

Photosensitizing porphyrin–triazine compound for bulk heterojunction solar cells†

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This report describes the synthesis of a novel porphyrin–triazine compound bearing three porphyrin macrocycles connected to each other *via* a triazine central unit, and investigation of its properties for possible use in bulk heterojunction solar cells (BHJ-SCs). The porphyrin macrocycles serve as light harvesting antennae, while the triazines have been widely known to be charge extracting promoters. According to cyclic voltammetric studies, the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels of the target compound were estimated to be at -5.4 and -3.5 eV *versus* vacuum, respectively. Photoluminescence measurements of the blended films of the porphyrin–triazine compound and phenyl-C₆₁-butyric acid methyl ester (PCBM) or poly(3-hexylthiophene) (P3HT) indicated that the charge transfer was possible when the target porphyrin was used as an electron donor together with PCBM as an acceptor. Additionally, the surface morphology of the films with different donor : acceptor ratios was investigated by atomic force microscopy (AFM). Upon variation of the donor : acceptor weight ratio and thickness of the organic layer, the short circuit current density (J_{SC}) of the BHJ-SCs fabricated herein improved up to approximately 2.25 mA cm⁻².

Introduction

Harvesting energy directly from sunlight using photovoltaic (PV) technology is recognized as one of the major global energy production approaches in future energy supply. Amongst all types of photovoltaic cells, organic solar cells have been of great interest due to their flexibility in chemical design and mechanical properties as well as ultrathin, roll-to-roll fabrication possibilities.¹ An impressive development of their efficiency took place in the last decade and organic solar cells pushed above the 10% power conversion efficiency.² Photosynthetic pigments related to the chlorophylls, such as porphyrins, are particularly good candidates for optical and optoelectronic applications, due to their large molar absorption coefficients, tuneable electrochemical and photophysical properties *via* central metal insertion and/or introduction of various substituents at the macrocycle

peripheral positions,³ thermal and photo-stabilities, and strong two-photon absorption.⁴ Porphyrins have long been of interest as light-harvesting initiators for charge separation⁵ in various optoelectronic devices, for example in photovoltaic cells,⁶ organic light-emitting diodes (OLEDs),⁷ and organic field-effect transistors (OFETs).⁸ Recently, porphyrins have been proven to be one of the most promising candidates for dye-sensitized solar cells (DSSCs)⁹ and bulk-heterojunction solar cells (BHJSCs).^{2,10}

In this study, we use porphyrin macrocycles as light harvesting antennae by attaching them *via* their *meso*-carbons on all three peripheral sites of an electron accepting triazine ring *via* amino groups. Triazine (or 1,3,5-triazine) and its derivatives have high thermal stability, molecular symmetry,¹¹ spatial co-planarity,¹² and great potential for structural modification.¹³ Triazine derivatives have been extensively studied as electron transporting and hole blocking layers,^{12b,c,14} as emissive materials,^{12f,14b,15} and as non-linear optical¹⁶ and two-photon absorbing compounds.¹⁷ Covalent connection of the porphyrins, which are known to be p-type semiconductors,¹⁸ with π -electron-deficient conjugated functionalities like the triazine unit is expected to provide functions in BHJ-SCs from the possibly enhanced charge extraction efficiency. Like other planar aromatic compounds, several porphyrin derivatives encounter low solubility due to molecular aggregation. As one of the most important requirements of the photoactive compounds for organic solar cell applications, high solubility is essential for synthetic transformations, purification

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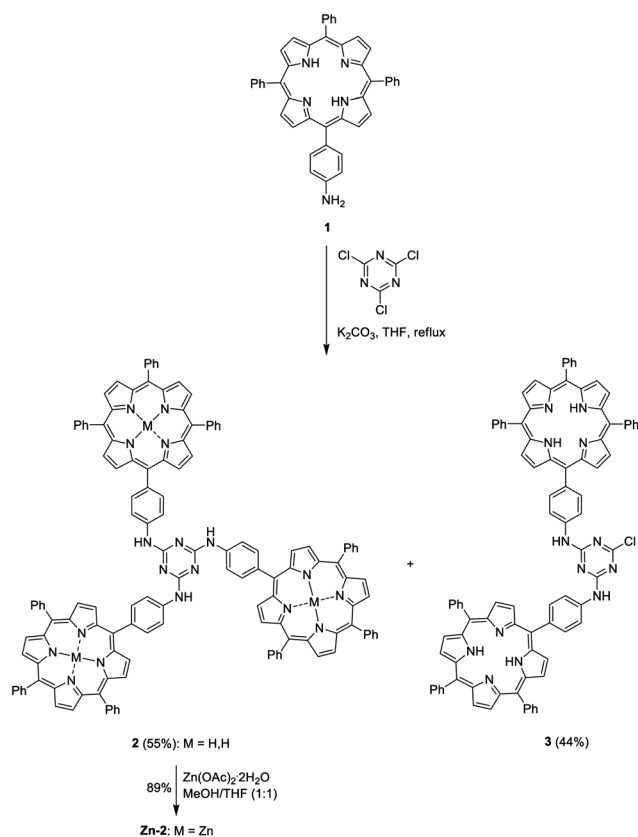
† Electronic supplementary information (ESI) available: spectral data, including ¹H-NMR spectra, ¹³C-NMR spectra and mass spectra for new compounds, and absorption and emission spectra of **Zn-2**, as well as the calibration curve of **Zn-2**. Absorption spectrum of a P3HT film. See DOI: 10.1039/c2jm33840h

procedures, diverse physical, photophysical and electrochemical studies, and device fabrication *via* a wet process. This three-pointed star architecture, presented here in this work, having three porphyrin rings attached on the triazine ring *via* a flexible amino group is expected to suppress the porphyrin aggregation without the use of solubilizing substituents on the porphyrin rings. To the best of our knowledge, there is no porphyrin–triazine derivative studied for organic solar cells yet. Therefore, this work aims to demonstrate the potential use of this class of material for BHJ SCs.

Results and discussion

1. Synthesis

The synthesis of the target porphyrin–triazine derivative for BHJ-SCs is illustrated in Scheme 1. Porphyrin **1**¹⁹ was readily condensed with cyanuric chloride in basic condition, resulting in compounds **2** and **3** in 55% and 44% yield, respectively. A three-column process is required to purify the target compounds. Firstly, the silica column was used to remove unreacted compound **1** and other polar byproducts. Secondly, size-exclusion chromatography separated pure compounds **2** and **3**. Finally, to further remove the remaining impurities another silica column chromatography followed by sonicating–centrifugating the resulting solids in hexane and methanol were performed. Mass spectra confirmed the formation of compounds **2** and **3** by showing their molecular ion peaks at m/z 1964.342 and 1371.742, respectively. Compound **2** was metallated by $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ to



Scheme 1 Synthesis of target compound **Zn-2**.

give **Zn-2** quantitatively, while compound **3** was kept for other syntheses. The disappearance of the singlet signal at $\delta -2.84$ ppm in a $^1\text{H-NMR}$ spectrum and an emission peak at about 720 nm indicated the completion of the reaction. According to the $^1\text{H-NMR}$ spectrum, small signals between $\delta 1.00$ – 1.50 ppm was observed, indicating a small amount of impurities that might be encompassed in the aggregates of **Zn-2** in the synthesis and purification processes. Solubility of **Zn-2** in several common organic solvents, such as CH_2Cl_2 , CHCl_3 , toluene, chlorobenzene, THF, *etc.* proved its utility for BHJ-SC preparation from a wet process by using various kinds of solvents. In chlorobenzene, which was a solvent employed in the device fabrication in this study, the solubility of **Zn-2** was found to be approximately 45 mg mL^{-1} , equivalent to about $6.3 \times 10^{-5} \text{ mol tetraphenylporphyrin rings per 1 mL}$, while that of its benchmark *meso*-tetraphenylporphyrinatozinc(II) (**Zn-TPP**) was approximately 36 mg mL^{-1} or $4.5 \times 10^{-5} \text{ mol mL}^{-1}$. This observation indicated the enhancement of the solubility of **Zn-2** due to the presence of the 2,4,6-triamino-1,3,5-triazine central unit that might lower the stacking effect of the porphyrin rings.

2. Photophysical properties of Zn-2

UV-Vis absorption spectra of a **Zn-2** solution in toluene and a **Zn-2** film are shown in Fig. 1. The **Zn-2** solution exhibited a characteristic absorption pattern of a Zn-chelated porphyrin ring having intense B-band at 431 nm and Q-bands at 552 and 601 nm with absorption coefficients of 6×10^5 , 2×10^4 and $9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, indicating that the photophysical properties of the individual porphyrin macrocycle were not significantly affected by the linking with the triazine unit, which is consistent with a previous report.²⁰ The absorption pattern of the film is similar, but broader than that of the solution most likely due to the aggregation of the macrocycle conjugation systems.

The photoluminescence spectra of **Zn-2** solution (toluene) and film are shown in Fig. 2. Upon excitation at 431 nm, emission of the **Zn-2** solution appeared at 611 nm with a small shoulder at 659 nm, while that of the film was found at 611 and 648 nm and the peaks were broader compared to those of the solution. The emission peak at 648 nm in the film spectrum was significantly more pronounced and blue shifted than that at 659 nm in the

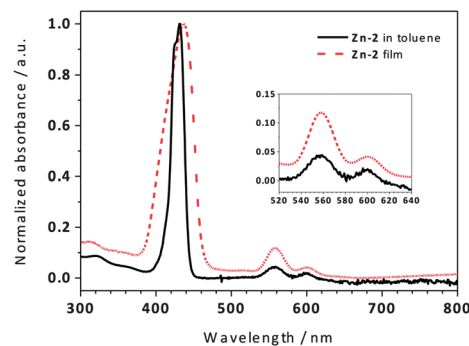


Fig. 1 Absorption spectra of a **Zn-2** solution in toluene (solid line) and a **Zn-2** film (dashed line). The inset shows a magnification of the region between 520 and 640 nm.

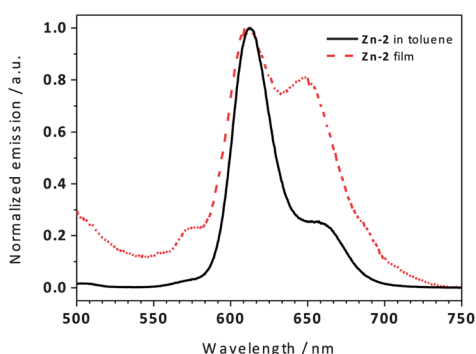


Fig. 2 Photoluminescence spectra of a **Zn-2** solution in toluene (solid line) and a **Zn-2** film (dashed line) upon photoexcitation at 431 nm.

solution spectrum, which is commonly observed when the aggregate is created in the bulk sample.

3. Electrochemistry

Based on cyclic voltammetry, the **Zn-2** film can be electrochemically oxidized and reduced (Fig. 3). The oxidation process of the molecule to a radical cation was observed at about +0.9 V *versus* a normal hydrogen electrode (NHE) and a second oxidation of the molecule to a dication was found at about +1.1 V *versus* NHE. The reduction of **Zn-2** to a radical anion and a dianion occurred at about -1.5 and -1.8 V *versus* NHE, respectively. These oxidation and reduction features are consistent with those of Zn-TPP, except that **Zn-2** can be reduced at a significantly lower potential than Zn-TPP (the onset potentials of the first reduction of **Zn-2** and Zn-TPP were -1.3 and -1.4 V *versus* NHE, respectively), indicating the higher electronegative nature of **Zn-2** compared to that of Zn-TPP due

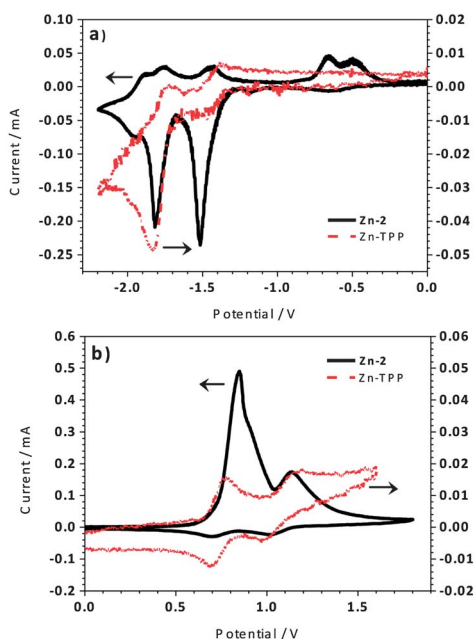


Fig. 3 Cyclic voltammograms of a **Zn-2** (solid line) and ZnTPP (dashed line) films in the range between (a) 0 and -2.2 V and (b) 0 and +1.8 V.

to the presence of the triazine unit. According to the previous report,^{12b} the reversible reduction peak at about -2.0 V *versus* NHE was likely to be reduction of the triazine unit. The indefinite anodic signal from -0.3 and -0.7 V *versus* NHE is likely to be resulted from the possible formation of unknown products from the reduction process(es) of **Zn-2**, which is attributed to molecular cleavage or deformation, as this feature was more conspicuous at higher cycle numbers and was not observed in the case of Zn-TPP.

The onset potentials of the first oxidation and reduction (E_{ox} and E_{red} , respectively) of **Zn-2** obtained from the cyclic voltammetric studies were found to be +0.7 and -1.3 eV, respectively. These values were used to determine an energy gap (E_g), and the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels (E_{HOMO} and E_{LUMO} , respectively) of **Zn-2** *versus* vacuum with an estimated energy for NHE of -4.75 eV *versus* vacuum.²¹ According to the equations:

$$E_g = E_{\text{ox}} - E_{\text{red}};$$

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.75) \text{ (eV); and}$$

$$E_{\text{LUMO}} = -(E_{\text{red}} + 4.75) \text{ (eV);}^{22}$$

the calculated E_g of **Zn-2** was 1.9 eV with E_{HOMO} and E_{LUMO} of -5.5 and -3.5 eV, respectively.

In Fig. 4, we display both HOMO and LUMO levels together with the work functions (WF) of ITO, poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) and Al, and the HOMO and LUMO levels of poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric acid methyl ester (PCBM). For a device with a P3HT : **Zn-2** active layer, the LUMO level of **Zn-2** is at a lower energy level than that of P3HT, which can allow the acceptance of electrons from P3HT and subsequent charge transfer to the Al electrode. Similarly, when **Zn-2** is blended with electron-accepting PCBM, the LUMO level of **Zn-2** was estimated to be at a higher energy than that of PCBM, while its HOMO level lies below the WF of PEDOT : PSS, suggesting the possibility of charge transfer in the system. The above-mentioned electrochemical behaviour of **Zn-2** and this estimation suggest that **Zn-2** should be able to serve both as donor (when used with PCBM) or acceptor (when used with P3HT) in **Zn-2**-based BHJ-SCs.

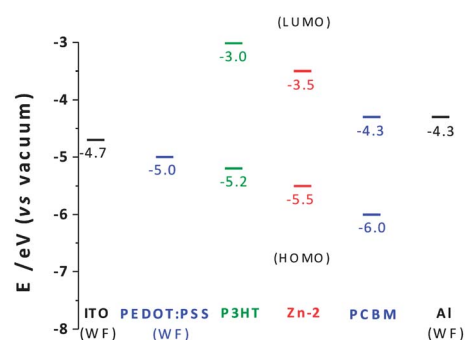


Fig. 4 Comparative energy diagram of a **Zn-2**-based BHJ-SC architecture.

4. Photoluminescence studies of the blend films

In order to study if **Zn-2** is able to serve as a donor and/or as an acceptor material, photoluminescence studies of the **Zn-2** : PCBM (1 : 1 w/w) and P3HT : **Zn-2** (1 : 1 w/w) blended films were performed. The photoactive layers were photoexcited at the absorption maximum of the donor, *i.e.* **Zn-2** ($\lambda_{\text{max}} = 431$ nm) in the case of the **Zn-2** : PCBM film and P3HT ($\lambda_{\text{max}} = 517$ nm, see ESI†) in the case of the P3HT : **Zn-2** film. The results shown in Fig. 5 reveal that the porphyrin emission was completely quenched by PCBM, indicating electron transfer from **Zn-2** (donor) to PCBM (acceptor). In the contrary, such complete emission quenching was not observed in the case of the P3HT : **Zn-2** blend, indicating that the charge transfer from P3HT (donor) to **Zn-2** (acceptor) was not efficient. Therefore, only the **Zn-2** : PCBM blended film were employed as a photoactive layer in the BHJ-SCs. The use of the blends of porphyrin derivatives and fullerenes as active layers in BHJ-SCs has been demonstrated to efficiently harvest solar energy and to facilitate the photo-induced charge separation process.^{6h,18b,23} Some reports described the formation of a crystallite network between porphyrins and fullerenes in the blends^{23,24} that have proven useful for BHJ-SCs.²⁵

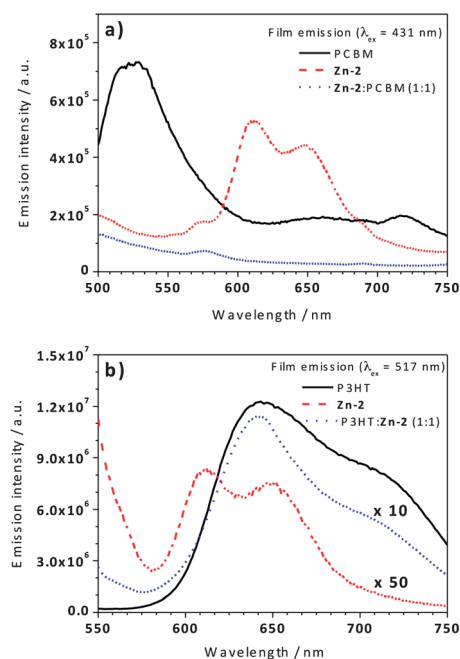


Fig. 5 Results of photoluminescence study of the (a) **Zn-2** : PCBM and (b) the P3HT : **Zn-2** blended films.

5. Photovoltaic characteristics

To determine the potential of **Zn-2** as the photoactive compound in the BHJ-SCs, **Zn-2**-based devices having different weight ratio of **Zn-2** : PCBM as well as thicknesses were fabricated. As shown in Fig. 6, a 60 nm layer of electron blocking PEDOT : PSS was patterned on an ITO-coated glass substrate. The **Zn-2** : PCBM blended film was sandwiched between the PEDOT : PSS layer and a 150 nm Al top contact layer.

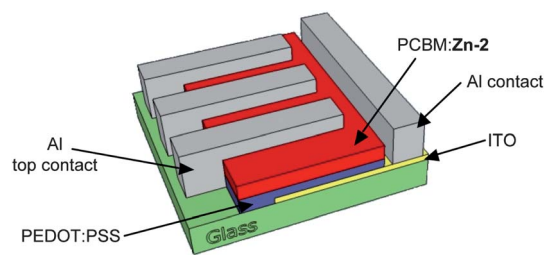


Fig. 6 Schematic setup of a BHJ-SC based on **Zn-2** : PCBM.

As a control experiment, a standard device having a P3HT : PCBM (2 : 1 w/w) active layer (device ‘Standard’, Table 1) was prepared in the same batch as the devices based on **Zn-2** : PCBM to ensure a high standard and reproducibility of the device fabrication procedure. The standard device exhibited a cell efficiency (η) of 3.4% with a short circuit current density (J_{SC}), and an open circuit voltage (V_{OC}) and a fill factor (FF) of 9.78 mA cm⁻², 0.6 V and 55%, respectively. These results are in good agreement with those of the ITO/PEDOT : PSS/P3HT : PCBM/Al device previously prepared by a similar procedure.²⁶

Table 1 Characteristics of **Zn-2** based BHJ-SCs

Device	Zn-2 : PCBM ratio		J_{SC} /mA cm ⁻²	V_{OC} /V	FF/%	η %
	By weight	By mol				
A	1 : 4	0.106 : 1	1.68	0.4	28	0.2
B	1 : 6	0.070 : 1	1.95	0.5	32	0.3
C	1 : 8	0.053 : 1	2.24	0.6	32	0.4
D	1 : 10 ^a	0.042 : 1	2.25	0.6	32	0.5
E	1 : 12	0.035 : 1	2.06	0.6	32	0.4
F	1 : 14	0.030 : 1	1.89	0.6	32	0.4
G	1 : 10 ^b	0.042 : 1	1.80	0.6	31	0.3
H	1 : 10 ^c	0.042 : 1	1.77	0.5	30	0.3
I	Zn-2			n/a ^d		
J	PCBM			n/a ^d		
P3HT : Zn-2 ratio						
K	1 : 10		<0.01	0.2	27	<0.1
L	1 : 1		0.12	0.4	31	<0.1
M	10 : 1		0.02	0.1	24	<0.1
Standard	P3HT : PCBM 2 : 1		9.78	0.6	55	3.4

^a A **Zn-2** : PCBM mixed solution was prepared from a 18 mg mL⁻¹ stock solution of each compound. ^b A **Zn-2** : PCBM mixed solution was prepared from a 9 mg mL⁻¹ stock solution of each compound. ^c A **Zn-2** : PCBM mixed solution was prepared from a 36 mg mL⁻¹ stock solution of each compound. ^d No significant J_{SC} and/or V_{OC} was measured.

The **Zn-2** : PCBM weight ratio was varied from 4 : 1 to 1 : 14, corresponding to a molar ratio from 1.70 : 1 to 0.030 : 1. The use of a ratio from 4 : 1 to 1 : 2 gave an η of less than 0.1% and therefore is not described in the table. The results clearly showed that the variation of the **Zn-2** : PCBM weight ratio from 1 : 4 to 1 : 10 (devices A–D) led to the increase in J_{SC} , while V_{OC} and FF increased and reached maximum values at weight ratios of 1 : 8 and 1 : 10, indicating the better charge transfer when the PCBM amount in the **Zn-2** : PCBM film is higher within this weight ratio range. The optimum η of 0.5% with J_{SC} of 2.25 mA cm⁻²,

V_{OC} of 0.6 V and FF of 32% was obtained when the **Zn-2** : PCBM weight ratio was 1 : 10 (device D, Table 1). Additional attempts to improve the cell efficiency by adjusting the thickness of the **Zn-2** : PCBM (1 : 10) film *via* the use of the two-fold lower (device G) and higher (device H) concentrations of the **Zn-2** : PCBM (1 : 10) spin-casting solution were done. The increase or decrease in thickness results mainly in the drop of J_{SC} and therefore the cell efficiencies. It should be noted that, for the optimum case, with the **Zn-2** : PCBM weight ratio of 1 : 10, the **Zn-2** : PCBM mole ratio is equivalent to 0.042 : 1 or, in other words, the porphyrin ring : PCBM mole ratio is approximately 0.13 : 1. It can also be considered that under this condition the porphyrin stacking effect tended to be reduced, leading to the increase in the porphyrin–PCBM interface and the improved donor–acceptor electronic communication.

As reference systems, solar cells based on pristine **Zn-2** and PCBM (devices I and J, respectively) were fabricated and characterized in the same manner. The results revealed that no significant current was generated from these devices under illumination, indicating that **Zn-2** and PCBM are not suitable for being used as a single component in the photoactive layer of organic solar cells. Additionally, BHJ-SC bearing P3HT : **Zn-2** blended films with the weight ratio of 1 : 10, 1 : 1 and 10 : 1 (devices K, L and M, respectively) were also prepared to examine whether the results correspond to those obtained from the above-mentioned photoluminescence study of the P3HT : **Zn-2** blended film. As a result, the J_{SC} , V_{OC} and FF of these devices were found to be relatively low compared to those of the BHJ-SCs based on **Zn-2** : PCBM, which is likely the result of poor charge transfer from P3HT to **Zn-2** as demonstrated in the photoluminescence study section.

Current density–voltage (J – V) curves of device D obtained from the measurement in the dark and under illumination are shown in Fig. 7a. The dark curve shows the diode performance. A rectification ratio of around 50 was obtained. Upon illumination, a photovoltaic effect was observed with moderate J_{SC}

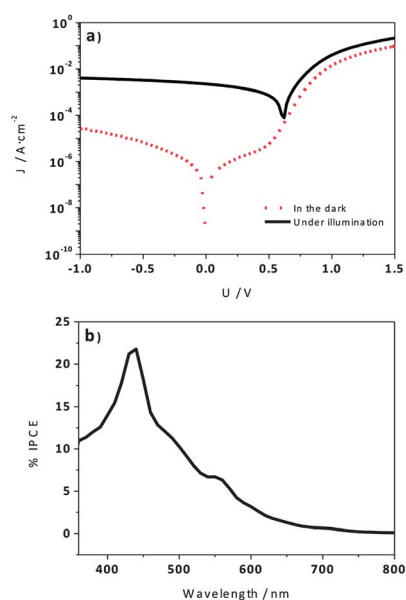


Fig. 7 (a) J – V curve and (b) IPCE plot of device D.

and V_{OC} . High series resistance and low parallel resistance worked as limiting factors in the cell performance. Incident photon-to-current efficiency (IPCE) spectrum of device D upon excitation at 431 nm exhibited a similar spectral behaviour as the absorption spectrum of **Zn-2** ($\lambda_{max} = 431$ nm) films (Fig. 7b). The maximum value of IPCE was found to be 22%.

6. Thin film nanomorphology

Nanoscale phase separation between the two compounds and film morphology were found to have significant importance for achieving efficient devices.²⁷ Surface topography of the **Zn-2** : PCBM films with different **Zn-2** : PCBM weight ratios was investigated by atomic force microscopy (AFM). The results showed that the surface morphology of the films looked very similar with no observable pinhole, suggesting good blending of the two materials. As shown in Fig. 8, an AFM image of the **Zn-2** : PCBM film of device D having the weight ratio of 1 : 10 indicates the relatively smooth and evenly distributed blend of **Zn-2** and PCBM with root-mean-square (rms) roughness of 0.5 nm. Additionally, the AFM technique was used to determine the film thickness of the **Zn-2** : PCBM film at the weight ratio of 1 : 10. The results showed that the use of the **Zn-2** and PCBM stock solutions at concentrations of 9, 18 and 36 mg mL^{−1} (devices G, D and H, respectively) gave the **Zn-2** : PCBM film a thickness of approximately 60, 80 and 120 nm, respectively.

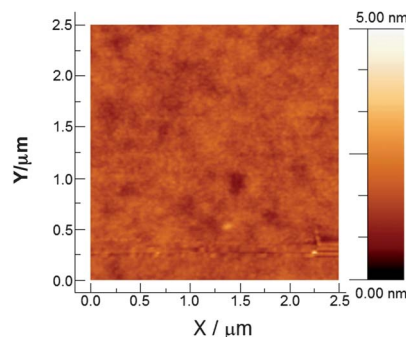


Fig. 8 AFM image of device D.

Experimental section

Material and methods

All chemicals were analytical grade, purchased from commercial suppliers and used as received without further purification. Chemical shifts (δ) of ¹H-NMR and ¹³C-NMR measurement are reported in parts per million (ppm) relative to the residual CHCl₃ peak (7.26 ppm for ¹H-NMR and 77.0 ppm for ¹³C-NMR). Coupling constants (J) are reported in Hertz (Hz). Mass spectra were obtained by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) using dithranol as a matrix and electron spray ionization mass spectrometry (ESI-MS). Absorption and emission spectra of the solutions were measured in toluene at room temperature, and those of the films were obtained from the drop-casted films on a glass substrate.

Non-commercial compound

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**1**) was prepared according to the previous published literature.¹⁷

Synthesis of compound Zn-2

Following a previously published procedure,²⁸ a solution of compound **1** (0.2317 g, 0.3684 mmol) and K₂CO₃ (0.5103 g, 0.3692 mmol) in THF (5 mL) was treated with cyanuric chloride (0.0175 g, 0.0949 mmol) at room temperature. The resulting solution was refluxed for 8 h and then cooled down to room temperature. After removal of the solvent, the crude product was purified by column chromatography [silica, 1% EtOH in CH₂Cl₂] and the purple fraction was collected. Compound **2** was isolated from **3** by consequent size-exclusion column chromatography using THF as eluent and then purified again by a silica column [1% EtOH in CH₂Cl₂], leading to compound **2** (0.1036 g, 56%) as a purple solid. MALDI-MS obsd 1964.241 ([M]⁺), calcd 1964.280 ([M]⁺; M = C₁₃₅H₉₀N₁₈). Compound **3** was treated in the same manner and obtained as a purple solid (0.0578 g, 44%). MALDI-MS obsd 1371.742 ([M]⁺), calcd avg mass 1371.998 ([M]⁺; M = C₉₁H₆₁ClN₁₃). Optimized synthesis and detailed characterization of compound **3** and its derivatives will be described elsewhere.

Following recently published procedure²⁹ with slight modification, compound **2** (0.1036 g, 0.05263 mmol) was dissolved in THF (10 mL) and then reacted with a solution of Zn(OAc)₂·2H₂O (0.1743 g, 0.5263 mmol) in methanol (10 mL) at room temperature for 8 h. After removal of the solvent, the reaction mixture was redissolved in CH₂Cl₂, washed with water, dried (Na₂SO₄), and concentrated to dryness. Purification by column chromatography [silica, 1% EtOH in CH₂Cl₂] followed by sonicating–centrifugating in hexane and methanol gave a purple solid (100.7 mg, 89%). δ_H (400 MHz; CDCl₃) 6.47 (3H, s), 7.29–7.59 (m, 6H), 7.60–7.75 (m, 27H), 7.75–7.88 (m, 6H), 7.90–8.29 (m, 18H), 8.76–8.97 (m, 18H), 8.97–9.15 (m, 6H); δ_C (100 MHz; CDCl₃) 119.0, 120.7, 121.1, 124.3, 126.4, 126.5, 127.3, 127.4, 132.0, 134.4, 134.9, 137.7, 138.0, 142.7, 142.8, 143.1, 150.1, 150.2, 150.3, 163.9; MALDI-MS obsd 2154.516; calcd avg mass 2154.462 ([M]⁺; M = C₁₃₅H₈₄N₁₈Zn₃); ESI-HRMS obsd 2177.5169 ([M + Na]⁺), calcd 2177.4513 ([M + Na]⁺), 2154.5145 ([M]⁺); λ_{abs}/nm 431, 552 and 601 (ε/dm³ mol⁻¹ cm⁻¹ 6 × 10⁵, 6 × 10⁴ and 9 × 10³); λ_{em}/nm 612 (λ_{ex} = 431 nm).

Electrochemical studies

Electrochemical properties of compound **Zn-1** were determined by cyclic voltammetry in acetonitrile containing 0.1 M Bu₄NPF₆ by using a ITO-coated glass working electrode, a Pt wire counter electrode and an Ag/AgCl quasi-reference electrode (QRE) with a scan rate of 20 mV s⁻¹. The resulting redox potentials were externally calibrated with a ferrocene/ferrocenium couple of which the potential value of 0.40 V *versus* NHE was used. The value of the NHE *versus* vacuum level used in this work is -4.75 eV.²¹

Photoluminescence studies

Stock solutions of **Zn-2**, P3HT and PCBM in chlorobenzene were prepared in the concentration of 18 mg mL⁻¹ and filtered

through 0.45 μm PTFE syringe filters. The solution of **Zn-2** was mixed with that of P3HT or PCBM in weight ratio of 1 : 1. The resulting P3HT : **Zn-2** and **Zn-2** : PCBM 1 : 1 (w/w) mixture was spin-coated on 15 mm × 15 mm glass substrates, that were cleaned by consecutive sonication in acetone, isopropanol and deionized water, and then dried by purging with air, with 800 rpm for 25 s.

Device fabrication and characterization

Following a previously reported procedure with slight modification,²⁶ the above-mentioned stock solutions of **Zn-2**, PCBM and P3HT in chlorobenzene were used to prepare the mixed solution of **Zn-2** : PCBM with the weight ratio varying from 4 : 1 to 1 : 14, that of P3HT : **Zn-2** with weight ratios of 1 : 10, 1 : 1 and 10 : 1, and that of P3HT : PCBM with the weight ratio of 2 : 1. The 15 mm × 15 mm ITO-coated glass substrates were first wiped with toluene and cleaned by consecutive sonication in acetone, isopropanol and deionized water, and then dried by purging with air. PEDOT/PSS solution (Heraeus Clevis™ PH1000 Clevis P VP AI 4083) was spin-coated on top of the ITO with 2000 rpm for 1 s and 4000 rpm for 45 s, followed by annealing at 150 °C for 10 min. After that, the organic mixed solution was spin-coated on top of this PEDOT/PSS layer at 800 rpm for 25 s. The resulting samples were dried under vacuum at ambient temperature for 1–2 h before a 150 nm thick Al top electrode was deposited by thermal evaporation in a vacuum of about 10⁻⁶ mbar in a glovebox. The active area of the devices was between 6 and 10 mm². Current–voltage (*I*–*V*) characteristics of the devices were measured in the dark and under simulated 100 mW cm⁻² AM 1.5 solar irradiation in a glovebox using a Keithley 236 source measurement unit. The intensity of the illumination was verified prior to each individual measurement using a calibrated silicon diode with known spectral response. Incident photon to current efficiency (IPCE) measurements were taken using a fiber optical light source from a 90 W Xenon lamp, which is connected to an ACTON Spectra Pro150 monochromator and EG & G 7260 DSP Lock amplifier to measure the current. Three to six samples for each cell condition were prepared to test the reproducibility and reliability of the results.

Film morphology study

An atomic force microscope setup with Digital Instruments Dimension 3100 (Veeco Metrology group), working in tapping mode, was used in order to investigate the surface morphology and determine the thickness of the samples.³⁰

Conclusions

The novel soluble porphyrin derivative having three porphyrin macrocycles linked by the triazine central unit (**Zn-2**) was successfully synthesized and characterized by spectroscopic techniques. Based on cyclic voltammetric analysis, **Zn-2** was found to have appropriate HOMO–LUMO energy levels to possibly serve as both donor and acceptor in ITO/PEDOT : PSS/**Zn-2** : PCBM/Al and ITO/PEDOT : PSS/P3HT : **Zn-2**/Al solar cells, respectively. However, photoluminescence measurements of the blended films of the organic active layers indicated that an electron transfer was observed in the **Zn-2** : PCBM film, but not

in the P3HT : **Zn-2** one. The results from the device study confirmed the possible usage of **Zn-2** as donor material in organic BHJ-SCs. Our best ITO/PEDOT : PSS/**Zn-2** : PCBM/Al device exhibited an energy conversion maximum efficiency of 0.5% with J_{SC} , V_{OC} and FF of 2.25 mA cm⁻², 0.6 V and 32%, respectively. The studies showed that porphyrin rings in the **Zn-2** molecule were useful as light-harvesting units in BHJ-SCs and, with the good collaboration of the triazine core, **Zn-2** could transfer electrons to PCBM, resulting in a photovoltaic effect.

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