Cite this: J. Mater. Chem., 2011, 21, 17209

www.rsc.org/materials

PAPER

Efficiency enhancement of P3HT/PCBM bulk heterojunction solar cells by attaching zinc phthalocyanine to the chain-end of P3HT[†]

Jea Uk Lee,[‡]^a Young Do Kim,[‡]^b Jea Woong Jo,^b Jae Pil Kim^b and Won Ho Jo^{*b}

Received 12th April 2011, Accepted 19th August 2011 DOI: 10.1039/c1jm11563d

A new solution processable zinc phthalocyanine dye (ZnPc), as an interface modifier between poly(3hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in bulk heterojunction solar cells, was successively synthesized and linked to the chain-end of P3HT through the formation of a coordination complex. ZnPc dye molecules do not aggregate but preferentially locate at the interface between P3HT and PCBM, and thus contribute to the photocurrent generation by both direct photoexcitation and enhancement of charge transfer between P3HT and PCBM. To localize the zinc phthalocyanine dyes at the donor–acceptor interface more effectively, another new organic dye molecule, fullerene-functionalized zinc phthalocyanine (ZnPc-C₆₀) was also synthesized and linked to the chain-end of the P3HT, where ZnPc-C₆₀ contributes not only to the photocurrent generation by direct photo-excitation, but also lowers the interfacial tension, resulting in the reduction of the domain size and the suppression of the macrophase separation of the P3HT/PCBM blend for prolonged thermal annealing. This leads to higher device efficiency with 20% enhancement of the short circuit current and to enhancement of long-term thermal stability of device performance as compared to that of the reference P3HT/PCBM device.

Introduction

Conjugated polymer-based solar cells have widely been studied as low-cost alternatives for renewable energy sources. Particularly, the polymer solar cell with bulk heterojunction (BHJ) structure based on poly(3-hexylthiophene) (P3HT) and [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) has intensively been investigated and almost reached the optimum device performance: power conversion efficiencies (PCEs) of 4–5% and an incident photon-to-current conversion efficiency (IPCE) of over 70% under AM 1.5 (AM = air mass) illumination.¹⁻⁵

In recent years, new device structures^{6,7} and novel active layer materials based on low-bandgap polymers^{8–10} have been developed to further enhance the performance of polymer solar cells. Although tandem architectures, in which two subcells with complementary absorption bands are connected in series through a recombination zone, lead to summation of the open-

circuit voltage (V_{OC}) of each subcell, there have been few successful reports on tandem solar cells with high efficiency because the overall current is limited by the subcell that delivers the smaller photocurrent.¹¹ Another avenue to achieve high efficiency is to develop donor–acceptor type low-bandgap polymers which have broader absorption range and consequently harvest solar light more efficiently than P3HT.¹² However, it is not always easy to synthesize low-bandgap conjugated polymers with high charge carrier mobility.¹³

A recent approach for improving the device performance of polymer solar cells is to employ the dye sensitization method, modifying the interface between the conjugated polymer and electron acceptor material in BHJ solar cells. A previous work has demonstrated that the addition of a small molecule chromophore with an energy level intermediate between P3HT and fullerene extends the absorption of P3HT to longer wavelength, and as a result improves the photocurrent of P3HT/PCBM solar cells.14-16 Very recently, other research groups have also reported that dye molecules can improve the photocurrent significantly by promoting charge separation and strongly suppressing back recombination at the donor-acceptor interface.17-19 However, the PCEs have not been enhanced. For the enhancement of the PCE, the following prerequisites should be taken into account for successful application of dye molecules as the interface modifier in BHJ solar cells. First, to effectively mediate charge transfer between the donor and acceptor, the energy level of the dye molecule must be located at the intermediate between those

^aComposite Materials Research Group, Korea Institute of Materials Science, Changwon, Gyeongnam, 642-831, Korea

^bWCU Hybrid Materials Program and Department of Materials Science and Engineering, Seoul National University, Seoul, 151-742, Korea. E-mail: whjpoly@snu.ac.kr; Fax: +82-2-876-6086; Tel: +82-2-880-7192
† Electronic supplementary information (ESI) available: Cyclic voltammetry data, ¹H NMR spectrum, XRD patterns, average photovoltaic parameters and deviations, and TEM image. See DOI: 10.1039/c1jm11563d

[‡] These authors contributed equally to this work.

of the donor and acceptor materials: the lowest unoccupied molecular orbital (LUMO) level of the organic dye should be lower than the donor LUMO level and higher than the acceptor LUMO level; the HOMO level of the dye should be lower than the HOMO level of the donor.²⁰ Second, dye molecules should not aggregate in the blend film. It has been generally accepted that dye molecules with a planar structure easily aggregate and consequently deteriorate the device performance by reducing the absorption efficiency and the charge mobility of the active layer, when blended as the third component of the active layer.¹⁸ Third, dye molecules should be located at the donor–acceptor interface.

In this study, for the ideal interface modifier to be realized, a novel material, tetra-tert-butyl zinc(II) phthalocyanine-end capped P3HT (P3HT-ZnPc) has been synthesized and used as an interface modifier in BHJ solar cells. Solution processable tetratert-butyl zinc(II) phthalocyanine (ZnPc), which has widely been used for dye sensitization, was linked to the chain-end of the pyridyl-terminated P3HT (P3HT-Py) through coordination of the zinc atom of phthalocyanine to the pyridyl group of P3HT-Py. Since some experimental and theoretical studies have demonstrated that the end group of the polymer chain preferentially migrates to the polymer-polymer interface in immiscible polymer blends,²¹ it is easily expected that the phthalocyanine dyes bound to the P3HT chain-end are located at the interface between P3HT and PCBM. Furthermore, to more effectively localize the zinc phthalocyanine dyes at the donor-acceptor interface, another new organic dye molecule, fullerene-functionalized ZnPc, $(ZnPc-C_{60})$ has been synthesized and also linked to the chain-end of the P3HT-Py. Since the ZnPc-C₆₀ molecule has better compatibility with PCBM than ZnPc, it is fully expected that the P3HT-ZnPc-C₆₀ complex is more effective for modification of the interface between P3HT and PCBM. In this paper, we report the synthesis of dye-end capped P3HTs, together with an extensive investigation on their optical properties, crystal structures, and their application to BHJ solar cells.

Results and discussion

The synthetic routes for preparation of ZnPc and ZnPc- C_{60} are shown in Scheme 1. Metal phthalocyanine (Pc) dyes such as CuPc, ZnPc, FePc, CoPc, and NiPc have well been recognized as electron donor materials (or p-type semiconductors) in organic solar cells. The central metals in these phthalocyanines are transition metals, with different electrochemical properties derived from the 3d orbitals. Among these metal phthalocyanines, ZnPc was selected in this study because of its broader absorption range and higher open circuit voltage than other metal phthalocyanines when it is used as an electron donor material in BHJ solar cells.^{22,23} Furthermore, the energy levels of the solution processable ZnPc (LUMO = -3.8 eV, HOMO = -4.9 eV) are located at the intermediate between those of P3HT (LUMO = -3.2 eV, HOMO = -4.7 eV) and PCBM (LUMO =-4.0 eV, HOMO = -6.0 eV) (see ESI[†]). For the purpose of further enhancing the probability for ZnPc dyes to locate at the interface between the P3HT and PCBM domain, fullerenemodified ZnPc was also synthesized, as represented in Scheme 1, where tri-*tert*-butyl-amino zinc(II) phthalocyanine (ZnPc-NH₂) was first synthesized and then coupled with carboxylate-functionalized fullerene, [6,6]-phenyl-C₆₁-butyric acid (PCBA). It

should be noted here that an amide bond formed between fullerene and ZnPc breaks the conjugation between ZnPc and fullerene, and thus the absorption and the energy levels of ZnPc and fullerene remain intact after coupling.

The chemical structure of ZnPc-C₆₀ is identified by comparing FT-IR spectra of ZnPc, ZnPc-NH₂, and ZnPc-C₆₀, as shown in Fig. 1. The characteristic absorption bands of ZnPc-NH₂ are observed at 3366 cm⁻¹ and 3221 cm⁻¹ (N–H stretch of primary amine), 3072 cm⁻¹ (aromatic C–H stretch), 2950–2850 cm⁻¹ (aliphatic C–H stretch), and 1612 cm⁻¹ (N–H bend), while the FT-IR spectrum of ZnPc-C₆₀ shows the appearance of a single N–H stretching vibration and C==O stretching vibration of amide bond at 3376 cm⁻¹ and 1661 cm⁻¹, respectively. The appearance of a sharp peak at 528 cm⁻¹, which is characteristic for fullerene, also confirms that PCBA is linked covalently to ZnPc.

As another evidence for successful synthesis of phthalocyanines, matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy and elementary analysis were carried out. Fig. 2 reveals that the mass spectra of all phthalocyanines match well with the calculated molecular weights.

A new pyridyl-terminated P3HT was synthesized through the controlled Grignard metathesis polymerization of 2,5-dibromo-3-hexylthiophene and subsequent post-polymerization functionalization (Scheme 2). Hydroxypropyl-terminated P3HT (P3HT-OH) was first synthesized according to the procedure reported in the literature,24-26 and then combined with isonicotinic acid by using the carbodiimide-activated Steglich esterification method to connect the pyridine unit to the chainend of the P3HT. The Steglich esterification is one of the most convenient and effective methods for end-group modification of polymer chains, because the reaction condition is mild nevertheless the conversion is very high due to the favorable catalytic action of dimethylaminopyridine.27,28 The pyridyl-terminated P3HT was then reacted with ZnPc or ZnPc-C₆₀ dye in refluxing anhydrous THF, affording the corresponding complexes in which the pyridyl end group forms a ligand with Zn in the axial direction of phthalocyanine dyes (Scheme 2). Since the solubility of phthalocyanine dyes with tert-butyl groups is much better than P3HT, the final complex materials are readily purified by filtering and washing the unreacted dye molecules with MeOH and dichloromethane after the reaction. The final products, P3HT-ZnPc and P3HT-ZnPc-C₆₀, are soluble in various organic solvents such as THF, toluene, chloroform, and 1,2dichlorobenzene.

The formation of pyridyl-terminated P3HT and polymer-dye complexes was identified by ¹H NMR. The down-field shift of the methylene proton signal adjacent to the hydroxyl group of P3HT-OH from 3.75 to 4.2 ppm and the appearance of two aromatic proton signals at 7.8 and 8.8 ppm due to the pyridine group provide a solid evidence that P3HT-Py was successfully synthesized through the esterification reaction between P3HT-OH and isonicotinic acid (see ESI[†]). When P3HT-Py is reacted with ZnPc, the ¹H NMR spectrum of the product unambiguously exhibits further down-field shift of the two proton signals of the pyridine group in P3HT-Py to 8.3 and 9.5 ppm, respectively, confirming the formation of a coordination complex between P3HT-Py and ZnPc (Fig. 3). The ¹H NMR spectrum of the P3HT-ZnPc-C₆₀ complex also shows both the down-field shift of



Scheme 1 Synthesis of ZnPc and ZnPc-C₆₀ dyes.



Fig. 1 FT-IR spectra of ZnPc, ZnPc-NH₂, and ZnPc-C₆₀.

the pyridine signals and the appearance of new proton signals at $\delta = 7.5$ –8 ppm due to the phenyl hydrogens of PCBA.

The formation of P3HT-dye complexes was further verified by using gel permeation chromatography (GPC) (Fig. 4). P3HT synthesized in this study has a reasonable molecular weight for the application of an electron donor in BHJ solar cells, with a narrow molecular weight distribution ($M_n = 24\ 000, M_w/M_n =$ 1.15). After P3HT was reacted with ZnPc and ZnPc-C₆₀, the GPC traces slightly shifted to higher molecular weights ($M_n =$ 25 000 for P3HT-ZnPc and $M_n = 27\ 000$ for P3HT-ZnPc-C₆₀), indicating that the ZnPc and ZnPc-C₆₀ dyes were linked to the P3HT chain. It should be mentioned here that the GPC trace of



Fig. 2 MALDI-TOF MS spectra of ZnPc (black line), ZnPc-NH₂ (red line), and ZnPc- C_{60} (blue line).

P3HT-Py has a very small shoulder at shorter elution times. This is due to the chain coupling that may occur during the end-group modification of P3HT, because the thiophene-bromine bond at the opposite chain-end is active in various side reactions.²⁹

When we measured the molecular weights of chain-end modified P3HTs using MALDI-TOF MS, it showed that the average number of the molecular weights of P3HT-Py, P3HT-ZnPc, and P3HT-ZnPc-C₆₀ were 17 250, 18 020, and 18 890 g mol⁻¹, respectively, as shown in Fig. 5. The molecular weight differences between these polymers (770 and 870 g mol⁻¹) are well matched with the molecular weight of ZnPc and PCBA, clearly indicating that most of the P3HT chain-ends are functionalized by the ZnPc and ZnPc-C₆₀ dyes.

Fig. 6 shows the UV-Vis absorption spectra of the dye molecules, P3HT-ZnPc, and P3HT-ZnPc- C_{60} in THF solution. The



Scheme 2 Synthesis of P3HT-Py, P3HT-ZnPc, and P3HT-ZnPc-C₆₀. DCC: 1,3-dicylohexylcarbodi-imide; DMAP: dimethylaminopyridine.

polymer-dye complexes absorb at 300–550 nm and 600–700 nm, corresponding to the typical absorption range of P3HT and phthalocyanine, respectively. A small red-shift of the maximum absorption wavelength (λ_{max}) of the dye molecules was observed, as the fullerene derivative was covalently bonded to a side arm of the phthalocyanine dye. When the amount of dye molecules bound at the polymer chain-end is estimated by comparing the absorbance of P3HT with that of the dye molecule, it reveals that 92% and 86% of the chain-ends of P3HT are modified by ZnPc and ZnPc-C₆₀, respectively. However, when the same amount of ZnPc dye as that in P3HT-ZnPc is simply mixed with P3HT, the simple mixture (P3HT + ZnPc) does not absorb at the ZnPc absorption range, probably because the dye molecules are aggregated in the mixture.

To investigate the effect of ZnPc dye attached at the chain-end of P3HT on the film morphology and the device performance, three blend films of P3HT/PCBM, P3HT-ZnPc/PCBM, and P3HT-ZnPc-C₆₀/PCBM were prepared. For comparison, another film was also prepared by simple mixing of P3HT/PCBM with the same amount of ZnPc dyes as that in P3HT-ZnPc (hereafter denoted by P3HT + ZnPc/PCBM). When the X-ray diffraction (XRD) patterns of four blend films are compared after thermal annealing at 150 °C for 5 min, as shown in Fig. 7, the P3HT/PCBM blend film shows a very sharp and intense (100) reflection peak at $2\theta = 5.4^{\circ}$ corresponding to the chain-chain interlayer distance, and weak (200) and (300) reflection peaks at $2\theta = 10.7$ and 15.9° , respectively. Although the (100) peak intensities are somewhat weaker than that of the P3HT/PCBM film, P3HT-ZnPc/PCBM and P3HT-ZnPc-C₆₀/PCBM blend films still show a strong (100) reflection peak, implying that the P3HT chains crystallize even after the chain-end of P3HT is modified by phthalocyanine dyes. However, when the ZnPc dyes are simply mixed with P3HT/PCBM, the blend film exhibits considerably lower crystallinity than the others, indicating that ZnPc dye molecules in the simple mixture of P3HT + ZnPc/PCBM disturb the crystallization of P3HT, presumably due to the formation of dye aggregation in the blend film.

Table 1 shows the average photovoltaic parameters and their deviations of BHJ devices fabricated from four different blends, where the average power conversion efficiency of each blend sample was evaluated from the values of 12 devices. The representative current density-voltage (*J-V*) curves were also compared in Fig. 8. The reference device of P3HT/PCBM has $V_{\rm OC} = 0.56$ V, $J_{\rm SC} = 9.23$ mA cm⁻², and *FF* = 0.61, yielding the PCE of 3.15%, which is slightly lower than the literature value. This lower PCE value can be explained as follows: the high crystallinity of P3HT synthesized in our laboratory may raise the HOMO level (-4.7 eV) due to increased inter-chain orbital delocalization (see ESI†),³⁰ and therefore the rise of the HOMO of P3HT results in a decrease of $V_{\rm OC}$.

After introducing ZnPc and ZnPc-C₆₀ to the chain-end of P3HT, the J_{SC} of both devices was substantially increased, while the fill factor was nearly unchanged, leading to PCEs of 3.28 and 3.56% for the P3HT-ZnPc/PCBM and P3HT-ZnPc-C₆₀/PCBM devices, respectively. It should be noted here that the J_{SC} of the P3HT-ZnPc-C₆₀/PCBM device was increased by *ca.* 20% in comparison with the reference device of P3HT/PCBM. On the other hand, the device fabricated by simple mixing with ZnPc exhibited a much lower PCE of 2.25%.

The IPCEs of the P3HT-dye/PCBM devices were measured and compared with that of the P3HT/PCBM device, as shown in Fig. 9. Both the P3HT-ZnPc/PCBM and P3HT-ZnPc- C_{60} /PCBM



Fig. 3 1 H NMR spectra of (a) P3HT-ZnPc and (b) P3HT-ZnPc-C₆₀ complexes.

devices exhibit an additional photocurrent at the ZnPc absorption range (650–800 nm), indicating that dye molecules attached at the polymer chain-end effectively absorb the incident light and contribute to the photocurrent generation. Furthermore, the IPCE value at 520 nm corresponding to the P3HT absorption also increases up to 66% and 74% for the P3HT-ZnPc/PCBM and P3HT-ZnPc-C₆₀/PCBM device, respectively, from 62% for the reference P3HT/PCBM device, suggesting that the phthalocyanine dye promotes charge generation from excitons in P3HT,³¹ whereas the P3HT + ZnPc/PCBM device shows a low IPCE at the P3HT absorption range and very small signal at the ZnPc absorption range, because the ZnPc dyes are easily aggregated in the simple blend of P3HT/PCBM.



Fig. 4 GPC traces of P3HT-Py (black line), P3HT-ZnPc (red line), and P3HT-ZnPc-C₆₀ (blue line).



Fig. 5 MALDI-TOF MS spectra of P3HT-Py, P3HT-ZnPc, and P3HT-ZnPc-C₆₀.



Fig. 6 UV-Visible absorption spectra of ZnPc (red dashed line), ZnPc- C_{60} (blue dashed line), P3HT-ZnPc (red line), P3HT-ZnPc- C_{60} (blue line), and P3HT + ZnPc (green line) in THF solution.



Fig. 7 XRD patterns of P3HT/PCBM (black line), P3HT-ZnPc/PCBM (red line), P3HT-ZnPc- C_{60} /PCBM (blue line), and P3HT + ZnPc/PCBM (green line) blend films after thermal annealing at 150 °C for 5 min.

When the nanoscale morphology of the active layer from each device after 5 min annealing is examined by TEM, as shown in Fig. 10, the TEM image of the P3HT/PCBM film shows the nanoscale phase morphology with network structure where well developed P3HT nanocrystals are clearly observed in the bright P3HT domain (Fig. 10a), whereas the thin film of P3HT + ZnPc/PCBM shows leaf-like aggregation of dye molecules after thermal annealing at 150 °C for 5 min (Fig. 10b). To more clearly



Fig. 8 Typical *J-V* curves of P3HT/PCBM (black line), P3HT + ZnPc/ PCBM (green line), P3HT-ZnPc/PCBM (red line), and P3HT-ZnPc-C₆₀/ PCBM (blue line) BHJ devices (100 mW cm⁻², AM 1.5 G). All the devices were thermally annealed at 150 °C for 5 min.



Fig. 9 IPCE spectra of P3HT/PCBM (black circle), P3HT + ZnPc/ PCBM (green circle), P3HT-ZnPc/PCBM (red circle), and P3HT-ZnPc-C₆₀/PCBM (blue circle) BHJ devices (100 mW cm⁻², AM 1.5 G). All the devices were thermally annealed at 150 °C for 5 min.

identify the aggregates formed from ZnPc dyes, we prepared separately another P3HT/PCBM sample blended with a larger amount of ZnPc and examined the thin film morphology. As the weight fraction of ZnPc is increased, the size of the aggregate becomes larger in the blend film (see ESI[†]). This observation leads us to conclude that ZnPc dyes, when blended as the third component of the active layer, form large aggregates after thermal annealing and this aggregation may suppress the

Table 1 The photovoltaic parameters of P3HT/PCBM, P3HT + ZnPc/PCBM, P3HT-ZnPc/PCBM, and P3HT-ZnPc-C₆₀/PCBM BHJ devices (100 mW cm⁻², AM 1.5 G). All the devices were thermally annealed at 150 °C for 5 min

Device	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)
P3HT/PCBM	0.56 ± 0.02	9.22 ± 0.7	61 ± 1.0	3.15 ± 0.15
P3HT + ZnPc/PCBM	0.54 ± 0.03	8.52 ± 0.8	49 ± 3.0	2.25 ± 0.25
P3HT-ZnPc/PCBM	0.56 ± 0.02	9.91 ± 0.5	59 ± 1.0	3.27 ± 0.20
P3HT-ZnPc-C ₆₀ /PCBM	0.56 ± 0.02	10.96 ± 0.4	58 ± 1.5	3.56 ± 0.18



Fig. 10 TEM images of (a) P3HT/PCBM, (b) P3HT + ZnPc/PCBM, (c) P3HT-ZnPc/PCBM, and (d) P3HT-ZnPc- C_{60} /PCBM blend films after thermal annealing at 150 °C for 5 min.

crystallization of P3HT, resulting in inefficient charge transport. On the other hand, the dye aggregation was not observed in P3HT-ZnPc/PCBM and P3HT-ZnPc-C₆₀/PCBM after thermal annealing, as shown in Fig. 10c and 10d, suggesting that dye molecules linked to the polymer chain-end do not aggregate upon thermal annealing and thus do not prohibit the crystallization of P3HT. It should be noted that the pyridine-Zn bond is not dissociated upon thermal annealing because the dissociation energy of pyridine-Zn metal (248 KJ/mol) is much larger than the thermal energy at 150 °C (RT \approx 3.5 kJ mol⁻¹).³² Furthermore, it is notable that the domain size of P3HT-ZnPc-C₆₀/PCBM is \sim 50 nm, which is much smaller than the domain size of P3HT/ PCBM (~ 200 nm). It has been well known that the addition of block copolymer compatibilizer to the corresponding homopolymer blend leads to reduction of interfacial tension and thus suppresses macrophase separation due to the attractive interaction between the block copolymer and the corresponding blend component at the interface.^{33,34} Hence, it is expected that the ZnPc-C₆₀ part in P3HT-ZnPc-C₆₀ interacts effectively with PCBM, and thus reduces the interfacial tension between P3HT and PCBM, resulting in the reduction of domain size. The high J_{SC} of the P3HT-ZnPc-C₆₀/PCBM device is attributed to the relatively small domain size.

The time-resolved photoluminescence spectroscopy (TRPL) was measured under different film conditions, as shown in Fig. 11, from which the fluorescence kinetic parameters of the blend films were evaluated and summarized in Table 2. The fluorescence at 650 nm of P3HT has the mono-exponential decay time of 700 ps whereas that of P3HT/PCBM has bi-exponential decay times of 190 ps and 450 ps at room temperature. The fast decay time (190 ps) is identical with the time of charge (exciton) separation at the interface between P3HT and PCBM, while the slow decay time (450 ps) is ascribed to the exciton-hole recombination time of P3HT. Whilst the P3HT + ZnPc/PCBM sample also exhibits bi-exponential decay with a lifetime of 180 and



Fig. 11 TRPL spectra of P3HT (gray line), P3HT/PCBM (black line), P3HT + ZnPc/PCBM (green line), P3HT-ZnPc/PCBM (red line), and P3HT-ZnPc-C₆₀/PCBM (blue line) blend films after thermal annealing at 150 °C for 5 min.

450 ps, which is nearly equal to that of P3HT/PCBM, both the P3HT-ZnPc/PCBM and P3HT-ZnPc-C₆₀/PCBM films have shorter charge separation time (140-160 ps) than the P3HT/ PCBM film. This is because excitons in P3HT-dye/PCBM are more efficiently dissociated into charge carriers while ZnPc molecules in the simple mixture of P3HT + ZnPc/PCBM are aggregated and thus do not contribute to the charge separation. In short, the ZnPc-C₆₀ dye molecules linked to the chain-end of P3HT do not aggregate but preferentially locate at the interface between P3HT and PCBM, and thereby contribute to the enhancement of J_{SC} via three different mechanisms: First, dye molecules absorb the incident light and contribute to the photocurrent generation; second, the dye molecule at the donoracceptor interface enhances the charge transfer from P3HT to PCBM by acting as an "electronic tunnel"; third, P3HT-ZnPc-C₆₀ acts as a "compatibilizer" to control the donor/acceptor morphology.35-37 Among these contributions, the first contribution to the enhancement of $J_{\rm SC}$ must be small because the photocurrent at the ZnPc absorption range is not so large in ICPE spectra, as shown in Fig. 9. On the other hand, more important contributions would be both charge transfer and morphology control by ZnPc-C₆₀, because differences in the TRPL decay time (20 ps) and J_{SC} (1.0 eV) between P3HT-ZnPc-C₆₀/PCBM and P3HT-ZnPc/PCBM are observed.

Another important role of the interface modifier is the improvement of the long-term stability of the nano-scaled morphology against macrophase separation. To examine the

Table 2 Fluorescence kinetic parameters of P3HT/PCBM, P3HT + ZnPc/PCBM, P3HT-ZnPc/PCBM, and P3HT-ZnPc- C_{60} /PCBM blend films after thermal annealing at 150 °C for 5 min

P3HT 532 650 700 P3HT/PCBM 190/450 P3HT + ZnPc/PCBM 180/450 P3HT-ZnPc/PCBM 160/470	ps)
P3HT-ZnPc- C_{60} /PCBM 140/430	

effect of the ZnPc-C₆₀ interface modifier on the long-term stability of the device performance, the PCEs of the P3HT-ZnPc-C₆₀/PCBM devices were measured as a function of annealing time at 150 °C and compared with those of devices without ZnPc-C₆₀ interface modifier. When the PCEs are plotted against the annealing time, as shown in Fig. 12, it is obvious that the PCE of the P3HT-ZnPc-C₆₀/PCBM device decreases much more slowly than the other devices with increasing the annealing time. This is probably because the ZnPc-C₆₀ dyes located at the interface between the P3HT and PCBM phases effectively act as a compatibilizer to suppress the macrophase separation.

Conclusions

We have synthesized two kinds of zinc phthalocyanine dyes and linked them to the chain-end of P3HT. It was found that the dye molecules linked to the chain-end of P3HT do not aggregate in the blend film and preferentially locate at the P3HT/PCBM interface. Hence, the dye molecules linked to P3HT do not disturb the crystallization of P3HT, and rather lower the interfacial tension, affording the reduction of the domain size of the P3HT/PCBM blend. More importantly, the ZnPc-C₆₀ dye located at the interface enhances the photocurrent generation by both direct photo-excitation and effective charge separation. The P3HT-ZnPc-C₆₀/PCBM devices achieved the PCE of 3.56% with 20% enhancement of $J_{\rm SC}$ compared to that of the reference P3HT/PCBM device. Furthermore, the P3HT-ZnPc-C₆₀/PCBM device exhibited remarkable enhancement of the long-term thermal stability of the device performance, because the ZnPc- C_{60} interface modifier suppresses large-scale phase separation of P3HT/PCBM blend even after prolonged annealing times. It is expected that our concept to attach dye molecules to the polymer chain-end can be applied to other low bandgap conjugated polymers to enhance the device performance of polymer solar cells.

Experimental section

Materials

4-*tert*-Butylphthalonitrile and 4-aminophthalonitrile were purchased from TCI and used without further purification.



annealing time at 150 °C.

Tetrahydrofuran (THF) was dried over sodium/benzophenone under nitrogen and freshly distilled before use. Buckminsterfullerene derivatives, PCBA (Materials Technologies Research) and PCBM (Nano-C) were used as received. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P VP AI 4083) was purchased from H. C. Stark and passed through a 0.45 μ m PES syringe filter before spin-coating. All other reagents were purchased from Sigma-Aldrich and used as received.

Synthesis of tetra-tert-butyl zinc(II) phthalocyanine (ZnPc)

A mixture of 4-*tert*-butylphthalonitrile (737 mg, 4 mmol) and ZnCl₂ (136 mg, 1 mmol) were refluxed in dimethylaminoethanol (DMAE, 1.5 mL) under argon for 15 h. After the reaction mixture was concentrated under reduced pressure, the blue solid was extracted with dichloromethane and then washed with water. Yield 85.5%; FT-IR (KBr, cm⁻¹): 2956 (C–H), 1613 (N–H); elementary analysis calcd (%) for C₄₈H₄₈N₈Zn (802.36): C 70.14, H 6.34, N 12.58, found: C 70.53, H 6.79, N 12.12; MALDI-TOF MS: *m/z* 800.3 (100%, [M + 2H]⁺).

Synthesis of tri-*tert*-butyl-amino zinc(II) phthalocyanine (ZnPc-NH₂)

A mixture of 4-*tert*-butylphthalonitrile (553 mg, 3 mmol) and 4-aminophthalonitrile (143 mg, 1 mmol) was refluxed in DMAE (1.5 mL) under argon for 15 h in the presence of ZnCl₂ (136 mg, 1 mmol). After the reaction mixture was concentrated under reduced pressure, the greenish blue solid was extracted with dichloromethane and then washed with water. The corresponding tri-*tert*-butyl-amino zinc(II) phthalocyanine was separated from tetra-*tert*-butyl zinc(II) phthalocyanine, di-*tert*-butyl-diamino zinc(II) phthalocyanine, and *tert*-butyl-tri-amino zinc(II) phthalocyanine by column chromatography using a mixed solvent of petroleum ether and dioxane (4 : 1/v:v) as an eluting solvent. Yield 18.5%; FT-IR (KBr, cm⁻¹): 3366, 3221, 1612 (N– H), 2955 (C–H); elementary analysis calcd (%) for C₄₄H₄₁N₉Zn (761.27): C 67.88, H 5.81, N 14.84, found: C 66.16, H 6.24, N 13.55; MALDI-TOF MS: *m*/*z* 760.0 (100%, [M + H]⁺).

Synthesis of tri-tert-butyl zinc(11) phthalocyanine-C_{60} (ZnPc-C_{60})

PCBA (150 mg, 0.17 mmol) was dissolved in 50 mL of dry CS₂ under argon atmosphere. Thionyl chloride (10 mL) was added using a syringe and the mixture was heated at 80 °C for 18 h. After the reaction mixture was cooled down to room temperature, the volatile compounds were removed under reduced pressure. The remaining solid ([6,6]-phenyl- C_{61} -acyl chloride) was washed with anhydrous THF three times and dried under vacuum. The tri-tert-butyl-amino zinc(II) phthalocyanine (155 mg, 0.18 mmol) and triethylamine (4.5 mL) were dissolved in dry CS_2 (60 mL), and the solution was dropwise added to [6,6]phenyl- C_{61} -acyl chloride using a syringe. After the reaction solution was refluxed for 24 h, the volatile CS2 was removed with a rotary evaporator. The crude product was suspended in diethyl ether using ultrasonication. The suspension was poured into 500 mL of water, and the precipitate was filtered and dried at 50 °C under vacuum. After the product was suspended in ethyl



Fig. 12 The power conversion efficiencies of P3HT/PCBM (black line),

P3HT + ZnPc/PCBM (green line), P3HT-ZnPc/PCBM (red line), and

P3HT-ZnPc-C₆₀/PCBM (blue line) BHJ devices as a function of

acetate using ultrasonication, the suspension was centrifuged at 3500 rpm, and the supernatant was decanted and dried at 50 °C under vacuum. Yield 30.5%; FT-IR (KBr, cm⁻¹): 3376, 1554 (N–H), 2925 (C–H), 1661 (C=O), 528 (C₆₀); elementary analysis calcd (%) for C₁₁₅H₅₁N₉OZn (1640.1): C 84.22, H 3.13, N 7.69, found: C 83.93, H 3.06, N 7.95; MALDI-TOF MS: m/z 1638.8 (100%, [M + H]⁺).

Synthesis of pyridyl-terminated P3HT (P3HT-Py)

Hydroxypropyl-terminated P3HT was synthesized by following the procedure reported in the literature,²⁵ before pyridyl-terminated P3HT was synthesized by the Steglich esterification between hydroxypropyl-terminated P3HT and isonicotinic acid. In a 100 mL round-bottom flask, 0.14 g of hydroxypropylterminated P3HT ($M_{\rm n} = 24\ 000,\ M_{\rm w}/M_{\rm n} = 1.15$ by GPC) and isonicotinic acid (0.04 g, 0.32 mmol) were added, and the flask was degassed under vacuum and backfilled with argon gas. 40 mL of CHCl₃ and 0.01 mg of dimethylaminopyridine (0.1 mmol) were added to the reaction mixture. Then, 0.07 mg of 1,3dicyclohexylcarbodiimide (0.32 mmol) dissolved in 10 mL of CHCl₃ was dropwise added using a syringe, and the solution was stirred at 30 °C for 2 days. The polymer was purified by soxhlet extraction consecutively with methanol, hexane, ethyl acetate, and toluene. The polymer was isolated from toluene solution, and dried under vacuum to afford 0.125 g (90% yield).

Synthesis of zinc(II) phthalocyanine-terminated P3HT (P3HT-ZnPc)

A mixture of tetra-*tert*-butyl zinc(II) phthalocyanine (0.1 g, 0.125 mmol) and pyridyl-terminated P3HT (0.1 g, 0.004 mmol) were refluxed in anhydrous THF (10 mL) under argon for 12 h. The polymer solution was precipitated into MeOH and filtered, and the precipitation and filtration step was repeated 3 times to remove the unreacted zinc(II) phthalocyanine. The precipitated polymer was dried under vacuum to afford 0.09 g (87% yield).

Synthesis of zinc(II) phthalocyanine-C₆₀-terminated P3HT (P3HT-ZnPc-C₆₀)

A mixture of tri-*tert*-butyl zinc(II) phthalocyanine- C_{60} (0.08 g, 0.05 mmol) and pyridyl-terminated P3HT (0.1 g, 0.004 mmol) were refluxed in anhydrous THF (10 mL) under argon for 24 h. The polymer solution was precipitated into dichloromethane and filtered, and this precipitation and filtration step was repeated three times to remove the unreacted zinc(II) phthalocyanine- C_{60} . The precipitated polymer was dried under vacuum to give 0.08 g (76% yield).

Photovoltaic cells fabrication

ITO-coated glass (15 Ω sq⁻¹) was cleaned with acetone and isopropyl alcohol, and then dried at 200 °C for 30 min. After complete drying, the ITO-coated glass was treated with UVozone for 15 min. PEDOT:PSS was spin coated onto the ITO with 40 nm in thickness, and the PEDOT:PSS film was annealed at 120 °C for 30 min in a N₂-filled glove box. The mixture of P3HT/PCBM (P3HT-ZnPc/PCBM, or P3HT-ZnPc-C₆₀/PCBM) was dissolved in 1,2-dichlorobenzene at a concentration of 4 wt%. For comparison, the solution of P3HT/PCBM blended with the same amount of ZnPc dyes as that in P3HT-ZnPc was also prepared. These solutions were stirred for at least 24 h at room temperature and then were passed through a 0.2 μ m PES syringe filter before spin coating. These solutions were coated on the top of PEDOT:PSS layer by spin-coating at 700 rpm for 60 s. Al (100 nm in thickness) was thermally evaporated on the top of the active layer under high vacuum lower than 10⁻⁶ Torr. The devices were then annealed at 150 °C for 5 min on a digital hot plate under nitrogen atmosphere inside a glove box.

Characterization and measurement

The chemical structure was identified by a 500 MHz ¹H NMR spectrometer (Avance 500, Bruker). FT-IR spectra of the synthesized materials were obtained on an IR spectrometer (FT/IR-660 plus, Jasco). The molecular weight and its distribution for all synthesized polymers was measured by GPC (Knauer K-501 pump with a K-2301 refractive index detector) using THF as an eluent. The molecular weights were reported relative to polystyrene standards. MALDI-TOF mass spectra were collected (Voyager-DE STR Biospectrometry Workstation, Applied Biosystems Inc.) with α -cyano-4-hydroxy-cynamic acid (CHCA) as a matrix. Elementary analyses of all synthesized dyes were performed by an elemental analyzer (Flash EA 1112, Thermo Electron Co.).

The UV-visible absorption and fluorescence spectra were obtained on a Perkin-Elmer Lambda 25 spectrometer and a Photon Technology International QM-4 fluorescence spectrometer, respectively. The morphology of the active layer films was observed by TEM (JEM-1010, JEOL) with an accelerating voltage of 120 kV. The crystallinity of the active layer was investigated by X-ray diffractometer (M18XHF-SRA, Mac Science Co.) using Cu-K α ($\lambda = 0.154$ nm) radiation. The cyclic voltammetry (CV) measurements were carried out using Pt working and counter electrodes and a Ag/AgCl (3 M NaCl) reference electrode. The photovoltaic performance was measured under nitrogen atmosphere inside a glove box. The current density-voltage (J-V) characteristics were measured with a Keithley 4200 source-meter under AM 1.5 G (100 mW cm⁻²) simulated by a Newport-Oriel solar simulator. The light intensity was calibrated using a NREL certified photodiode and light source meter prior to each measurement. The active area was determined at 0.04 cm² by attaching a shadow mask onto the solar cell device. The IPCE was measured using a lock-in amplifier with a current preamplifier (K3100, Mac Science Co.) under short circuit current state with illumination of monochromatic light.

TRPL measurement

A mode-locked Nd:YAG laser (Pizzicato, Quantel) with the pulse duration of 25 ps was employed for excitation, and a streak camera of 10 ps (C2830, Hamamatsu) attached to a CCD detector (RTE128H, Princeton Instruments) was used for detection. Samples were excited with the second harmonic pulses (532 nm) of the laser. Emission wavelengths were collected at near magic angle for the fluorescence kinetic measurements and selected by combining band-pass filters and cut-off filters.

Fluorescence kinetic constants were extracted by fitting the measured kinetic profiles to computer-simulated kinetic curves convoluted with the instrument temporal response functions.³⁸

Acknowledgements

The authors thank the Ministry of Education, Science and Technology (MEST), Korea for financial support through the Global Research Laboratory (GRL) and the World Class University (WCU) programs.

References

- 1 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.
- 2 W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, Adv. Funct. Mater., 2005, 15, 1617.
- 3 J. A. Jo, S. S. Kim, S. I. Na, B. K. Yu and D. Y. Kim, *Adv. Funct. Mater.*, 2009, **19**, 866.
- 4 C. Lin, E. Y. Lin and F. Y. Tsai, *Adv. Funct. Mater.*, 2010, 20, 834.
 5 G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang and Y. Yang, *Adv. Funct. Mater.*, 2007, 17, 1636.
- 6 J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. Ma, X. Gong and A. J. Heeger, *Adv. Mater.*, 2006, **18**, 572.
- 7 J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222.
- 8 L. Huo, J. Hou, S. Zhang, H. Y. Chen and Y. Yang, Angew. Chem., Int. Ed., 2010, 49, 1500.
- 9 N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. N. Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, J. Am. Chem. Soc., 2008, 130, 732.
- 10 Y. Lee, T. P. Russell and W. H. Jo, Org. Electron., 2010, 11, 846.
- 11 S. Sista, Z. Hong, M. H. Park, Z. Xu and Y. Yang, *Adv. Mater.*, 2010, 22, E77.
- 12 H. Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649.
- 13 D. Mühlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, 18, 2884.
- 14 H. Neugebauera, M. A. Loib, C. Windera, N. S. Sariciftcia, G. Cerulloc, A. Gouloumisd, P. Vázquezd and T. Torres, *Sol. Energy Mater. Sol. Cells*, 2004, 83, 201.
- 15 J. Peet, A. B. Tamayo, X. D. Dang, J. H. Seo and T. Q. Nguyen, *Appl. Phys. Lett.*, 2008, **93**, 163306.
- 16 E. M. J. Johansson, A. Yartsev, H. Rensmo and V. Sundström, J. Phys. Chem. C, 2009, 113, 3014.

- 17 Y. Y. Lin, T. H. Chu, S. S. Li, C. H. Chuang, C. H. Chang, W. F. Su, C. P. Chang, M. W. Chu and C. W. Chen, *J. Am. Chem. Soc.*, 2009, 131, 3644.
- 18 S. Honda, T. Nogami, H. Ohkita, H. Benten and S. Ito, ACS Appl. Mater. Interfaces, 2009, 1, 804.
- 19 S. Honda, H. Ohkita, H. Benten and S. Ito, *Chem. Commun.*, 2010, 46, 6596.
- 20 G. K. Mor, S. Kim, M. Paulose, O. K. Varghese, K. Shankar, J. Basham and C. A. Grimes, *Nano Lett.*, 2009, 9, 4250.
- 21 D. Kawaguchi, K. Tanaka, N. Torikai, A. Takahara and T. Kajiyama, *Langmuir*, 2007, 23, 7269.
- 22 R. Koeppe, N. S. Sariciftci, P. A. Troshin and R. N. Lyubovskaya, *Appl. Phys. Lett.*, 2005, **87**, 244102.
- 23 P. A. Troshin, R. Koeppe, A. S. Peregudov, S. M. Peregudova, M. Egginger, R. N. Lyubovskaya and S. Sariciftci, *Chem. Mater.*, 2007, **19**, 5363.
- 24 C. R. Craley, R. Zhang, T. Kowalewski, R. D. McCullough and M. C. Stefan, *Macromol. Rapid Commun.*, 2009, 30, 11.
- 25 M. C. Iovu, M. Jeffries, E. E. Sheina, J. R. Cooper and R. D. McCullough, *Polymer*, 2005, 46, 1483.
- 26 J. U. Lee, A. Cirpan, T. Emrick, T. P. Russell and W. H. Jo, J. Mater. Chem., 2009, 19, 118.
- 27 B. Neises and W. Steglich, Angew. Chem., Int. Ed. Engl., 1978, 17, 522.
- 28 J. U. Lee, J. W. Jung, T. Emrick, T. P. Russell and W. H. Jo, J. Mater. Chem., 2010, 20, 3287.
- 29 Y. Lee, K. I. Fukukawa, J. Bang, C. J. Hawker and J. K. Kim, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 8200.
- 30 K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. V. Severen, L. Lutsen, T. J. Cleij, D. Vanderzande and J. V. Manca, *Adv. Funct. Mater.*, 2008, 18, 2064.
- 31 R. Zhu, C. Y. Jiang, B. Liu and S. Ramakrishna, Adv. Mater., 2009, 21, 994.
- 32 M. T. Rodgers, J. R. Stanley and R. Amunugama, J. Am. Chem. Soc., 2000, **122**, 10969.
- 33 J. U. Lee, J. W. Jung, T. Emrick, T. P. Russell and W. H. Jo, *Nanotechnology*, 2010, 21, 105201.
- 34 J. Washiyama, C. Creton and E. J. Kramer, *Macromolecules*, 1992, 25, 4751.
- 35 N. Kudo, S. Honda, Y. Shimazaki, H. Ohkita, S. Ito and H. Benten, *Appl. Phys. Lett.*, 2007, **90**, 183513.
- 36 Y. Liu, M. A. Summers, C. Edder, J. M. J. Fréchet and M. D. McGehee, *Adv. Mater.*, 2005, 17, 2960.
- 37 S. R. Scully, P. B. Armstrong, C. Edder, J. M. J. Fréchet and M. D. McGehee, *Adv. Mater.*, 2007, **19**, 2961.
- 38 B. Valeur, Molecular Fluorescence: Principles and Applications, Wiley-VCH, Weinheim, 2001.