

Thin Film of a Porphyrin-End-Functionalized Poly(cyclohexane)/ Fullerene-End-Functionalized Poly(4-diphenylaminostyrene) Blend: Control of Microphase Separation in a Light-Harvesting System for Polymer Solar Cells

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ABSTRACT: Thin films of a tetraphenylporphyrin-end-functionalized polycyclohexane zinc complex (ZnTPP-PCHE)/fullerene- C_{60} (C_{60}) end-functionalized poly(4-diphenylaminostyrene) (C_{60} -PDAS) were prepared to investigate their potential as a light-harvesting system for polymer solar cells (PSCs). The microphase separation in the ZnTPP-PCHE/ C_{60} -PDAS blends had a significant effect on the optical properties; the absorption band of the microphase separation structure that overlaps the visible-light region was considerably enhanced with an increase in the C_{60} concentration in the polymer film, although both pristine ZnTPP-PCHE and C_{60} -PDAS thin films had only weak absorption bands in that region. Therefore, this polymer blend is considered to be suitable for use as a light-harvesting system for PSCs. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4212–4216, 2013

KEYWORDS: films; morphology; adsorption; blends; optical and photovoltaic applications

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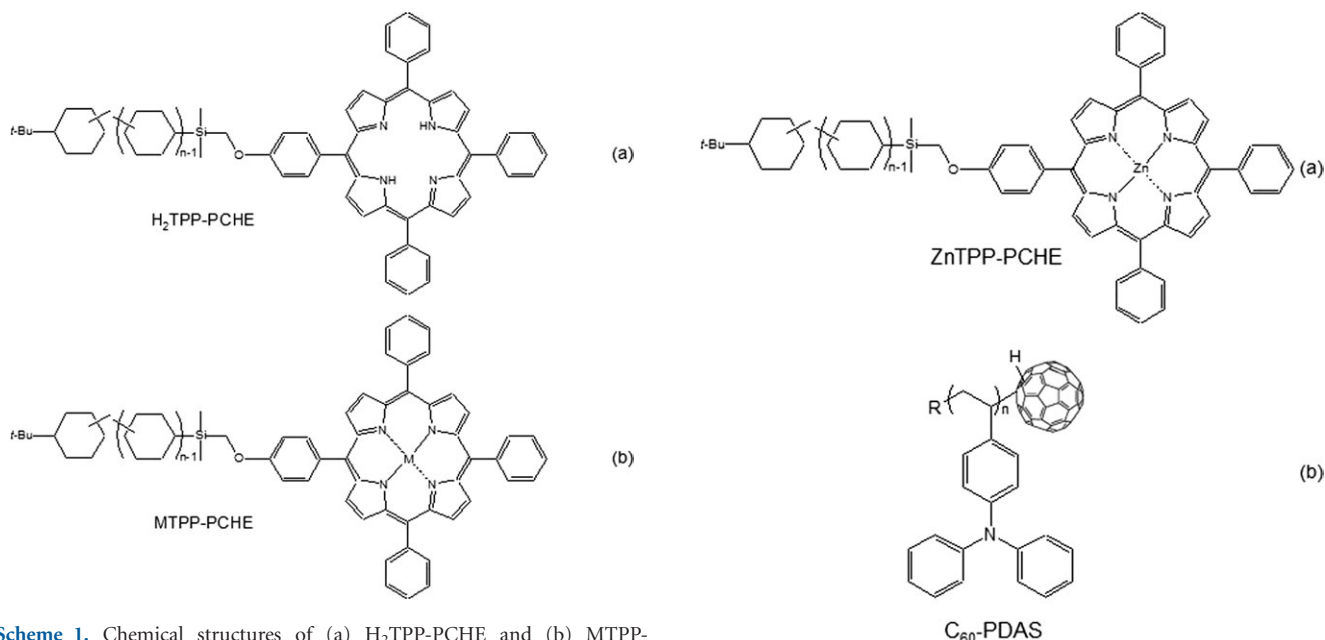
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INTRODUCTION

Polymer solar cells (PSCs) have generated considerable interest due to their potential as renewable, alternative sources of electrical energy. The unique advantages of PSCs, such as their low cost, light weight, and potential application in flexible large-area devices, are the driving force behind studies into the development of new PSCs. In particular, there has been increased effort to develop PSCs based on soluble semiconducting polymers and fullerene derivatives.^{1–5} However, the power conversion efficiency of PSCs is still significantly lower than that of inorganic solar cells, such as amorphous silicon (A-Si), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS), which has prevented their practical application on a large scale. One of the factors that limits the performance of PSCs is their absorption mismatch to the terrestrial solar spectrum⁶; therefore, there has been a variety of approaches to expand the spectral region of PSCs, such as the introduction of photosensitizers^{7–10} or semiconducting polymers with wide range of absorption.^{11–13} For example, the incorporation of porphyrins (a typical photosensitizer) has been considered as an effective method to improve the properties of PSCs.^{8,10,14,15} However, previous attempts to incorporate porphyrins into PSCs have resulted in limited success due to the uncontrolled dispersion of porphyrin molecules

into the polymer thin films. The realization of a broad absorption band that completely overlaps the visible-light region in PSCs that contain porphyrins has been very difficult. Therefore, new concepts for the light-harvesting system of PSCs have been required.

Recently, we reported the synthesis of tetraphenylporphyrin-end-functionalized polycyclohexane (H_2 TPP-PCHE) [Scheme 1(a)] and its metal complexes (MTPP-PCHE) [Scheme 1(b)] with a well-controlled and defined polymer chain structure.¹⁶ The π -conjugated system in the H_2 TPP (or MTPP) end-groups were expected to have strong π - π interaction with the π -conjugated system of a soluble semiconducting polymer and fullerene derivative (a typical active layer of PSCs). Thus, the end-groups are expected to assemble at the border between the soluble semiconducting polymer/fullerene derivative phase and the polycyclohexane (PCHE) phase, as shown in Scheme 2. This layer appears to have an expanded π -conjugated system due to the continuous porphyrin molecules, and it is thought that such layer should exhibit a broader absorption band than that of isolated porphyrin molecules. The preparation of polymer blends consisting of a H_2 TPP-PCHE zinc complex (ZnTPP-PCHE) [Scheme 3(a)] and fullerene- C_{60} (C_{60}) end-functionalized poly(4-diphenylaminostyrene) (C_{60} -PDAS, a soluble semiconducting polymer with attached



Scheme 1. Chemical structures of (a) H₂TPP-PCHE and (b) MTPP-PCHE.

C₆₀ [Scheme 3(b)]^{17,18} was attempted to confirm this hypothesis.

In this article, we report on preparation of a ZnTPP-PCHE/C₆₀-PDAS blend thin film for application as a light-harvesting system in PSCs. The control of microphase separation in the thin film for realization of a broad absorption band that completely overlaps the visible-light region is also discussed in detail.

EXPERIMENTAL

Materials

Toluene ($\geq 99.8\%$) was refluxed over calcium hydride (CaH₂, 95%) and then distilled under dry argon. C₆₀ (99.5%) was washed with tetrahydrofuran (THF) and dried under reduced pressure. 4-Diphenylaminostyrene (DAS) was prepared via a

Scheme 3. Chemical structures of (a) ZnTPP-PCHE and (b) C₆₀-PDAS.

previously reported standard Wittig reaction.¹⁹ ZnTPP-PCHE (M_n 1990, PDI 1.24,) was obtained as reported in our previous paper.¹⁶ C₆₀-PDAS (M_n 4530, PDI 1.39) was prepared by the addition of poly(4-diphenylaminostyryl)lithium (PDASLi, M_n 3890, PDI 1.31),^{*} which was initiated with *tert*-butyllithium (*t*-BuLi) in toluene, onto C₆₀ [Scheme 3(b), PDASLi/C₆₀ = 1/1, mol/mol, R = *t*-Bu] according to our previously reported procedure.^{17,18} All other reagents (Sigma–Aldrich) were used as received unless otherwise stated.

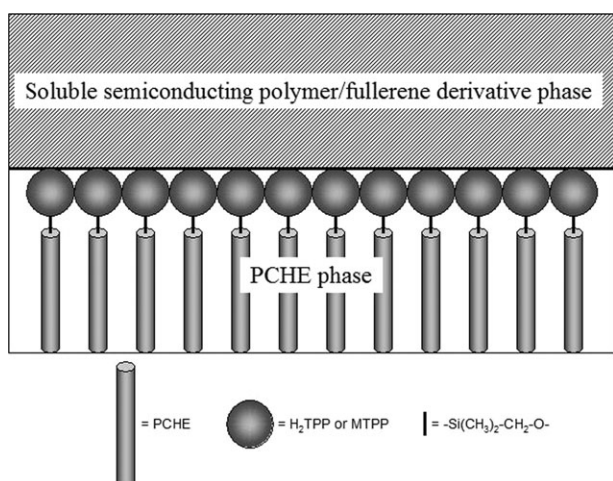
Preparation of Polymer Thin Films

ZnTPP-PCHE, C₆₀-PDAS, the zinc tetraphenylporphyrin (ZnTPP)/ C₆₀-PDAS blend, and the ZnTPP-PCHE/C₆₀-PDAS blend were dissolved in chlorobenzene, and were spin-coated onto glass substrates at 3000 rpm to form polymer thin films.

Measurements

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI; M_w/M_n) were determined using gel permeation chromatography (GPC) apparatus equipped with a differential refractive index (RI) detector and a Shimadzu Shim-pack GPC-80M column (column length: 300 mm; diameter: 8 mm; effective molecular weight range: 100–4,000,000) at 40°C. THF was used as the eluent at a flow rate of 1.00 mL min⁻¹. A molecular weight calibration curve was obtained using polystyrene (PSt) standards. ¹H nuclear magnetic resonance (NMR; Jeol ECA500) spectra of the polymers were measured in deuterated chloroform (CDCl₃) at 500 MHz. UV–vis absorption spectra of the polymer solutions and films were obtained with a spectrometer (Shimadzu UV-3101PC). Micro-phase separation of polymer films was observed using atomic force microscopy (AFM; Jeol JSPM-4200).

* M_n and PDI were measured after deactivation with methanol.



Scheme 2. Assembly of the H₂TPP- or MTPP- end-groups at the border between the soluble semiconducting polymer/fullerene derivative phase and the PCHE phase.

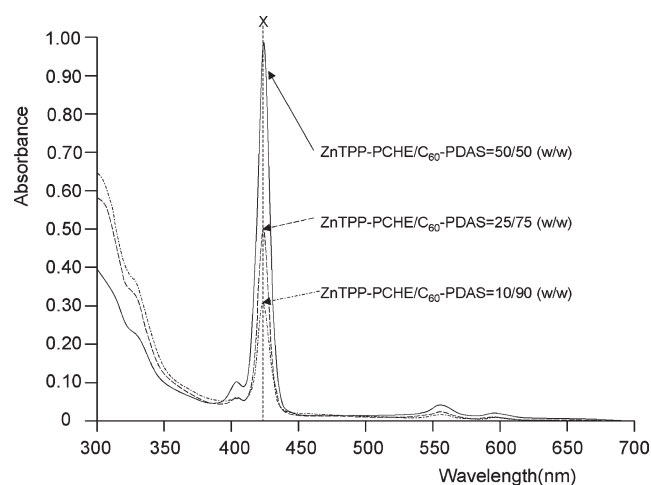


Figure 1. UV-vis spectra of the ZnTPP-PCHE/ C_{60} -PDAS blend in THF (sample/THF = 0.010 mg mL⁻¹).

RESULTS AND DISCUSSION

Optical Properties of the ZnTPP-PCHE/ C_{60} -PDAS Blend in THF

The optical properties of the thin films were considered to be the most important for practical use as light-harvesting systems for PSCs. Before the examination of polymer thin films, UV-vis spectroscopy measurements for the THF solutions of the ZnTPP-PCHE/ C_{60} -PDAS blend were performed to obtain the basic information (Note: THF is an inert solvent for PDAS. Meanwhile the color of PADS is gradually changed by the halogenated solvents under UV light.).

Figure 1 shows typical UV-vis spectra for the ZnTPP-PCHE/ C_{60} -PDAS blend in THF (polymer/THF = 0.010 mg mL⁻¹). As previously reported, the absorption band for the THF solution of PCHE was not observed in the region >300 nm; therefore, PCHE does not inhibit the optical properties of the ZnTPP end-groups which has the absorption bands around 425, 560, and 590 nm.¹⁶ The THF solution of C_{60} -PDAS has an absorption band around 300 nm, which is attributed to the C_{60} end-groups and PDAS moiety.¹⁷ For the THF solutions of the ZnTPP-PCHE/ C_{60} -PDAS blend, the absorption bands around 425 nm (line X) is the Soret-band of the porphyrin moiety, and the bands around 560 and 590 nm are the Q-bands of the porphyrin moiety.¹⁶ The absorption band around 300 nm is the C_{60} end-groups and PDAS moiety.¹⁷ The Soret- and Q-bands of the porphyrin moiety were simply enhanced with an increase in the ratio of ZnTPP-PCHE. However, the remarkable change of the absorption band in the region between 450 and 540 nm was not observed. Therefore, the π - π interaction between ZnTPP-PCHE and C_{60} -PDAS appears to be faint in the THF solutions.

Direct Contact of ZnTPP and C_{60} -PDAS

As shown in Scheme 2, if ZnTPP end-groups are assembled at the border between the C_{60} -PDAS phase and the PCHE phase, the direct contact of ZnTPP end-groups and C_{60} -PDAS is thought to occur. Therefore, as a model of this border, it was very important to reveal the nature of ZnTPP/ C_{60} -PDAS blends. To examine the effect of direct contact of ZnTPP and C_{60} -PDAS

on the optical properties, ZnTPP and C_{60} -PDAS were blended in chlorobenzene [ZnTPP (mg)/ C_{60} -PDAS (mg)/chlorobenzene (mL) = (a) 0.00/0.50/1.00, (b) 0.50/0.50/1.00, (c) 1.00/0.50/1.00]. Thin films of the ZnTPP/ C_{60} -PDAS blend were then prepared by spin-coating of the chlorobenzene solutions of the blend onto a glass substrate.[†]

Figure 2 shows typical UV-vis spectra of the ZnTPP/ C_{60} -PDAS blend thin films. The thin film of C_{60} -PDAS [Figure 2(a)] has an absorption band around 310 nm, which is attributed to the C_{60} end-groups and PDAS moiety. For the thin films of ZnTPP/ C_{60} -PDAS blend [Figure 2(b,c)], the Soret-band was shifted to the longer wavelength region (around 440 nm, line Y) due to the direct contact of ZnTPP and C_{60} -PDAS as a ZnTPP- C_{60} charge-transfer complex. The Q-bands remained around 560 and 590 nm. The Soret- and Q-bands of the porphyrin moiety were enhanced with an increase in the ratio of ZnTPP. In the thin films of ZnTPP/ C_{60} -PDAS blend, the control dispersion of ZnTPP molecules was very difficult although a ZnTPP- C_{60} charge-transfer complex seemed to form in the polymer thin films.[†] That is, only limited part of ZnTPP molecules is thought to be used as the self-assembled ZnTPP. In addition, this uncontrolled dispersion of ZnTPP gave many defects into the polymer thin film.

Effect of Microphase Separation on the Optical Properties of the ZnTPP-PCHE/ C_{60} -PDAS Blend

The π -conjugated system in the ZnTPP end-groups is expected to have strong π - π interaction with the π -conjugated system of C_{60} -PDAS (a combination of soluble semiconducting polymer and fullerene derivative) in polymer thin films. Therefore, if the microphase separation is formed, the end-groups seem to assemble at the border between the C_{60} -PDAS phase and the ZnTPP-PCHE phase, as shown in Scheme 2. To examine the effect of microphase separation on the optical properties of polymer thin films, ZnTPP-PCHE and C_{60} -PDAS were blended in chlorobenzene [ZnTPP-PCHE (mg)/ C_{60} -PDAS (mg)/chlorobenzene (mL) = (a) 0.50/0.00/1.00, (b) 0.50/0.25/1.00, (c) 0.50/0.50/1.00, (d) 0.50/1.00/1.00]. The thin films of the ZnTPP-PCHE/ C_{60} -PDAS blend were then prepared by spin-coating of the chlorobenzene solutions of the blend onto a glass substrate.

Figure 3 shows typical UV-vis spectra of the ZnTPP-PCHE/ C_{60} -PDAS blend thin films. For the thin film of ZnTPP-PCHE [Figure 3(a)], the absorption bands around 425 nm (line X) is the Soret-band of the porphyrin moiety, and the bands around 560 and 590 nm are the Q-bands of the porphyrin moiety.¹⁶ In the case of the ZnTPP-PCHE/ C_{60} -PDAS (=1/0.5) blend thin film [Figure 3(b)], the Soret- and Q-bands of the porphyrin moiety were almost same as the ZnTPP-PCHE thin film (An absorption band around 310 nm is attributed to the C_{60} end-groups and PDAS moiety.¹⁷). The remarkable change of the absorption band in the region between 450 and 540 nm was not observed in this film. Meanwhile, the thin films of the ZnTPP-PCHE/ C_{60} -PDAS [=1/1 and 1/2 (w/w)] blend

[†]The ZnTPP/ C_{60} -PDAS blend thin films had many defects due to the low solubility and self-aggregation of ZnTPP.

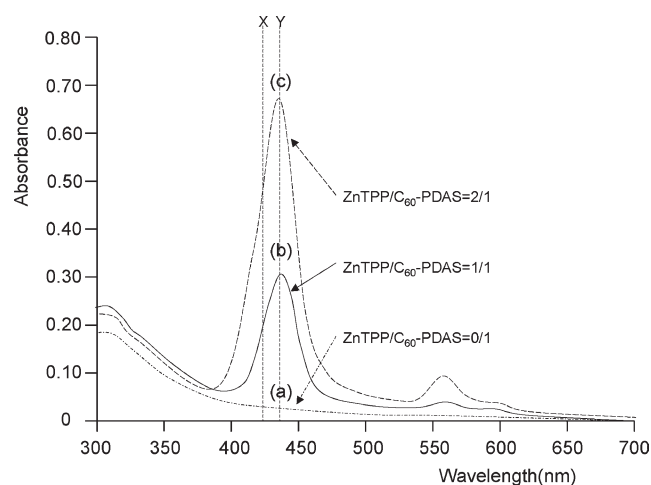


Figure 2. UV-vis spectra of the ZnTPP/C₆₀-PDAS blend films prepared from chlorobenzene solution [ZnTPP (mg)/C₆₀-PDAS (mg) /chlorobenzene(mL) = (a) 0.00/0.50/1.00, (b) 0.50/0.50/1.00, (c) 1.00/0.50/1.00].

[Figure 3(c,d)] exhibited a shift in the Soret-band (around 425 nm, line X) to the longer wavelength region (around 440 nm, line Y) due to the direct contact of ZnTPP end-groups and C₆₀-PDAS as a ZnTPP-C₆₀ charge-transfer complex. Furthermore, the absorption band in the region >450 nm was considerably enhanced with an increase in the C₆₀ concentration in the polymer film. When ZnTPP-PCHE was blended to C₆₀-PDAS, the net absorption of the polymer thin films appeared to be increased although the absorption of the Soret-band was somewhat diminished. In a previous paper,²⁰ we found that the self-assembled porphyrin-end-groups of porphyrin-end-functionalized polymers had a broad absorption band that well overlaps the terrestrial solar spectrum in the polymer thin film. In the case of the ZnTPP-PCHE/C₆₀-PDAS blends, it was thought that this broad absorption band is due to the self-assembled ZnTPP end-groups of ZnTPP-PCHE.

Figure 4 shows the AFM image of the ZnTPP-PCHE/C₆₀-PDAS [=1/1 (w/w)] blend thin film. In this film, the microphase separation is clearly formed.[‡] The ZnTPP end-groups presumably assemble at the border of microphase separation of ZnTPP-PCHE and C₆₀-PDAS as a ZnTPP-C₆₀ charge-transfer complex, as shown in Scheme 2. In this case, the ZnTPP-end-groups of ZnTPP-PCHE seem to be used as the self-assembled ZnTPP-end-groups, efficiently. That is, the microphase separation of the ZnTPP-PCHE/C₆₀-PDAS blends leads to the well-controlled self-assembled ZnTPP-end-groups having the broad absorption band in the visible-light region. In other words, the role of PCHE in ZnTPP-PCHE is to form a controlled microphase separation having the controlled self-assembled ZnTPP-end-groups. This self-assembled porphyrin layer seems to have an expanded π -conjugated system with a broader absorption band than that of isolated porphyrin molecules. Thus, the thin films of the ZnTPP-PCHE/C₆₀-PDAS [=1/1 and 1/2 (w/w)] blend have a

[‡]From the results of our preliminary study for the PCHE/PDAS blends; the dark phase corresponds to the PCHE phase and the bright phase to the PDAS phase.

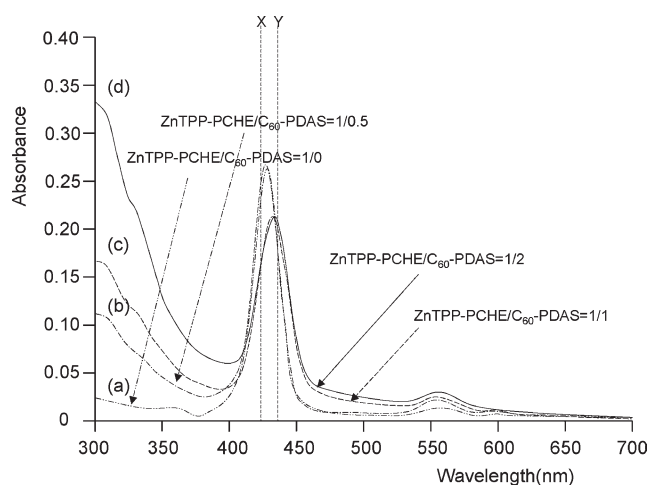


Figure 3. UV-vis spectra of the ZnTPP-PCHE/C₆₀-PDAS blend films prepared from chlorobenzene solution [ZnTPP-PCHE (mg)/C₆₀-PDAS (mg)/chlorobenzene (mL) = (a) 0.50/0.00/1.00, (b) 0.50/0.25/1.00, (c) 0.50/0.50/1.00, (d) 0.50/1.00/1.00].

broad absorption band that completely overlaps the visible-light region, and are therefore suitable for use as a light harvesting system in PSCs.

CONCLUSIONS

The preparation and optical properties of the ZnTPP-PCHE/C₆₀-PDAS blend thin films were examined in an attempt to obtain a light-harvesting system for PSCs. Films of ZnTPP-PCHE, C₆₀-PDAS, ZnTPP/C₆₀-PDAS blend, and the ZnTPP-PCHE/C₆₀-PDAS blends were prepared by spin-coating onto a glass substrate. The ZnTPP-PCHE thin film had only a weak absorption band in the region >450 nm and the thin film of C₆₀-PDAS had only a faint absorption band in the region >400 nm. In the case of a thin film of the ZnTPP-PCHE/C₆₀-PDAS [=1/0.5 (w/w)] blend, the absorption band in the region greater than 450 nm was not enhanced over that of individual thin films of ZnTPP-PCHE and C₆₀-PDAS. Meanwhile, the thin films of the ZnTPP-PCHE/C₆₀-PDAS [=1/1 and 1/2 (w/w)] blend exhibited a shift in the Soret-band to the longer wavelength

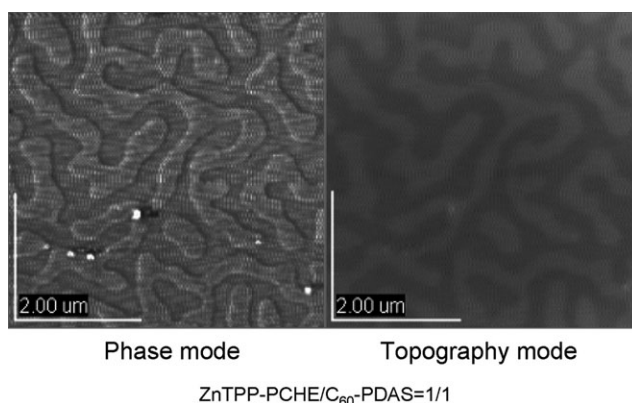


Figure 4. AFM image of the ZnTPP-PCHE/C₆₀-PDAS [=1/1 (w/w)] blend film prepared from chlorobenzene solution (sample/solvent = 1.00 mg mL⁻¹).

region due to the direct contact of ZnTPP end-groups and C₆₀-PDAS as a ZnTPP-C₆₀ charge-transfer complex. Furthermore, the absorption band in the region >450 nm was considerably enhanced with an increase in the C₆₀ concentration in the polymer film. The ZnTPP end-groups appeared to assemble at the border of the microphase separation. This self-assembled porphyrin layer has an expanded π -conjugated system with a broader absorption band that completely overlaps the visible-light region, and these films are therefore suitable for use as a light-harvesting system in PSCs.

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