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Ball-Type Dioxy-o-Carborane Bridged Cobaltphthalocyanine: Synthesis, Characterization and DFT Studies For Dye-Sensitized Solar Cells as Photosensitizer

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Abstract: The synthesis and spectroscopic characterization of an innovative ball-type cobalt metallophthalocyanine **4**, bridged by four 1,2-bis(2-hydroxymethyl)-*O*-carborane (HMO) **1** units, has been achieved. The synthesized compound **4** was characterized structurally and electronically using elemental analysis, UV-Vis absorption spectroscopy, FT-IR spectroscopy, MALDI-TOF mass spectrometry, EPR spectroscopy and magnetic susceptibility. 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, 5.41 mA cm⁻²; overall conversion efficiency, 3.42%). Computational UV-Vis absorption spectra of the molecule was calculated using time dependent density functional theory and was found consistent with measured UV-Vis spectra.

Keywords: metallophthalocyanine, carborane, photovoltaic, dye-sensitized solar cell, density functional theory

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 the two general approaches or using a suitable combination: 1) 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 co-facially 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 strongly with each other in these compounds, and these interactions were detected 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], preparing organic and organometallic compounds that can be used to perform polymeric syntheses [17-19] and biological/

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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 are dicarbo-closododecaboranes, which are 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) have 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 factors is the physicochemical properties of the dye molecule for the development of efficient DSSC [30,31]. Polypyridylruthenium complexes are reported to be the most successful charge-transfer sensitizers that are used in DSSC systems [32]. 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 M_2Pc_2 , **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.

Results and discussion

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 $Co(OAc)_2$.

Spectroscopic data of the newly synthesized compound was in agreement with the predicted structures in Scheme 1. Compound **3** was obtained in 35% yield after work up. FT-IR Spectra of compounds **3** and **4** are given in Figure S1 and Figure S2, respectively. The IR spectrum of **3** confirms the presence of the C≡N group as an intense and sharp stretching band at 2225 cm^{-1} , and the typical $\nu(B-H)$ absorption frequency at 2533 cm^{-1} and 2366 cm^{-1} that is characteristic of *clos*-carboranes [33,34]. The characteristic C–O–C bridging group bands were observed at 1099 cm^{-1} for compound **3** and at 1095 cm^{-1} for compound **4**. 1H -NMR and ^{13}C -NMR Spectra of compound **3** are given in Figure S3 and Figure S4. In the 1H -NMR spectrum of **3**, the aromatic protons appeared at 8.77 and 8.45 ppm in the form of doublets, the phenyl proton appeared at 8.95 ppm as a singlet, and the C–H protons appeared at 3.11 ppm as a singlet. The ^{13}C -NMR spectrum of **3** shows signals in the aromatic carbons and nitrile carbons at 136.47, 129.61, 121.73, 118.03, 115.12 ppm respectively, and the CH_2 carbon at 48.9 ppm.

In the 1H NMR spectrum of **4** (Figure S5), it is rather difficult to even identify aromatic protons of phthalocyanine groups because of the large number of protons of substituted o-carborane groups [35]. Therefore, aromatic protons for compound **4** are not observed. The C–H protons for the CH_2-O group are observed at 5.72 ppm as a singlet and are in agreement with the structure shown in Scheme 1.

Phthalocyanine complexes are expected to have positional isomers due to the presence of a single substituent on either the peripheral or non-peripheral positions. Fewer or more positional isomers are expected for the non-peripherally or peripherally substituted complexes due to steric effects. This situation is effective on NMR spectra. Dioxy-o-carborane, substituted complex **4** which is at the peripheral position, hampered the vibrations of Pc ring proton and in the NMR spectrum [36].

Compound **4** is diamagnetic because no cobalt traces were observed at 100 K in the EPR spectrum. This is also supported by the magnetic susceptibility and NMR measurements. The results presented here suggest that efforts to Ball-type Cobalt phthalocyanine systems should focus on magnetic property.

The positive ion and linear mode MALDI-MS spectrum of compound **3** is presented in Figure S6, 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.

Co-Pc **4** was synthesized in low yield and demonstrated solubility in dimethyl sulfoxide (DMSO). The melting point of **4** was found to exceed $200\text{ }^\circ\text{C}$. Characterization

Scheme 1 Synthesis of the phthalocyanine complex: (i) Cs_2CO_3 , N_2 , ACN, 80°C , 72 h, (ii) $\text{Co}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$, 300°C , DMAE, N_2 , 24 h.

was achieved using a combination of methods including elemental analysis, FT-IR spectroscopy (Figure S2), ^1H -NMR spectroscopy (Figure S5), UV-Vis spectroscopy (Figure 1) and MALDI-TOF mass spectroscopy (Figure S7).

The positive ion and linear mode MALDI-MS spectrum of the synthesized Co-Pc complex are presented in Figure S7. 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 1945 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 S7). The combined results indicate that the corresponding metallophthalocyanine was synthesized in the desired manner.

Electronic spectra are very important to verify the structure of phthalocyanine compounds. Phthalocyanines show typical UV-Vis spectra with two absorption

regions, the Q band around 600-700 nm and the B band in the near UV region around 300-400 nm. The Q band of all the compounds are attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. B band of all the phthalocyanines arise from the deeper π levels / LUMO transitions. The split form of Q band for **2**, is a characteristic for metal-free phthalocyanines [36].

The ball-type metallophthalocyanine **4**, in DMSO, had a typical UV-Vis spectra which demonstrated the expected absorption bands for phthalocyanines (with a Soret band centered 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 [37]. The energy band gap (E_g) is calculated using the following equation,

$$E_{\text{gap}} = 1239/\lambda$$

The extrapolation of absorption spectra towards horizontal axis (wavelength) is 720 nm (Figure 1). Accordingly, the energy band gap (E_g) is 1.72 eV for compound **4**.

Figure 1 Experimental UV-Vis spectra (1.72×10^{-6} M, solid line) and calculated oscillator strengths with TD-DFT method at B3LYP/6-31G(d,p)/LANL2DZ for **4** in DMSO.

This value is very suitable for titanium dioxide applications [38-41]. Figure 1 also displays calculated oscillator strengths. These results are discussed in the DFT calculations section.

Photovoltaic performance

To record the absorption spectra of the films, $\sim 5\text{-}\mu\text{m}$ -thick TiO_2 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 $\sim 5\text{-}\mu\text{m}$ -thick TiO_2 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 TiO_2 surface. Furthermore, light scattering and re-absorption from the nanoparticle surface of TiO_2 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) [42]. 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):

$$\text{FF} = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{sc}} \times V_{\text{oc}}} \quad (1)$$

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):

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

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 2 and the device performance parameters are provided in Table 1.

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 2 and the performance parameters at AM 1.5 G sunlight are listed in Table 1.

As it is clear from Table 1, the DSSC for compound **4** exhibits good photovoltaic properties (V_{oc} of 0.80 V, J_{sc} of 5.41 mA cm^{-2} , FF of 0.79 and η of 3.42% under AM 1.5 G

Figure 2 J–V characteristics of DSSCs sensitized with **4** at room temperature for different adsorption times.

Table 1 Photovoltaic parameters of DSSCs sensitized with **4** for different sensitization times

Sensitization time (h)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	J_{max} (mA cm ⁻²)	V_{max} (V)	FF	η (%)
12	4.13	0.81	3.75	0.64	0.72	2.4
24	4.47	0.79	4.07	0.65	0.74	2.62
36	5.41	0.80	5.52	0.62	0.79	3.42
48	5.10	0.74	4.51	0.57	0.69	2.58
60	4.32	0.80	3.90	0.62	0.70	2.42

irradiation) which are much better than polypyrrylruthenium complex photovoltaic properties [32] (V_{oc} of 0.72 V, J_{sc} of 20.5 mA cm⁻², FF of 0.7 and η of 0.1 under AM 1.5 G solar irradiance 1000 W m⁻²).

Analysis of the performance parameters (Table 1) shows that V_{oc} is relatively insensitive to sensitization time. V_{oc} , which can be considered as 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 [53]. When the same electrolyte is used, the V_{oc} can be expressed as follows [44]:

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

where E_{cb} is the potential that is observed at the conduction band edge, α shows a characteristic constant of the tailing states of TiO₂ (k : the Boltzmann constant; T : temperature, N_c : the effective density of the states at the TiO₂ conduction band edge, and n : electron number in TiO₂).

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 TiO₂ was expected to increase with increasing sensitization time because more dye was expected to adsorb onto the TiO₂ film. However, it is formerly determined that η 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 (TiO₂) and when the highest occupied molecular orbital (HOMO) is observed to be more positive than the redox potential of the electrolyte [45]. The observed J_{sc} increased with increasing dye-sensitization time with the maximum t_{max} at 36 h (Table 1). 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 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. 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 by the multilayer formation or dye aggregation. The decrease in J_{sc} value can be explained by the contribution of the multilayer formation to the series resistance increase. Also, Polypyridylruthenium complexes are reported to be the most successful sensitizers and their absorption wavelengths are in the range of 570–600 nm [28,32]. In this study, the absorption wavelength of the synthesized Co-Pc complex was observed to be in the range of 612–673 nm. This can be explained as a result of the decrease in J_{sc} . For a related dye, ZnPc, it has been reported that dye aggregation led to self-quenching enhancements of the excited singlet state [46].

DFT Studies

Spartan08 [47], Gaussian09 [48] and Gaussview5.0 [49] software packages were used in the calculations. The DFT approach was used to optimize ground state geometries [50]. Calculations were carried out using Becke's three-parameter nonlocal exchange functional [51,52] with the Lee–Yang–Parr correlation function [53] (hybrid B3LYP functional) for DFT and TDDFT with 6-31G(d,p) and LANL2DZ (for metal) basis sets [54–57]. The ground-state structure of **4** was optimized in DMSO and the minima were verified with positive calculated frequencies (Figure S8). Solvent effects were investigated using the Polarizable Continuum Model (PCM) [58,59] in ground state as implemented in Gaussian09.

The dipole moment (μ), 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 4.44 Debye, -5857.9572 Hartree, and -5858.0852 Hartree, respectively. The first frequency was found at 8.12 cm^{-1} . As expected, **4** has a peripheral structure. The closest

distance was observed between the two central Co atoms (3.03 Å), and the distance between Co and the Pc N atoms was nearly 3.63 Å .

Experimental and calculated UV-Vis absorption spectra were found in agreement in DMSO (Figure 1). The first 100 singlet states were calculated to analyse the electronic transitions and Table S1 shows the list of selected transitions of compound **4**. Maximum peak at longer wavelength appears at 680 nm and it belongs to the local excitation of the Pc core (LE1). At longer wavelengths of electronic transitions, shifts to IR region are observed. At shorter wavelengths (616.5 nm, 499.3 nm), UV spectrum displays ligand-to-metal charge transition (LMCT) character and d-d transition (LE2) is observed between metal d orbitals at 572 nm. Additionally, intramolecular charge transfer (ICT) is observed on the bridging oxygen atoms between carborane groups and Pcs towards Pc core in many electronic transitions.

Experimental

Materials

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**) was purchased from Katchem. 4-nitrophthalonitrile (**2**) was purchased from Sigma Aldrich. All the reactions were performed under a dinitrogen atmosphere.

Characterization techniques

Microanalyses were performed using a CHNS-932 (LECO) elemental analyzer. The ^1H -NMR and ^{13}C -NMR were measured on Varian Innova 600 MHz spectrometer. Chemical shift values for ^1H -NMR and ^{13}C -NMR were referenced relative to $\text{Si}(\text{CH}_3)_4$. 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^{-1} . The MALDI sample was prepared by combining sample solutions (1.5

mg mL⁻¹ 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. JEOL JESFa-300 X-band EPR spectrometer was used for EPR measurements. The magnetic susceptibility measurements were made with the Sherwood Scientific MX1 model Gouy magnetic susceptibility scale.

Chemical synthesis

Synthesis [{bis(2-oxymethyl-4-phthalonitrile)} O-carborane] (3)

Finely ground anhydrous Cs₂CO₃ (2.0 g, 15.0 mol) was added to 1,2-bis(2-hydroxymethyl)-O-carborane (HMOC) **1** (0.204 g, 1mol) and 4-nitrophthalonitrile **2** (0.346 g, 2 mol) in a solution of acetonitrile (25 ml), and the mixture was magnetically stirred at reflux for 72 h under a dry N₂ atmosphere at 85 °C. After cooling to room temperature, the reaction mixture was filtered to eliminate the undissolved salt; further, the filtrate was evaporated to dryness to produce an oily residue. Compound **3** was precipitated using petroleum ether (30 mL) and was collected. This compound was washed with plenty of petroleum ether and tetrahydrofuran successively and air-dried. Compound **3** was readily soluble in acetone.

The Compound **3** was obtained in 62% (286 mg) yield as a yellow color; ¹H NMR (600 MHz, *d*₆ – acetone, 25 °C, Si(CH₃)₄) δ/ppm: 8.95 (s, 1H; Ar–H), 8.77 (d, 1H, Ar–H); 8.45 (d, 1H, Ar–H), 3.11 (s, 4H; CH₂–H); ¹³C NMR (600 MHz, *d*₆ – acetone, 25 °C, Si(CH₃)₄) δ/ppm 136.47, 129.61, 121.73 (Ar–C), 118.03, 115.12 (Ar–CN) and 48.9 (O–CH₂); IR (KBr pellets) ν⁻¹ / cm⁻¹: 2969 (Ar–CH), 2533 and 2366 (Ar–BH), 2225 (Ar–C≡N), 1596 and 1496 (Ar–C=C), 1347 and 1256 (Ar–C–N), 1099 (C–O–C); m.p.: 146–153 °C; Anal. Calcd for compound **3** [C₂₀H₂₀O₂N₄B₁₀] (M=456.52) are C 52.57, H 4.38, N 12.27; found: C 53.07, H 4.92, N 12.4; MS m/z: 456.52 (M⁺, 100%) and 457 (M+H)⁺.

[2',10',16',24'-tetrakis{bis(2-oxymethyl-4-phenyl-O-carborane)}bisphthalocyaninato-dicobalt] (4)

A mixture of **3** (0.182 g, 0.4 mmol) and Co(OAc)₂·6H₂O (0.01 g, 0.2 mmol) was dissolved in dimethylaminoethanol (DMAE) under a dry N₂ atmosphere in a sealed glass tube and was heated for 24 h at 300 °C. After reaching room temperature, the dark-green mixture was washed with distilled water to eliminate the excess cobalt acetate

and was further filtered and washed repeatedly using hot water and different solvents (ethanol, chloroform, and diethyl ether) before drying under vacuum at 70 °C. Compound **4** was soluble in DMSO.

The Compound **4** was obtained in 4% (66 mg) yield as a yellow color; ¹H-NMR (600 MHz, *d*₆ – DMSO, 25 °C, Si(CH₃)₄) δ/ppm : 5.72 (s, 4H, CH₂–H); UV (DMSO) λ_{max} / nm : 310, 612 and 673 (log ε/ M⁻¹ cm⁻¹: 5.97, 5.48 and 5.88); IR (KBr pellets) ν⁻¹ / cm⁻¹: 3828, 3436 (H₂O), 2924 and 2857 (Ar–CH), 2539 and 2366 (Ar–B–H), 1611 (Ar–C=N), 1465 (Ar–C=C), 1390 (Ar–C–N), 1239 (Ar–C=N), 1095 (C–O–C); μ_{eff} (BM): Diamagnetic; m.p.: >250 °C; Anal. Calcd for compound **4** [C₈₀H₈₀B₄₀Co₂N₁₆O₈] (M=1943.98) are C 49.38, H 4.12, N 11.52; found: C 50.2, H 4.4, N 11.98; MS m/z : 1943.98 (M⁺, 100%), and 1945 (M+H).

DSSC fabrication and characterization

DSSCs were produced using fluorine-doped tin oxide (FTO)-coated glass substrates. Before coating the nanoporous TiO₂ paste onto the FTO substrates, the FTO substrates were cleaned as follows: First, ultrasonic treatment for 40 min in a detergent solution; second, ultrasonic bath treatment for 15 min in deionized (DI) water; third, ultrasonic bath treatment in isopropyl alcohol for 15 min; and fourth, drying under flowing dry nitrogen. The porous TiO₂ layer was prepared by applying a paste of TiO₂ nanoparticles onto the FTO glass substrates using a surgical blade and was annealed at 450 °C in air for 30 min. The annealed substrates were allowed to reach 60 °C and were further dipped into the dye solution. The TiO₂ electrodes were immediately immersed in a 0.4 mM solution of **4** in DMSO (dye solution) for various immersion times between 12 and 60 h. On completion of dye sensitization, the photoanodes were removed from the dye solution, washed thoroughly with DMSO to eliminate the non-adsorbed dye molecules, and dried under a stream of high-purity nitrogen. The **4**-sensitized TiO₂ photo-anodes and thermally platinum-plated counter electrode were assembled into a sealed sandwich-type cell using the gap of a hot-melt ionomer film. An iodide-based electrolyte containing 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.3 M lithium iodide, 0.07 M iodine, and 0.6 M *tert*-butylpyridine in a mixture of acetonitrile:valeronitrile (80:20) was used. The devices were characterized by means of current–voltage (I–V) measurements using a Keithley 6517 A electrometer under solar simulator illumination (100 mW cm⁻² irradiance, AM 1.5 G). The diode parameters of fabricated n SnS₂ /p-Si were measured under illumination with a Xenon lamp (150 W short-area) equipped portable solar simulator

(PEC-L01). The conversion efficiency (η) and the fill factor (FF) of the prepared DSSCs were estimated using the measured I–V characteristics.

Conclusions

A novel ball-type Co-containing metallophthalocyanine with peripheral carborane units was successfully synthesized. The synthesized compounds were structurally and electronically characterized using elemental analysis, UV–Vis spectroscopy, FT-IR spectroscopy, ^1H -NMR spectroscopy, MALDI-TOF mass spectrometry, EPR spectroscopy, and magnetic susceptibility. Additionally, calculated UV-Vis absorption spectra of the molecule were compared with experimental spectra and found in agreement with each other. The newly synthesized phthalocyanine **4** was 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, 5.41 mA cm^{-2} ; overall conversion efficiency, 3.42%) and then decreased with prolonged dye-sensitization time.

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