

Polydiacetylene-nested porphyrin as a potential light harvesting component in bulk heterojunction solar cells†

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A *meso*-substituted zinc-porphyrin embedded in a polydiacetylene web was prepared and tested for its potential in bulk heterojunction solar cells (BHJ-SCs). Light assisted formation of the polyenyne from diacetylenes coupled to the *meso*-position of the porphyrin were observed after UV-radiation, as evidenced by double and triple bond Raman-bands at 1446 and 2080 cm⁻¹, respectively, and *via* UV absorption enhancement at 530–600 nm. Using cyclic voltammetry, Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels were determined to be in an appropriate range for the photoactive materials in BHJ-SCs. Indeed, photoluminescence quenching indicated energy and/or charge transfer when the target material was used as a donor in combination with phenyl-C₆₁-butyric acid methyl ester as acceptor in a blend. A photovoltaic effect of the BHJ-SCs was observed.

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Introduction

Among organic light harvesting semiconductors porphyrins are especially interesting due to their photophysical and electrochemical properties,¹ thermal and photo-stability, and high two-photon absorption cross sections.² All these parameters may be modulated using porphyrin substituents and complexed metals. Consequently, porphyrins are used as key constituents in many photovoltaic cells,³ organic light-emitting diodes (OLEDs),⁴ and organic field-effect transistors (OFETs).⁵ They have proven to be one of the most promising candidates for dye-sensitized- and bulk-heterojunction-solar cells (DSSCs⁶ and BHJ-SCs⁷).

Since only a small fraction of solar irradiation can be absorbed by pristine porphyrins in their Q-band region, several chromophores have been proposed as co-absorbers for the porphyrins to broaden their absorption profile. The objective of this work is to create a photoactive system having zinc porphyrin macrocycle in a polydiacetylene (PDA)-web and to assess the possibility of this material for using BHJ-SCs. Zinc

porphyrin was selected because the complex is robust, and it is the most widely studied metalloporphyrin in BHJ-SCs. A previous report has shown that π -stacking of copper and free-base porphyrins can orient local diacetylene (DA) substituents in favorable ways for photopolymerization, leading to PDA that exhibited absorption at 550–650 nm.⁸ However, that work was not extended to investigate the use of such materials for BHJ-SCs. Another prior work described that photoinduced electron transfer from PDA to C₆₀ could not efficiently occur.⁹ The hypothesis of this work is that the photoinduced electron transfer *would* occur in a tripartite photoactive layer composed of PDA, porphyrin and a C₆₀ derivative, phenyl-C₆₁-butyric acid methyl ester (PCBM), with porphyrin serving as a stepping stone for electron transfer. Moreover, the PDA structure should decrease π - π stacking of the porphyrin units, which should afford the material favorable solubilities in organic solvents.

This work describes synthesis of a zinc-porphyrin bearing *meso*-C₂₅ alkyl chains with diacetylene units, polymerized to give a porphyrin embedded PDA web. The resulting material was tested for its photophysical and electrochemical properties, and for potential use in BHJ-SCs.

Experimental section

Materials and methods

All chemicals were of analytical grade, purchased from commercial suppliers and used as received without further purification. ¹H-NMR and ¹³C-NMR spectra were obtained in deuterated chloroform (CDCl₃) using an NMR spectrometer

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operated at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual CHCl_3 peak (7.26 ppm for ^1H -NMR and 77.0 ppm for ^{13}C -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. Absorption and emission spectra of the solutions were measured in toluene at room temperature, while those of the films, including a film sample for Raman spectroscopic measurement, were obtained from a drop-casting process on a pre-cleaned glass substrate.

Non-commercial compound

5,10,15,20-Tetra(4-carboxyphenyl)porphyrin (**1**)¹⁰ and 1-amino-10,12-pentacosadiyne (**3**)¹¹ were prepared following literature procedures.

Synthesis of Zn-4

Following a previously published procedure¹² with a slight modification, compound **1** (0.134 g, 0.170 mmol) was stirred in THF (10 mL) and *N*-hydroxysuccinimide (NHS) (0.128 g, 1.12 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (0.222 g, 1.16 mmol) were added. The reaction mixture was refluxed for 2 days, and the solvent was then removed under reduced pressure. The resulting crude containing compound **2** was dissolved in THF (10 mL) and treated with diacetylene **3** (0.565 g, 1.57 mmol) and triethylamine (TEA, 5 mL). The reaction mixture was refluxed for 1 day. After the solvent was removed under reduced pressure, the crude mixture was purified by column chromatography [silica, CH_2Cl_2 : EtOH : TEA (96 : 3 : 1)], resulting in a purple solid that gave a molecular ion peak with m/z consistent with a molecular mass of **4** in its mass spectrum. MALDI-MS m/z obsd 2158.056 [M^+], calcd avg mass 2157.240 ($\text{M} = \text{C}_{148}\text{H}_{202}\text{N}_8\text{O}_4$). Following a previously published procedure,¹³ the purple solid was re-dissolved in CHCl_3 (3 mL) and treated with a solution of zinc acetate dihydrate (0.050 g, 0.23 mmol) in methanol (1 mL). The reaction mixture was stirred at room temperature for 3 h and then extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$. The organic phase was collected, dried over anhydrous magnesium sulfate and concentrated to dryness. The resulting crude was purified by a short silica column [CH_2Cl_2 : EtOH : TEA (96 : 3 : 1)] to afford compound **Zn-4** as a purple solid (0.058 g, 15%). ^1H -NMR δ 0.77–0.94 (m, 12H), 1.10–1.76 (m, 128H), 2.25 (m, 16H), 3.50–3.63 (m, 8H), 6.36–6.51 (m, 8H), 8.06 (d, $J = 7.6$ Hz, 8H), 8.26 (d, $J = 7.9$ Hz, 8H), 8.88 (s, 8H) ppm; ^{13}C -NMR δ 14.1, 19.2, 22.7, 25.7, 27.1, 28.3, 28.4, 28.8, 28.9, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9, 32.8, 40.4, 63.1, 65.2, 65.3, 120.2, 125.1, 132.1, 134.1, 134.5, 145.9, 149.9, 167.6; MALDI-TOF-MS m/z obsd 2220.831 [M^+], calcd avg mass 2220.633 ($\text{M} = \text{ZnC}_{148}\text{H}_{200}\text{N}_8\text{O}_4$). Due to inevitable partial photopolymerization of **Zn-4** under ambient conditions during the measurement, high resolution mass spectrometric data could not be obtained. λ_{abs} 426, 557, 596 nm; λ_{em} ($\lambda_{\text{ex}} = 424$ nm) 607, 649 nm.

Electrochemical studies

Electrochemical properties of poly-**Zn-4** were determined by cyclic voltammetry in the three electrode configuration using acetonitrile containing 0.1 M Bu_4NPF_6 as an electrolyte, an indium tin oxide (ITO)-coated glass covered with poly-**Zn-4** as a working electrode (WE), a Pt wire counter electrode (CE) and a Ag/AgCl quasi-reference electrode (QRE). All measurements were performed with a scan rate of 20 mV s^{-1} . The QRE was externally calibrated with a ferrocene/ferrocenium redox couple of which the potential value of 0.40 V *versus* NHE was used. For the determination of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels, the value of the NHE *versus* vacuum level of -4.75 eV was used.¹⁴

Photoluminescence studies

Glass substrates ($15 \times 15 \text{ mm}^2$) were pre-cleaned by consecutive sonication in acetone, isopropanol and deionized water, and then dried by purging with air, with 800 rpm for 25 s. Stock solutions of **Zn-4**, P3HT and PCBM in chlorobenzene with the concentration of 18 mg mL^{-1} were prepared and filtered through 0.45 μm PTFE syringe filters. The solution of **Zn-4** was mixed either with poly(3-hexylthiophene) (P3HT) or PCBM in a weight ratio of 1 : 1. The resulting P3HT : **Zn-4** and **Zn-4** : PCBM (1 : 1 w/w) mixtures were drop-casted onto the glass substrates, left to dry at room temperature in the dark and then irradiated by a 254 nm light for 15 min.

Fabrication and characterization of poly-Zn-4-based BHJ-SCs

The above-mentioned stock solutions of **Zn-4** and PCBM were used to prepare solutions of **Zn-4** : PCBM with the weight ratios from 4 : 1 to 1 : 4. The $15 \times 15 \text{ mm}^2$ 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. A solution of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) (Heraeus Clevious™ P VP Al 4083) was spin-coated on top of 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 drop-casted on top of this PEDOT : PSS layer and the solvent was slowly evaporated for 30 min in a closed 150 mm \times 25 mm Petri dish in the dark. The resulting samples were dried under vacuum at ambient temperature for 1–2 h and then exposed to the 254 nm light for 15 min. After that, a 150 nm thick Al top electrode was deposited by thermal evaporation in vacuum of about 10^{-6} mbar in a glovebox. The active area of the devices was determined between 4 and 10 mm^2 . 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. Three to six samples for each cell condition were prepared to test the reproducibility of the results.

Results and discussion

Synthesis

The synthesis of **Zn-4** started with a reaction of the tetracarboxylic acid **1**¹⁰ with NHS and EDC·HCl to yield ester **2** (Scheme 1). Due to its hygroscopicity, ester **2** was freshly prepared and immediately reacted with 9 equivalents of diacetylene **3**¹¹ to afford compound **4**. The subsequent Zn-metallation of **4** gave **Zn-4** in 15% yield overall. The completion of the metalation step was indicated by the absence of an emission peak at about 720 nm and the disappearance of ¹H-NMR peak of the inner protons at δ -2.89 ppm in the spectra of compound **Zn-4**. The resulting sample of **Zn-4** was soluble in common organic solvents at the levels required for the preparation of the BHJ-SCs by routine wet processes (*i.e.* up to 40 mg mL⁻¹ in CH₂Cl₂, CHCl₃ and dichlorobenzene).

Based on Raman spectroscopy, the polymerization of **Zn-4** upon UV-irradiation to give poly-**Zn-4** was evidenced by the pronounced peaks of the C=C and C≡C stretches at 1446 and 2080 cm⁻¹ corresponding to the ene-yne conjugate (Fig. 1a and b).¹⁵

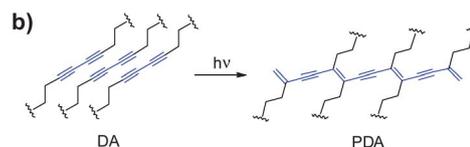
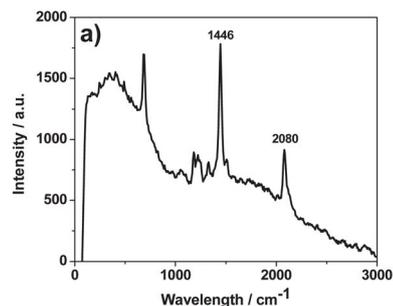
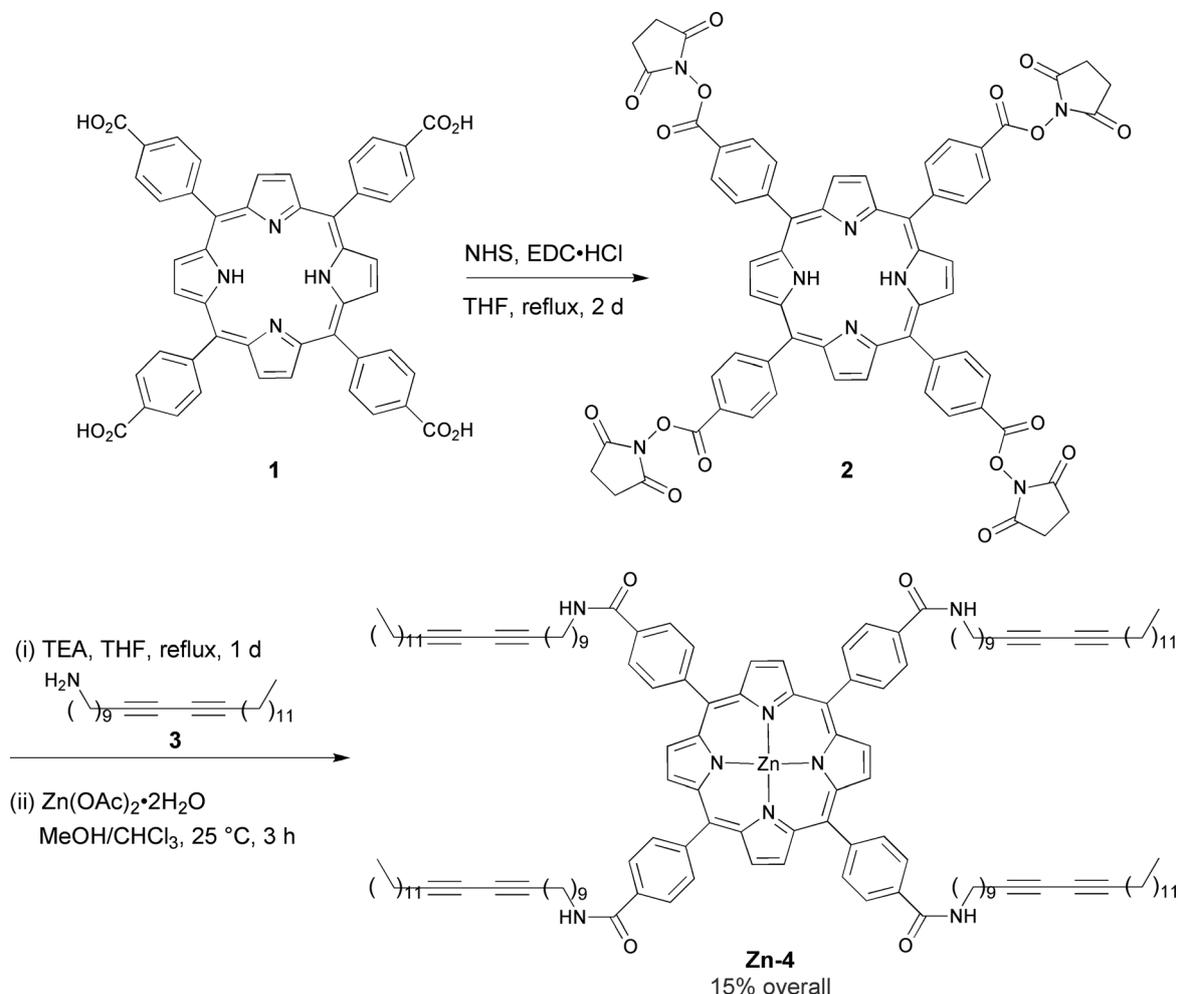


Fig. 1 (a) Raman spectrum of poly-**Zn-4**. (b) Photopolymerization of DA to form PDA.

Photophysical and electrochemical properties

UV-Vis absorption spectra of a poly-**Zn-4** film and a **Zn-4** solution in toluene are shown in Fig. 2. The **Zn-4** solution exhibited a B-band at 426 nm and Q-bands at 557 and 596 nm which are



Scheme 1 Synthesis of the target compound.

characteristic absorption patterns for a Zn-chelated porphyrin ring. After irradiation of the **Zn-4** film at 254 nm for 15 min, the resulting poly-**Zn-4** film gave the similar absorption pattern with significantly more pronounced Q-bands (Fig. 2, inset), indicating the absorption enhancement due to the presence of the PDA. The broadening of its B-band compared to that of the solution is most likely resulting from the aggregation of the macrocycle conjugation systems.

Based on cyclic voltammetry, the poly-**Zn-4** film can be electrochemically oxidized and reduced (Fig. 3). Oxidation process of the molecule to a radical cation was observed at +1.0 V (*versus* a normal hydrogen electrode, NHE, throughout) and a second oxidation to a dication was found at +1.3 V. Reduction of poly-**Zn-4** to a radical anion and a dianion occurred at -1.5 and -1.9 V, respectively. Compared with the benchmark *meso*-tetraphenylporphyrinatozinc(II) (Zn-TPP), both oxidation potentials of poly-**Zn-4** were at approximately 0.2 V higher potentials with the onset potential of the first oxidation (E_{ox}) of +0.9 V. As for the reduction, poly-**Zn-4** was reduced at approximately 0.1 V higher potentials than Zn-TPP with an equal onset potential of the first reduction (E_{red}) of -1.4 V. These small shifts indicate a significant effect of the presence of the PDA and/or the alkyl long chains on the electrochemical characteristics of the porphyrin ring. The indefinable anodic signal from -0.4 and -0.8 V is likely to be from the possible formation of unknown products from the reduction process(es) of poly-**Zn-4**, which is attributed to the molecular cleavage or deformation due to the presence of the PDA *meso* substituents, as this feature was more conspicuous at higher cycle numbers and was not observed in the case of Zn-TPP.

The above mentioned E_{ox} and E_{red} were used to determine an electrochemical energy gap (E_{g}), and HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO} , respectively) of poly-**Zn-4** *versus* vacuum with an estimated energy of NHE of -4.75 eV *versus* vacuum.¹⁴ According to the equations:

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

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

$$E_{\text{LUMO}} = -(E_{\text{red}} + 4.75) \text{ (eV);}^{16}$$

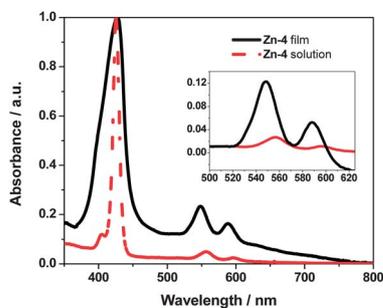


Fig. 2 Absorption spectra of a poly-**Zn-4** film (solid line) and a Zn-4 solution in toluene (dashed line). The inset shows a magnification of the region between 500 and 625 nm with baseline calibration for a comparison purpose.

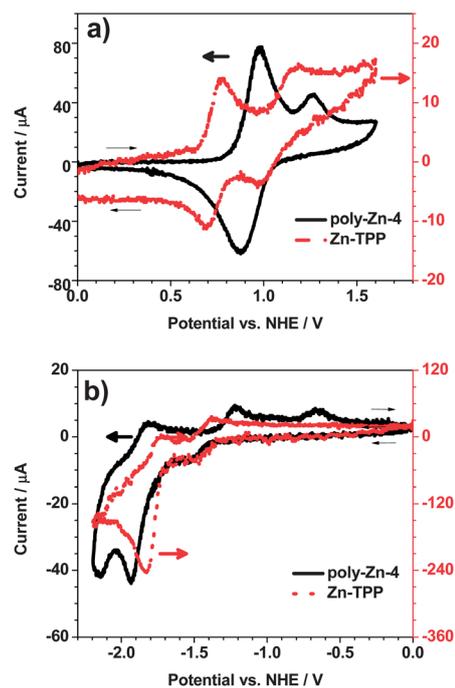


Fig. 3 Cyclic voltammograms of a poly-**Zn-4** film in the ranges between (a) 0 and +1.6 V and (b) 0 and -2.2 V.

the calculated E_{g} of poly-**Zn-4** was 2.2 eV with E_{HOMO} and E_{LUMO} of -5.6 eV and -3.4 eV, respectively.

Fig. 4 illustrates the HOMO and LUMO levels of poly-**Zn-4** in comparison with work functions (WFs) of ITO, PEDOT : PSS and Al, and the HOMO and LUMO levels of P3HT and PCBM.

For the ITO/PEDOT : PSS/P3HT : poly-**Zn-4**/Al solar cell, the LUMO level of poly-**Zn-4** is at a lower energy level than that of P3HT, enabling the electron transfer from P3HT to poly-**Zn-4** and then to Al electrode after photoexcitation of P3HT. In a similar manner, the ITO/PEDOT : PSS/poly-**Zn-4** : PCBM/Al device has the LUMO level of poly-**Zn-4** locating at higher energy level than that of PCBM and its HOMO level lying below the WF of PEDOT : PSS, allowing the electron transfer from poly-**Zn-4** to PCBM and from PEDOT : PSS to poly-**Zn-4** after photoexcitation

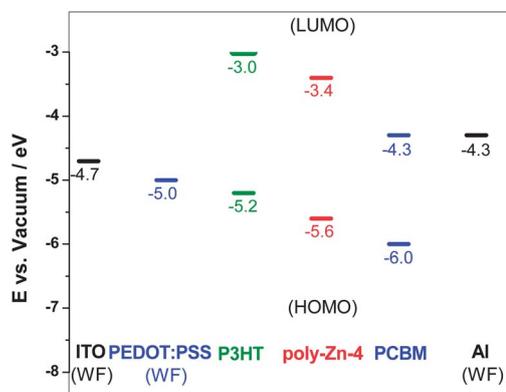


Fig. 4 Comparative energy diagram of a possible poly-**Zn-4**-based BHJ-SCs architecture.

of poly-Zn-4. The above-mentioned electrochemical characteristics of poly-Zn-4 and this calculation suggest the possibility of poly-Zn-4 to serve both as a donor and an acceptor in poly-Zn-4-based BHJ-SCs when used with PCBM and P3HT, respectively.

Photoluminescence studies of the blend films

To test for the possibility of the charge transfer from poly-Zn-4 to PCBM and from P3HT to poly-Zn-4 as suggested above, photoluminescence studies of poly-Zn-4 : PCBM (1 : 1 w/w) and P3HT : poly-Zn-4 (1 : 1 w/w) as the blended films were performed. Upon photoexcitation at the absorption maximum of the donor, *i.e.*, poly-Zn-4 ($\lambda_{\text{max}} = 426 \text{ nm}$) in case of the poly-Zn-4 : PCBM film and P3HT ($\lambda_{\text{max}} = 517 \text{ nm}$) in case of the P3HT : poly-Zn-4 film, the emission spectra of the films as shown in Fig. 5 were obtained.

In Fig. 5a, the emission spectra of poly-Zn-4 and PCBM, upon the excitation at 426 nm, are shown in red and black lines, respectively. Upon excitation at the same wavelength, the poly-Zn-4 : PCBM film (blue line) exhibited the complete quenching of the porphyrin emission by PCBM, presumably due to the efficient energy and/or charge transfer from poly-Zn-4 (donor) to PCBM (acceptor). However, Fig. 5b shows that the P3HT emission (as shown in a black line) was not completely quenched by poly-Zn-4 in the P3HT : poly-Zn-4 film (blue line), suggesting that the energy/charge transfer from P3HT (donor) to poly-Zn-4 (acceptor) was not efficient. Therefore the poly-Zn-4 : PCBM film was selected for the device studies as described below.

Preliminary device studies

In this study, the thickness and type of a metal top contact (PEDOT : PSS and ITO-coated glass) were kept constant. Upon

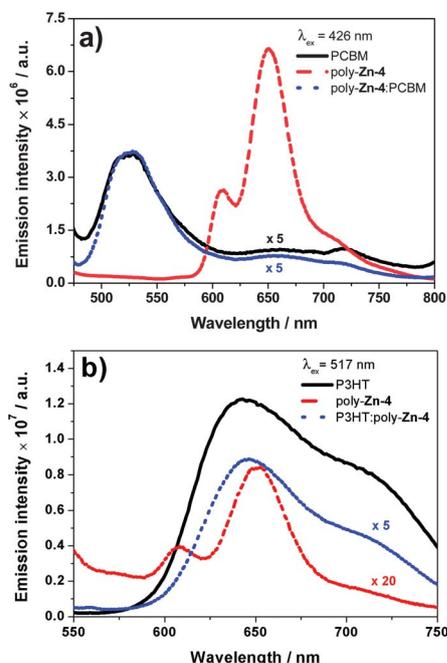


Fig. 5 Results of photoluminescence studies of (a) the poly-Zn-4 : PCBM and, (b) the P3HT : poly-Zn-4 blended films.

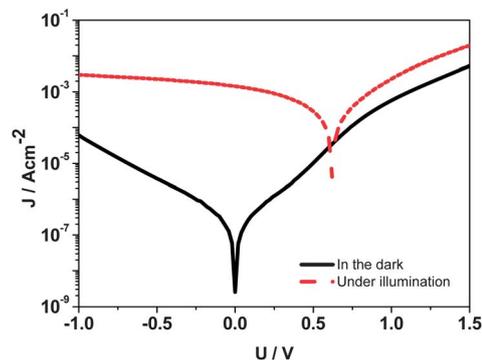


Fig. 6 J - V curves of the poly-Zn-4-based BHJ-SC.

variation of poly-Zn-4 : PCBM weight ratio from 4 : 1 to 1 : 4, the resulting cell efficiency was found to be highest at 0.2% with J_{SC} of 1.44 mA cm^{-2} , V_{OC} of 0.6 V and FF of 28%, when poly-Zn-4 : PCBM weight ratio of 1 : 1 was used. Fig. 6 shows current density-voltage (J - V) curves of the above-mentioned device obtained from the measurement in the dark and under illumination. To validate the beneficial effect of the presence of PDA in the photoactive layer, BHJ-SCs based on zinc tetraphenylporphyrin (ZnTPP) were fabricated under the same condition and investigated for comparison. In this case, the ZnTPP-based device did not exhibit the significant photovoltaic effects.

In all devices fabricated, the photovoltaic effect was observed. However, reproducibility of the experiments, especially those involving the poly-Zn-4 : PCBM film preparation, was poor likely due to aggregation of the material in the blend. Consequently, further experiments are required to understand the photovoltaic characteristics of the poly-Zn-4-based BHJ-SCs, and will be described elsewhere.

Conclusions

The featured PDA-nested porphyrin had enhanced absorption of poly-Zn-4 at the Q-band region relative to the parent porphyrin, and satisfactory solubility characteristics. Based on cyclic voltammetry, poly-Zn-4 exhibited the proper HOMO-LUMO levels for serving both as donor and acceptor for PCBM and P3HT, respectively, in BHJ-SCs. Photoluminescence studies of the poly-Zn-4 : PCBM and P3HT : poly-Zn-4 blended films indicated that the charge transfer was efficient in the poly-Zn-4 : PCBM film. Preliminary studies indicated poly-Zn-4 could be used as photoactive electron donating material for the BHJ-SCs.

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Notes and references

- 1 K. M. Kadish, E. V. Caemelbecke and G. Royal, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2000, vol. 8, ch. 55.
- 2 F. C. Krebs and H. Spanggaard, *Sol. Energy Mater. Sol. Cells*, 2005, **88**, 363.
- 3 Selected publications: (a) K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier and M. Grätzel, *J. Phys. Chem.*, 1987, **91**, 2342; (b) A. Kay and M. Grätzel, *J. Phys. Chem.*, 1993, **97**, 6272; (c) D. Wohrle, B. Tennigkeit, J. Elbe, L. Kreienhoop and G. Schurpfeil, *Mol. Cryst. Liq. Cryst.*, 1993, **230**, 221; (d) S. Cherian and C. C. Wamser, *J. Phys. Chem. B*, 2000, **104**, 3624; (e) F. Odobel, E. Blart, M. Lagree, M. Villieras, H. Boujtita, N. El Murr, S. Caramori and C. A. Bignozzi, *J. Mater. Chem.*, 2003, **13**, 502; (f) W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolly, *Coord. Chem. Rev.*, 2004, **248**, 1363; (g) H. Imahori, *J. Phys. Chem. B*, 2004, **108**, 6130; (h) T. Hasobe, P. V. Kamat, M. A. Absalom, Y. Kashiwagi, J. Sly, M. J. Crossley, K. Hosomizu, H. Imahori and S. Fukuzumi, *J. Phys. Chem. B*, 2004, **108**, 12865; (i) Q. Wang, W. M. Campbell, E. E. Bonfantani, K. W. Jolley, D. L. Officer, P. J. Walsh, K. Gordon, R. Humphry-Baker, M. K. Nazeeruddin and M. Grätzel, *J. Phys. Chem. B*, 2005, **109**, 15397; (j) T. Hasobe, S. Fukuzumi and P. V. Kamat, *J. Phys. Chem. B*, 2006, **110**, 25477; (k) W. M. Campbell, K. W. Jolly, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. S. Mende, M. K. Nazeerruddin, Q. Wang and M. Grätzel, *J. Phys. Chem. C*, 2007, **111**, 11760; (l) H. Imahori, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809; (m) R. M. Ma, P. Guo, H. J. Cui, X. X. Zhang, K. N. Mohammad and M. Grätzel, *J. Phys. Chem. A*, 2009, **113**, 10119.
- 4 Selected publications: (a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; (b) R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest and M. E. Thompson, *Chem. Mater.*, 1999, **11**, 3709; (c) T. F. Guo, S. C. Chang, Y. Yang, R. C. Kwong and W. E. Thompson, *Org. Electrochem.*, 2000, **1**, 15; (d) E. M. Gross, N. R. Armstrong and R. M. Wightman, *J. Electrochem. Soc.*, 2002, **149**, E137; (e) V. A. Montes, C. Perez-Bolivar, N. Agarwal, J. Shinar and P. Anzenbacher, *J. Am. Chem. Soc.*, 2006, **128**, 12436; (f) X. Wang, H. Wang, Y. Yang, Y. He, L. Zhang, Y. Li and X. Li, *Macromolecules*, 2010, **43**, 709.
- 5 Selected publications: (a) Y. Y. Noh, K. Yase and S. Nagamatsu, *Appl. Phys. Lett.*, 2003, **83**, 1243; (b) Y. Y. Noh, J. J. Kim, Y. Yoshida and K. Yase, *Adv. Mater.*, 2003, **15**, 699; (c) P. Checcoli, G. Conte, S. Salvatori, R. Paolesse, A. Bolognesi, A. Berliocchi, F. Brunetti, A. D'Amico, A. Di Carlo and P. Lugli, *Synth. Met.*, 2003, **138**, 261; (d) P. B. Shea, J. Kanicki and N. Ono, *J. Appl. Phys.*, 2005, **98**, 014503; (e) C.-M. Che, H.-F. Xiang, S. S.-Y. Chui, Z.-X. Xu, V. A. L. Roy, J. J. Yan, W.-F. Fu, P. T. Lai and I. D. Williams, *Chem.-Asian J.*, 2008, **3**, 1092; (f) X. B. Huang, C. L. Zhu, S. M. Zhang, W. W. Li, Y. L. Guo, X. W. Zhan, Y. Q. Liu and Z. Z. Bo, *Macromolecules*, 2008, **41**, 6895; (g) P. Ma, Y. Chen, X. Cai, H. Wang, Y. Zhang, Y. Gao and J. Jiang, *Synth. Met.*, 2010, **160**, 510.
- 6 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diao, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
- 7 (a) Mitsubishi Chemical Holdings Corporation, <http://www.m-kagaku.co.jp/english/aboutmcc/RC/special/feature1.html>, accessed 17 April 2012; (b) R. F. Service, *Science*, 2011, **332**, 293.
- 8 M. Shirakawa, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2006, **127**, 4164.
- 9 N. S. Sariciftci, B. Kraabel, C. H. Lee, K. Pakbaz, A. J. Heeger and D. J. Sandman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 12044.
- 10 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
- 11 N. M. Howarth, W. E. Lindsell, E. Murray and P. N. Preston, *Tetrahedron*, 2005, **61**, 8875.
- 12 S. J. Kew and E. A. H. Hall, *J. Mater. Chem.*, 2006, **16**, 2039.
- 13 J. Jiao, P. Thamyongkit, I. Schmidt, J. S. Lindsey and D. F. Bocian, *J. Phys. Chem. C*, 2007, **111**, 12693.
- 14 (a) R. Gomer and G. Tryson, *J. Chem. Phys.*, 1977, **66**, 4413; (b) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.
- 15 (a) D. Bloor and R. Chance, in *Polydiacetylenes*, ed. D. Bloor and R. Chance, NATO ASI Series E: Applied Sciences – No. 102, Martinus Nijhoff Publishers, Boston, MA, 1985, pp. V–VII; (b) Y. Wang, L. Li, K. Yang, L. A. Samuelson and J. Kumar, *J. Am. Chem. Soc.*, 2007, **129**, 7238.
- 16 D. Baran, A. Balan, S. Celebi, B. M. Esteban, H. Neugebauer, N. S. Sariciftci and L. Toppare, *Chem. Mater.*, 2010, **22**, 2978.