

Broad-absorbing tetrabenzocorrolazine green photosensitizer for the enhanced conversion efficiency in dye-sensitized solar cells

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ABSTRACT: Novel tetrabenzocorrolazine green photosensitizer was designed and synthesized to enhance the solar energy-to-electricity conversion efficiency of dye-sensitized solar cells. This near-infrared absorbing dye exhibited superior short-circuit photocurrent density induced from the additional absorption compared to the phthalocyanine dye commonly applied as a photosensitizer covering the near-infrared region in dye-sensitized solar cells. The introduction of bulky peripheral groups and axial substituents to the novel dye led to the increase of open-circuit photovoltage. As a result, the novel tetrabenzocorrolazine dye achieved a solar energy-to-electricity conversion efficiency of 3.78% under AM 1.5G conditions which was much higher than that of the phthalocyanine reference dye.

KEYWORDS: dye-sensitized solar cell, tetrabenzocorrolazine, ring-contraction reaction, bathochromic shift, aggregation, phthalocyanine.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have recently attracted great attention because of their ease of fabrication, lightweight, and cost-effectiveness compared with silicon (Si)-based photovoltaic devices [1]. Upon optical excitation, the dye injects an electron into the conduction band of a nanocrystalline film of a wide band gap oxide, such as titanium dioxide (TiO₂), and is subsequently regenerated back to the ground state by electron donation from a redox couple present in the electrolyte [2]. For higher efficiency, many sensitizers with high short-circuit photocurrent density (J_{sc}) values and high open-circuit photovoltage (V_{oc}) values have been extensively investigated [3–7]. J_{sc} value can be improved by the red-shift of the absorption region towards the long wavelength end of the solar spectrum through the

introduction of additional donors [8] or extension of the donor chromophore's π -conjugation system [9] to have a broadened absorption spectrum for absorbing more light. V_{oc} value can be improved by suppressing charge recombination between injected electrons on the TiO₂ surface and the holes in the electrolyte with prohibiting dye aggregation though the introduction of alkyl chains or bulky aromatic rings on the donor and/or the π -conjugation linker [10]. Overall, J_{sc} and V_{oc} values can be improved by simple structural modifications of the dye molecule.

Although Ru complex sensitizers (N3, N719 and black dye) have been reported to give high photoelectric conversion efficiencies of over 11% under AM 1.5 conditions [11], their use of rare and expensive metals and the difficulty of obtaining purified dyes have limited their commercial applicability. On the other hand, sensitizers without Ru such as metal-free organic dyes or organometallic dyes are relatively inexpensive and easily synthesized, purified, and modified. However, an

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issue with respect to these dyes is their weak absorption coefficient of above 650 nm. Therefore, to achieve not only the enhancement of the photovoltaic performance but also the esthetic appreciation of the DSSCs, this nearinfrared (NIR) region absorbing green photosensitizer should be developed. Because of their excellent lightharvesting property with intense absorption throughout the NIR region, various phthalocyanines (PCs) have been designed and applied for DSSC. Recently, there was a report of a high conversion efficiency ($\eta = 4.6\%$) for DSSCs using the unsymmetrical zinc phthalocyanine dye having three bulky aryl groups and a carboxylic acid group [12]. However, their lack of absorption in the visible area (400-600 nm) and the natural tendency of forming aggregates induced from planar molecular structure are detrimental to solar energy-to-electricity conversion efficiency. In order to overcome these limitations, we have designed and developed a tetrabenzocorrolazine (TBC) green sensitizer modified from PCs as shown in Fig. 1. In addition to the conventional absorption range of PCs (600-700 nm), they also showed prominent absorption from 400 nm to 500 nm where the high solar photon flux occurs. Such expanded light absorption led to the higher J_{sc} value. In addition, their bulky peripheral groups and the axial substituents introduced to the phosphorus core metal prevented the formation of π - π stacks among the molecules which led to the higher V_{oc} value. These effects were investigated by the dye photophysical and electrochemical properties, and the cells' photovoltaic performance. Electrochemical impedance spectroscopy (EIS) was used to study their interfacial charge transfer.

RESULTS AND DISCUSSION

Synthesis

The novel TBC phosphorus compounds, TBC2, with enhanced solubility and broadened absorption peak for DSSC was designed and synthesized as shown in Scheme 1. The detailed synthesis route of reference dye PcS2, accomplished by the cyclization reaction between phthalonitrile 1 and tert-butylphthalonitrile and subsequently treated by NaOH in THF according to the previously reported procedures [12], also appeared in Scheme 1. The precursor of TBC2, the phthalonitrile (2), was synthesized through a nucleophilic aromatic substitution reaction between nitro phthalonitrile and phenol with the bulky functional substituents, and its structure was confirmed by ¹H NMR [13]. The metalfree PC (3) was synthesized by the cyclization reaction between the phthalonitrile 1 and twice the amount of the phthalonitrile 2. Phenol was used as a cosolvent instead of ethanol to prevent the transesterification. After the cooling of the resulting slurry, the crude product contained several kinds of metal-free PCs and this was purified by column chromatography on silica gel using dichloromethane as the eluent [14]. The band containing a compound synthesized only from four phthalonitriles 2 could be separated firstly. Subsequently, the second band containing bright green metal-free PC 3 was collected. The TBC phosphorus compound was synthesized via a ring-contraction reaction mediated by PBr₃ in pyridine in which a meso-nitrogen atom was extruded from an appropriate metal-free PC precursor 3. In order to ensure a good yield of TBC, the pyridine must be carefully distilled over CaH₂, and the phthalocyanine starting material must be dried in a heated (50°C) vacuum oven for several hours immediately prior to use [15]. After the ring-contraction reaction, the TBC compound was successfully precipitated by quenching with a MeOH/CH₂Cl₂ mixture to introduce the methoxy axial substituent. Purification by silica gel chromatography was carried out by using ethyl acetate/hexane solution as the eluent. After the column chromatography, the resulting compound was treated with an aqueous solution of NaOH to hydrolyze the esteric part [12]. Purification by silica gel chromatography was then carried out again by using MeOH/CH₂Cl₂ solution as the eluent. The TBC compound synthesized can theoretically have two



Fig. 1. Molecular structures of PcS2, TBC2, and N719

isomers as shown in Scheme 1, and their properties were observed without further attempts to separate these isomers in this work. The structure of the synthesized TBC2 was confirmed by MALDI-TOF spectroscopy and elemental analysis.

Photophysical properties of the dyes

The absorption spectra of the synthesized dyes in THF or CH_2Cl_2 solution and on TiO₂ films are shown in Figs 2(a) and 2(b), respectively. The dyes' absorption and emission properties are listed in Table 1. As reported

elsewhere, the absorption peak of the dye TBC2 had a red-shifted Soret band and a slightly blue-shifted Q-band compared to that of the dye PcS2 [16–18]. Therefore, the absorption peak of the dye TBC2 became closer to that of the panchromatic dye which is ideal for the high photovoltaic performance of DSSC. In particular, the conspicuous growth and bathochromic shift of the Soret band induced from the conversion from PC compound to TBC compound was extremely crucial for exhibiting high solar energy-to-electricity conversion efficiency. When it came to the aesthetic appreciation of the DSSCs' application, TBC dyes exhibited much more



Scheme 1. Synthesis of PcS2 and TBC2







Fig. 2. UV-visible absorption spectra of (a) PcS2 in THF and TBC2 in CH_2Cl_2 , and (b) both on TiO₂ films

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Table 1. Absorption and emission properties of PcS2 and TBC2

Dye		Emission		
	λ_{max}	ϵ_{max} , M ⁻¹ .cm ⁻¹	λ_{max} (on TiO ₂) ^c	λ_{max}
PcS2 ^a	676 nm	240,530	662 nm	694 nm
TBC2 ^b	452, 640 nm	311,582	423, 639 nm	676 nm

^aAbsorption and emission spectra were measured in THF solution at room temperature (5 × 10⁻⁶ M). ^bAbsorption and emission spectra were measured in CH₂Cl₂ solution at room temperature (5 × 10⁻⁶ M). ^cAbsorption spectra were obtained through measuring the dye absorbed onto TiO₂ film.

vivid green colors compared with the PC dyes. Such a bathochromic shift of the Soret band was likely to be the result of the destabilization of the HOMO⁻¹ (a2u) orbital caused by the removal of a meso-nitrogen atom [15]. The absorption maxima (λ_{max}) of the Soret band of TBC2 was at 452 nm, and that of the Q-band at 640 nm in CH₂Cl₂ solution. The molar extinction coefficient at λ_{max} of TBC2 was 311,582 M⁻¹.cm⁻¹, and included in Table 1, which was higher than that of PcS2. This was also desirable as a photosensitizer for large photocurrent generation. On TiO₂ films, the absorption maxima (λ_{max}) of PcS2 and TBC2 were shown in Fig. 2(b). They exhibited blue-shifts (14–29 nm) due to the H-aggregation of the dyes [19–21], or deprotonation of carboxylic acid upon adsorption onto the TiO_2 surface [22]. However, these hypsochromic shifts of the absorption spectra for the prepared dyes were

Dye	Oxidation potential data ^a							
	E _{ox} (=HOMO) (vs. NHE)	$E_{0\!-\!0}{}^b$	E _{ox} -E ₀₋₀ (=LUMO) (<i>vs.</i> NHE)					
PcS2	0.95 eV	1.81 eV	-0.86 eV					
TBC2	0.97 eV	1.86 eV	-0.89 eV					

 Table 2. Electrochemical properties of PcS2 and TBC2

^aMeasured in CH₂Cl₂ containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag/Ag⁺; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference, and converted to NHE by addition of 630 mV [25]). ^bEstimated from intersection wavelengths between absorption and emission spectra.



Fig. 3. CV and DPV (inset) curves of Fc/Fc⁺, PcS2, and TBC2 in CH₂Cl₂

smaller than those generally observed in other organic dyes when dyes were attached to the TiO_2 surface.

Electrochemical properties of the dyes

The first oxidation potential (E_{ox}) , corresponding to each dye's HOMO level, was measured in CH₂Cl₂ by CV and DPV. The excited state oxidation potential (E_{ox}^* = $E_{0x} - E_{0-0}$, corresponding to each dye's LUMO level, was obtained by subtracting the zeroth–zeroth energy ($E_{0=0}$), estimated from the intersection between the normalized absorption and emission spectra (Fig. S1) from E_{ox}. The electrochemical properties of the dyes and their CV with DPV curves are shown in Table 2 and Fig. 3, respectively. The HOMO levels of the prepared dyes ranged from 0.95 to 0.97 eV (vs. NHE) and were much more positive than the redox potential of $I^{/I^{3-}}$ (0.4 V vs. NHE) [23]. The LUMO levels of the dyes ranged from -0.86 to -0.89 eV and were more negative than the conduction band energy level of TiO₂ (-0.5 V vs. NHE) [23], thus indicating that the excited electrons of the dyes can be efficiently injected into the conduction band of TiO₂.

The HOMO level of the ring-contracted dye TBC2 was slightly more positive than that of the PcS2 while the LUMO level of TBC2 was slightly more negative than that of PcS2, resulting in the increase of the energy band gap (E_{gap}) of the HOMO-LUMO level. This may be attributed to the blue-shifted Q-band of dye TBC2 compared with that of PcS2. Consequently, the dye TBC2 might act as a more efficient photosensitizer for DSSCs, compared with PcS2 because its absorption spectra are in the wavelength range where the higher solar photon flux occurs [24].

Photovoltaic properties of DSSCs

DSSCs were fabricated using the synthesized dyes according to the methods described in the experimental section, and their photovoltaic properties were measured under standard AM 1.5G irradiation conditions (100 mW.cm⁻²). The effects on cell performance by the modifications of the dye structure were assessed by measuring the conversion efficiencies. The capabilities of the prepared dyes as possible photosensitizers were compared with the N719 cell's

Table 3. Photovoltaic performance data of the cells with the prepared dyes^a

Dye ^b	J _{sc} , mA.cm ⁻²	V _{oc} , V	FF, %	Area, cm ²	IPCE _{max} , %	η, %
PcS2	3.27	0.56	0.71	0.283	21	1.30
TBC2	7.08	0.65	0.69	0.298	59	3.78
N719	13.34	0.72	0.71	0.278	72	7.09

^aMeasured under AM 1.5 irradiation G (100 mW.cm⁻¹), with 0.278–0.298 cm² working area. ^bDyes were maintained at 0.5 mM in CH_2Cl_2 -acetonitrile (1:1) solution, with 10 mM CDCA as co-adsorbent. Electrolyte comprised 0.7 M 1-methyl-3-propylimidazolium iodide (MPII), 0.2 M LiI, 0.05 M I₂, 0.5 M TBP in acetonitrile-valeronitrile (v/v, 85/15) for organic dyes.



Fig. 4. (a) Incident photo-to-current conversion efficiency (IPCE) spectra for DSSCs based on **PcS2**, **TBC2**, and **N719** (b) Photocurrent-voltage curves for DSSCs based on **PcS2**, **TBC2**, and **N719** under illumination of AM 1.5G simulated sunlight (100 mW.cm⁻²)

performance as listed in Table 3. Figures 4(a) and 4(b) show the incident photon-to-current conversion efficiency (IPCE) spectra and photocurrent-voltage (J-V) curves, respectively. Compared to the reference dye PcS2, the dye TBC2 could effectively convert

visible light to photocurrent at ca. 400-500 nm and at ca. 600-700 nm due to the increased directional electron-transfer property (pushing ability) of the substituents, as well as the prevention of aggregation [12]. The IPCE value of the cell with TBC2 reached the highest value of 59% at 420 nm and 57% at 660 nm. Although the dye TBC2 exhibited superior IPCE values compared to the reference dye PcS2, its IPCE did not exceed that of the dye N719 except the NIR region (ca. 650-800 nm). This outcome was not very comprehensible since this near-IR photosensitizer had excellent absorption at *ca*. 400–500 nm (ε_{max} = 311,582), as well as throughout the near-IR region $(\varepsilon_{\text{max}} = 180,924)$. This result could be attributed to the poor adsorption of the dye TBC2 to the TiO_2 surfaces because the steric hindrance induced by the bulky peripheral groups and the axial substituents of this dye inhibited close π - π aggregation between the dye molecules, and may decrease the amount of dye adsorbed [26].

The positive effects on the cell performance by the dye structural modification were also appeared in J-V curves. The ring-contracted dye TBC₂ exhibited a much higher J_{sc} value of 7.08 mA.cm⁻² compared to the dye PcS2 owing to the expanded light absorption in the wavelengths where the high solar photon flux occurring as previously mentioned. The higher molar extinction coefficient of the dye TBC2 also affected the improvement of the J_{sc} value of it. In case of open-circuit photovoltage, the dye TBC2 also exhibited higher V_{oc} value of 0.65 V compared with the dye PcS2 owing to decreased molecular aggregation by the introduction of bulky peripheral groups and the axial substituents to the phosphorus core metal of it. The suppressed dye aggregation prevented the recombination between the injected electrons on TiO_2 and the holes of the electrolyte which raised the V_{oc} value [10].

Electrochemical impedance spectroscopy (EIS) analysis [27] was employed to investigate the electron recombination and interfacial charge transfer process in DSSCs. The EIS spectra for the DSSCs based on PcS2 and TBC2 were performed under forward bias (-0.55 V) in the dark and the Nyquist plots are shown in Fig. 5. The major semicircles in the Nyquist plots indicate the



Fig. 5. Electrochemical impedance spectra (Nyquist plots) of DSSCs based on PcS2 and TBC2 measured at -0.55 V forward bias in the dark

charge transfer resistance at the $TiO_2/dye/electrolyte$ interface. The radius of the major semicircle in the Nyquist plot of TBC2 was larger than that of PcS2, indicating that the electron recombination resistance of TBC2 was bigger than that of PcS2 [28]. This result coincided with the increase of V_{oc} in the DSSCs based on these dyes as the suppression of electron recombination between the injected electrons and the electrolyte improved V_{oc}.

Consequently, the overall conversion efficiency value of 3.78% achieved by the cell fabricated with TBC2 was much higher than that of the cell with the reference dye PcS2. Without the co-adsorbent CDCA, the cell with TBC2 showed the conversion efficiency value of 3.72%, which is not very distinctive. The co-adsorbent CDCA did not play a crucial role since the attachment of peripheral bulky units and methoxy axial groups already prevented the stacking of the dye molecules. In addition to that, the dye TBC2 was expected to be really suitable to the co-sensitization in DSSC since there were plenty of highly efficient sensitizers which absorbed light in the range of 500–600 nm [2, 10, 29–31].

EXPERIMENTAL

Materials and reagents

1,8-Diazabicyclo-7-undecene (DBU), 4-nitrophthalonitrile, and 2,5-bis-(1,1-dimethylbutyl)-methoxyphenol from TCI and 4-iodophthalonitrile, 4-(methoxy carbonyl phenyl) boronic acid, Pd(PPh₃)₄, NaCO₃, *tert*-butylphthalonitrile, ZnCl₂, NaOH, K₂CO₃, Li, NaCl, pyridine, PBr₃ and HCl from Sigma-Aldrich were purchased and used as received without further purification. All the other reagents and solvents were of reagent-grade quality and obtained from commercial suppliers.

Analytical instruments and measurements

¹H NMR spectra were recorded on a Bruker Avance 500 MHz (Seoul National University National Center for inter-University Research Facilities) with the chemical shifts against TMS. Matrix Assisted Laser Desorption/ Ionization Time Of Flight (MALDI-TOF) mass spectra were collected on a Voyager-DE STR Biospectrometry Workstation with a-cyano-4-hydroxy-cynamic acid (CHCA) as the matrix. Elemental analysis was carried out with a Flash EA 1112 CNH analyzer. UV-vis spectra and photoluminescence spectra were recorded on a Hewlette Packard 8452A spectrophotometer and Shimadzu RF-5301PC spectrofluorometer, respectively. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using a three-electrode cell with a 273A potentiostat (Princeton Applied Research, Inc.). The measurement was carried out using an Ag wire (Ag/Ag⁺), a glassy carbon and a platinum wire as a reference, a working and a counter electrode, respectively, in CH₂Cl₂ solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. A standard ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used to calibrate the oxidation peak. DPV scan rate was 100 mV.s⁻¹. Photocurrent-voltage measurements were performed using a Keithley model 2400 source measure unit. Incident photon-to-current conversion efficiency was measured as a function of wavelength from 300 nm to 1000 nm using a specially designed system for the DSSCs (PV Measurements, Inc.). Electrical impedance spectra of DSSCs under dark with -0.55 V forward bias were measured with an impedance analyzer (Compactstat, IVIUM Tech) at frequencies of 10⁻¹–10⁶ Hz.

Fabrication of dye-sensitized solar cells and measurements

 TiO_2 working electrode The nanocrystalline comprised a TiO₂ transparent layer (20 nm, synthesized) and a TiO₂ scattering layer (250 nm, G1). The Pt-coated counter electrode was prepared by a reported procedure [8b]. TiO₂ electrodes were immersed in *tert*-butanolacetonitrile (1:1) solution containing the dyes at 0.5 mM for 40 h at ambient temperature. They were then washed with ethanol and dried under a stream of nitrogen. The working and counter electrodes were sealed with Surlyn $(60 \,\mu\text{m}, \text{Dupont})$ and the electrolyte was injected through a hole in the counter electrode. The electrolyte comprised 0.7 M 1-methyl-3-propylimidazolium iodide (PMII), 0.2 M LiI (Aldrich), 0.05 M I₂ (Aldrich), and 0.5 M 4-tert-butylpyridine (TBP, Aldrich) in a mixed solvent of acetonitrile and valeronitrile (v/v, 85/18). The active area of the dye-coated TiO₂ film was 0.269-0.284 cm² working area, measured by analyzing images from a CCD camera (moticam 1000). TiO₂ film thickness was measured by an α -step surface profiler (KLA tencor).

Synthesis of dyes

Phthalonitrile 1 were accomplished by the Suzuki coupling reaction between 4-iodo phthalonitrile and 4-(methoxy carbonyl phenyl) boronic acid or 3-(methoxy carbonyl phenyl) boronic acid according to the previously reported procedures [12].

PcS2 were accomplished by the cyclization reaction between phthalonitrile 1 and *tert*-butylphthalonitrile and subsequently treated by NaOH in THF according to the previously reported procedures [12].

Preparation of 4-(2,5-Bis(1,1-dimethylbutyl)-4methoxyphenoxy)phthalonitrile (2). 4-Nitrophthalonitrile (1 g, 5.77 mmol) and 2,5-bis-(1,1-dimethylbutyl)methoxyphenol (1.68 g, 5.77 mmol) were dissolved in 30 mL of dry DMF and anhydrous K₂CO₃ (1.06 g, 7.66 mmol) was added in portions during 4 h. The mixture was stirred at 80 °C for 8 h under nitrogen atmosphere. After filtering the reaction mixture, the residue was extracted with CH₂Cl₂ and dried by rotary evaporation. After removal of the solvent, the crude product was purified on a silica gel column (CHCl₃) to afford the target compound as a light brown solid (2.13 g, 88.47%). ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ, ppm 7.69 (d, 1H), 7.22 (s, 1H), 7.14 (d, 1H), 6.82 (s, 1H), 6.63 (s, 1H), 3.08 (s, 3H, -O-CH₃), 1.71 (m, 2H), 1.56 (m, 2H), 1.26 (d, 12H), 1.04 (m, 2H), 0.96 (m, 2H), 0.81 (t, 3H), 0.71 (t, 3H).

Preparation of unsymmetrical metal-free phthalocyanine (3). Phthalonitrile 1 (0.3 g, 1.08 mmol) and phthalonitrile 2 (0.9 g, 2.15 mmol) was dissolved in 50 mL of anhydrous xylene and 10 mL of phenol under nitrogen atmosphere and Li (0.16 g, 22.63 mmol) was added in the solution. The reaction mixture was stirred at 150 °C for 5 h. After cooling the solution, the resulting slurry was extracted with 100 mL of CH₂Cl₂ and washed with saturated NaCl solution. After removal of the solvent, the crude product was purified on a silica gel column (CH₂Cl₂) to afford the target compound as a bright green solid (0.61 g, 55.60%). MALDI-TOF MS: m/z 1520.40 (100%, [M]⁺). Found C, 76.37; H, 7.60; N, 7.35. Calcd. for C₉₇H₁₁₄N₈O₈: C, 76.65; H, 7.56; N, 7.37.

Preparation of unsymmetrical phosphorus triazatetrabenzcorrole (TBC2). Phthalocyanine 3 (1.12 g, 0.74 mmol) was placed in a 100 mL flask equipped with a condenser and gas inlet adapter and dissolved in 30 mL of pyridine. An amount of PBr₃ (9.0 g, 33.0 mmol) was added and the resulting solution heated to 120 °C and stirred for 2 h. After 2 h, the volume of the reaction mixture was reduced by vacuum distillation to 1–2 mL and then treated with a 50/50 solution of CH₂Cl₂/MeOH for 2 h. The resulting green solid was dissolved in CH₂Cl₂ and filtered to remove excess pyridinium bromide as a white crystalline solid. The filtrate was reduced in volume under reduced pressure and loaded onto a silica gel column for purification with 1/7 ethyl acetate/hexane as the eluent.

An aqueous solution of NaOH (1.0 M, 2 mL) was added to the solution of unsymmetrical phosphorus

triazatetrabenzcorrole having an ester in THF (9 mL). The mixture was stirred at 70 °C for 24 h. The solvent was removed *in vacuo* and the residue was dissolved in aqueous solution of HCl (1.0 M, 20 mL) and 20 mL of CH₂Cl₂. The resulting solution was extracted and washed with saturated NaCl solution. After removal of the solvent, the crude product was purified on a silica gel column with 1/1 CH₂Cl₂/MeOH as the eluent to afford the target compound as a bright green solid (0.24 g, 20.19%). MALDI-TOF MS: *m*/*z* 1582.25 (100%, [M]⁺). Found C, 73.97; H, 7.49; N, 6.31. Calcd. for C₉₈H₁₁₆N₇O₁₀P: C, 74.36; H, 7.39; N, 6.19.

CONCLUSION

Novel TBC green sensitizer was designed and synthesized to investigate the effects of an expanded absorption range induced from the ring-contraction reaction and an anti-aggregation by the bulky peripheral groups and the axial substituents on the performance of DSSCs. To the best of the authors' knowledge, this is the first report of applying TBC moieties exhibiting vivid green colors as a sensitizer of DSSCs.

As we expected, the ring-contraction reaction of phthalocyanine precursor made its Soret band largely bathochromic-shifted and its Q-band hipsochromic-shifted. The additional strong absorption from 400 nm to 500 nm of tetrabenzocorrolazine dye TBC2 induced increase of its J_{sc} and IPCE compared with the phthalocyanine dye PcS2. In addition to that, the introduction of bulky peripheral groups and axial substituents at the core metal of phthalocyanine triggered decreased molecular aggregation which led to the increased V_{oc} . The radius of the semicircle in the intermediate frequency regime of the Nyquist plot of TBC2 was bigger than that of PcS2 which coincided with the trend of V_{oc} values.

As a result, the superior solar energy-to-electricity conversion efficiency was achieved with TBC2, which had the η value of 3.78% under AM 1.5G irradiation. However, the fabrication of the DSSCs with these sensitizers should be thoroughly optimized since all the conversion efficiencies of the cells even with the dye N719 ($\eta = 7.09\%$) were not high enough as reported elsewhere.

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