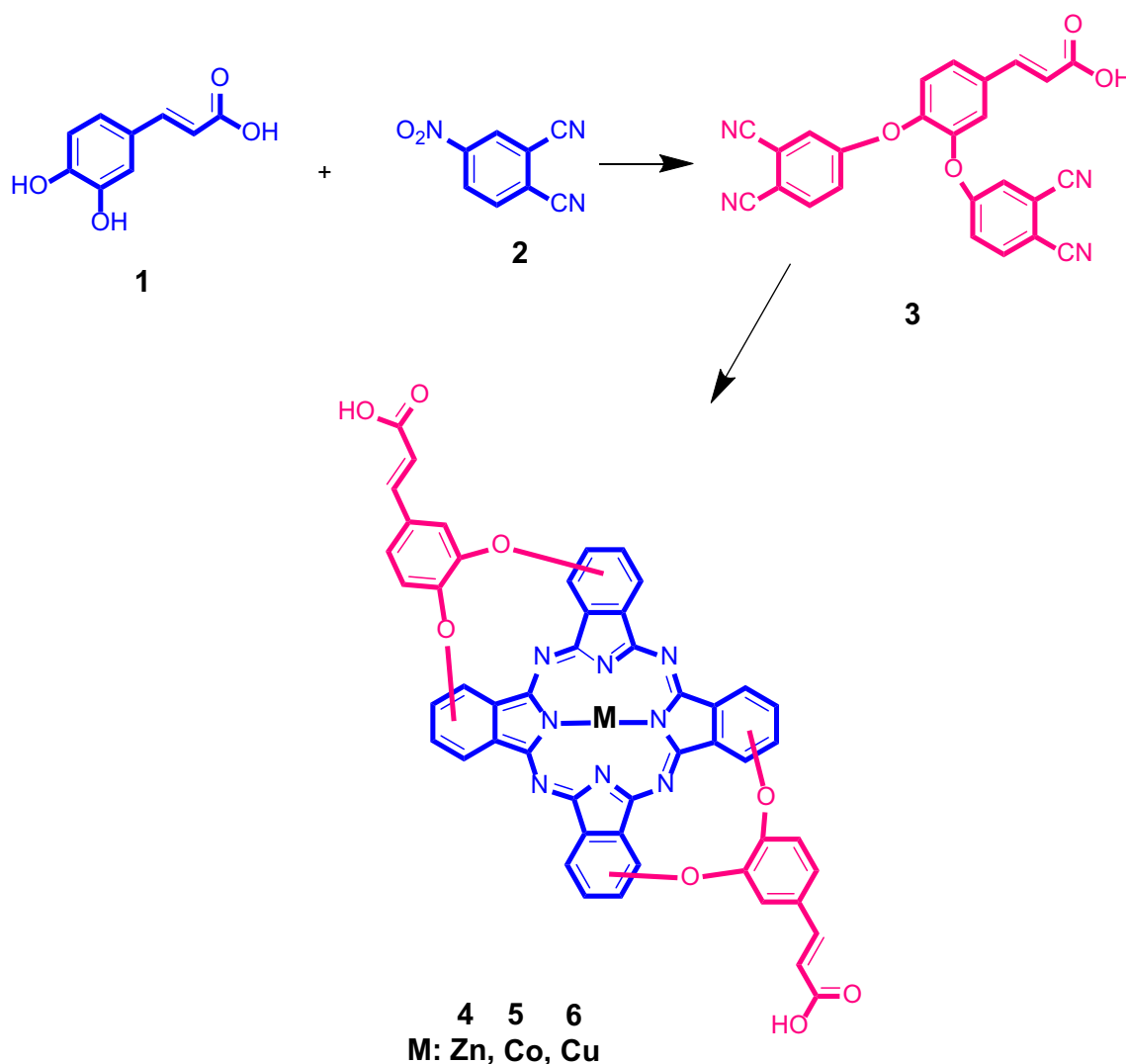
Results and discussion

The (E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid compound (**3**) was obtained by reacting caffeic acid with 4-nitrophthalonitrile in DMF. The reaction was carried

out at 70 °C. When the reaction was terminated, it was brought to room temperature. Then HCl was used so that the pH was 2–3. The product precipitated in water was washed with pure water until neutrality. The synthesis scheme of the (E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid compound (**3**) and phthalocyanines compounds (**4–6**) is given in Schema 1. Zinc, cobalt, and copper phthalocyanine complex compounds were obtained as a result of reactions of (E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid with metal salts. Spectroscopic methods such as IR, NMR, UV Vis, Mass spectroscopy were used in the characterization of the new compounds.

(E)-3-(3,4-bis(3,4-dicyanophenoxy)phenyl)acrylic acid as expected in the IR spectrum OH group peak at 3523 cm^{-1} , nitrile peak at 2231 cm^{-1} , aromatic H peaks at $3072\text{--}3035\text{ cm}^{-1}$, C=O peak at 1691 cm^{-1} , C=C peaks at $1641\text{--}1577\text{ cm}^{-1}$, Ar–O–Ar peak at 1242 cm^{-1} was

observed. The change observed in the IR spectrum in the formation of the metal phthalocyanine compounds from the (E)-3-(3, 4-bis (3, 4-dicyanophenoxy) phenyl) acrylic acid compound is the disappearance of the nitrile peak in 2231 cm^{-1} . Peaks of zinc phthalocyanine, as expected, are observed at OH peak 3523 cm^{-1} , at aromatic CH peaks $3078\text{--}3032\text{ cm}^{-1}$, $2881(\text{aliphatic-CH})$, C=O peaks at 1689 cm^{-1} , C=C peaks at 1535 cm^{-1} , Ar–O–Ar peak at 1288 cm^{-1} . Peaks of cobalt phthalocyanine, as expected, are observed at OH peak 3523 cm^{-1} , at aromatic CH peaks $3066\text{--}3032\text{ cm}^{-1}$, $2881(\text{aliphatic-CH})$, C=O peaks at 1691 cm^{-1} , C=C peaks at 1535 cm^{-1} , Ar–O–Ar peak at 1271 cm^{-1} . Peaks of copper phthalocyanine, as expected, are observed at OH peak 3523 cm^{-1} , at aromatic CH peaks $3072\text{--}3032\text{ cm}^{-1}$, $2883(\text{aliphatic-CH})$, C=O peaks at 1691 cm^{-1} , C=C peaks at 1535 cm^{-1} , Ar–O–Ar peak at



Schema 1 Reaction route of newly synthesized compounds (3–6)

1288 cm^{-1} . The FTIR spectra of the compounds are shown in Figs. 1–4.

Mass spectra of compounds (3–6) confirmed the proposed structure with the molecular ion being identified at 455.07 $[\text{M} + \text{Na}]^+$, 951.09 $[\text{M} + \text{Na}]^+$, 946.08 $[\text{M} + \text{Na}]^+$, and 928.10 $[\text{M} + \text{H}]^+$ respectively.

In the ^1H NMR spectrum of Compound 3, OH peak was observed as a singlet at 12.45 ppm, while other aromatic protons were observed as multiplets in the range 8.04–6.58 ppm. In the ^{13}C NMR spectrum, peaks of carbon atoms were observed in the range of 167.81–109.28 ppm in accordance with the structure. In the ^1H NMR spectrum of compound number 5, aromatic protons were observed as multiplets in the range 7.93–7.24 ppm.

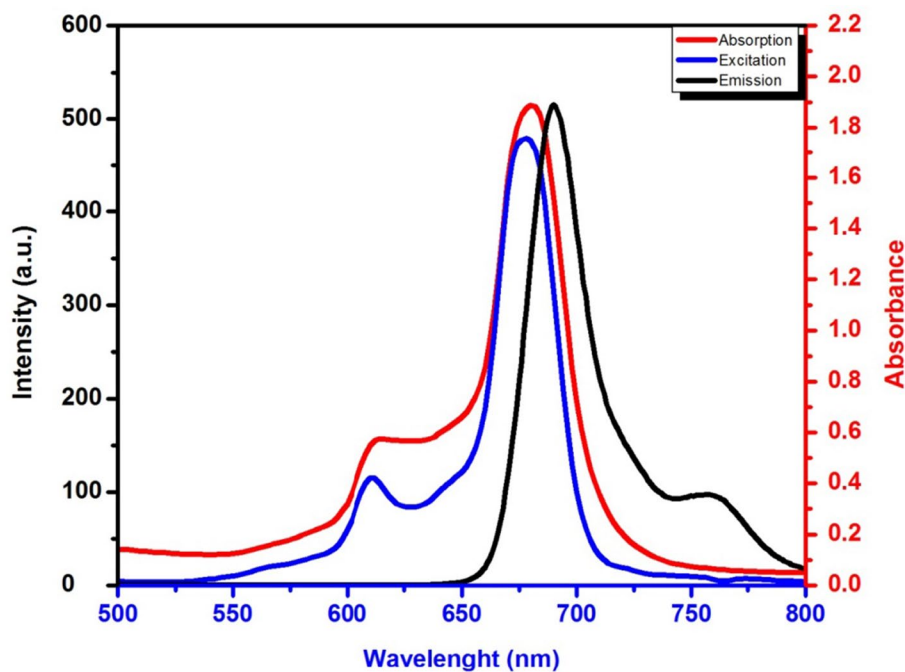
UV–vis is mainly used to examine the electronic properties of phthalocyanines. With this spectroscopic method, characteristic *Q* and *B* bands for phthalocyanines are observed. In addition, the observation of the *Q* band as a single peak or a split peak is evaluated as an indication of whether the metal is attached to the phthalocyanine ring. In this study, the electronic properties of phthalocyanine complexes were investigated in DMF solvent. The *Q* band for zinc, cobalt, and copper phthalocyanine compounds was observed at 678, 670 and 680 nm, respectively. The electronic transition band values determined for phthalocyanine compounds are compatible with the existing literature information for phthalocyanine compounds (Salih Ağırtaş 2007). This confirms the expected structure of the phthalocyanine compounds. Large aromatic molecules such as phthalocyanines and porphyrins systems can stack on each other due to much more π electrons. This stacking is generally called

aggregation. Phthalocyanine derivatives show two types of aggregation, *H* and *J* type, which are mentioned in the literature. The aggregation can vary depending on factors such as the structure of the molecules, solvent type, and polarity. These effects reduce the solubility of phthalocyanine compounds, molecules in organic solvents (Özdemir et al. 2021).

For today, phthalocyanine-based fluorescent compounds are not only the subject of medical diagnostics and sensing agents, but also the subject of interesting research such as patterning, detection, and data storage in polymer films (Li et al. 2017). It manifests itself in metals with diamagnetic properties such as zinc, where phthalocyanine compounds are expected to show fluorescence properties. Fluorescence spectra are known as mirror images of absorption spectra. The fluorescence spectrum is slightly wider compared to the absorption spectrum. In this study, the fluorescence excitation, emission, and absorption values of the zinc phthalocyanine compound are shown in Fig. 1.

It is known that the fluorescent Stokes shift values of zinc phthalocyanine change more or less depending on the solvent effect. The Stokes shift value for this compound was found to be 8 nm in DMF solvent. Fluorescence excitation, emission, and absorption values of phthalocyanine compound 4 values were determined as 678, 686, and 680 nm, respectively. The fluorescence quantum efficiency (Φ_F) of zinc phthalocyanine is 0.26. The fluorescence quantum efficiency (Φ_F) of zinc phthalocyanine was higher in DMF than std-ZnPc (0.17) (Saka et al. 2011). In general, it is expected that the substituted phthalocyanines are higher than the standard. This situation can be regarded as the effect of the substituent. The parameters found indicate that the

Fig. 1 Emission, excitation, and absorption spectra of zinc phthalocyanine (4) in DMF



fluorescent activity of the compound may be suitable for a detection agent.

Photovoltaic properties

Solar cells in Dye-Sensitized Solar Cell (DSSC) structure were prepared to examine the photovoltaic performance of phthalocyanine compounds produced. Fluorine doped tin oxide (FTO) coated microscope glasses were used as the substrate of DSSC structures, which were prepared with great care and traditional cleaning at every stage. The 18 nm anatase TiO₂ paste was left to have an effective circular area of 0.2 cm² by the doctor blade technique. After drying at room temperature, it was annealed in a quartz oven at 450 °C for 15 min the phthalocyanine solutions of compound **4**, compound **5**, and compound **6** prepared as 1 mM were sensitized to TiO₂ photoanodes using the dripping-drying technique. It was left to dry at room temperature for 24 h after each drop for sensitization. It was repeated 4 times to determine the amount of sensitization at the highest conversion efficiency. The current density–voltage plot of the 4 times repeated trickle drying process for compound **6** is given in Fig. 2. As can be seen from Fig. 2, the highest conversion efficiency was obtained by repeating the dripping drying 3 times. To form strong covalent bonding with TiO₂, the drop drying process was repeated 3 times for the solutions of compound **4**, compound **5**, and compound **6**. An I[−]/I₃[−] electrolyte containing 50 mM iodide/tri-iodide was dropped to the prepared samples and combined with a platinum-coated electrode, they were turned into sandwiches (Ağırtaş et al. 2020).

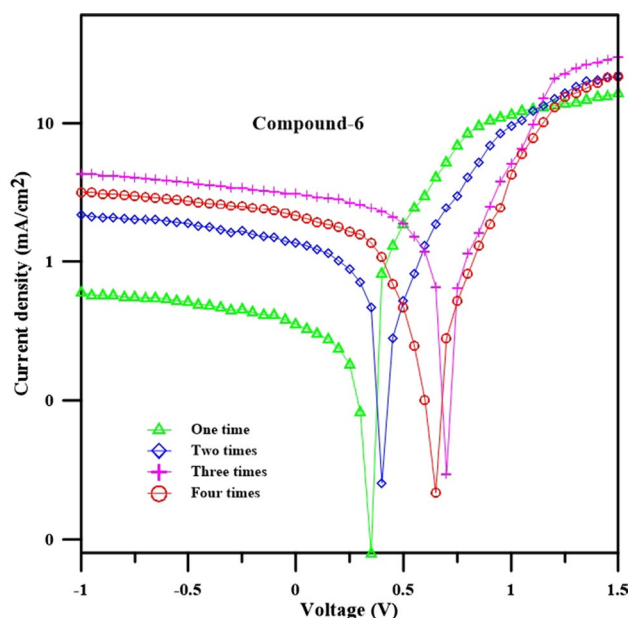


Fig. 2 *J*–*V* plot of the amount of sensitization for Compound 6

The current–voltage (*I*–*V*) measurements of the prepared DSSC structures were carried out with Keithley (model 6487) picoampermeter/voltage source at room temperature, under a solar simulator with 100 mW/cm² illumination.

The graph obtained from the current–voltage measurements of compound **4**, compound **5**, and compound **6** is given in Fig. 3. Short circuit current density (*J*_{sc}), open-circuit voltage (*V*_{oc}), *V*_m, and *J*_m values of the samples are obtained from Fig. 3.

$$FF = \frac{I_{\max} V_{\max}}{I_{sc} V_{oc}} \quad (1)$$

$$\eta = \frac{I_{sc} V_{oc}}{P_{in}} FF \quad (2)$$

Filling factor (FF) and energy conversion efficiency (*η*) values of the produced samples calculated with the help of Eqs. (1) and (2) are given in Table 1. With a value of 2.66, the highest energy conversion efficiency belongs to compound **6**. The results obtained here suggest that if the heterojunction perovskite is formed with perovskite, the photovoltaic performance of solar cells will further improve (Wu et al. 2017). Another feature of phthalocyanines is that they are good chromophores. Besides DSSCs, photovoltaic devices are being studied extensively for their promise for applications such as electrochemical, absorption in intense red/NIR, photochemical, thermal stability (O'Regan et al. 2008; Yum et al. 2008). The energy power conversion

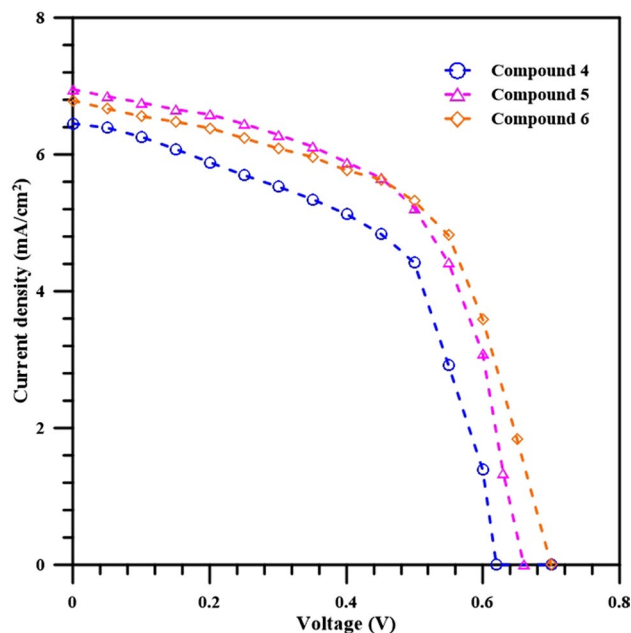


Fig. 3 *J*–*V* curves of DSSCs based on phthalocyanine compounds 4–6

efficiencies obtained here were found to be higher than our previous studies (Martín-Gomis et al. 2017; Güngördü Solğun et al. 2018; Ağırtaş et al. 2020; Cabir et al. 2020). In this way, it can be said that the energy power conversion efficiency increases depending on the group being substituted. Here, it is clear that the most effective factor in the high power conversion effect is the carboxyl group. This indicates that the compounds can be evaluated commercially. There is an expectation that the efficiency will increase even more when other additives are added to it. The results obtained in this research are also expected to contribute to renewable energy. The photovoltaic performance obtained in this study is promising for dye-sensitized solar cells.

DFT studies of phthalocyanines

The structure of the phthalocyanine compounds was optimized by using the LanL2DZ basis set of the B3LYP method from Gaussian 09 software at the groundstate gas phase (Frisch and Gaussian 09. 2009; Priya et al. 2019). The parameters HOMO–LUMO, NBO, DOS, and MEP, etc. were calculated on the ground state optimized structure. Frontier orbital energy spectra were obtained using Gausssum 3.0 software (O’Boyle et al. 2008).

Orbitals of molecular HOMO–LUMO

Orbital energies of a molecular system are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their energy gap (Mumit et al. 2020; Sherin and Manojkumar 2020; Shukla and Yadava 2020). HOMO are electrons in the outermost highest energy orbital that are the electron donor. LUMO is the lowest energy orbital that can accept electrons. The HOMO and LUMO value of Zn–Pc were calculated -5.60 eV and -3.57 eV in Fig. 4 a, respectively. The energy value of Co–Pc was calculated -5.63 eV and -3.42 eV in Fig. 5 a, respectively. The parameters of Cu–Pc were calculated -5.64 eV and -3.48 eV (Fig. 6). The bandgap is calculated close to each other in both basic sets. The HOMO–LUMO energy gap obtained around 2.03–2.21 eV and indicates that the molecule is softer, more reactive, and more polarizable (Maidur et al. 2017).

Table 1 The photovoltaic parameters for DSSCs are based on phthalocyanine 4–6 complexes

Samples	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)
Compound 4	6.45	0.62	0.52	2.04
Compound 5	6.95	0.66	0.55	2.54
Compound 6	6.78	0.70	0.56	2.66

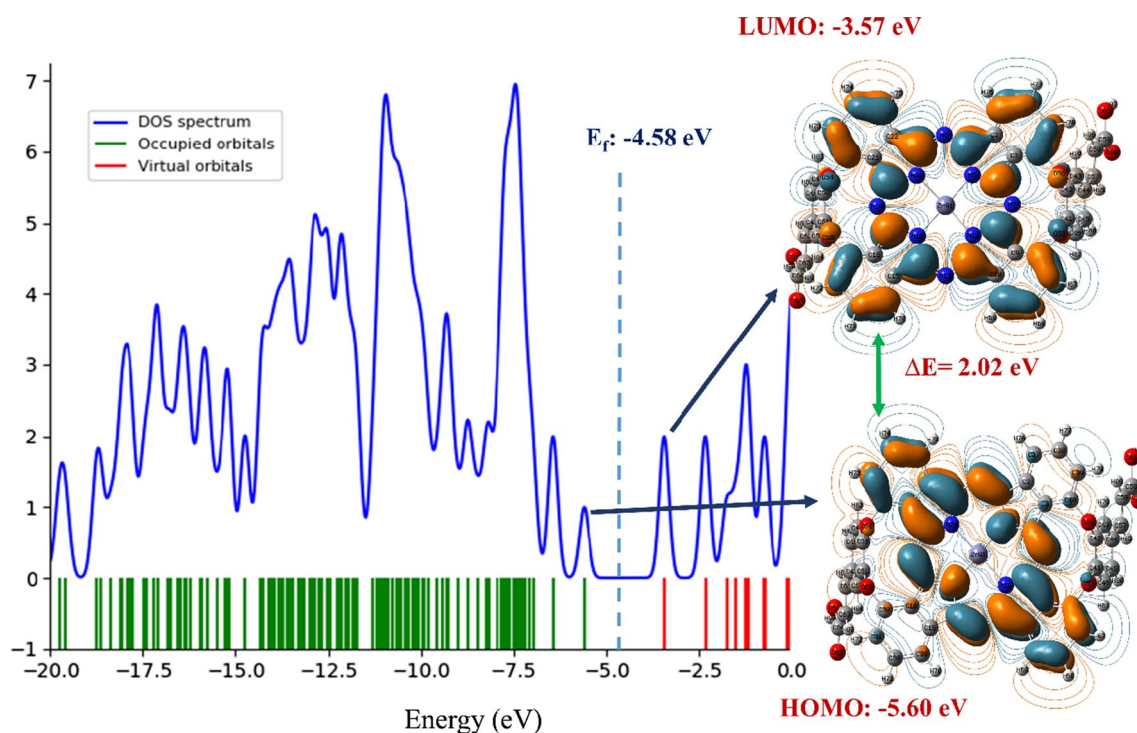


Fig. 4 HOMO–LUMO energy orbitals, Fermi energy (E_F) and bandgap of Zn–Pc with B3LYP/LanL2DZ basis set

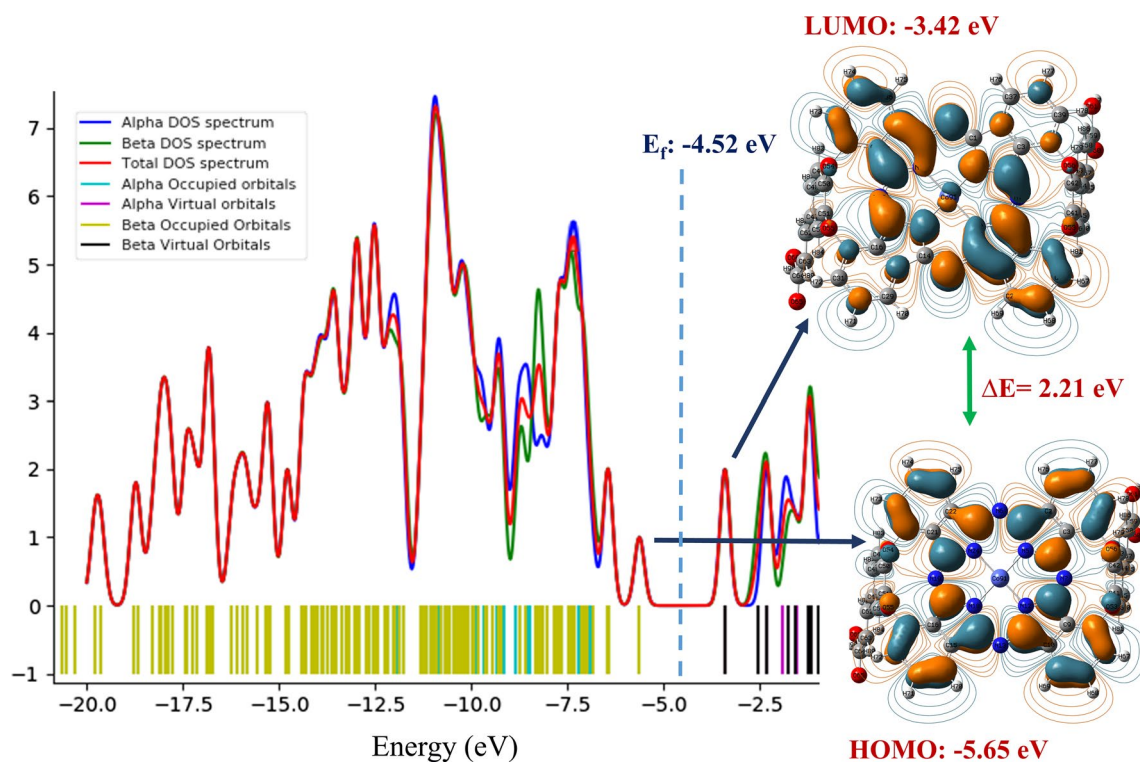


Fig. 5 HOMO–LUMO energy orbitals, Fermi energy, and bandgap of Co-Pc with B3LYP/LanL2DZ basis set

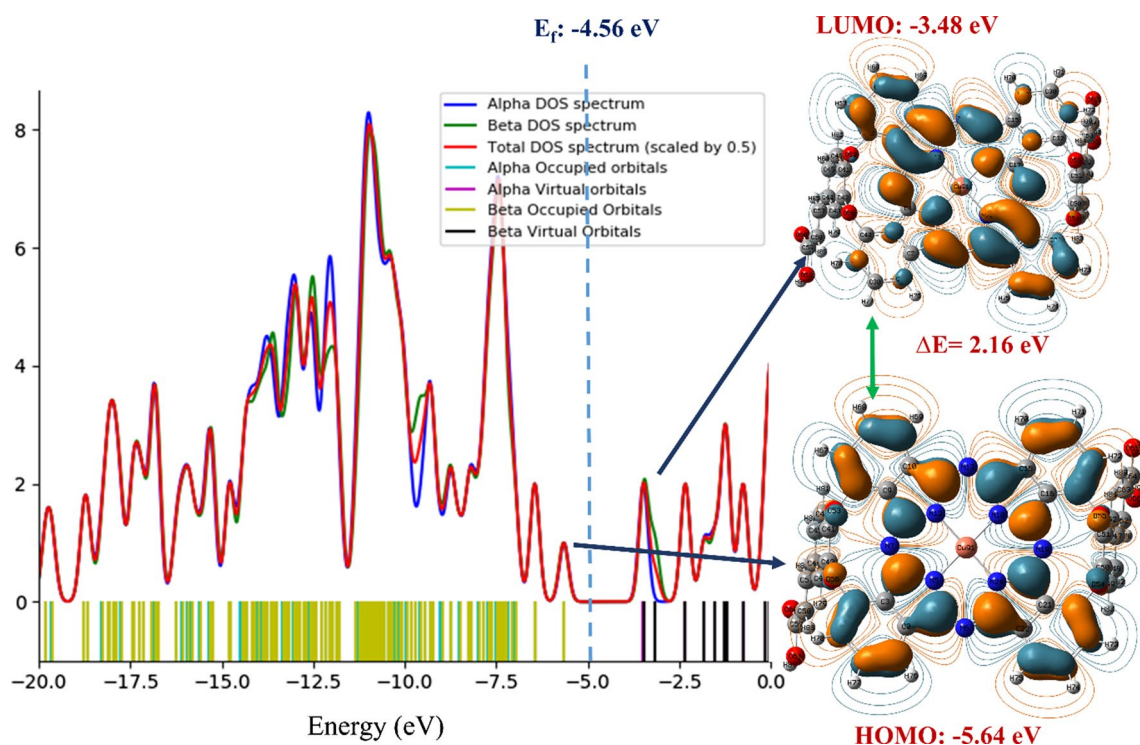


Fig. 6 HOMO–LUMO energy orbitals, Fermi energy and DOS diagram of Cu-Pc with B3LYP/LanL2DZ basis set

In order to understand the electronic states of phthalocyanines with central metal atom in detail, the results of the electronic total DOS of different sizes are visualized as shown in Figs. 4–6. The density of localized states of metal atoms most effectively in the phthalocyanine nucleus increases the energy level due to the presence of N atoms. Here the intensity of localized states is seen between -7.5 and -15 eV with a high increasing trend. This situation has close values for three phthalocyanines with different central atoms. DOS analysis shows that M–Pc has energy gap, therefore it shows semiconductor character. There is an increase in HOMO, LUMO and Fermi energies with the increase of 8 N content in the phthalocyanine structure. As can be seen in the table, the Fermi energy levels of the compounds were found to be closer to the HOMO values, which are the middle of the valence and conduction band (Rad and Aghaei 2018).

HOMO and LUMO frontiers orbitals, the chemical bonding potential of the molecule plays an active role. The bandgap between the maximum full orbital and the minimum energy orbital indicates kinetic stability and chemical reactivity. At the same time, Fermi energies, the polarization, stiffness, electronegativity, and other reactive indices of a molecule using these energies were calculated. Table 2 shows the chemical character indices.

Molecular electrostatic potential (MEP)

MEP maps are calculated to determine the amount and distribution of electrostatic potential of the molecular structure (Moghadam et al. 2019). This map deals with electron density and is an important descriptor for understanding the electrophilic and nucleophilic potential, reaction activity, and hydrogen bond interaction sites of compounds. MEP reactive sites calculated at DFT/B3LYP methods with LanL2DZ basis sets in Fig. 7 respectively. The different colors traced in the molecule indicate different electrostatic potentials and the potential level shifts to a more negative region, such as blue > green > yellow > orange > red. The negative potential (red regions) $V(r)$ values are -6.01 e $^{-2}$ and the majorly positive potentials (blue regions) are around 6.01 e $^{-2}$ on phthalocyanine. These results provided information on the intramolecular interaction site of the phthalocyanine compound (Cabir et al. 2019, 2020; Ağırtaş et al. 2021). These active sites of the title compound indicate high both chemical and biological activity.

Natural bond orbital (NBO) analysis

NBO analysis, which is based on quantum data, is a useful method to show the electron transfer between electron donor and electron acceptor atom groups in a compound (Singh et al. 2020). The stabilization energy $E(2)$ is obtained for the donor (i) and the acceptor (j) with the NBO analysis calculated with the formula given below.

Table 2 Comparison of HOMO, LUMO, Fermi Energies, and chemical reactivity descriptors of phthalocyanine

Energy											
Molecule	LUMO	HOMO	^a Δ	^b E_f	^c I	^d η	^e s	^f χ	^g μ	^h ω	ⁱ A
Zn–Pc	– 3.57	– 5.60	2.03	– 4.58	5.60	1.015	0.507	4.58	– 4.58	10.3	3.57
Co–Pc	– 3.42	– 5.63	2.21	– 4.52	5.63	1.105	0.532	4.52	– 4.52	9.24	3.42
Cu–Pc	– 3.48	– 5.64	2.16	– 4.56	5.64	1.080	0.54	4.56	– 4.56	9.62	3.48

^aEnergy Gap, ^bFermi Energy, ^cIonization Potential, ^dChemical hardness, ^eChemical softness, ^fElectronegativity, ^gChemical Potential, ^hElectrophilicity index, ⁱElectron Affinity

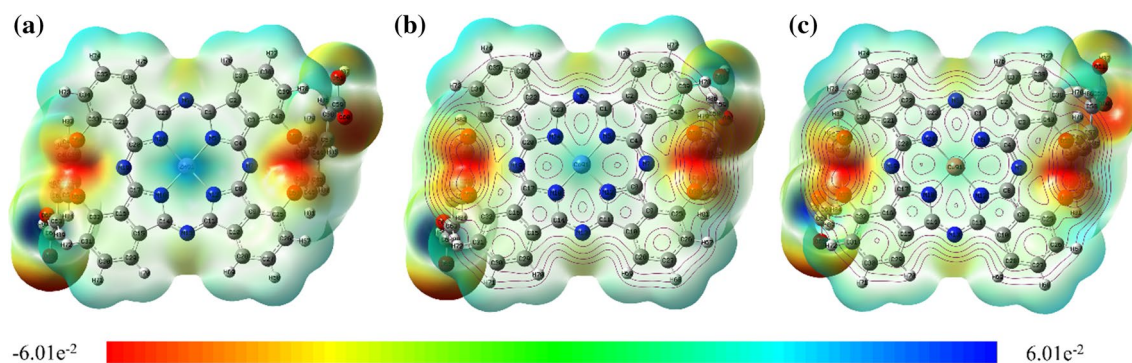


Fig. 7 MEP reactive sites calculated at DFT / B3LYP methods with **a** 6–311 G (d, p) **b** LanL2DZ basis sets

$$E(2) = \Delta E_{ij} = q_i \left(\frac{F_{(ij)}^2}{E_j - E_i} \right)$$

In the formula, E_i and E_j diagonal elements, q_i donor orbital occupancy value, $F(i, j)$ is the NBO Fock matrix element (Rahaman et al. 2020). The higher the value of stabilization $E(2)$ indicates the strong interaction. Electron density, hybridization, and excitation potentials of the phthalocyanine core and substituted groups, NBO analysis were performed at the DFT (B3LYP)/LanL2DZ basis set. NBO 3.1 programs included in the Gaussian 09 package were used and listed at Table 3. The electronic configuration of optimized Zn-Pc was obtained Zn 91 [core]4s^(0.30)3d^(9.96)4p^(0.37), Co 91 [core]4s^(0.10)3d^(3.31)4p^(0.03)5p^(0.12) and Cu 91 [core]4s^(0.37)3d^(9.22)4p^(0.01).

The 18 π electron system of the phthalocyanine compound forms the center with or without metal. Here the metal atom is held in a strong sheath. The stabilization of the groups surrounding the central atom was compared with the neutral bond analysis. The strongest stabilization energy was calculated in Zn-Pc. The interaction stabilization energy of

the Zn central atom between the surrounding atom groups, for example, the transition N 19—C 20 $\rightarrow$ C 17—N 18 $\pi \rightarrow \pi^*$, has been calculated to be the highest 40.12 kcal/mol. The stabilization energy obtained in phthalocyanine with Cu central atom was calculated as C 4—N 7 $\rightarrow$ C 8—N 12 19.34 kcal/mol. In the Co-centered compound, N 6—C 23 $\rightarrow$ C 1—N 5 $\pi \rightarrow \pi^*$ transitions have maximum stabilization energy of 19.02 kcal/mol. NBO analysis parameters and other transition examples are listed in Table 3.

Conclusions

Here, firstly, (E)-3-(3,4-bis(3,4-dicyanophenoxy) phenyl) acrylic acid was synthesized. New zinc, cobalt, and copper phthalocyanine complexes were obtained from the reaction of synthesized starting compounds with metal salts. All new compounds were characterized by spectroscopic methods. Metal phthalocyanines were calculated using the B3LYP method LanL2DZ basis set. Optimization energy calculations have shown that the phthalocyanine structures are stable. In addition to other properties of zinc phthalocyanine,

Table 3 NBO analysis of phthalonine compounds, donor and acceptor interaction, and bond type energy values

Donor NBO(<i>i</i>)	Type	ED/ <i>e</i>	Acceptor NBO(<i>j</i>)	Type	ED/ <i>e</i>	$E(2)^a$ (Kcal/mol)	$E(j)-E(i)^b$ (a.u.)	$F(i, j)^c$ (a.u.)
Cu 91	CR(3)	0.99960	C 1—N 5	σ^*	0.02326	0.65	6.31	0.081
			C 4—N 5	σ^*	0.02410	0.46	6.34	0.069
			C 8—N 12	σ^*	0.02416	0.46	6.34	0.069
C 1—C 2	σ	0.98322	Cu 91 (6)	LP*	0.15996	1.08	37.91	0.279
			C 2—C 37	σ^*	0.01127	1.80	1.22	0.059
			C 3—C 40	σ^*	0.01873	2.33	1.22	0.067
C 2—C 3	π	0.97851	C 1—N 5	π^*	0.29998	15.01	0.21	0.074
			C 4—N 7	π^*	0.22805	14.21	0.25	0.076
			C 37—C 38	π^*	0.15213	0.28	9.47	0.066
			C 39—C 40	π^*	0.17246	10.82	0.27	0.069
C 4—N 7	π	0.84755	C 8—N 12	π^*	0.29653	19.34	0.28	0.100
C 9—C 10	π	0.80053	C 8—N 12	π^*	0.29653	17.12	0.21	0.080
			C 11—N 13	π^*	0.22536	12.43	0.24	0.070
			C 25—C 26	π^*	0.17255	10.84	0.27	0.069
			C 27—C 28	π^*	0.15192	9.48	0.28	0.066
C 14—C 15	σ	0.98322	C 16—C 32	σ^*	0.01872	2.33	1.22	0.067
C 16—C 32		0.98597	C 15—C 16	σ^*	0.01305	2.61	1.25	0.072
			C 16—C 17	σ^*	0.02145	2.59	1.20	0.071
C 37—C 38	σ	0.98892	C 1—C 2	σ^*	0.02058	2.88	1.14	0.073
			C 2—C 37	σ^*	0.01127	1.68	1.26	0.058
Co 91	CR(2)	0.99916	C 1—N 5	σ^*	0.30454	0.94	4.05	0.079
	CR (1)	0.99679	Co 91	LP*	0.05877	1.50	3.87	0.104
N 6—C 23	π	0.98990	C 1—N 5	π^*	0.88573	19.02	0.27	0.098
Zn 91	LP*		C 8—N 12	σ^*	0.04934	1.77	0.11	0.040
C 1—N 6	π	1.69669	C 23—N 24	π^*	0.59688	38.72	0.27	0.099
N 19—C 20	π	1.69039	C 17—N 18	π^*	0.58711	40.12	0.28	0.102

fluorescence was characteristic. The properties of this compound depending on the fluorescence emission and absorption spectra were investigated. The solar conversion efficiency of DSSC devices based on zinc, cobalt, and copper phthalocyanine compounds was reported as 2.04%, 2.54%, and 2.66%, respectively. It was determined that the trickle drying process used for the sensitization of TiO₂ was 3 times. The measurement results show that the compounds can be beneficial in dye-sensitive solar cell technology.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11696-021-01786-6>.

Acknowledgements We would like to thank Van Yüzüncü Yıl University Scientific Research Projects Unit for their contribution (Project Number: FDK-2019-8105).

Declarations

Conflict of interest The authors declare no conflict of interest.

References

- Ağırtaş MS (2007) Synthesis and characterization of novel symmetrical phthalocyanines substituted with four benzo [d] [1,3] dioxol-5-ylmethoxy groups. *Inorganica Chim Acta* 360(7):2499–2502. <https://doi.org/10.1016/j.ica.2006.12.029>
- Ağırtaş MS (2020) Fluorescence properties in different solvents and synthesis of axially substituted silicon phthalocyanine bearing bis-4-tritylphenoxy units. *J Heterocycl Commun* 26(1):130–136. <https://doi.org/10.1515/hc-2020-0113>
- Ağırtaş MS, Cabir B, Yıldık U, Özdemir S, Gonca S (2021) Synthesis, antioxidant, DNA cleavage and antimicrobial properties of phthalocyanine complexes bearing the poly-hydroxyl groups. *Chem Pap* 75(4):1749–1760. <https://doi.org/10.1007/s11696-020-01432-7>
- Ağırtaş MS, Güngördü Solğun D, Yıldık U, Özkartal A (2020) Design of novel substituted phthalocyanines; synthesis and fluorescence, DFT, photovoltaic properties. *Türk J Chem* 44:1574–1586
- Amitha GS, Ameen MY, Reddy VS, Vasudevan S (2019) Synthesis of peripherally tetra substituted neutral azophenoxy zinc phthalocyanine and its application in bulk hetero junction solar cells. *J Mol Struct* 1185:425–431. <https://doi.org/10.1016/j.molstruc.2019.02.086>
- Arslantas A, Agirtas MS (2018) Investigation of DNA binding activities of peripherally 2,10,16,24-Tetrakis Dimethyl 5-(Phenoxy)-Isophthalate-Substituted Ni(II) Phthalocyanine complex. *ChemistrySelect* 3(11):3155–3160. <https://doi.org/10.1002/slct.201800572>
- Attia MS, Ali K, El-Kemary M, Darwish WM (2019) Phthalocyanine-doped polystyrene fluorescent nanocomposite as a highly selective biosensor for quantitative determination of cancer antigen 125. *Talanta* 201:185–193. <https://doi.org/10.1016/j.talanta.2019.03.119>
- Cabir B, Yıldık U, Ağırtaş MS (2019) Synthesis, DFT analysis, and electronic properties of new phthalocyanines bearing ETAEO substituents on peripheral position. *J Coord Chem* 72(17):2997–3011. <https://doi.org/10.1080/00958972.2019.1680832>
- Cabir B, Yıldık U, Ağırtaş MS, Horoz S (2020) Computational DFT calculations, photovoltaic properties and synthesis of (2R, 3S)-2, 3, 4-trihydroxybutoxy substituted phthalocyanines. *Inorg Nano-Met Chem* 50(9):816–827. <https://doi.org/10.1080/24701556.2020.1725051>
- Cozzolino M, Pesce L, Pezzuoli D, Montali C, Brancalione L, Cavanna L, Abbruzzetti S, Diaspro A, Bianchini P, Viappiani C (2019) Apomyoglobin is an efficient carrier for zinc phthalocyanine in photodynamic therapy of tumors. *Biophys Chem* 253:106228. <https://doi.org/10.1016/j.bpc.2019.106228>
- Frisch MJ, GAUSSIAN09. <http://www.gaussian.com/>.
- Ghadari R, Saei P-S, Sabri A, Ghasemi Z and Kong F, (2020). Enhanced phthalocyanine-sensitized solar cell efficiency via cooperation of nitrogen-doped carbon dots. *J Clean Prod* 2020 v.268. DOI: <https://doi.org/10.1016/j.jclepro.2020.122236>
- Güngördü Solğun D, Horoz S, Ağırtaş MS (2018) Synthesis of novel tetra (4-tritylphenoxy) substituted metallophthalocyanines and investigation of their aggregation, photovoltaic, solar cell properties. *Inorg Nano-Met Chem* 48(10):508–514. <https://doi.org/10.1080/24701556.2019.1572624>
- Janas K, Boniewska-Bernacka E, Dyrda G, Słota R (2021) Porphyrin and phthalocyanine photosensitizers designed for targeted photodynamic therapy of colorectal cancer. *Bioorg Med Chem* 30:115926. <https://doi.org/10.1016/j.bmc.2020.115926>
- Kong S, Wang X, Bai L, Song Y, Meng F (2019) Multi-arm ionic liquid crystals formed by pyridine-mesophase and copper phthalocyanine. *J Mol Liq* 288:111012. <https://doi.org/10.1016/j.molliq.2019.111012>
- Li B, Wei P, de Leon A, Frey T, Pentzer E (2017) Polymer composites with photo-responsive phthalocyanine for patterning in color and fluorescence. *Eur Polym J* 89:399–405. <https://doi.org/10.1016/j.eurpolymj.2017.02.042>
- Lin K-C, Doane T, Wang L, Li P, Pejic S, Kenney ME, Burda C (2014) Laser spectroscopic assessment of a phthalocyanine-sensitized solar cell as a function of dye loading. *Sol Energy Mater Sol Cells* 126:155–162. <https://doi.org/10.1016/j.solmat.2014.03.025>
- Luo S, Zhang E, Su Y, Cheng T, Shi C (2011) A review of NIR dyes in cancer targeting and imaging. *Biomaterials* 32(29):7127–7138. <https://doi.org/10.1016/j.biomaterials.2011.06.024>
- Maidur SR, Patil PS, Rao SV, Shkir M, Dharmaparakash SM (2017) Experimental and computational studies on second- and third-order nonlinear optical properties of a novel D- π -A type chalcone derivative: 3-(4-methoxyphenyl)-1-(4-nitrophenyl) prop-2-en-1-one. *Opt Laser Technol* 97:219–228. <https://doi.org/10.1016/j.optlastec.2017.07.003>
- Martín-Gomis L, Parejo C, Álvarez JC, Fernández-Lázaro F, Sastre-Santos Á (2017) Dye sensitized solar cells (DSSCs) based on bulky tert-octylphenoxy-carboxyphenyl substituted phthalocyanine without the presence of co-adsorbents. *Inorganica Chim Acta* 468:327–333. <https://doi.org/10.1016/j.ica.2017.07.043>
- Matshitse R, Nwaji N, Mananga M, Prinsloo E, Nyokong TJJoP and A-chemistry P, (2018). Effect of number of positive charges on the photophysical and photodynamic therapy activities of quaternary benzothiazole substituted zinc phthalocyanine. 367: 253–260.
- Moghadam G, Tirgiri F, Reshak AH, Khorshidi M (2019) Specific features of 3, 6-bis (4-hydroxy phenyl)-piperazine-2, 5-dione (BHPPD) diphenolic monomer and compared with toxic industrial bisphenol-A (BPA): DFT calculation. *Mater Chem Phys* 236:121780. <https://doi.org/10.1016/j.matchemphys.2019.121780>
- Mumit MA, Pal TK, Alam MA, Islam MA-A-A-A, Paul S, Sheikh MC (2020) DFT studies on vibrational and electronic spectra, HOMO–LUMO, MEP, HOMA, NBO and molecular docking analysis of benzyl-3-N-(2,4,5-trimethoxyphenylmethylene)hydrazinecarbo-dithioate. *J Mol Struct* 1220:128715. <https://doi.org/10.1016/j.molstruc.2020.128715>
- O’Boyle NM, Tenderholt AL, Langner KM (2008) cclib: a library for package-independent computational chemistry algorithms. *J Comput Chem* 29(5):839–845. <https://doi.org/10.1002/jcc.20823>

- O'Regan BC, López-Duarte I, Martínez-Díaz MV, Forneli A, Alberio J, Morandeira A, Palomares E, Torres T, Durrant JR (2008) Catalysis of recombination and its limitation on open circuit voltage for dye sensitized photovoltaic cells using phthalocyanine dyes. *J Am Chem Soc* 130(10):2906–2907. <https://doi.org/10.1021/ja078045o>
- Ou C, Lv W, Chen J, Yu T, Song Y, Wang Y, Wang S, Yang G (2021) Structural, photophysical and nonlinear optical limiting properties of sandwich phthalocyanines with different rare earth metals. *Dyes Pigm* 184:108862. <https://doi.org/10.1016/j.dyepig.2020.108862>
- Özdemir M, Köksoy B, Yalçın B, Taşkın T, Selçuki NA, Salan Ü, Durmuş M, Bulut M (2021) Novel lutetium(III) phthalocyanine-coumarin dyads; synthesis, characterization, photochemical, theoretical and antioxidant properties. *Inorganica Chim Acta* 517:120145. <https://doi.org/10.1016/j.ica.2020.120145>
- Panwar V, Kumar P, Ray SS, Jain SL (2015) Organic inorganic hybrid cobalt phthalocyanine/polyaniline as efficient catalyst for aerobic oxidation of alcohols in liquid phase. *Tetrahedron Lett* 56(25):3948–3953. <https://doi.org/10.1016/j.tetlet.2015.05.003>
- Priya MK, Revathi BK, Renuka V, Sathya S, Asirvatham PS (2019) Molecular structure, spectroscopic (FT-IR, FT-Raman, ¹³C and ¹H NMR) analysis, HOMO-LUMO energies, Mulliken, MEP and thermal properties of new chalcone derivative by DFT calculation. *Mater Today* 8:37–46. <https://doi.org/10.1016/j.matpr.2019.02.078>
- Rad AS, Aghaei SM (2018) Potential of metal–fullerene hybrids as strong nanocarriers for cytosine and guanine nucleobases: a detailed DFT study. *Curr Appl Phys* 18(2):133–140. <https://doi.org/10.1016/j.cap.2017.11.016>
- Rahuman MH, Muthu S, Raajaraman BR, Raja M, Umamahesvari H (2020) Investigations on 2-(4-Cyanophenylamino) acetic acid by FT-IR, FT-Raman, NMR and UV-Vis spectroscopy, DFT (NBO, HOMO-LUMO, MEP and Fukui function) and molecular docking studies. *Heliyon* 6(9):e04976. <https://doi.org/10.1016/j.heliyon.2020.e04976>
- Reddy G, Gaspera ED, Jones LA, Giribabu L (2021) Self-assembly of a symmetrical dimethoxyphenyl substituted Zn(II) phthalocyanine into nanoparticles with enhanced NIR absorbance for singlet oxygen generation. *J Photochem Photobiol* 408:113123. <https://doi.org/10.1016/j.jphotochem.2020.113123>
- Saka ET, Durmuş M, Kantekin H (2011) Solvent and central metal effects on the photophysical and photochemical properties of 4-benzoyloxybenzoxy substituted phthalocyanines. *J Organomet Chem* 696(4):913–924. <https://doi.org/10.1016/j.jorganchem.2010.10.024>
- Salih Ağırtaş M (2007) Non-aggregating phthalocyanines with bulky 2,4-di-tert-butylphenoxy-substituents. *Dyes Pigm* 74(2):490–493. <https://doi.org/10.1016/j.dyepig.2006.03.009>
- Sherin DR, Manojkumar TK (2020) Significance of five membered heterocycles in fine tuning of HOMO-LUMO gap of simple donor-acceptor system as organic solar cell material: a DFT approach. *Mater Today* 33:1229–1233. <https://doi.org/10.1016/j.matpr.2020.03.482>
- Shukla BK and Yadava U, (2020). DFT calculations on molecular structure, MEP and HOMO-LUMO study of 3-phenyl-1-(methylsulfonyl)-1H-pyrazolo[3,4-d]pyrimidine-4-amine. *Mater Today*. <https://doi.org/10.1016/j.matpr.2020.10.903>
- Singh K, bala I and Kataria R, (2020) Crystal structure, Hirshfeld surface and DFT based NBO, NLO, ECT and MEP of benzothiazole based hydrazone. *Chem Phys* 538:110873. <https://doi.org/10.1016/j.chemphys.2020.110873>
- Suzuki A, Okumura H, Yamasaki Y, Oku T (2019) Fabrication and characterization of perovskite type solar cells using phthalocyanine complexes. *Appl Surf Sci* 488:586–592. <https://doi.org/10.1016/j.apsusc.2019.05.305>
- Urbani M, Ragoussi M-E, Nazeeruddin MK, Torres T (2019) Phthalocyanines for dye-sensitized solar cells. *Coord Chem Rev* 381:1–64. <https://doi.org/10.1016/j.ccr.2018.10.007>
- Wu S, Liu Q, Zheng Y, Li R, Peng T (2017) An efficient copper phthalocyanine additive of perovskite precursor for improving the photovoltaic performance of planar perovskite solar cells. *J Power Sources* 359:303–310. <https://doi.org/10.1016/j.jpowsour.2017.05.083>
- Xu J, Yang W, Chen R (2020) The photovoltaic performance of highly asymmetric phthalocyanine-sensitized brookite-based solar cells. *Optik* 200:163413. <https://doi.org/10.1016/j.ijleo.2019.163413>
- Yum JH, Jang SR, Humphry-Baker R, Grätzel M, Cid JJ, Torres T, Nazeeruddin MK (2008) Effect of coadsorbent on the photovoltaic performance of zinc phthalocyanine-sensitized solar cells. *Langmuir: The ACS J Surf Colloids* 24(10):5636–5640. <https://doi.org/10.1021/la800087q>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.