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ARTICLE

Synthesis and Characterization of Simple Cost-Effective *Trans*-A₂BC Porphyrins with Various Donor Groups for Dye-Sensitized Solar Cells[†]

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We have designed and synthesized a series of simple cost-effective 'push-pull' Zn(II) porphyrin dyes containing various electron donors such as 2-thienyl, pyrenyl, phenyl, 4'-bromophenyl and 4'-^tbutylphenyl and 4'-carboxyphenyl acceptor moieties in three steps. Their optical absorption spectra, electrochemical redox and photovoltaic properties have been investigated in detail. The overall power conversion efficiencies (η) of DSSCs based on these dyes are in the range of 2.1 to 4.2% and highly depend on their donor moiety. The incorporation of *trans*-10,20-dimesityl groups is highly beneficial to prevent the π - π aggregation among the porphyrin moieties, thus favorably suppressing the charge recombination and intermolecular interaction. Among all, pyrenyl appended Zn(II) porphyrin has exhibited higher power conversion efficiency of 4.2% under 1 sun illumination due to extended π -conjugation and electron donating ability of pyrenyl moiety.

Introduction

Development of a sustainable society and growing global energy consumption demands clean and renewable energy resources. Several environmental issues aroused by consumption of a large amount of fossil fuel in the recent years. Artificial photosynthesis and photovoltaics technologies are desirable to harvest substantially inexhaustible solar energy. Dye-sensitized solar cells (DSSCs)¹ are one of the promising alternatives to conventional photovoltaic devices based on silicon which can convert sunlight efficiently to electricity owing to their high power conversion efficiency (PCE), ease of fabrication and potential low cost compared with traditional silicon-based solar cells. In this respect for the past two decades, polypyridyl ruthenium complexes^{1c,2} have been utilized to achieve electric power conversion efficiency up to 11% due to their broad absorption spectrum through metal-to-ligand charge transfer (MLCT), the longer exciton lifetime, and their long-term chemical stability.³ Despite their overwhelming performance, Ru-polypyridyl sensitizers encounter several drawbacks^{2a-c} such as the high cost of noble metal ruthenium, the requirement for careful synthesis, hefty purification steps, toxicity to environment and low molar extinction coefficients in the red region of visible spectrum hampers their large-scale application in DSSCs.

Organic dyes⁴ such as coumarin, indoline, oligoene, thiophene, triarylamine, perylene, cyanine, fluorine, merocyanine and hemicyanine derivatives are of great interest owing to their modest cost, ease of synthesis and structural modification, large molar absorption coefficients, and satisfactory stability.⁵ Some organic dyes with the conversion efficiencies in a range of 5-9% have been prepared.⁴ Recently, carboxy anchoring dye, **LEG4** collaboratively working with alkoxysilylether dye, **ADEKA1** exhibited 14.3% power conversion efficiency (PCE) under one sun illumination. However, porphyrins and phthalocyanines are best dyes due to their high thermal and photochemical stability, strong absorption in visible region as well as their intriguing optical, photophysical and electrochemical properties can be tuned by peripheral substitutions.^{6,7} The most efficient porphyrin sensitizers feature 'push-pull Donor- π -Acceptor (D- π -A)' structures and/or π -extensions that made porphyrins panchromatic in visible and even near infrared regions.⁷ Consequently, porphyrin sensitizers have exhibited power conversion efficiencies that are comparable to or even higher than those of well-established highly efficient DSSCs based on ruthenium complexes. For example, remarkable power conversion efficiency (η) of 12.3%, was achieved by Zn(II) porphyrin sensitizer (YD2-*o*-C8) co-sensitized with an organic dye (YD123) using a cobalt-based electrolyte which is superior to those based on Ru complexes.⁸

Recently, a class of 'push-pull' porphyrins with an electron-donating diarylamino group and an electron-withdrawing carboxyphenylethynyl anchoring group, GY50 and SM315 have revealed remarkable high efficiencies of 12% and 13% with

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[†]Electronic Supplementary Information (SI) available: ¹H NMR and mass spectra of synthesized dyes. See DOI: 10.1039/x0xx00000x

cobalt electrolyte under standard one sun illumination.⁹ However, synthesis of these bridged conjugated 'push-pull' porphyrin sensitizers involves multistep synthesis involving expensive metal (Pd)-catalyzed C-C and C-N coupling reactions under stringent reaction conditions leading to overall low yield of final product. All these aspects demand a simple and efficient synthetic methodology to address the practical future applications of porphyrin-based DSSCs. He and co-workers reported a power conversion efficiency of 5.1% using a simple architecture having *trans*-mesityl groups and *meso*-acrylic acid substituted zinc porphyrin sensitizer.¹⁰ However, the synthesis of *meso*-bromosubstituted porphyrin followed by Pd[0]-catalyzed Heck coupling to introduce the acrylic acid anchoring group involves multistep synthesis under inert and dry environment leading to high cost DSSCs. These findings encourage us to develop simple, efficient sensitizers involving fewer synthetic steps.

Herein, we report, five simple *trans*-mesityl A₂BC porphyrin Zn(II) complexes having different donor groups and carboxylate as the anchoring group (Chart 1). A benzene ring between the carboxylic acid and the porphyrin ring functions as a spacer. To prevent dye aggregation, usually alkyl and alkoxy chains have been introduced on the *meso*-phenyl rings of porphyrinic sensitizers leading to high cell performance.¹¹ Bulky *trans*-*meso*-dimesityl groups are introduced to provide the oxidative stability¹² to porphyrins and to suppress the self-quenching by dye aggregation between the neighboring molecules adsorbed onto the TiO₂ surface by the steric hindrance around the porphyrin core and also provides an effective shielding to electron recombination with the electrolyte.¹⁰ This leads to an increase of electron injection efficiency (ϕ_{inj}). The overall power conversion efficiencies (η) of DSSCs based on these dyes are in the range of 2.1 to 4.2% and highly depend upon their donor moiety. Among all, pyrenyl appended Zn(II) porphyrin has exhibited higher power conversion efficiency of 4.3% under 1 sun illumination which is attributed to strong π -conjugated character of pyrene¹³ that interacts with porphyrin effectively.

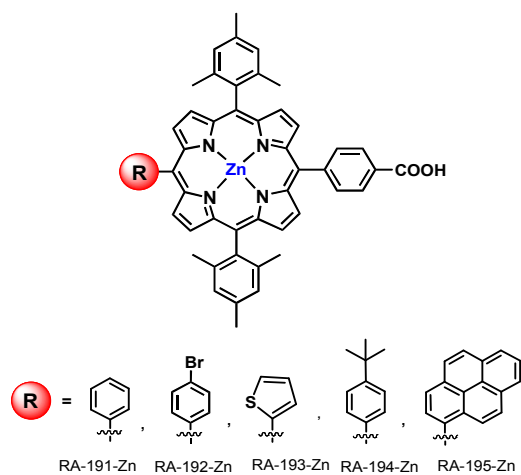
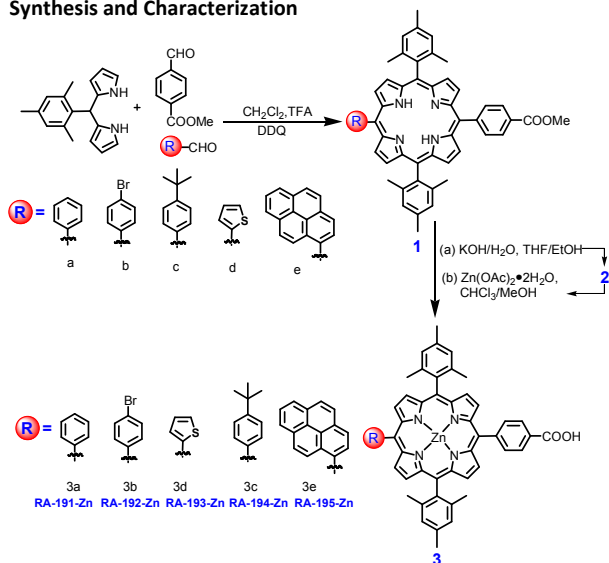


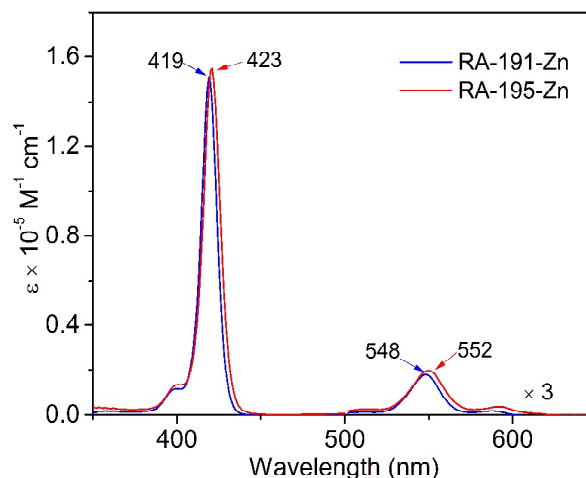
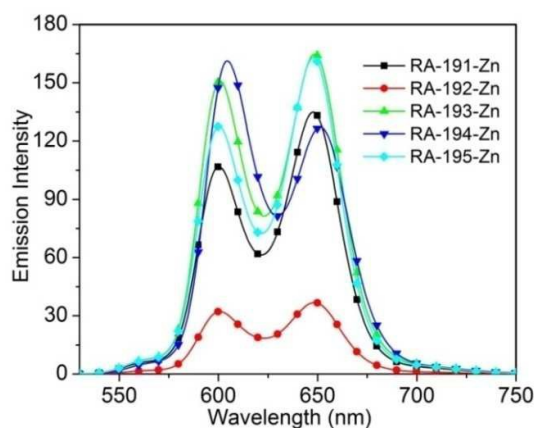
Chart1. Molecular structure of synthesized porphyrinic dyes.

Results and Discussion

Synthesis and Characterization



Scheme 1. Synthetic route for the preparation of porphyrinic dyes.

Figure 1. Electronic absorption spectra of dyes RA-191-Zn (9 μ M) and RA-195-Zn (9 μ M) in CH₂Cl₂ at 298 K.Figure 2. Fluorescence spectra of Zn(II) porphyrin dyes in CH₂Cl₂ at 298 K.

Trans-A₂BC-esterporphyrins (**1a-1e**) were synthesized *via* modified MacDonald [2+2] condensation between 5-mesityl dipyrromethane and two different types of aromatic aldehydes viz. aryl aldehyde (B) having different donor groups (R-CHO) and 4-carbomethoxybenzaldehyde (C) to afford monoester porphyrins in good yields. Then monoester porphyrins (**1a-1e**) were subjected to base hydrolysis to afford the corresponding carboxyporphyrins (**2a-2e**) (Scheme 1) in quantitative yields. The subsequent metallation using Zn(OAc)₂•2H₂O yielded the target porphyrinic dyes **RA-191-Zn**, **RA-192-Zn**, **RA-193-Zn**, **RA-194-Zn** and **RA-195-Zn** in 90-92% yield. Detailed synthetic procedures are given in the experimental section. All the intermediates and final Zn(II) porphyrin dyes were characterized by UV-Vis, fluorescence and ¹H NMR spectroscopic techniques (Figures S1-S10 in the electronic supplementary information (SI)) and mass spectrometry (Figures S11-S24, SI). Further, electronic, photophysical, structural properties and computational studies of these dyes were investigated by optical absorption and fluorescence spectroscopic techniques, density functional theory (DFT), cyclic voltammetry and photocurrent–voltage measurements.

Optical Absorption and Emission Spectral Properties

The UV-Vis spectra of the synthesized Zn(II) porphyrin dyes were recorded in distilled CH₂Cl₂ at 298 K and the absorption data is listed in Table 1. Representative absorption spectra of dyes **RA-191-Zn** and **RA-195-Zn** are shown in Figure 1. All these synthesized dyes exhibited an intense Soret band in the range 400–450 nm and moderate absorbing two Q bands in the range 525–625 nm, which are attributed to the π–π* electronic transitions. Dyes containing 2-thienyl and pyrenyl as donor groups (**RA-Zn-193** and **RA-Zn-195**) showed marginal red shift (3-4 nm) in Soret and Q bands than those of **RA-191-Zn**, **RA-192-Zn** and **RA-194-Zn**.

The synthesized dyes were also characterized by fluorescence spectroscopy to elucidate the role of different donor groups. Figure 2 represents the steady state emission spectra of Zn(II) porphyrin dyes in CH₂Cl₂ at 298 K and the emission data is listed in Table 1. No significant shifts in emission bands were observed for these dyes except **RA-193-Zn** which exhibited a red shift of 4 nm in emission bands as compared to **RA-191-Zn**. However, the fluorescence quenching was observed for **RA-192-Zn** which leads to the decrement in the quantum yield due to the heavy atom effect of bromo group.

Table 1. Optical absorption and emission spectral data of synthesized dyes in CH₂Cl₂ at 298 K. Values in parentheses refer to log ε (ε in Mol⁻¹ cm⁻¹).

Porphyrin	B band(s), nm	Q band(s), nm	λ _{em} , nm	Φ _f
RA-191-Zn	419(5.17)	548(4.77), 587(4.00)	600, 648	0.037
RA-192-Zn	420(5.24)	549(4.86), 588(4.04)	600, 648	0.019
RA-193-Zn	420(5.23)	549(4.85), 588(4.03)	600, 648	0.031
RA-194-Zn	421(5.18)	550(4.80), 592(4.04)	604, 652	0.041
RA-195-Zn	423(5.17)	552(4.76), 593(4.01)	601, 649	0.041

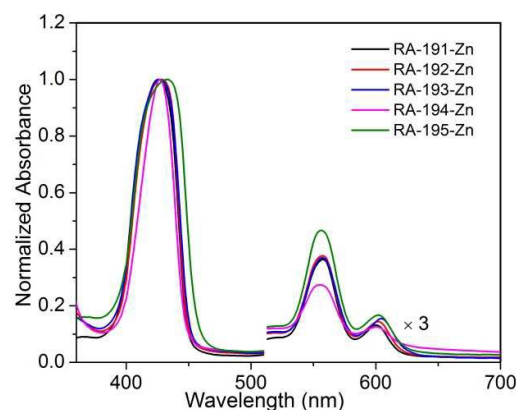


Figure 3. Normalized UV-Vis absorption spectra of Zn(II) porphyrin dyes on the TiO₂ films.

The UV-Vis absorption spectra of porphyrin **RA-191-Zn** to **RA-195-Zn** adsorbed on TiO₂ films is shown in Figure 3. All of these porphyrins show broadened and red shifted Soret and Q bands after adsorption on TiO₂ films as compared to corresponding absorption spectra in solution. The observed red shifted bands provide an indication of J-type aggregation of the porphyrinic dyes onto the TiO₂ surface.^{14a} Notably, these dyes after adsorption onto the TiO₂ film exhibits stronger absorption in Q bands region, indicating strong electronic coupling between the porphyrin ring and the TiO₂ conduction band and alteration of porphyrin geometry^{14b} as well as an enhanced light harvesting capacity of the low energy photons, which is highly desirable for efficient sensitizers in DSSCs. Among all, **RA-195-Zn** exhibited broader absorption spectral features possibly due to extended π-conjugation which leads to higher light harvesting capacity.

Cyclic Voltammetric (CV) Studies

The electrochemical properties of these Zn(II) porphyrinic dyes (**RA-191-Zn** to **RA-195-Zn**) were investigated by cyclic voltammetric studies in CH₂Cl₂ containing 0.1 M TBAPF₆ with a scan rate of 0.1 V/s at 298 K as shown in Figure 4 and the data is listed in Table 2. The reduction potentials of these Zn(II) dyes are 20-80 mV cathodically shifted indicating the influence of electron donor moieties as compared to ZnTPP whereas oxidation potentials are anodically shifted (10-40 mV). Among all, *tert*-butylphenyl and pyrenyl appended porphyrins showed larger cathodic shift 50-80 mV in their reduction potentials indicating their effective donor ability. Among all, pyrenyl appended porphyrin (**RA-195-Zn**) showed 40 mV cathodic shift indicating the possibility of extended conjugation from pyrenyl moiety to porphyrin π-system.^{6a,6b} Figure 5 depicts the HOMO-LUMO energy levels of Zn(II) porphyrin dyes and compared with conduction band of TiO₂ and electrolyte which clearly indicate that the feasibility of electron transfer (down-hill process).

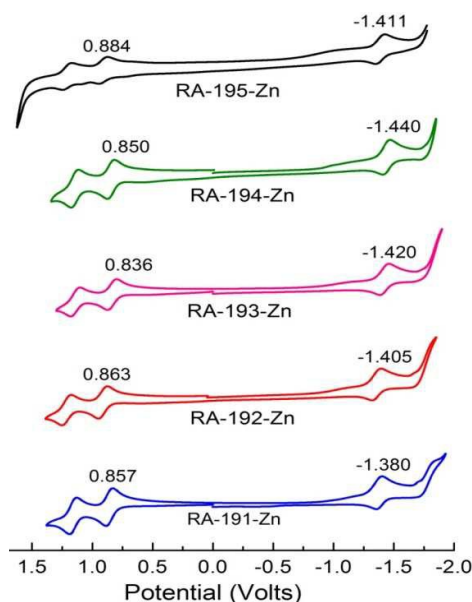


Figure 4. Cyclic voltammograms of zinc porphyrin dyes (~ 1 mM) in CH_2Cl_2 containing 0.1 M TBAPF₆ using Ag/AgCl as reference electrode with a scan rate of 0.1 V/s at 298 K.

Table 2. Electrochemical redox potentials (in V vs Ag/AgCl) of zinc porphyrin dyes in CH_2Cl_2 containing 0.1 M TBAPF₆ with a scan rate of 0.1 V/s at 298 K.

Porphyrin	Oxidation (V)		Reduction (V)		$\Delta E(\text{V})$
	I	II	I	II	
RA-191-Zn	0.857	1.157	-1.380	-1.775	2.237
RA-192-Zn	0.863	1.163	-1.405	-	2.268
RA-193-Zn	0.836	1.141	-1.420	-	2.256
RA-194-Zn	0.850	1.148	-1.440	-	2.287
RA-195-Zn	0.884	1.183	-1.411	-	2.295

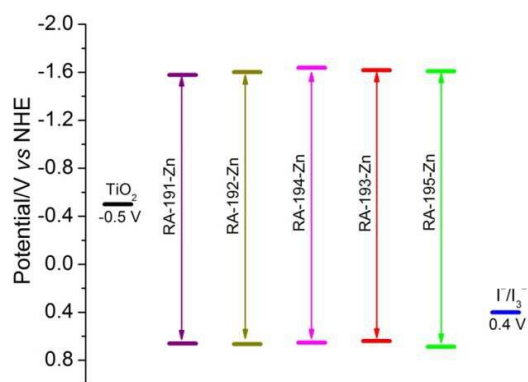


Figure 5. Energy level diagram of dyes and compared with nanocrystalline TiO_2 and iodide/triiodide electrolyte.

Photovoltaic studies

Dye-sensitized solar cells (DSSCs) were prepared using *trans*-A₂BC Zn(II)-porphyrin-dyed 12 μm thick TiO_2 photoanodes (0.16 cm^2) assembled into standard sealed sandwiched cells with Pt

sheet counter electrode, iodide/triiodide electrolyte was introduced into the space between the photoanodes. Figure 6 shows the typical I-V characteristics of the dye-sensitized solar cells using various Zn(II) porphyrin dyes using iodide/triiodide electrolyte. Table 3 lists the photovoltaic parameters of Zn(II) dyes under AM 1.5G solar light illumination (power 100 mW cm^{-2}) with an active area of 0.16 cm^2 . We have obtained the photon-to-current efficiency (PCE) in the range of 2.1 to 4.2%. Among all, the best performance of was obtained with **RA-195-Zn** after soaking for 20 hours. **RA-195-Zn** exhibited V_{oc} , J_{sc} and fill factor values of 560 mV, 10.8 mA/cm^2 and 0.70, respectively with the PCE value of (η) 4.23% at AM 1.5G full sunlight illumination. Similar open circuit voltage (V_{oc}) was observed for these dyes, as expected since they have similar electronic configuration whereas much higher short circuit current density (J_{sc}) was observed for **RA-195-Zn** due to extended π -conjugation between pyrene and Zn(II) porphyrin.^{6a,6b} The power conversion efficiency (η) of these dyes follows the order:

phenyl ($\eta = 2.11\%$) < 4'-*tert*-butylphenyl ($\eta = 2.19\%$) < 4'-Bromophenyl ($\eta = 3.07\%$) < 2'-thienyl ($\eta = 3.13\%$) < pyrenyl ($\eta = 4.23\%$)

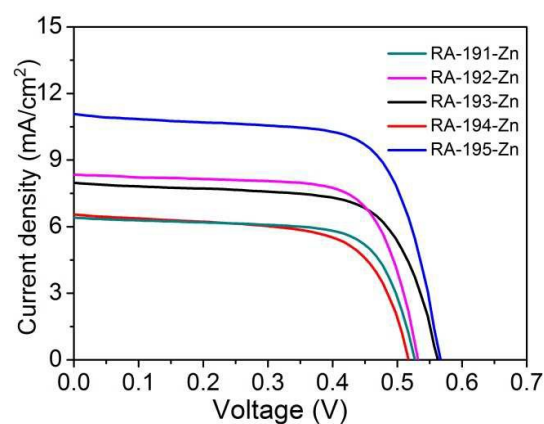


Figure 6. The typical I-V characteristics of the DSSCs using various Zn(II) porphyrin dyes.

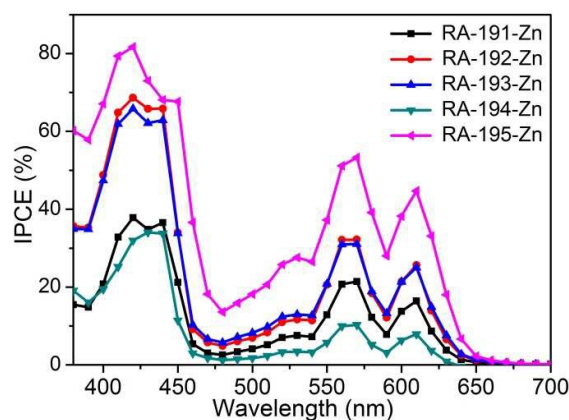


Figure 7. IPCE action spectra of Zn(II) porphyrin dyes (RA-191-Zn to RA-195-Zn).

Table 3. Photovoltaic parameters of Zn(II) porphyrins under AM 1.5G sun illumination (power 100 mW cm^{-2}) with an active area of 0.16 cm^2 .

Zn-Porphyrin	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)	IPCE (%)
RA-191-Zn	0.53	5.7	70	2.11	21
RA-192-Zn	0.53	8.3	70	3.07	31
RA-193-Zn	0.56	8.0	70	3.13	29
RA-194-Zn	0.52	6.5	65	2.19	13
RA-195-Zn	0.55	11.0	70	4.23	52

The variation in η values clearly indicates the effect extended π -conjugation and donor ability of **R** groups appended on porphyrin π -skeleton. Further, we are trying to probe for the possibility of enhanced charge separation and broad absorption of pyrenyl dye (**RA-195-Zn**) on TiO_2 surface. The attempts to improve the efficiencies of these dyes by appending various efficient electron donors are in progress.

The Incident photon to current efficiency (IPCE) spectra were measured using a Newport IPCE system. The IPCE was performed as a function of incident wavelength to evaluate the photovoltaic performance. The IPCE spectra of fabricated solar cells is shown in Figure 7 which resemble the absorption spectra of the Zn(II) porphyrins adsorbed on TiO_2 films (Figure 3), exhibiting characteristic peaks of moderate intensity in the 400-470 and 500-650 nm region. The IPCE values are listed in Table 3. Among all, the solar cell **RA-195-Zn** exhibited good IPCE response (52%) which is consistent with a higher J_{sc} value (Table 3) as compared to other dyes. **RA-192-Zn** and **RA-193-Zn** possess moderate while **RA-191-Zn** and **RA-194-Zn** exhibit lower IPCE values at the Soret and Q absorption bands which is consistent with the trends of the corresponding Soret and Q absorption bands. The I-V curves under standard AM 1.5G illumination are in qualitative agreement with the photoaction spectra of these porphyrin dyes. Notably, **RA-195-Zn** exhibited high plateau at Soret and Q band region as compared to other dyes which is responsible for highest current density for **RA-195-Zn**. This observation may be ascribed to the enhanced conjugation by pyrene moiety to the porphyrin π -system which obviously led to red-shift and broadened absorption bands and thus as enhance the current density.

DFT Studies

We have optimized the geometries of synthesized Zn(II) porphyrin dyes using B3LYP functional and LanL2DZ basis set. All these porphyrins are exhibiting planar confirmation of the porphyrin core. The *meso*-substituents (mesityl, different donor moieties and carboxyphenyl) are nearly perpendicular to the porphyrin plane. Figures S25 and S26 in the SI depict the frontier molecular orbitals (FMOs) of synthesized Zn(II) porphyrin dyes having various donor moieties. In general, these porphyrins show typical TPP (having acceptor groups) type molecular orbitals a_{1u} , a_{2u} and e_g , i.e HOMO is a_{2u} , HOMO-1 is a_{1u} ; LUMO and LUMO+1 are e_g orbitals, respectively (Figures S25 and S26, SI). Further, LUMO+2 represents the

acceptor carboxy phenyl moiety. This study clearly indicates that there could be the possibility of charge transfer from HOMO (porphyrin core) to LUMO+2 (carboxyphenyl moiety).

Conclusions

We have designed and synthesized a new series of *trans*- A_2BC porphyrins having various donor groups in three steps with good yields. These porphyrins were characterized by UV-Visible, fluorescence and ^1H NMR spectroscopic techniques and mass spectrometry. CV studies revealed the cathodic shift in reduction potentials as compared to ZnTPP indicating electron donation from **R** groups. These dyes exhibited the power conversion efficiency from 2.1 to 4.2% which depend upon electron donating ability of R group. Among all, pyrenyl appended porphyrin (**RA-195-Zn**) exhibited 4.2% power conversion efficiency possibly due to extended π -conjugation. The systematic studies to support extended π -conjugation between porphyrin π -system and pyrenyl moiety is in progress. The attempts to improve the efficiencies of these dyes by appending various efficient electron donors are in progress.

Experimental Section

Chemicals and materials

All aromatic aldehydes employed in present work were purchased from Alfa Aesar, India and used as received. Silica gel (100 - 200 mesh) used for column chromatography was purchased from Rankem, India and used as received. TBAPF₆ used in cyclic voltammetric studies was obtained from Alfa Aesar, India and recrystallized twice from ethanol followed by drying under vacuum at 60 °C for 10 h.

Instrumentation and methods

UV-Vis absorption spectra were measured in distilled CH_2Cl_2 using a Agilent Cary 100 spectrophotometer with a pair of quartz cells of 10 mm path length and the fluorescence emission spectra were recorded on a Hitachi F-4600 spectrofluorometer using a quartz cell of 10 mm path length. Elemental analysis was carried out using ElementarVario EL II instrument. ^1H NMR spectra were recorded on a Bruker AVANCE 500 MHz and JEOL ECX 400 MHz spectrometers using CDCl_3 as a solvent containing 0.03% TMS (v/v). MALDI-TOF-MS spectra were measured using a BrukerUltrafleXtreme-TN MALDI-TOF/TOF spectrometer using HABA as a matrix and the ESI mass spectra were recorded on a Bruker Daltonics microTOF mass spectrometer in positive ion mode using acetonitrile as solvent. DFT studies were carried out using B3LYP functional with LANLD2Z basis set with Gaussian 03 software package. Cyclic voltammetric measurements were carried out using CHI 620E instrument in triple distilled CH_2Cl_2 containing 0.1 M TBAPF₆ as supporting electrolyte under argon atmosphere. A three electrode assembly was used consisting of a Pt disk working electrode, Ag/AgCl as a reference electrode and a Pt-wire as a counter electrode. UV-Vis absorption spectra of Zn(II) porphyrins on TiO_2 films were recorded on a Analytik Jena spectrophotometer (model

specord 210). IPCE was measured using a 150 W Xe lamp (ORIEL) fitted with a monochromator (Corerstone 260) as the monochromatic light source.

The fabrication of DSSCs

Fluorine-doped SnO₂ glass (TEC-15, 2.2 mm thickness, Solaronix) was used for transparent conducting electrodes. The substrate was first cleaned in an ultrasonic bath using a detergent solution, acetone and ethanol, respectively (each step was 20 min long). The FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. A screen-printed double layer film of interconnected TiO₂ particles were used as mesoporous negative electrode. A 7 μm thick film of 20-nm-sized TiO₂ particles was first printed on the fluorine-doped SnO₂ conducting glass electrode and further coated by a 5 μm thick second layer of 400-nm sized light scattering anatase particles.

The TiO₂-coated electrodes (active area 0.16 cm²) were gradually heated under air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and 500 °C for 15 min. After the sintering process, the TiO₂ film was treated with 40 mM TiCl₄ solution, then rinsed with water and ethanol. The electrodes were heated at 500 °C for 30 min and after cooling (80 °C) were immersed for 16 h into sensitizing baths containing EtOH/THF (volume ratio: 1/4) solutions of the porphyrin in 0.2 mM concentration and when required with 0.4 mM of 3a,7a-dihydroxy-5b-cholic acid (CDCA) (Solaronix, Switzerland) was added. After washing with THF and drying by air flow, electrolyte (AN-50, Solaronix, Switzerland) solution was introduced into the space between the photoanodes and Pt-sheet counter electrode.

Synthetic Procedures

5-Mesityldiopyromethane was prepared using literature methods.¹⁵ 5g of mesitaldehyde (0.034 mol) was taken in 300 mL of 0.18 M aqueous HCl. To this, 7 ml of pyrrole (0.101 mol) was added. The reaction mixture was purged with argon and then stirred in dark for overnight at room temperature. At the end of this period, the reaction mixture was extracted with CHCl₃, washed with water and dried over anhydrous sodium sulphate. The product was purified by silica column using CHCl₃ as eluent. The yield of the desired product was found to be 4.5 g, 0.017 mol (50% yield).

¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.94 (s, 2H, NH), 6.87 (s, 2H, *meso*-phenyl-H), 6.66 (d, 2H, *J* = 1.5 Hz, α-pyrrole-H), 6.18 (q, 2H, *J* = 3 Hz, β-pyrrole-H), 6.01 (s, 2H, β'-pyrrole-H), 5.93 (s, 1H, *meso*-CH), 2.28 (s, 3H, *p*-CH₃ of Mesityl), 2.07 (s, 6H, *o*-CH₃ of Mesityl).

General procedure for the synthesis of 1:

5-Mesityldiopyromethane (3.78mmol), 4-formylbenzoate (1.89 mmol) and the corresponding aromatic aldehyde (1.89 mmol) were taken in a two-neck RB flask containing 800 ml of distilled CHCl₃. The reaction mixture was purged with argon for 20 minutes followed by addition of trifluoroacetic acid (2.26

mmol). The resulting reaction mixture was stirred in dark for 3 hours. At the end of this period, DDQ (3.78 mmol) was added and allowed to stir for 1 hour. The reaction mixture was neutralized with triethylamine, concentrated to small volume and loaded on silica column, eluted using 1:1 hexane/chloroform mixture. The desired product was obtained as second fraction (Scheme 2) which was further recrystallized from CHCl₃/CH₃OH mixture (1:3, v/v). The yield was found to be 10-12%.

5-(4'-carbomethoxyphenyl)-10,20-(dimesityl)-15-phenyl-

porphyrin (1a): 0.14 g, 0.184 mmol (10% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.80 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.74 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.70 (t, 4H, *J* = 4.5 Hz, β-pyrrole-H), 8.42 (d, 2H, *J* = 8.5 Hz, *meso*-*o*-carbomethoxyphenyl-H), 8.31 (d, 2H, *J* = 8.5 Hz, *meso*-*m*-carbomethoxyphenyl-H), 8.22 (dd, 2H, *J* = 8.5 Hz, *meso*-*o*-phenyl-H), 7.79-7.72 (m, 3H, *meso*-*m* and *p*-phenyl-H), 7.28 (s, 4H, *meso*-*m*-mesityl-H), 4.10 (s, 3H, OCH₃), 2.63 (s, 6H, *meso*-*p*-CH₃mesityl-H), 1.84 (s, 12H, *meso*-*o*-CH₃mesityl-H), -2.64 (s, 2H, N-H). MALDI-TOF-MS (m/z): found 757.82 [M+H]⁺, calcd. 757.35 for C₅₂H₄₄N₄O₂.

5-(4'-carbomethoxyphenyl)-10,20-(dimesityl)-15-(4'-

bromophenyl)porphyrin (1b): 0.16 g, 0.157 mmol (10.1% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.78 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.74 (d, 2H, *J* = 5 Hz, β-pyrrole-H), 8.71 (asym t, 4H, *J* = 4.5 Hz, β-pyrrole-H), 8.43 (d, 2H, *J* = 8.5 Hz, *meso*-*o*-carbomethoxyphenyl-H), 8.31 (d, 2H, *J* = 8.5 Hz, *meso*-*m*-carbomethoxyphenyl-H), 8.09 (d, 2H, *J* = 8.5 Hz, *meso*-*o*-bromophenyl-H), 7.88 (d, 2H, *J* = 8.5 Hz, *meso*-*m*-bromophenyl-H), 7.29 (s, 4H, *meso*-*m*-mesityl-H), 4.11 (s, 3H, OCH₃), 2.63 (s, 6H, *meso*-*p*-CH₃mesityl-H), 1.83 (s, 12H, *meso*-*o*-CH₃mesityl-H), -2.66 (s, 2H, N-H). MALDI-TOF-MS (m/z): found 836.89 [M]⁺, calcd. 836.29 for C₅₂H₄₃BrN₄O₂.

5-(4'-carbomethoxyphenyl)-10,20-(dimesityl)-15-(2'-thienyl)-

porphyrin (1c): 0.155 g, 0.157 mmol (11.1% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.01 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.73 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.72-8.67 (m, 4H, β-pyrrole-H), 8.42 (d, 2H, *J* = 7.5 Hz, *meso*-*o*-carbomethoxyphenyl-H), 8.31 (d, 2H, *J* = 8 Hz, *meso*-*m*-carbomethoxyphenyl-H), 7.91 (d, 1H, *J* = 3 Hz, α-thienyl-H), 7.82 (d, 1H, *J* = 5 Hz, γ-thienyl-H), 7.49 (t, 1H, *J* = 4 Hz, β-thienyl-H), 7.28 (s, 4H, *meso*-*m*-mesityl-H), 4.11 (s, 3H, OCH₃), 2.63 (s, 6H, *meso*-*p*-CH₃mesityl-H), 1.84 (s, 12H, *meso*-*o*-CH₃mesityl-H), -2.58 (s, 2H, N-H). MALDI-TOF-MS (m/z): found 763.99 [M+H]⁺, calcd. 763.31 for C₅₀H₄₂N₄O₂S.

5-(4'-carbomethoxyphenyl)-10,20-(dimesityl)-15-(4'-tert-

butylphenyl)porphyrin (1d): 0.180 g, 0.221mmol (11.7% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.85 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.72 (d, 2H, *J* = 4.5 Hz, β-pyrrole-H), 8.69 (t, 4H, *J* = 4 Hz, β-pyrrole-H), 8.42 (d, 2H, *J* = 8 Hz, *meso*-*o*-carbomethoxyphenyl-H), 8.31 (d, 2H, *J* = 8 Hz, *meso*-*m*-carbomethoxyphenyl-H), 8.14 (d, 2H, *J* = 8 Hz, *meso*-*o*-^tbutylphenyl-H), 7.75 (d, 2H, *J* = 8.5 Hz, *meso*-*m*-^tbutylphenyl-H), 7.28 (s, 4H, *meso*-*m*-mesityl-H), 4.10 (s, 3H, OCH₃), 2.63 (s,

6H, *meso-p*-CH₃mesityl-H), 1.84 (s, 12H, *meso-o*-CH₃mesityl-H), 1.60n (s, 12H, CH₃-^tbutylphenyl-H), -2.62 (s, 2H, N-H). MALDI-TOF-MS (m/z): found 814.05 [M+H]⁺, calcd. 814.42 for C₅₆H₅₄N₄O₂.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(2'-pyrenyl)-porphyrin (1e): 0.172 g, 0.195mmol (10.3% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.80 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.77 (d, 2H, J = 5 Hz, β-pyrrole-H), 8.73 (d, 2H, J = 5 Hz, β-pyrrole-H), 8.59 (d, 2H, J = 5 Hz, β-pyrrole-H), 8.51 (d, 1H, J = 6 Hz, β-pyrrole-H), 8.47-8.43 (m, 4H, *meso-o*- and *m*-carboxyphenyl-H), 8.40 (d, 1H, J = 9 Hz, pyrenyl-H), 8.37-8.30 (m, 4H, pyrenyl-H), 8.15-8.05 (m, 2H, pyrenyl-H), 7.72 (d, 1H, J = 9 Hz, pyrenyl-H), 7.51 (d, 1H, J = 9.5 Hz, pyrenyl-H), 7.26 (s, 4H, *meso-m*-mesityl-H), 4.12 (s, 3H, OCH₃), 2.60 (s, 6H, *meso-p*-CH₃ mesityl-H), 1.89 (s, 6H, *meso-o*-CH₃ mesityl-H), 1.84 (s, 6H, *meso-o*-CH₃mesityl-H), -2.42 (s, 2H, N-H). MALDI-TOF-MS (m/z): found 882.08 [M+H]⁺, calcd. 881.39 for C₆₂H₄₈N₄O₂.

General procedure for the synthesis of 2:

Monoester porphyrin (0.10 mmol) (**1a-1e**) was dissolved in 20 ml of THF. To this, KOH (10 mmol) in 0.5 ml water was added and heated at 80 °C for 24 h. At the end of this period, THF was removed under vacuum. The crude porphyrin was treated with 15 ml of 2N HCl affording green precipitate which was filtered and washed with excess of water thrice and dried. The product was purified by silica gel column chromatography using 3% methanol in chloroform as eluent. The yield of the product was found to be quantitative.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-phenylporphyrin (2a): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.81 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.77 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.73 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.71 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.54 (d, 2H, J = 8 Hz, *meso-o*-carboxyphenyl-H), 8.38 (d, 2H, J = 8 Hz, *meso-m*-carboxyphenyl-H), 8.23 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.79-7.73 (m, 3H, *meso-m*- and *p*-phenyl-H), 7.30 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃mesityl-H), 1.86 (s, 12H, *meso-o*-CH₃mesityl-H), -2.61 (s, 2H, N-H). ESI-MS (m/z): found 743.33 [M+H]⁺, calcd. 743.34 for C₅₁H₄₂N₄O₂. Elemental analysis calcd for C₅₁H₄₂N₄O₂: C, 82.45%; H, 5.70%; N, 7.54% and found: C, 82.61%; H, 5.78%; N, 7.35%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(4'-bromophenyl)-porphyrin (2b): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.78 (t, 4H, J = 4 Hz, β-pyrrole-H), 8.73 (t, 4H, J = 4 Hz, β-pyrrole-H), 8.54 (d, 2H, J = 8 Hz, *meso-o*-carboxyphenyl-H), 8.38 (d, 2H, J = 8 Hz, *meso-m*-carboxyphenyl-H), 8.10 (d, 2H, J = 8 Hz, *meso-o*-bromophenyl-H), 7.90 (d, 2H, J = 8 Hz, *meso-m*-bromophenyl-H), 7.30 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃mesityl-H), 1.85 (s, 12H, *meso-o*-CH₃mesityl-H), -2.64 (s, 2H, N-H). ESI-MS (m/z): found 823.23 [M+H]⁺, calcd. 823.27 for C₅₁H₄₁BrN₄O₂. Elemental analysis calcd. For C₅₁H₄₁BrN₄O₂: C, 74.54%; H, 5.03%; N, 6.82% and found: C, 74.37%; H, 5.15%; N, 6.89%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(2'-thienyl)-porphyrin (2c): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.03 (d, 2H, J

= 4.5 Hz, β-pyrrole-H), 8.77 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.72 (d, 4H, J = 4.5 Hz, β-pyrrole-H), 8.55 (d, 2H, J = 8 Hz, *meso-o*-carboxyphenyl-H), 8.38 (d, 2H, J = 8 Hz, *meso-m*-carboxyphenyl-H), 7.93 (d, 1H, J = 8 Hz, α-thienyl-H), 7.85 (d, 1H, J = 5 Hz, γ-thienyl-H), 7.50 (t, 1H, J = 4 Hz, β-thienyl-H), 7.30 (s, 4H, *meso-m*-mesityl-H), 2.65 (s, 6H, *meso-p*-CH₃mesityl-H), 1.86 (s, 12H, *meso-o*-CH₃mesityl-H), -2.55 (s, 2H, N-H). ESI-MS (m/z): found 749.28 [M+H]⁺, calcd. 749.30 for C₄₉H₄₀N₄O₂S. Elemental analysis calcd. For C₄₉H₄₀N₄O₂S: C, 78.58%; H, 5.38%; N, 7.48%; S, 4.28% and found: C, 78.83%; H, 5.65%; N, 7.34%; S, 4.16%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(4'-^tbutylphenyl)-porphyrin (2d): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.86 (d, 2H, J = 4 Hz, β-pyrrole-H), 8.75 (d, 2H, J = 4 Hz, β-pyrrole-H), 8.71 (asym t, 4H, β-pyrrole-H), 8.49 (d, 2H, J = 8 Hz, *meso-o*-carboxyphenyl-H), 8.36 (d, 2H, J = 8 Hz, *meso-m*-carboxyphenyl-H), 8.14 (d, 2H, J = 8 Hz, *meso-o*-^tbutylphenyl-H), 7.75 (d, 2H, J = 8 Hz, *meso-m*-^tbutylphenyl-H), 7.29 (s, 4H, *meso-m*-mesityl-H), 2.63 (s, 6H, *meso-p*-CH₃mesityl-H), 1.84 (s, 12H, *meso-o*-CH₃mesityl-H), 1.61 (s, 9H, CH₃-^tbutylphenyl-H), -2.62 (s, 2H, N-H). ESI-MS (m/z): found 799.39 [M+H]⁺, calcd. 799.40 for C₅₅H₅₀N₄O₂. Elemental analysis calcd. For C₅₅H₅₀N₄O₂: C, 82.68%; H, 6.31%; N, 7.01% and found: C, 82.90%; H, 6.20%; N, 6.81%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(2'-pyrenyl)-porphyrin (2e): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.81 (s, 1H, β-pyrrole-H), 8.78 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.74 (d, 2H, J = 4 Hz, β-pyrrole-H), 8.59 (d, 2H, J = 4.5 Hz, β-pyrrole-H), 8.51 (s, 1H, β-pyrrole-H), 8.50 (d, 2H, J = 8 Hz, *meso-o*-carboxyphenyl-H), 8.45 (d, 2H, J = 8 Hz, *meso-m*-carboxyphenyl-H), 8.41-8.38 (m, 2H, pyrenyl-H), 8.37-8.30 (m, 3H, pyrenyl-H), 8.13-8.03 (m, 2H, pyrenyl-H), 7.73 (d, 1H, J = 8 Hz, pyrenyl-H), 7.51 (d, 1H, J = 8 Hz, pyrenyl-H), 7.26 (s, 4H, *meso-m*-mesityl-H), 2.60 (s, 6H, *meso-p*-CH₃mesityl-H), 1.89 (s, 6H, *meso-o*-CH₃ mesityl-H), 1.84 (s, 6H, *meso-o*-CH₃mesityl-H), -2.44 (s, 2H, N-H). ESI-MS (m/z): found 867.36 [M+H]⁺, calcd. 867.37 for C₆₁H₄₆N₄O₂. Elemental analysis calcd. For C₆₁H₄₆N₄O₂: C, 84.50%; H, 5.35%; N, 6.46% and found: C, 84.62%; H, 5.49%; N, 6.55%.

General procedure for the synthesis of 3:

2a-2e (0.066 mmol) was dissolved in 15 mL CHCl₃. To this, 10 equivalent of Zn(OAc)•2H₂O (0.66 mmol) in methanol was added and refluxed on water bath for 30 minutes. At the end of this period, the reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in CHCl₃, washed with water, dried over anhydrous sodium sulphate. The crude product was purified by column chromatography on silica column using CHCl₃ as eluent. The product was recrystallized from CHCl₃/CH₃OH mixture (1:3, v/v) to give a purple solid with 92-95% yield.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-phenyl-porphyrinatozinc(II) (RA-191-Zn): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.89 (s, 2H, β-pyrrole-H), 8.84 (s, 2H, β-pyrrole-H), 8.77 (t, 4H, J = 4 Hz, β-pyrrole-H), 8.50 (d, 2H, J = 7.5 Hz, *meso-o*-

carbomethoxyphenyl-H), 8.38 (d, 2H, $J = 7.5$ Hz, *meso-m*-carbomethoxyphenyl-H), 8.24 (d, 2H, $J = 6.5$ Hz, *meso-o*-phenyl-H), 7.80-7.72 (m, 3H, *meso-m*- and *p*-phenyl-H), 7.29 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃ mesityl-H), 1.84 (s, 12H, *meso-o*-CH₃ mesityl-H). ESI-MS (m/z): found 804.23 [M+]⁺, calcd. 804.24 for C₅₁H₄₀N₄O₂Zn. Elemental analysis calcd. For C₅₁H₄₀N₄O₂Zn: C, 75.97%; H, 5.00%; N, 6.95% and found: C, 75.79%; H, 5.11%; N, 7.17%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(4'-bromophenyl)-porphyrinato zinc(II) (RA-192-Zn): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.86 (d, 4H, $J = 4.5$ Hz, β -pyrrole-H), 8.82 (s, 4H, β -pyrrole-H), 8.51 (d, 2H, $J = 7.5$ Hz, *meso-o*-carbomethoxyphenyl-H), 8.38 (d, 2H, $J = 8$ Hz, *meso-m*-carbomethoxyphenyl-H), 8.12 (d, 2H, $J = 7.5$ Hz, *meso-o*-bromophenyl-H), 7.89 (d, 2H, $J = 7.5$ Hz, *meso-m*-bromophenyl-H), 7.29 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃mesityl-H), 1.84 (s, 12H, *meso-o*-CH₃mesityl-H). ESI-MS (m/z): found 884.14 [M]⁺, calcd. 884.19 for C₅₁H₃₉BrN₄O₂Zn. Elemental analysis calcd. For C₅₁H₃₉BrN₄O₂Zn: C, 69.20%; H, 4.44%; N, 6.33% and found: C, 69.35%; H, 4.61%; N, 6.37%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(2'-thienyl)-porphyrinato zinc(II) (RA-193-Zn): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.10 (d, 2H, $J = 4$ Hz, β -pyrrole-H), 8.84 (d, 2H, $J = 3.5$ Hz, β -pyrrole-H), 8.79 (d, 4H, $J = 3.5$ Hz, β -pyrrole-H), 8.50 (d, 2H, $J = 7.5$ Hz, *meso-o*-carbomethoxyphenyl-H), 8.37 (d, 2H, $J = 7.5$ Hz, *meso-m*-carbomethoxyphenyl-H), 7.93 (s, 1H, α -thienyl-H), 7.83 (d, 1H, $J = 5.5$ Hz, γ -thienyl-H), 7.5 (s, 1H, β -thienyl-H), 7.29 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃ mesityl-H), 1.84 (s, 12H, *meso-o*-CH₃mesityl-H). ESI-MS (m/z): found 810.19 [M]⁺, calcd. 810.20 for C₄₉H₃₈N₄O₂SZn. Elemental analysis calcd. For C₄₉H₃₈N₄O₂SZn: C, 72.45%; H, 4.72%; N, 6.90%; S, 3.95% and found: C, 72.52%; H, 4.74%; N, 6.78%; S, 3.81.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(4'-^tbutylphenyl)-porphyrinato zinc(II) (RA-194-Zn): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.94 (d, 2H, $J = 4$ Hz, β -pyrrole-H), 8.83 (d, 2H, $J = 4$ Hz, β -pyrrole-H), 8.78 (t, 4H, $J = 4$ Hz, β -pyrrole-H), 8.48 (d, 2H, $J = 8$ Hz, *meso-o*-carbomethoxyphenyl-H), 8.37 (d, 2H, $J = 8$ Hz, *meso-m*-carbomethoxyphenyl-H), 8.16 (d, 2H, $J = 8$ Hz, *meso-o*-^tbutylphenyl-H), 7.75 (d, 2H, $J = 8$ Hz, *meso-m*-^tbutylphenyl-H), 7.29 (s, 4H, *meso-m*-mesityl-H), 2.64 (s, 6H, *meso-p*-CH₃mesityl-H), 1.83 (s, 12H, *meso-o*-CH₃mesityl-H), 1.61(s, 9H, CH₃-^tbutylphenyl-H). ESI-MS (m/z): found 862.30 [M]⁺, calcd. 862.32 for C₅₅H₄₈N₄O₂Zn. Elemental analysis calcd. For C₅₅H₄₈N₄O₂Zn: C, 76.60%; H, 5.61%; N, 6.50% and found: C, 76.84%; H, 5.70%; N, 6.39%.

5-(4'-carboxyphenyl)-10,20-(dimesityl)-15-(2'-pyrenyl)-porphyrinato zinc(II) (RA-195-Zn): ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.88 (bs, 2H, β -pyrrole-H), 8.84-8.78 (m, 3H, β -pyrrole-H), 8.66 (d, 2H, $J = 3.5$ Hz, β -pyrrole-H), 8.51 (d, 1H, $J = 4.5$ Hz, β -pyrrole-H), 8.50-8.45 (m, 4H, *meso-o*- and *m*-carbomethoxyphenyl-H), 8.41 (d, 1H, pyrenyl-H), 8.38-8.29 (m, 4H, pyrenyl-H), 8.15-8.05 (m, 2H, pyrenyl-H), 7.71 (d, 1H, $J = 8.5$ Hz, pyrenyl-H), 7.53 (d, 1H, $J = 8.5$ Hz, pyrenyl-H), 7.26 (s, 4H, *meso-m*-mesityl-H), 2.60 (s, 6H, *meso-p*-CH₃mesityl-H), 1.89 (s, 6H, *meso-o*-CH₃mesityl-H), 1.82 (s, 6H, *meso-o*-CH₃

mesityl-H). MALDI-TOF-MS (m/z): found 928.28 [M]⁺, calcd. 928.28 for C₆₁H₄₄N₄O₂Zn. Elemental analysis calcd. For C₆₁H₄₄N₄O₂Zn: C, 78.74%; H, 4.77%; N, 6.02% and found: C, 78.83%; H, 4.87%; N, 6.10%.

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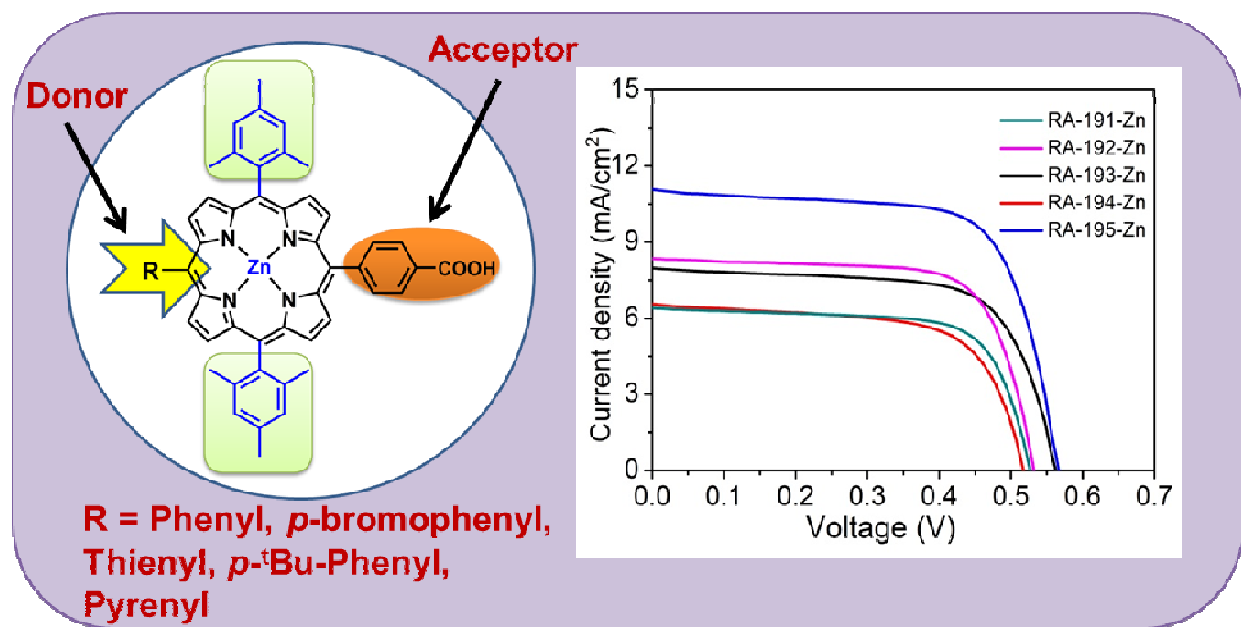
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Notes and references

- (a) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; (b) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (c) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382; (d) Z. Ning, Y. Fuand and H. Tian, *Energy Environ. Sci.*, 2010, **3**, 1170; (e) M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613; (f) M. Grätzel, *Acc. Chem. Res.*, 2009, **42**, 1788; (g) B. E. Hardin, H. J. Snaith and M. D. McGehee, *Nat. Photonics*, 2012, **6**, 162; (i) S. Zhang, X. Yang, Y. Numata and L. Han, *Energy Environ. Sci.*, 2013, **6**, 1443.
- (a) M. K. Nazeeruddin, F. D. Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835; (b) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720; (c) L. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. Zhang, X. Yang and M. Yanagida, *Energy Environ. Sci.*, 2012, **5**, 6057; (d) Q. Yu, Y. Wang, Z. Yi, N. Zu, J. Zhang, M. Zhang and P. Wang, *ACS Nano*, 2010, **4**, 6032; (e) C.-Y. Chen, M. Wang, J.-Y. Li, N. Pootrakulchote, L. Alibabaei, C.-H. Ngoc-le, J.-D. Decoppet, J.-H. Tsai, C. Grätzel, C.-G. Wu, S. M. Zakeeruddin and M. Grätzel, *ACS Nano*, 2009, **3**, 3103.
- (a) P. Wang, C. Klein, J.-E. Moser, R. Humphry-Baker, N.-L. Cevey-Ha, R. Charvet, P. Comte, S. M. Zakeeruddin and M. Grätzel, *J. Phys. Chem. B* 2004, **108**, 17, 553; (b) P. Wang, S. M. Zakeeruddin, R. Humphry-Baker, J. E. Moser, and M. Grätzel, *Adv. Mater.*, 2003, **15**, 2101; (c) P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Grätzel, *Nat. Mater.*, 2003, **2**, 402.
- (a) T. Horiuchi, H. Miura and S. Uchida, *Chem. Commun.*, 2003, 3036; (b) T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, 2004, **126**, 12218; (c) S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Pechy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**, 1202; (d) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara and H. Arakawa, *J. Phys. Chem. B*, 2003, **107**, 597; (e) A. Morandeira, G. Boschloo, A. Hagfeldt and L. Hammarstrom, *J. Phys. Chem. B*, 2005, **109**, 19403; (f) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.*, 2006, **128**, 14256; (g) S. Kim, H. Choi, D. Kim, K. Song, S. O. Kang and J. Ko, *Tetrahedron*, 2007, **63**, 9206; (h) I. Jung, J. K. Lee, K. H. Song, K. Song, S. O. Kang and J. Ko, *J. Org. Chem.*, 2007, **72**, 3652;

- (i) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.* 2006, 2245; (j) M. Velusamy, K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu and K.-C. Ho, *Org. Lett.*, 2005, **7**, 1899; (k) M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, *J. Phys. Chem. C*, 2007, **111**, 4465; (l) S. Ferrere, A. Zaban and B. A. Gregg, *J. Phys. Chem. B*, 1997, **101**, 4490; (m) S. Ferrere and B. A. Gregg, *New J. Chem.*, 2002, **26**, 1155; (n) Y. Shibano, T. Umeyama, Y. Matano and H. Imahori, *Org. Lett.*, 2007, **9**, 1971; (o) A. Ehret, L. Stuhl and M. T. Spitler, *J. Phys. Chem. B*, 2001, **105**, 9960; (p) S. Ushiroda, N. Ruzycski, Y. Lu, M. T. Spitler and B. A. Parkinson, *J. Am. Chem. Soc.*, 2005, **127**, 5158; (q) S. Tatay, S. A. Haque, B. O'Regan, J. R. Durrant, W. J. H. Verhees, J. M. Kroon, A. Vidal-Ferran, P. Gavina and E. Palomares, *J. Mater. Chem.*, 2007, **17**, 3037; (r) Q.-H. Yao, L. Shan, F.-Y. Li, D.-D. Yin and C.-H. Huang, *New J. Chem.*, 2003, **27**, 1277; (s) Y.-S. Chen, C. Li, Z.-H. Zeng, W.-B. Wang, X.-S. Wang and B.-W. Zhang, *J. Mater. Chem.* 2005, **15**, 1654; (t) K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa and M. Hanaya, *Chem. Commun.*, 2015, **51**, 15894.
- 5 (a) Y. Bai, J. Zhang, D. Zhou, Y. Wang, M. Zhang and P. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 11442; (b) D. Joly, L. Pellejà, S. Narbey, F. Oswald, J. Chiron, J. N. Clifford, E. Palomares and R. Demadrille, *Sci. Rep.*, 2014, **4**, 4033; (c) Y. Wu, M. Marszalek, S. M. Zakeeruddin, Q. Zhang, H. Tian, M. Grätzel and W. Zhu, *Energy Environ. Sci.*, 2012, **5**, 8261.
- 6 (a) L.-L. Li and E. W.-G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291; (b) J. Lu, S. Liu, H. Li, Y. Shen, J. Xu, Y. Cheg and M. Wang, *J. Mater. Chem. A*, 2014, **2**, 17495; (c) M. G. Walter, A. B. Rudine and C. C. Wamser, *J. Porphyrins Phthalocyanines*, 2010, **14**, 760; (d) R. Kumar and M. Sankar, *Inorg. Chem.*, 2014, **53**, 12706.
- 7 (a) T. Wei, X. Sun, X. Li, H. Ågren and Y. Xie, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21956; (b) Y. Wang, B. Chen, W. Wu, X. Li, W. Zhu, H. Tian and Y. Xie, *Angew. Chem. Int. Ed.*, 2014, **53**, 10779; (c) T. Higashino and H. Imahori, *Dalton Trans.*, 2015, **44**, 448; (d) W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, **248**, 1363; (e) M. Urbani, M. Grätzel, M. K. Nazeeruddin and T. Torres, *Chem. Rev.*, 2014, **114**, 12330; (f) X. Sun, Y. Wang, X. Li, H. Ågren, W. Zhu, H. Tian and Y. Xie, *Chem. Commun.*, 2014, **50**, 15609; (g) H. Imahori, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809; (h) B. Liu, W. Zhu, Y. Wang, W. Wu, X. Li, B. Chen, Y.-T. Long and Y. Xie, *J. Mater. Chem.*, 2012, **22**, 7434; (i) M. V. Martinez-Diaz, G. de la Torre and T. Torres, *Chem. Commun.* 2010, **46**, 7090; (j) M. J. Griffith, K. Sunahara, P. Wagner, K. Wagner, G. G. Wallace, D. L. Officer, A. Furube, R. Katoh, S. Mori and A. J. Mozer, *Chem. Commun.*, 2012, **48**, 4145; (k) Y. Wang, X. Li, B. Liu, W. Wu, W. Zhu and Y. Xie, *RSC Adv.*, 2013, **3**, 14780 (l) K. Ladomenou, T. N. Kitsopoulos, G. D. Sharma and A. G. Coutsolelos, *RSC Adv.*, 2014, **4**, 21379.
- 8 A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
- 9 (a) A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh and M. Grätzel, *Angew. Chem. Int. Ed.*, 2014, **53**, 2973; (b) S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, **6**, 242.
- 10 H. He, A. Gurung, L. Si and A. G. Sykes, *Chem. Commun.*, 2012, **48**, 7619.
- 11 (a) C. Y. Lee and J. T. Hupp, *Langmuir*, 2010, **26**, 3760; (b) C. Y. Lee, C. X. She, N. C. Jeong and J. T. Hupp, *Chem. Commun.*, 2010, **46**, 6090; (c) Y. C. Chang, C. L. Wang, T. Y. Pan, S. H. Hong, C. M. Lan, H. H. Kuo, C. F. Lo, H. Y. Hsu, C. Y. Lin and E. W.-G. Diau, *Chem. Commun.*, 2011, **47**, 8910; (d) C.-L. Wang, C.-M. Lan, S.-H. Hong, Y.-F. Wang, T.-Y. Pan, C.-W. Chang, H.-H. Kuo, M.-Y. Kuo, E. W.-G. Diau and C.-Y. Lin, *Energy Environ. Sci.*, 2012, **5**, 6933; (e) T. Ripolles-Sanchis, B. C. Guo, H. P. Wu, T. Y. Pan, H. W. Lee, S. R. Raga, F. Fabregat-Santiago, J. Bisquert, C. Y. Yeh and E. W.-G. Diau, *Chem. Commun.*, 2012, **48**, 4368.
- 12 (a) L. L. Chng, C. J. Chang and D. G. Nocera, *J. Org. Chem.*, 2003, **68**, 4075; (b) H. Imahori, S. Hayashi, T. Umeyama, S. Eu, A. Oguro, S. Kang, Y. Matano, T. Shishido, S. Ngamsinlapasathian and S. Yoshikawa, *Langmuir*, 2006, **22**, 11405; (c) S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y. Matano and H. Imahori, *J. Phys. Chem. C*, 2007, **111**, 3528; (d) S. Eu, S. Hayashi, T. Umeyama, Y. Matano, Y. Araki and H. Imahori, *J. Phys. Chem. C*, 2008, **112**, 4396; (e) S. Hayashi, Y. Matsubara, S. Eu, H. Hayashi, T. Umeyama, Y. Matano and H. Imahori, *Chem. Lett.*, 2008, **37**, 846; (f) A. Kira, M. Tanaka, T. Umeyama, Y. Matano, N. Yoshimoto, Y. Zhang, S. Ye, H. Lehtivuori, N. V. Tkachenko, H. Lemmetyinen and H. Imahori, *J. Phys. Chem. C*, 2007, **111**, 13618.
- 13 (a) O. Taratula, J. Rochford, P. Piotrowiak, E. Galoppini, R. A. Carlisle and G. J. Meyer, *J. Phys. Chem. B*, 2006, **110**, 15734; (b) T.-I. Ho, A. Elangovan, H.-Y. Hsu and S.-W. Yang, *J. Phys. Chem. B*, 2005, **109**, 8626; (c) B. N. Boden, K. J. Jardine, A. C. W. Leung and M. MacLachlan, *J. Org. Lett.*, 2006, **8**, 1855; (d) C.-W. Wan, A. Burghart, J. Chen, F. Bergstrom, L. B.-A. Johansson, M. F. Wolford, T. G. Kim, M. R. Topp, R. M. Hochstrasser and K. Burgess, *Chem.-Eur. J.*, 2003, **9**, 4430; (e) P. G. Hoertz, R. A. Carlisle and G. J. Meyer, *Nano Lett.*, 2003, **3**, 325.
- 14 (a) J.-J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S. O. Kang and J. Ko, *J. Mater. Chem.*, 2008, **18**, 5223; (b) J. A. Shelnutt, K. D. Straub, P. M. Rentzepis, M. Gouterman and E. R. Davidson, *Biochemistry*, 1984, **23**, 3946.
- 15 (a) T. Rohand, E. Dolusic, T. H. Ngo, W. Maes and W. Dehaen, *Arkivoc*, 2007, 307; (b) B. Kaszarna and D. T. Gryko, *J. Org. Chem.*, 2006, **71**, 3707.

Graphical Abstract



Zn(II) porphyrin dyes have been synthesized in three steps and exhibited power conversion efficiencies of 2.1 to 4.2% which depends on electron donating ability of **R** group.