**Novel ball-type dioxy-O-carborane bridged cobaltphthalocyanine: Synthesis, DFT studies and characterization for dye-sensitized solar cells as photosensitizers**

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**Abstract:** The synthesis and spectroscopic characterization of an innovative ball-type cobalt (II) metallophthalocyanine 4, bridged by four 1,2-bis(2-hydroxymethyl)-O-carborane (HMOC) 1 units has been achieved. The structure of 4 was characterized via elemental analysis, UV–visible absorption spectroscopy, FT-IR spectroscopy, and MALDI-TOF mass spectrometry. The photovoltaic performance of the newly synthesized compound in dye-sensitized solar cells was investigated. In order to clarify the effect of dye-sensitization time on photovoltaic performance parameters, the sensitization time was varied from 12 to 60 h and the performance parameters were investigated. It was found that sensitization time had a strong effect on the main performance parameters. The best photovoltaic performance was achieved after sensitization for 36 h (short circuit current density, 6.41 mA cm⁻²; overall conversion efficiency, 3.42%). Geometry optimization of the molecule was performed using density functional theory and shows a peripheral structure.

**Keywords:** carboranes; density functional calculations; dye-sensitized solar cell; Photovoltaics; phthalocyanines

1. Introduction

Phthalocyanines (Pcs) are compounds that have an 18 π-electron system. This electron system provides Pcs with their unique conductometric, photophysical, and optoelectronic properties [1]. The photophysical and photochemical properties of Pcs can be controlled and modified using either of the two general approaches or using a suitable combination: 1) by varying the metal 2) the nature of the substituents in the peripheral or non-peripheral groups [2]. Any change in substituents depicts significant effects on various parameters for applications such as molecular electronic devices, non-linear optical devices, liquid crystals, gas sensors, photosensitizers, catalysts, semi-conductive materials, and electrochromic displays [3-8]. In this respect, the synthesis and electro-catalytic behaviour of metallophthalocyanine (MPC) derivatives have been extensively investigated [9].
Multi-nuclear MPcs with different linker groups have been extensively studied to be specifically used as highly efficient catalysts to perform electro-catalysis of the oxygen reduction reaction (ORR) and organic field effect transistors [10].

Ball-type Pcs, which is a new category of Pcs, were initially investigated in 2002 [11, 12]. This new Pc-type depicts four bridging substituents on the peripheral positions of every benzene ring in the two cofacially arranged Pc monomers. The length between the two Pc rings and the resulting chemical and physical properties are dependent on the components of those linkers and depict a significant deviation from the initial monomers. The two face-to-face arranged Pc rings or the two metal centres are observed to interact very strongly with each other in these compounds, and these interactions were detected using spectroscopically and electrochemically. Based on the nature of the bridging compounds, the chemical and physical properties can change dramatically [13].

The synthesis of carboranyl derivatives is of considerable significance due to their similarity with some organic compounds that contain electron accepting groups [14-15]. Over the previous few decades, carbon-substituted carboranes have been investigated using new models by performing theoretical investigations [16] and by preparing organic and organometallic compounds that can be used to perform polymeric material syntheses [17-19] and biological/medicinal investigations [20]. Carbon-substituted carboranes have been effectively used for cancer treatment by boron neutron capture therapy (BNCT) [21-23].

Over the previous four decades, polyhedral heteroboranes have been extensively investigated. One of the members of this group of compounds is dicarbo-closo-dodecaboranes, which is commonly named as carboranes. Carborane chemistry is especially concerned with C–H or B–H substitution reactions at the vertices of these clusters [15], and the reaction products may be potentially used in different applications, including medicinal chemistry, BNCT [24], polymer chemistry [25], adsorption/extraction of metal ions [26], supramolecular chemistry [27] and as metal ligands.

After the work of M. Grätzel and co-workers [28] dye sensitized solar cells (DSSCs) has gained has gained much attention as an alternative to traditional silicon-based photovoltaic devices. The working mechanism is based on a photoelectrochemical mechanism that resembles plant photosynthesis [29]. It is reported that one of the most important factor is the physicochemical properties of the dye molecule for the development of efficient DSSC. Polypyridylruthenium complexes are reported to be the most successful charge-transfer sensitizers that are used in DSSC systems [30]. Although important advances have been made with polypyridylruthenium complexes toward high-performance solar cells, the Ru complexes have drawbacks such as the limited absorption wavelength [28]. Therefore, there is a strong need to develop new sensitizers with broader absorption profiles in the longer wavelength regions.

The present study reports a method for synthesizing a novel binuclear ball-type M2Pc2, 4 from commercial starting materials: 1,2-bis(2-hydroxymethyl)-o-carborane (HMOC) 1 and 4-nitrophthalonitrile 2. Binuclear ball-type metallophthalocyanine 4 was characterized spectroscopically and was then used to fabricate a DSSC.
2. Results

2.1. Syntheses and compound characterization

The synthesis of the target compound Co-Pc 4 is depicted in Scheme 1. The key starting material compound 3 could be obtained using a single step reaction of HMOC (1) and 4-nitrophthalonitrile (2) and could result in 35% yield. Co-Pc 4 was readily obtained in 34.74% yield by the metal-templated cyclotetramerization of 3 with the metal salt Co(OAc)₂·6H₂O.


Spectroscopic data for the newly synthesized compound was in agreement with the predicted structures in Scheme 1. Compound 3 was obtained in 35% yield after work up. The IR spectrum of 3 confirms the presence of the C≡N group as an intense and sharp stretching band at 2223 cm⁻¹, and the typical ν(B‒H) absorption frequency at 2539 cm⁻¹ and 2365 cm⁻¹ that is characteristic of closo-carboranes [31, 32]. The characteristic C–O–C bridging group bands were observed at 1090 cm⁻¹ for Compound 3 and at 1095 cm⁻¹ for Compound 4. In the ¹H-NMR spectrum of 3, the aromatic protons appeared at 7.62 and 7.00 ppm in the form of doublets, the benzylic proton appeared at 6.62 ppm as a singlet, and the C–H protons appeared at 3.28 ppm as a singlet. ¹H-NMR analysis of 4 was excluded due to its paramagnetic nature.

The positive ion and linear mode MALDI-MS spectrum of Compound 3 is presented in Figure 1, and the expected value of the protonated molecular ion at m/z 457 (calc. m/z 456.519) was confirmed. Only the 2,5-dihydroxybenzoic acid MALDI matrix yielded an intense molecular ion signal.
Figure 1. Positive ion and linear mode MALDI mass spectrum of 3 obtained from nitrogen laser (at 337 nm wavelength) ablation of a 2,5-dihydroxybenzoic acid MALDI matrix. Accumulation from 100 laser shots.

Co-Pc 4 was synthesized in low yield and demonstrated solubility in dimethyl sulfoxide (DMSO). The melting point of 4 was found to exceed 200 °C. The paramagnetic nature of 4 prevented the 1H-NMR measurements; thus, characterization was achieved using a combination of methods, including elemental analysis, FT-IR spectroscopy, UV–Vis spectroscopy (Figure 3), and MALDI-TOF mass spectroscopy (Figure 2).

The positive ion and linear mode MALDI-MS spectrum of the synthesized Co-Pc complex is presented in Figure 2. Several novel MALDI matrices were tested to obtain the molecular ion peak, and 1,8-dihydroxy-9(10H)-anthracenone (Dithranol) yielded the best MALDI-MS spectrum. Beside the protonated molecular ion peak of the complex that was observed at 1956.2 Da, a few low-intensity fragment ions were observed at masses between 900 and 1400 Da. The other peaks at around 600 Da represent the various clusters of MALDI matrix Dithranol used in this study. The complex depicted low fragmentation under linear MALDI-MS conditions. The isotopic distribution of the experimental molecular ion overlapped the theoretical isotopic peak pattern for this complex (Figure 2). The combined results indicate that the corresponding metallophthalocyanine was synthesized in the desired manner.

Figure 2. Linear mode and positive ion MALDI-MS spectrum of 4 obtained from a Dithranol MALDI matrix using nitrogen laser (at 337 nm wavelength) ablation. Accumulation from 100 laser shots. Inset is an expansion of the molecular ion peak region with the theoretical isotopic pattern.

The ball-type metallophthalocyanines, 4 in DMSO, had a typical UV–Vis spectra which demonstrated the expected absorption bands for phthalocyanines (with a Soret band centred at 310 nm) and Q-bands at 612 and 673 nm, respectively; both Q-band values were in good agreement with the literature relative to the absorption properties of tetrasubstituted phthalocyanines [33].
Figure 3. UV–Vis spectra of 4 (1.72 × 10^{-6} M) in DMSO

2.2. Photovoltaic performance

To record the absorption spectra of the films, ∼5-μm-thick TiO2 films were immersed in DMSO solutions containing Pcs for various time intervals between 12 and 60 h at 60 °C. The absorption spectra of 4 adsorbed onto the ∼5-μm-thick TiO2 electrodes were very similar to the in-solution spectra. A small red shift was observed with much broader bands. This may be due to the aggregation of dyes on the TiO2 surface. Furthermore, light scattering and re-absorption from the nanoparticle surface of TiO2 may cause significant broadening of the spectra.

The main performance for a DSSC are determined using standard test conditions under specific illumination based on four main parameters: short circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and photovoltaic conversion efficiency (η) [34]. FF defines the maximum power output of the solar cell per unit area divided by the product of J_{sc} and V_{oc} and can be expressed by equation (1)

\[ FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \]  

(1)

J_{max} and V_{max} are the current and voltage at the point on the J–V curve where the maximum power density is delivered by the cell. The photovoltaic conversion efficiency (η) is defined as the ratio of the maximum electrical power output of the photovoltaic cell to the energy of the incident sunlight (P_{in}) and can be defined with the formula given in equation (2):

\[ η = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \]  

(2)

The fabricated cells were characterized by measuring the current density as a function of the applied voltage in ambient air when subjected to an illumination of 100 mW cm^{-2}. The resulting J–V curve of the DSSCs based on 4 after 36 h of sensitization is presented in Figure 4 and the device performance parameters are provided in Table 1.
Figure 4. J–V characteristics of the DSSC containing 4 after 36 h of sensitization

As is clear from Table 1, the DSSC with compound 4 exhibits good photovoltaic properties: $V_{oc}$ of 0.80 V, $J_{sc}$ of 6.41 mA cm$^{-2}$, FF of 0.62 and η of 3.42% under AM 1.5 G irradiation.

Table 1. Photovoltaic parameters of the DSSC containing 4 under AM 1.5 G irradiation

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{max}$ (mA cm$^{-2}$)</th>
<th>$V_{max}$ (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6.41</td>
<td>0.8</td>
<td>5.52</td>
<td>0.62</td>
<td>0.67</td>
<td>3.42</td>
</tr>
</tbody>
</table>

* $J_{sc}$ = short circuit current density, $V_{oc}$ = open-circuit voltage, FF = fill factor, η = photovoltaic conversion efficiency

One of our primary objectives was to investigate the effect of sensitization time on the photovoltaic performance of the 4-sensitized DSSCs. To obtain more insight into the effect of sensitization time on the solar cell parameters, DSSC devices were fabricated with various sensitization times, between 12 to 60 h. A comparison of the J–V curves of these DSSC devices is given in Figure 5, and the performance parameters at AM 1.5 G sunlight are listed in Table 2.

Figure 5. J–V characteristics of DSSCs sensitized with 4 at room temperature for different adsorption times

Analysis of the performance parameters (Table 2) shows that $V_{oc}$ is relatively insensitive to sensitization time. $V_{oc}$, which can be considered the point where the photocurrent generation and dark current processes compensate for each other, is reportedly determined by the Fermi level of the electrons and the electrolyte redox potential [35]. When the same electrolyte is used, the $V_{oc}$ can be expressed as follows [36]:
where $E_{cb}$ is the potential that is observed at the conduction band edge, $\alpha$ shows a characteristic constant of the tailing states of TiO$_2$. ($k$: the Boltzmann constant; $T$: temperature, $N_c$: the effective density of the states at the TiO$_2$ conduction band edge, and $n$: electron number in TiO$_2$)

\[ V_{oc} = \frac{E_{cb}}{q} + \alpha \frac{kT}{q} \ln \frac{N_c}{n} \quad (3) \]

It is clear from Equation (3) that the observed $V_{oc}$ at a given constant voltage strongly depends on the potential of the $E_{cb}$ and the number of electrons injected from the metal-oxide. This means that the values of $E_{cb}$ and $n$ are the limiting factors for achieving a high $V_{oc}$. (Note that the $E_{cb}$ and the number of the injected electrons are correlated to the surface charge and charge recombination rate, respectively). Under a steady-state illumination condition, the number of electrons transferred into the conduction band of TiO$_2$ was expected to increase with increasing sensitization time because more dye was expected to adsorb onto the TiO$_2$ film. However, it is formerly determined that $\eta$ strongly depends on the balance between injected electrons and charge recombination. Furthermore, recombination processes are known to cause a decrease in the charge-carrier population and $V_{oc}$. Therefore, the $V_{oc}$ in 4-sensitized DSSC devices is limited by the recombination processes.

One of the performance parameters for a solar cell is the $J_{sc}$. To realize current generation in a DSSC device, three basic processes should be considered: adsorption of incident light by dye molecules, charge collection by the electrodes, and the dye regeneration process. Combination of these three processes may cause the short circuit current for a photovoltaic device. An efficient exciton dissociation occurs when the lowest unoccupied molecular orbital (LUMO) of the photosensitizer is observed to be more negative than the conduction band of the semiconductor (TiO$_2$) and when the highest occupied molecular orbital (HOMO) is observed to be more positive than the redox potential of the electrolyte \[37\]. The observed $J_{sc}$ increased with increasing dye-sensitization time with the maximum $t_{max}$ at 36 h (Table 2). Thereafter, the $J_{sc}$ decreased. The same measurements were then repeated for another 4-sensitized DSSC device taken from the same batch of samples to verify the repeatability of the observed sensitization time-dependence. These measurements verified that the observed J–V behaviours were repeatable, except for a small shift in the $V_{oc}$. In this respect, the low $J_{sc}$ in a 4-based device can be attributed to recombination of

### Table 2. Photovoltaic parameters of DSSCs sensitized with 4 for different sensitization times

<table>
<thead>
<tr>
<th>Sensitization time (h)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{max}$ (mA cm$^{-2}$)</th>
<th>$V_{max}$ (V)</th>
<th>FF$^*$</th>
<th>$\eta^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>4.13</td>
<td>0.81</td>
<td>3.75</td>
<td>0.64</td>
<td>0.72</td>
<td>2.4</td>
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<tr>
<td>24</td>
<td>4.47</td>
<td>0.79</td>
<td>4.07</td>
<td>0.65</td>
<td>0.74</td>
<td>2.62</td>
</tr>
<tr>
<td>36</td>
<td>6.41</td>
<td>0.8</td>
<td>5.52</td>
<td>0.62</td>
<td>0.67</td>
<td>3.42</td>
</tr>
<tr>
<td>48</td>
<td>5.1</td>
<td>0.74</td>
<td>4.51</td>
<td>0.57</td>
<td>0.69</td>
<td>2.58</td>
</tr>
<tr>
<td>60</td>
<td>4.32</td>
<td>0.8</td>
<td>3.9</td>
<td>0.62</td>
<td>0.7</td>
<td>2.42</td>
</tr>
</tbody>
</table>

$^*$ $J_{sc}$ = short circuit current density, $V_{oc}$ = open-circuit voltage, FF = fill factor, $\eta$ = photovoltaic conversion efficiency
injected electrons either radiatively or non-radiatively. The increase in short circuit current with increasing sensitization time can be attributed to the decrease in charge-transfer resistance at the interface, which facilitates transport of the injected electrons in the photoanode layer, and affords improved short circuit current. That the maximum J_{sc} value and conversion efficiency of the solar cell could be found after sensitization for 36 h suggests that monolayer dye adsorption on the TiO_2 film was nearly complete after this duration. The gradual reduction in J_{sc} value and conversion efficiency could be ascribed the multilayer formation or dye aggregation. For a related dye, ZnPc, it has been reported that dye aggregation led to self-quenching enhancements of the excited singlet state [38].

2.3. DFT Studies

The DFT calculations suggested that the intermolecular interactions of dimeric molecules would form hydrogen bonds between the hydrogen atoms of the polar groups and an isoindole nitrogen atom of a neighbouring molecule. This interaction is the main driving force behind Pc aggregation in solution [39].

Spartan08 [40], Gaussian09 [41] and Gaussview5.0 [42] software packages were used in the calculations. The DFT approach was used to optimize ground state geometries [43]. Calculations were carried out using Becke’s three-parameter nonlocal exchange functional [44, 45] with the Lee–Yang–Parr correlation function [46] (hybrid B3LYP functional) for DFT and TDDFT with the LanL2DZ basis set [47-50]. The ground-state structure of 4 was optimized in the gas phase and the minima were verified with positive calculated frequencies (Figure 6).

The dipole moment (\mu), sum of electronic and zero point energies (E_{elec}+ZPE), and sum of electronic energy and thermal free energy (E_{elec}+\Delta G) were calculated to be 2.75 Debye, −5856.625170 Hartree, and −5856.754576 Hartree, respectively. The first frequency was found at 7.86 cm\(^{-1}\).

As expected, 4 has a peripheral structure. The closest distance was observed between the two central Co atoms (2.75 Å), and the distance between Co and the Pc N atoms was 3.37 Å.

![Figure 6. Optimized ground-state structure of 4 (top and side views) at the B3LYP/LanL2DZ level of theory.](image)

3. Discussion

A novel ball-type Co-containing metallophthalocyanine with peripheral carborane units was successfully synthesized. The synthesized compounds were structurally characterized using elemental analysis, UV–Vis spectroscopy, FT-IR spectroscopy, MALDI-TOF mass spectrometry,
and gas-phase DFT calculations. The DFT-calculated structure confirmed that the molecule has a peripheral structure. The newly synthesized phthalocyanines 4 were combined with anatase TiO$_2$ nanoparticle films to construct a working dye-sensitized solar cell. The performance of the resulting photovoltaic cells (photovoltaic conversion efficiency, short circuit current, and fill factor) was highly dependent on the dye-sensitization time. The photocurrent of 4 increased with sensitization time up to 36 h (short circuit current density, 6.41 mA cm$^{-2}$; overall conversion efficiency, 3.42%) and then decreased with prolonged dye-sensitization time.

4. Materials and Methods

All the initial materials and solvents were high purity commercial products that were obtained from Merck or Aldrich and were used as supplied unless otherwise pointed. Commercial 1,2-bis(2-hydroxymethyl)-O-carborane (HMOC) (1) and 4-nitrophthalonitrile (2) were used as purchased. All the reactions were performed under a dinitrogen atmosphere.

Microanalyses were performed using a CHNS-932 (LECO) elemental analyzer. The $^1$H-NMR spectra were measured on a Agilent 600 MHz or Varian Innova 400 MHz spectrometer. Chemical shift values for $^1$H-NMR were referenced relative to Si(CH$_3$)$_4$. The UV–Vis spectra were recorded using a Perkin Elmer lambda 35 spectrophotometer with 1-cm quartz cuvettes at room temperature. The IR spectra were obtained in the form of KBr pellets on a Perkin Elmer Spectrum FT-IR spectrophotometer. Mass spectra were obtained in linear mode with an average of 100 shots on a Voyager-DE™ Pro MALDI-TOF mass spectrometer (Applied Biosystems, USA) that was combined with a nitrogen UV-laser (337 nm). The MALDI matrix, 1,8-dihydroxy-9(10H)-anthracenone (dithranol), was prepared in tetrahydrofuran at a concentration of 10 mg/mL. The MALDI sample was prepared by combining sample solutions (1.5 mg/mL in dimethyl sulfoxide (DMSO)) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf® micro tube, and 1.0 μL of this mixture was deposited on the sample plate, dried at room temperature, and then analyzed.

Funding: I am gratefully acknowledge the financial support for Ayşe Ilgan Necipoğlu

Acknowledgments: I also thank computer time on FenCluster provided by Ege University Faculty of Science and TUBITAK-ULAKBIM Tuba Resources.

Conflicts of Interest: This manuscript has not been published elsewhere and is not under consideration by another journal. I have approved the manuscript and agree with submission to International Journal of Molecular Sciences. There are no conflicts of interest to declare. I briefly confirm all the work myself no other co workers were involved. I'm only one authors

Abbreviations

HMOC 1,2-bis(2-hydroxymethyl)-O-carborane or 1
Co-Pc cobalt (II) metallophthalocyanine or 4
Pcs Phthalocyanines
MPc metallophthalocyanine
ORR oxygen reduction reaction
BNCT boron neutron capture therapy
DSSCs dye sensitized solar cells
M$_2$Pc$_2$ ball-type metallophthalocyanine=
J$_{sc}$ short circuit current density
\[ V_{oc} \]  open-circuit voltage

\[ FF \]  fill factor

\[ \eta \]  photovoltaic conversion efficiency

\[ P_n \]  incident sunlight

\[ K \]  the Boltzmann constant;

\[ T \]  temperature,

\[ N_c \]  the effective density of the states at the TiO\textsubscript{2} conduction band edge,

\[ N \]  electron number in TiO\textsubscript{2}

DFT  Density Functional Theory

TDDFT  Time Density Differantional Functional Theory

\[ E_{\text{elec}+ZPE} \]  sum of electronic and zero point energies =

\[ E_{\text{elec}+\Delta G} \]  sum of electronic energy and thermal free energy

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