

Synthesis, Characterizations, and Properties of a P3HT-Hemin Covalent System for Solar Energy Conversions

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Abstract

Organic solar cells based on conjugated materials have widely been studied as potential renewable and low-cost alternatives for future solar energy conversions. The power conversion efficiency (PCE) of the best organic solar cells-bulk heterojunction (BHJ) cell reached to about 10%. However, there is room for improvements. In this study, we intend to address the critical “photon loss” problem and the germinate charge carriers recombination problem via an energy level matched dye molecular units sensitized polymer approach, *i.e.*, a “three-component” approach. Specifically, a covalent P3HT-Hemin system was synthesized and characterized successfully via esterification between HO/HO-P3HT and Hemin. The optoelectronic performance of P3HT-Hemin/PCBM cell is improved over the corresponding simple blend system, and this can be attributed to both improved photon capture and reduced charge recombination.

Keywords: Conjugated polymers; Molecular dyes; Light harvesting; Optoelectronics; Photovoltaics; Solar cells; Energy conversions

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Introduction

Organic solar cells based on donor/acceptor (D/A) conjugated molecular bulk-heterojunction (BHJ) blend system have achieved a best photoelectric power conversion efficiencies (PCEs) of about 10% [1,2]. Among those BHJ systems, regio-regular poly-(3-hexylthiophene) (P3HT) is a conjugated polymer exhibiting one of the best values for polymer charge-carrier mobility, producing about 5% power conversion efficiency and an incident photon-to-current conversion efficiency (IPCE) of over 70% with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) under one Sun intensity and 1.5 AM solar radiation, which can be used as a reference solar cell. Some principle explanations for the unique characteristics of P3HT, in comparison to other polymers, are high degree of solid state crystallinity, excellent charge mobility, extended absorption in the red region, and good chemical stability [3-5].

To develop high efficiency polymer photoelectric conversion systems, as elaborated earlier, among the five organic photovoltaic transformation steps and the three major losses, it was believed that the “photon loss” in the first sunlight harvesting step and the carrier loss in the carrier transport step are the bottle neck steps. In this study, we intent to address the critical “photon loss” problems and the germinate charge carrier recombination problem via an energy level matched dye molecular units sensitized “three-component” polymer approach. This “three-component” system can further minimize the photon loss via

better energy matched and high light absorption coefficient dye molecular units, and also simultaneously minimize the photo generated opposite charge pair recombination via further separation of photo generated opposite charges into the donor and the acceptor moieties apart from the dyes similar like in a natural photosynthetic process.

Regio-regular poly-(3-hexylthiophene) (P3HT) and a serious of derivatives with subsequent end-group functionalization of the polymers have been studied by McCullough and his co-workers [6-10]. In the past ten years, many other researchers have developed the method to synthesize a serious of polythiophene derivatives and polythiophene diblock copolymers [11-13]. In order to capture more photon and prevent charge carriers from recombination, Hemin molecule was desirably to be attached covalently to the P3HT chains, and the (di) hydroxyl-terminated P3HT (HO/HOP3HT) was synthesized using Grignard metathesis (GRIM) polymerization, which was reported in the literature [7,14].

In this study, commercial Hemin with two -COOH groups provides convenient conditions of esterification with -OH group terminated P3HT, while the reaction of -COOH with -OH

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is not a spontaneous reaction in mild conditions and at room temperature. To enhance the reactivity of the alcohol group to the protoporphyrin, Sami Boufi used carbonyldiimidazole (CDI) as an activator and 1,8-diaminooctane and 1,4-phenylenediamine as spacer to overcome molecular hindrance problem [15], but the synthesis procedure was complicated. As one way to circumvent this problem, the Steglich esterification method, which was first described by Wolfgang Steglich in 1978 is a different process of dicyclohexylcarbodiimide as a coupling reagent and 4-dimethylaminopyridine as a catalyst [16]. Steglich esterification was accepted in this study due to the mild reaction condition and high conversion because of the favorable catalytic action of dimethyl aminopyridine.

Hemin contains a porphyrin ring with a ferric iron ion and a chloride ligand. Although the NMR spectra of synthetic and natural porphyrin complexes of high-spin and low-spin have been investigated, [16,17] Characterization of Hemin by NMR is still difficult in our case due to Hemin's poor solubility and molecular aggregation in solution. The good solvents for Hemin include DMSO, DMF, 5% aqueous sodium dodecyl sulfate, [16,17] etc., but polymer P3HT is insoluble in those solvent. On the other hand, because iron (III) is paramagnetic material, the porphyrin proton resonances are shifted due to the metal element, generally outside the normal diamagnetic region [17]. Because of the discussions above, NMR was not utilized in characterization of Hemin and monitoring esterification between hydroxyl-terminated P3HT and Hemin, alternative methods shall be utilized.

Experimental Section

Materials

2,5-Dibromo-3-hexylthiophene, isopropylmagnesium chloride solution in THF, [1,3-Bis(diphenylphosphino) propane] dichloronickel(II)(Ni(dppp)Cl₂), Phosphorus oxychloride (POCl₃), Dicyclohexylcarbodiimide(DCC), 4-(Dimethylamino)pyridine (DMAP), anhydrous Tetrahydrofuran(THF) were purchased from Sigma-Aldrich without further purification. [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) was used as received from Nano-C. N-Methylformanilide was purchased from Acros. Chloroporphyrin IX iron(III) (Hemin) and Lithium aluminum hydride(LiAlH₄) were purchased from Pfaltz and Bauer and used as received. Poly (3,4-ethylenedioxythiophene) (PEDOT):poly(styrene sulfonate) (PSS) (Clevios P VP Al 4083) was purchased from H. C. Stark and passed through a 0.25 μm filter before spin-coating.

Characterization

¹H NMR spectrums were obtained by a Bruker Advance 300 MHz spectrometer, and all NMR samples were dissolved in CDCl₃, unless

otherwise stated. Molecular weights of polymer samples were measured on a Viscotek Gel permeation Chromatography (GPC) system with a UV-VIS absorption detector at room temperature, and standard polystyrene (PS) was used as conventional calibration. Photoluminescence measurements were performed on an ISA Fluoromax-3 luminescence spectrofluorometer THF as solvent. UV-VIS spectrometer was obtained absorption maximum peak wavelength (λ_{max}) and optical energy gap (E_g^{opt}) of these polymers in THF solutions (PerkinElmer Lambda-1050 UV-VIS-NIR spectrometer). The current-voltage curves of the cells produced were measured under an AM 1.5G solar simulator with 100 mW/cm² intensity. The active areas of the cells were 0.2025 cm².

Fabrication of solar cell devices

For comparison studies, 11.55 mg P3HT-Hemin and 10 mg PCBM, 10 mg P3HT and 10 mg PCBM were dissolved in 1 mL 1,2-Dichlorobenzene (DCB) respectively, and the mixture solutions were stirred at room temperature for 24 hrs. 10 mg P3HT, 0.155 mg Hemin and 10 mg PCBM were dissolved in 1 mL mixture solvent of DCB and DMF (3:1, v/v).

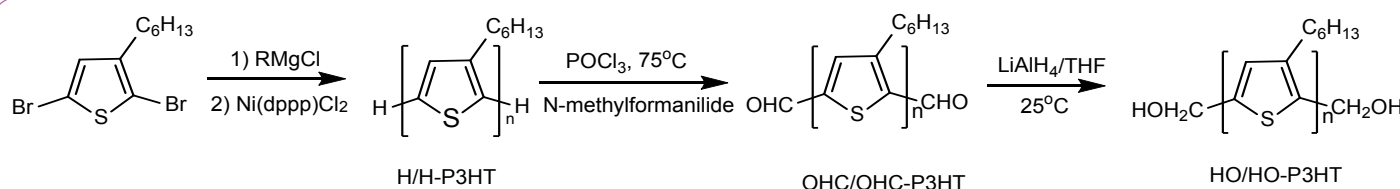
The ITO glass ($R_s=8-12 \Omega$) was cleaned by sequential 5 mins sonication in solutions of detergent, acetone, isopropyl alcohol and deionized water. The cleaned ITO glass was treated 15 mins UV-ozone to improve the wettability of PEDOT:PSS. Spin coat PEDOT:PSS aqueous solution (Clevios P VP Al 4083, from H.C. Starck) onto clean ITO glasses in 5000 rpm for 30 s forming 30 nm thin film in thickness, followed by drying in vacuum oven at 90°C for 1 hour to further get rid of the water in the PEDOT:PSS thin film. After cooling down to room temperature, the polymer mixture solution was spun on the top of dried "ITO/PDOT:PSS" film in 1000 rpm for 60 s, and when dried the polymer films by putting them in a high vacuum oven at 80°C for 30 mins. All solution samples were through 0.2 μm filter before spin coating. After cooling down to room temperature, evaporation of metal Al was performed in a glove box device with the pressure as low as $1-2 \times 10^{-7}$ mbar till the film thickness of 100 nm.

Synthetic Schemes and Procedures

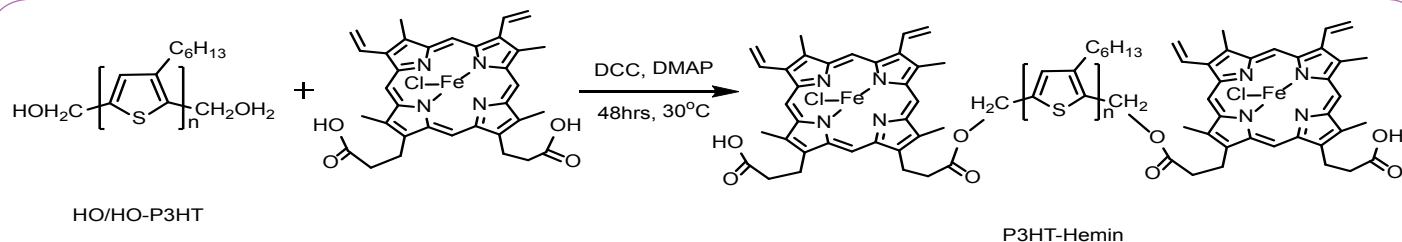
Synthetic scheme for hydroxyl terminated P3HT and P3HT-Hemin are given in Schemes 1 and 2

H/H Group Terminated Poly(3-hexylthiophene)

2,5-Dibromo-3-hexylthiophene (2.273 g, 6.96 mmol, 1 equiv.) was dissolved in anhydrous THF (50 mL) in a dry 100 mL three-neck flask under Argon. 2 M isopropylmagnesium chloride solution (3.48 mL, 6.96 mmol, 1 equiv.) in THF was added via a syringe, and the mixture was refluxed for 2 h. After cooling down



Scheme 1 Synthetic scheme for hydroxyl terminated P3HT.



Scheme 2 Synthetic scheme for the P3HT-Hemin.

to room temperature, Ni (dppp)Cl₂ (0.15 g, 0.27 mmol, 0.039 equiv.) was added to the flask. The reaction mixture was stirred at room temperature for 30 mins followed by the addition of 2 M isopropylmagnesium chloride solution (0.5 mL, 1 mmol, 0.14 equiv.) in THF. The reaction mixture was stirred at 70°C for 15 mins followed by adding 2 M HCl solution. Methanol was added after mixture cooling down room temperature, and brown precipitate polymer formed. The brown product was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform to gain H/H-P3HT (yield 36.4%). ¹H NMR (300 MHz, CDCl₃, ppm): δ=6.98 (s, 49H), 2.81 (t, J=8.0 Hz, 98H), 1.71 (m, 98H), 1.50-1.25 (m, 294H), 0.91 (t, J=7.0 Hz, 147H); GPC: Mn=8430, PDI=1.15.

OHC/OHC Group Terminated Poly(3-hexylthiophene) (OHC/OHC-P3HT)

H/H-P3HT (0.2 g) was dissolved in 50 mL anhydrous toluene in a dry flask under Argon. N-methylformanilide (2 mL, 18.4 mmol) and POCl₃ (1.4 mL, 15.1 mmol) were then added to the solution, and the reaction was stirred at 75°C for 24 hrs. After cooling to room temperature, saturated aqueous solution of sodium acetate was added and kept stirring for another 2 hrs, at which time methanol was added to reaction mixture to precipitate brown product. The polymer was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform. After removing chloroform in a vacuum, 0.195 g (yield 97.5%) of OHC/OHC-P3HT was obtained. ¹H NMR (300 MHz, CDCl₃, ppm): δ=10.02 and 9.99 (2H totally), 6.98 (s, 49H), 2.81 (t, J=8.0 Hz, 98H), 1.71 (m, 98H), 1.50-1.25 (m, 294H), 0.91 (t, J=7.0 Hz, 147H); GPC: Mn=8400, PDI=1.15.

CH₂OH/CH₂OH Group Terminated Poly(3-hexylthiophene) (HO/HO-P3HT)

A 100 mL three-neck flask was charged with OHC/OHC-P3HT (0.158 g) and anhydrous THF (40 mL) under argon, followed by addition of LiAlH₄ solution in THF (1 M, 1.2 mL) via a syringe. The mixture solution was stirred at room temperature for 1 h, at which time HCl (1 M, 2 mL) was added. The crude was precipitated in methanol and purified by sequential Soxhlet extraction with methanol, hexanes and chloroform to gain 0.15 g (yield 95%) HO/HO-P3HT. ¹H NMR (300 MHz, CDCl₃, ppm): δ=6.98 (s, 49H), 4.75 (s, 4H), 2.81 (t, J=8.0 Hz, 98H), 1.71 (m, 98H), 1.50-1.25 (m, 294H), 0.91 (t, J=7.0 Hz, 147H); GPC: Mn=8400, PDI=1.15.

Poly(3-Hexylthiophene)-Hemin (P3HT-Hemin)

In a 250 mL round-bottom flask, HO/HO-P3HT (50 mg, Mn=8400, Mw/Mn=1.15 by GPC) and Hemin (65.2 mg, 0.1 mmol) were

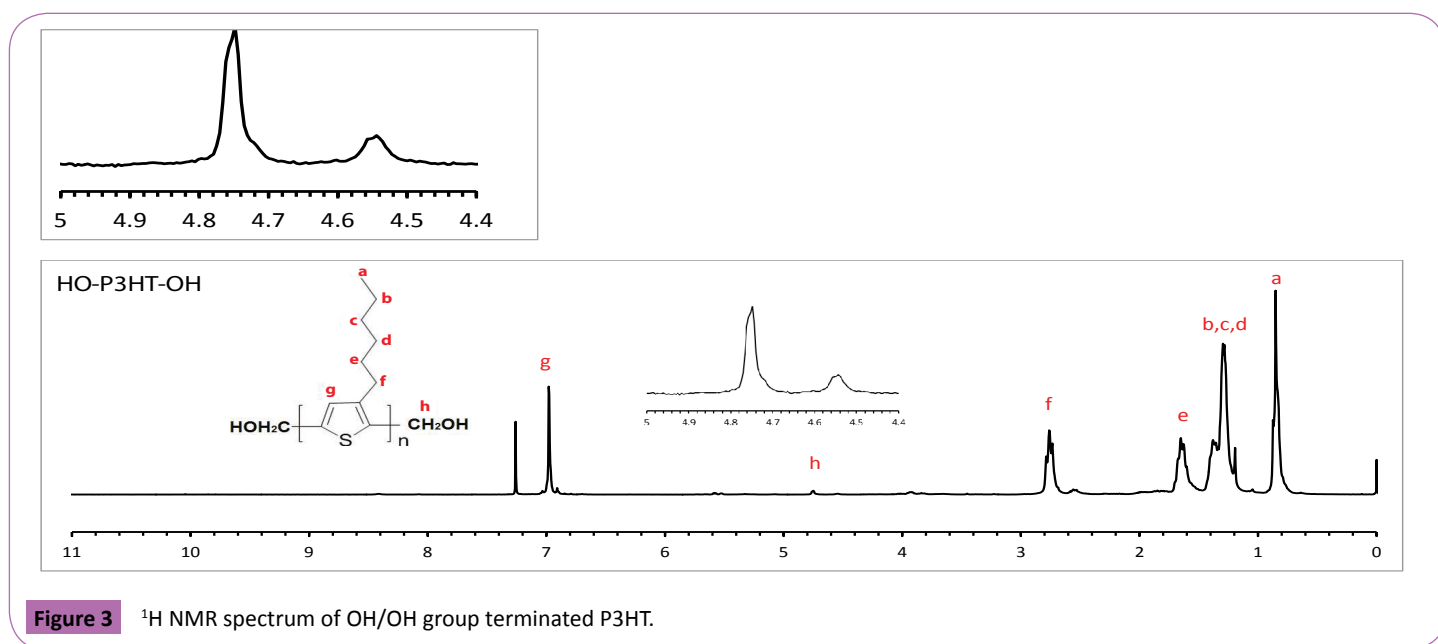
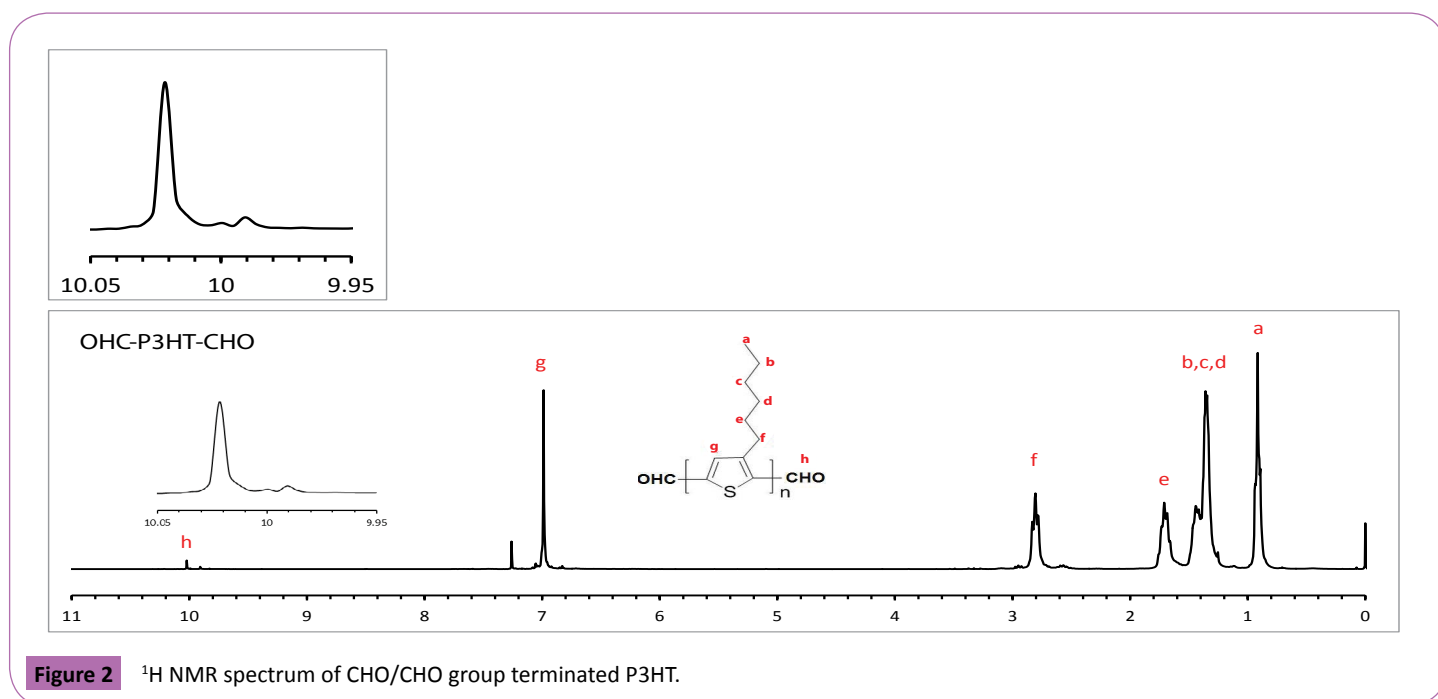
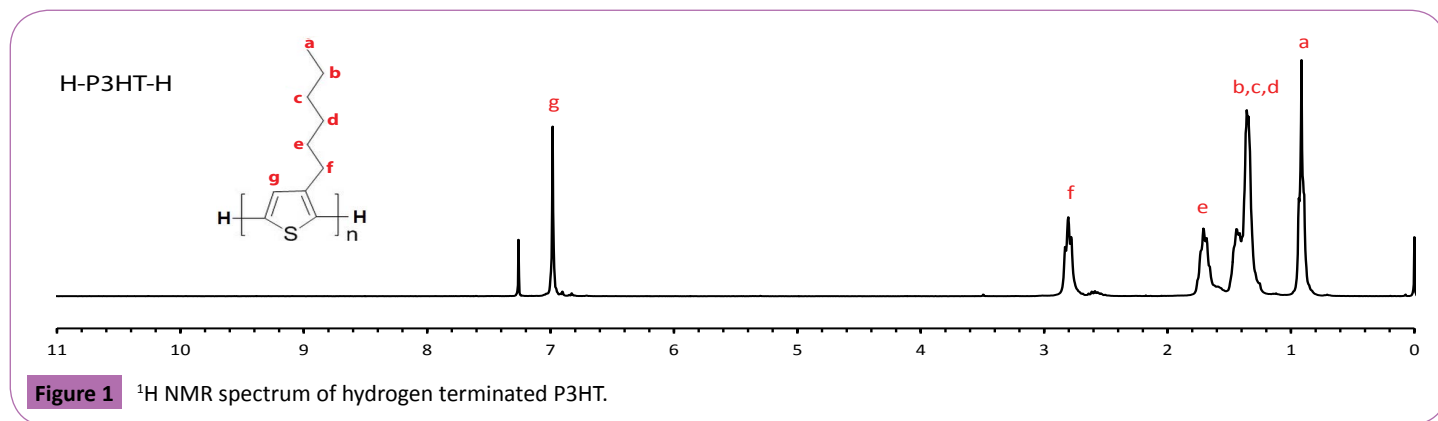
dissolved in anhydrous THF (160 ml) under Argon at 65°C and the reaction mixture was stirred for 1 h. After cooling down to room temperature, 4-Dimethylaminopyridine (DMAP, 3.66 mg, 0.03 mmol) were added to the reaction mixture. The mixture was kept stirring at room temperature for 30 mins, followed by the adding of 1,3-dicyclohexylcarbodiimide (DCC, 30.9 mg, 0.15 mmol) dissolved in anhydrous THF (10 mL), which was added dropwise using a syringe. The mixture was stirred at 40°C for 48 hrs. Brown precipitate polymer formed in methanol and purified by sequential Soxhlet extractions with methanol, hexanes. The polymer was isolated from the chloroform solution and dried under vacuum to give 48 mg (yield=83%) of desired product P3HT-Hemin. GPC: Mn=9600, PDI=1.15.

Results and Discussion

The synthetic routes for preparation of HO/HO-P3HT and P3HT-Hemin were shown in **Schemes 1 and 2**. The covalent P3HT-Hemin was prepared in four steps: (1) Synthesis of H/H-P3HT, (2) Synthesis of OHC/OHC-P3HT, (3) Synthesis of HO/HO-P3HT and (4) synthesis of P3HT-Hemin. By following the procedure reported in the literature [7,14], two sided hydroxypropyl-terminated P3HT (HO/HO-P3HT) was synthesized first, and then reacted with Hemin using the Steglich esterification, which preferred for its convenience and effectiveness. The reaction condition was mild, yet the conversion was high because of the favorable catalytic action of dimethylaminopyridine [16-19]. The formation of H/H-P3HT was identified by ¹H NMR (Figure 1). Two δ -CHO peaks of different intensity could be found from ¹H NMR spectrum of OHC/OHC-P3HT (Figure 2). The peak at δ 10.02 with highly dominant should be from the proton of -CHO at the 2-position end, and the other small peak at δ 9.99 was presumably assigned to the -CHO at the 5-position end. The NMR data of those two peaks indicated that 2-position chain ends had much higher abundance than 5-position ends in the product. The ¹H NMR integration indicated the polymer having 48 repeat units.

Figure 3 indicated that the OHC/OHC-P3HT was reduced by LiAlH₄ to HO/HO-P3HT. ¹H NMR spectra had confirmed the accomplishment of the reduction. The δ CHO peaks at 10.2 disappeared, and a new doublet peak at δ 4.75 was absorbed which belonged to the -CH₂OH [7] (Figure 3).

In this study, P3HT synthesized with a narrow molecular weight distribution (Mw/Mn=1.15) and reasonable molecular weight (Mn=8430, repeat unit=49) for solar cells application was obtained via precise controlling amount of Ni(dppp)Cl₂. The molecular weight difference between P3HT-Hemin and P3HT was 1200 Daltons, which was about the molecular weight summation of two Hemin molecules, indicating that P3HT chain was terminated



by two Hemin molecules. The repeat unit number of 49 obtained via gel permeation chromatography (GPC) (Table 1) very closed to 48 repeat units in ^1H NMR (Figure 1). P3HT-Hemin molecules with one response peak had short elution time comparing to P3HT/Hemin blend with two response peaks, which also testified that P3HT-Hemin was not simply physical mixture of P3HT/Hemin. (Figure 4)

Figure 5 showed the UV-visible absorption spectra of P3HT, Hemin, P3HT-Hemin and P3HT/Hemin blend in THF solution. The maximum absorption wavelength (λ_{max}) of P3HT-Hemin at 419 nm was blue shifted comparing to pure P3HT molecules with λ_{max} at 445 nm, and also was different with the absorption spectra of P3HT/Hemin blend and pure Hemin molecules, which implied that covalent P3HT-Hemin was synthesized successfully via the Steglich esterification.

The photoluminescence (PL) comparison of P3HT and P3HT-Hemin in THF solution was shown in **Figure 6**. P3HT and P3HT-Hemin samples with the same concentration (1.0×10^{-4} M) were excited respectively using the same excitation wavelength of 400 nm. The photoluminescence of P3HT-Hemin solution exhibited dramatically quenching performance, and the maximum PL intensity was more than 58% PL quenching compared to pure P3HT solution at 470 nm and 468 nm, respectively. The PL quenching was because electrons transferred from P3HT section as donor to Hemin section as acceptor in P3HT-Hemin molecules.

The performance of the fabricated solar cell devices was

Table 1: GPC parameters of HO-P3HT-OH and P3HT-Hemin.

	HO-P3HT-OH	P3HT-Hemin
Mn - (Daltons)	8430	9638
Mw - (Daltons)	9666	11012
Mz - (Daltons)	10860	12345
Mp - (Daltons)	9398	10663

measured using an AM 1.5 G solar simulator with about one Sun intensity (100 mW/cm^2), where the device scheme are shown in Figure 7.

Figure 8 and Table 2 indicated that P3HT-Hemin/PCBM solar cell devices exhibited 63% enhancement of power conversion efficiency (PCE), 9.8% enhancement of J_{sc} , and 28.6% enhancement of V_{oc} than the P3HT/Hemin/PCBM blend cells, and 16% enhancement of V_{oc} than P3HT/PCBM cells. Better photo induced charge separation appears to be the key factor in P3HT-Hemin/PCBM cells due to more convenient reach of photo generated excitons toward the P3HT-Dye interface.

Conclusions

The NMR, GPC, UV-vis, and PL quenching data provided evidences that P3HT-Hemin covalent system was synthesized successfully via esterification between HO/HO-P3HT and Hemin. P3HT-Hemin/PCBM solar cell devices exhibited 63% enhancement of PCE and 9.8% enhancement of J_{sc} than the P3HT/Hemin/PCBM blend cells, and 16% enhancement of V_{oc} than P3HT/PCBM cells. Better photo induced charge separation appears to be the key factor in P3HT-Hemin/PCBM cells due to more convenient reach of photo generated excitons toward the P3HT-Hemin interface. Further systematic optimizations involving better molecular dye units, and better polymer solid state morphologies are expected to further increase the overall device optoelectronic efficiencies.

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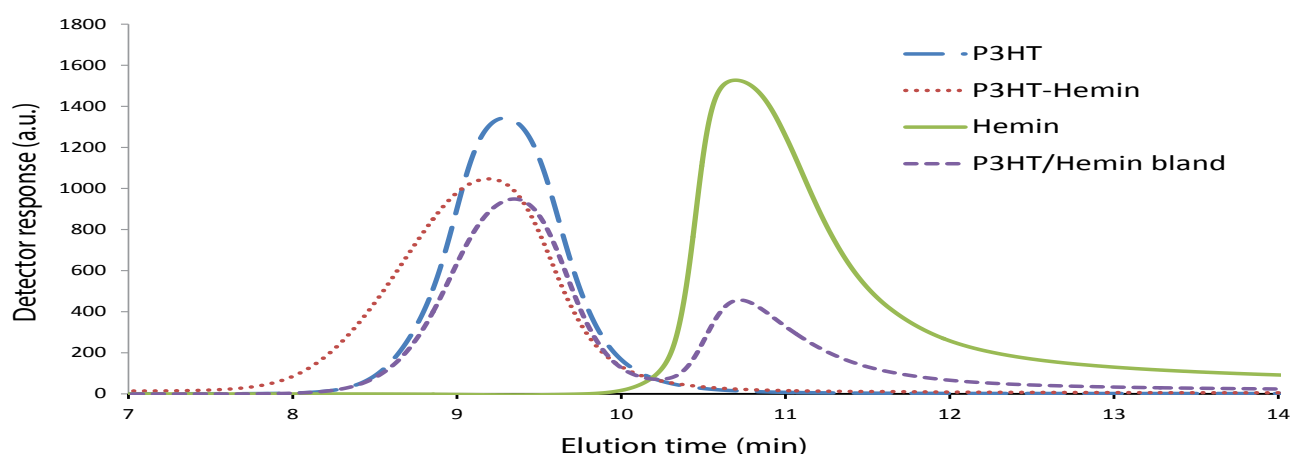


Figure 4 GPC traces of HO-P3HT-OH, Hemin, P3HT/Hemin blend and P3HT-Hemin covalent system.

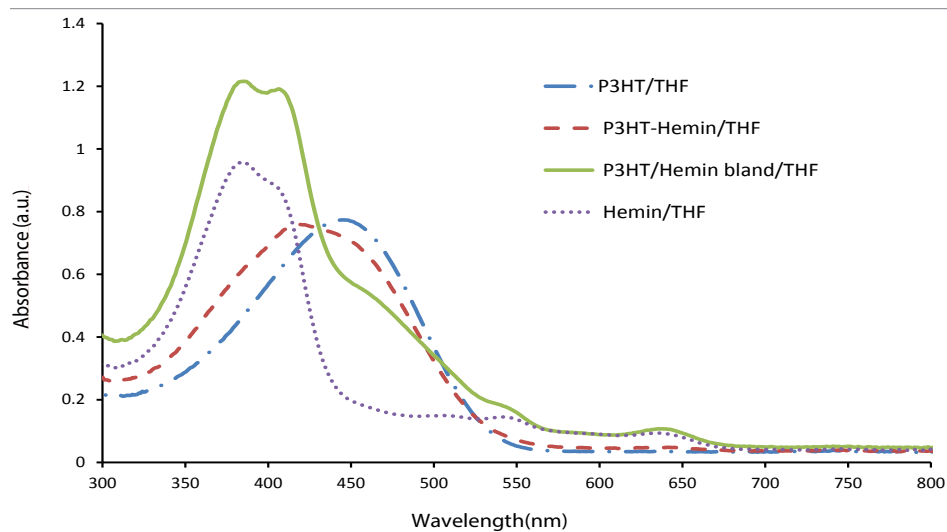


Figure 5 UV-visible absorption spectra of P3HT, Hemin, P3HT-Hemin covalent system and P3HT/Hemin blend in THF.

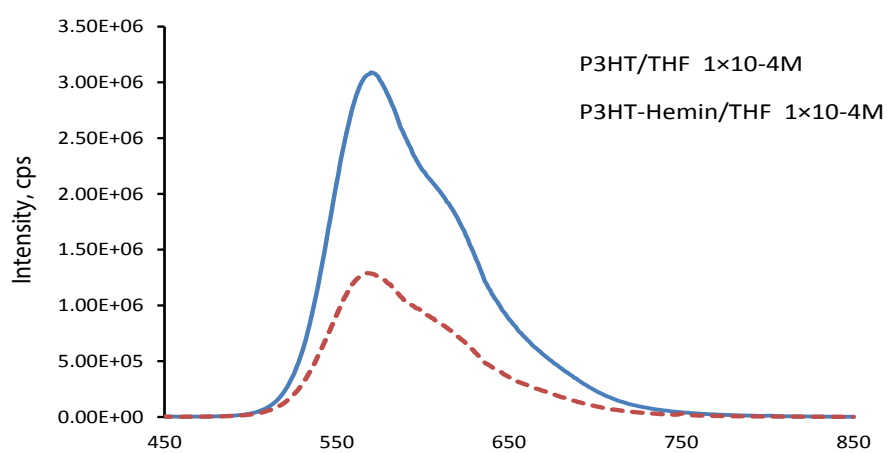


Figure 6 PL spectrum of P3HT and P3HT-Hemin, $1 \times 10^{-4} M$.

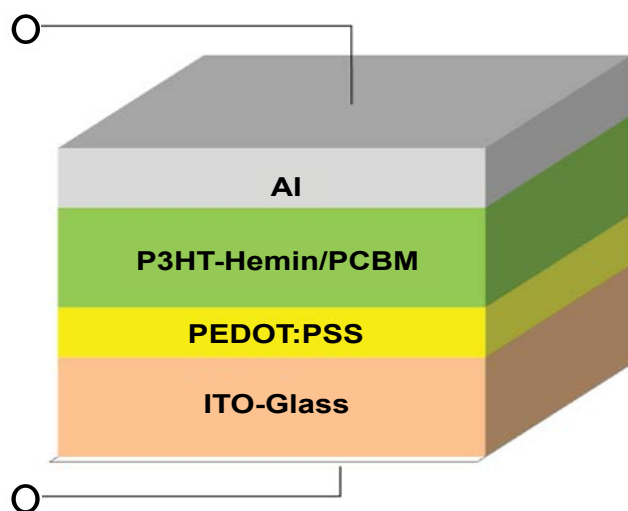


Figure 7 Schematic of device structure of P3HT-Hemin/PCBM.

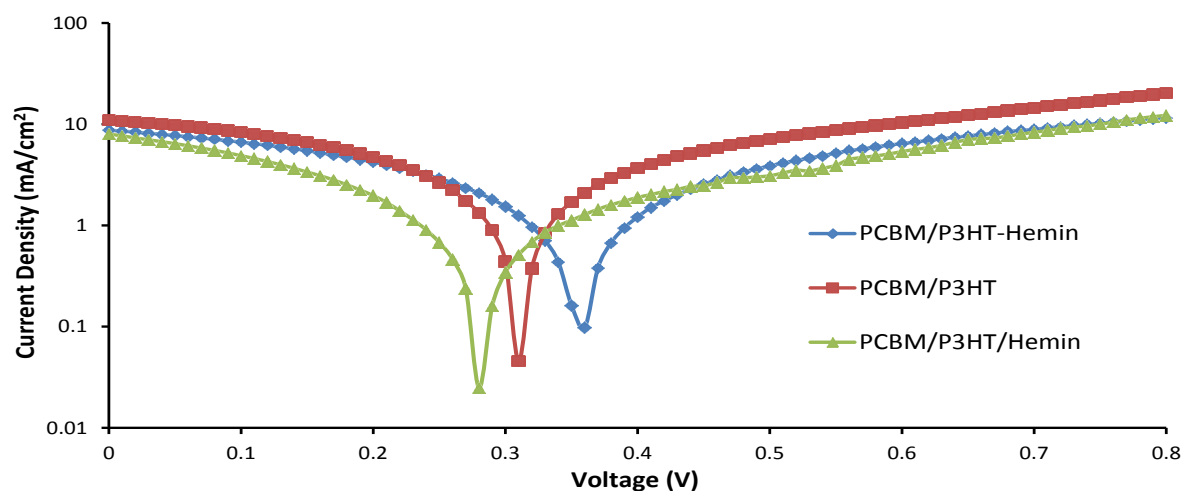


Figure 8 The J-V curves of P3HT/PCBM, P3HT-Hemin/PCBM and P3HT/Hemin/PCBM solar cells.

Table 2 The photovoltaic parameters of P3HT-Hemin/PCBM, P3HT/PCBM and P3HT/PCBM/Hemin (Un-calibration).

	P3HT-Hemin/ PCBM	P3HT/PCBM	P3HT/PCBM/ Hemin
J_{sc} , mA/cm ²	8.74	11.00	7.96
Voc, V	0.36	0.31	0.28
FF, %	27.14	29.61	23.17
PCE, %	0.86	1.02	0.53

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