Synthesis and Characterization of Polythiophene Block Copolymer and Fullerene Derivative Capable of "Three-Point" Complementary Hydrogen Bonding Interactions and Their Application in Bulk-Heterojunction Solar Cells

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ABSTRACT: We report the synthesis and characterization of a polythiophene block copolymer (P4) selectively functionalized with diaminopyrimidine moieties and a thymine tethered fullerene derivative (F1). Self-assembly between P4 and F1 through "three-point" complementary hydrogen bonding is studied by ¹H NMR spectroscopy and differential scanning calorimetry. A large Stern-Volmer constant (K_{SV}) of 1.2×10^5 M⁻¹ is observed from fluorescence quenching experiments, revealing strong complexation between these two components. Solar cells employing P4 and F1 at different weight ratios as active layers are fabricated and tested; corresponding thin film

INTRODUCTION Best performing polymer solar cell (PSC) devices¹⁻⁴ are typically fabricated by blending conjugated polymers and fullerene derivatives to form the so-called bulk heterojunction (BHJ) morphology characterized as an interpenetrating donor-acceptor binary network with domain sizes on the nanometer scale.⁵⁻⁸ However, BHJ is intrinsically at a thermodynamic meta-stable state that causes environmental instability and reduced cell lifetimes.9,10 One of the most studied methodologies toward stable BHJs in PSCs is selfassembly of conjugated block copolymers (BCPs) having electron acceptors selectively attached to one block.11-16 Most existing examples of this type have fullerene derivatives attached to conjugated backbones via covalent linkages.^{13,17-21} Fullerene concentrations in these examples are generally low due to limited solubility and strong aggregation tendency of fullerenes. An intriguing alternative approach is to attach fullerene acceptors onto conjugated polymer backbones non-covalently, by which fullerene loading percentages can be easily adjusted and solubility of the resulting complexes can be enhanced. Several recent reports have described complexation between fullerene derivatives and polythiophene based diblock and random copolymers

morphologies are studied in detail by optical imaging and atomic force microscopy. Correlations between polymer complex structures, film morphologies, and device performance are discussed. Thermal stability of benchmark poly(3-hexylthiophene) bulk heterojunction solar cells is found to be improved by the addition of a few weight percent of P4/F1 complexes as compatibilizers. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

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through "single-point" hydrogen bonding^{22,23} and π - π ²⁴ interactions. However, these interactions are relatively weak. Complementary hydrogen bonding is among the strongest and most studied non-covalent interactions and has found widespread applications in supramolecular chemistry.²⁵ In this article, we describe the synthesis and characterization of a polythiophene diblock copolymer and a fullerene derivative bearing diaminopyrimidine and thymine moieties, respectively. Complexation between these two components via "three-point" complementary hydrogen bonding^{26,27} was studied in detail, which showed strong interactions leading to stabilized morphologies. We also investigated the solar cell device performance employing P4/F1 blends at varied weight ratios. Additionally, P4/F1 complexes were applied as compatibilizers in order to improve the stability of benchmark BHJ PSCs.

EXPERIMENTAL

Materials and General Methods

All reagents and solvents were used as received from Sigma-Aldrich or VWR unless otherwise noted. 2-Bromo-3-hexyl-5-iodo-thiophene (M1),²⁸⁻³¹ ((6-(2-bromo-5-chloromagnesiothiophen-

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1

3-yl)hexyl)oxy)(*tert*-butyl)dimethylsilane (M2),^{32,33} 4-((6-bromohexyl)oxy)benzaldehyde (M4)^{34–36} were synthesized according to previously reported procedures. THF was distilled from Na/benzophenone prior to use. Anhydrous chloroform was obtained by distillation over CaH₂ and degassed through several freeze-pump-thaw cycles. ¹H (300.13 MHz) and ¹³C NMR (75.48 MHz) spectra were recorded on a Bruker Avance III Solution 300 spectrometer. All solution ¹H and ¹³C NMR spectra were referenced internally to solvent signals. Size exclusion chromatography (SEC) analyses were performed in chloroform with 0.5% (v/v) triethylamine (1 mL/ min) using a Waters Breeze system equipped with a 2707 autosampler, a 1515 isocratic HPLC pump, and a 2414 refractive index detector. Two styragel columns (Polymer Laboratories; 5 μ m Mix-C), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with polystyrene standards (Varian). Ultraviolet-visible (UVvis) absorption spectra were recorded on a Shimadzu UV-2401 PC spectrometer over a wavelength range of 240-800 nm. Fluorescence emission spectra were obtained using a Varian Cary Eclipse Fluorimeter. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC STAR^e system with about 10 mg sample and at a scan rate of 10 °C/min. The results reported are from the first cooling and second heating cycles. High resolution mass spectrometry (HRMS) was performed on a Waters/Micromass LCT Premier system operating under electrospray ionization (ESI) mode. Cyclic Voltammetry was performed at 25 °C on a CH Instrument CHI604xD electrochemical analyzer using a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode calibrated using ferrocene redox couple (4.8 eV below vacuum). Optical Microscopy images were taken from an Axio Imager A2 instrument under bright field. Powder X-ray diffraction measurements were performed on a Rigaku SmartLab instrument. Atomic force microscopy (AFM) images were obtained on a Thermomicroscopes Autoprobe CP Research AFM instrument operated under tapping mode. For the solution binding constant studies, an S5 solution in CDCl₃ (0.2 M) was gradually added into a F1 solution in $CDCl_3$ (4 mM) in a NMR tube. After each addition, the solution was allowed to equilibrate for 5 min and subjected to ¹H NMR measurements.

Solar Cell Fabrication and Testing

Blend solutions were prepared by dissolving **P4** and **F1** at predetermined weight ratios in chlorobenzene and the concentration of **P4** was kept at 1 wt %. Poly(3-hexylthiophene) (P3HT; synthesized in-house; $M_n = 26,077$, $M_w = 27,120$, PDI: 1.04)/phenyl-C61-butyric acid methyl ester (PCBM; American Dye Source) blend solutions were prepared by dissolving P3HT/PCBM (1:1 in weight) in chlorobenzene at a total concentration of 20 mg/mL. The compatibilizer solution was prepared by dissolving **P4** and **F1** (1:1 in weight) in chlorobenzene at a total concentration of 2 wt %, and stirred at 100 °C for 3 h. The compatibilizer solutions of predetermined volumes were then added to the P3HT/PCBM solution using microsyringes to form mixture solutions. All solutions were stirred at 100 °C for 10 h in a nitrogen glove box

(Innovative Technology, model PL-He-2GB, O₂ < 0.1 ppm, $H_2O < 0.1$ ppm) before device fabrication. Solar cell devices were fabricated according to the following procedure: ITOcoated glass substrates (China Shenzhen Southern Glass Display, 8 Ω/\Box) were cleaned by ultrasonication sequentially in detergent, DI water, acetone, and isopropyl alcohol, each for 15 min. These ITO-coated glass substrates were further treated by UV-ozone (PSD Series, Novascan) for 45 min before being transferred to a nitrogen glove box (Innovative Technology, model PL-He-4GB-1800, $O_2 < 0.1$ ppm, $H_2O <$ 0.1 ppm) for MoO₃ deposition. MoO₃ (10 nm) was deposited using an Angstrom Engineering Åmod deposition system at a base vacuum level $< 7 \times 10^{-8}$ Torr. The polymer/fullerene blend solution was first filtered through a 1 μ m PTFE filter and spin-coated on top of the MoO₃ layer at 400 rpm for 30 s. Al (100 nm) was thermally evaporated through patterned shadow masks as anodes. Current-voltage (I-V) characteristics were measured by a Keithley 2400 source-measuring unit under simulated AM1.5G irradiation (100 mW/cm⁻²) generated by a Xe arc-lamp based Newport 67005 150-W solar simulator equipped with an AM1.5G filter. The light intensity was calibrated by a Newport thermopile detector (model 818P-010-12) equipped with a Newport 1916-C optical power meter.

2,6-Bis(hexylamino)pyrimidin-4-ol (M3)

To a 100 mL flask was added 3 g 2,6-diaminopyrimidin-4-ol (23.8 mmol) and 17 mL hexanoic anhydride (71.4 mmol). The solution was refluxed for 4 h with vigorous stirring. During the reflux, the solution may become solidified. The solid was washed with copious CHCl₃ and isolated by gravity filtration. The product, N,N'-(6-hydroxypyrimidine-2,4-diyl)dihexanamide, was isolated by recrystallization from MeOH/ $CHCl_3$ as a white powder (6.8 g, 89%). ¹H NMR (300.13) MHz, DMSO-d₆, δ): 0.84-0.88 (m, 6H), 1.25-1.30 (m, 8H), 1.52-159 (m, 4H), 2.39 (t, 2H, J = 7.5 Hz), 2.46 (t, 2H, J = 7.5 Hz), 6.67 (s, 1H),9.93 (s, 1H), 11.23 (s, 1H), and 11.68 (s, 1H). ¹³C NMR (75.48 MHz, DMSO-d₆, δ): 176.6, 173.1, 161.7, 156.6, 150.4, 92.7, 36.2, 36.0, 30.8, 30.6, 24.4, 24.0, 21.9, 21.8, and 13.8. To a 250 mL, Schlenk flask equipped with a septum and a stir bar was added under nitrogen 1.0 g N,N'-(6-hydroxypyrimidine-2,4-diyl)dihexanamide (6.20 mmol) and about 100 mL anhydrous THF and the flask was placed in an ice bath for 10 min. $NaBH_4$ (0.59 g; 31.02 mmol) was added into the solution portion-wise during a period of 5 min, and the resulting solution was kept at 0 °C for 10 min before 1.92 mL (31.02 mmol) BF₃•Et₂O was added to the solution dropwise. The reaction mixture was kept at 0 $^\circ$ C for 1 h and then warmed up to room temperature. The reaction mixture was stirred for another 5 h and poured into a large excess of water. The water solution was extracted with EtOAc (50 mL \times 2) and the combined organic layers were washed with saturated NaHCO₃ (50 mL) solution and brine (50 mL). The organic layer was dried over Na₂SO₄ and volatile materials were removed under reduced pressure. M3 was obtained as a white solid (550 mg, 60%) through column chromatography with DCM/MeOH (100/3, v/v) as the eluent. ¹H NMR (300.13 MHz, CDCl₃, δ): 0.83–0.89 (m, 6H),

1.25–1.36 (m, 12H), 1.38–1.57 (m, 4H), 3.08 (d, 2H, J = 6.0 Hz), 3.23–3.29 (m, 2H), 4.66 (s, 1H),4.73 (t, 1H, NH), 6.42 (s, 1H, NH), 11.06 (s, 1H, OH). ¹³C NMR (75.48 MHz, CDCl₃, δ): 165.8, 164.9, 154.3, 75.4, 42.1, 40.8, 31.7, 31.6, 29.5, 29.3, 26.8, 26.7, 22.7, 14.2, and 14.1. HRMS (ESI): calcd. for C₁₆H₃₀N₄O, 295.2420 [M + H]; found, 295.2491 [M + H].

4-((6-(5-Methyl-2,4-dioxo-3,4-dihydro pyrimidin-1(2H)yl)hexyl)oxy)benzaldehyde (M5)

The synthsis of M5 is similar to previously reported literature procedures.³⁷ K₂CO₃ (3.18 g, 23 mmol) was added to a solution of thymine (2.92 g, 23 mmol) in 200 mL DMF and the solution was stirred at 80 °C for 1 h. 4-((6-Bromohexyl)oxy)benzaldehyde (M4) (6.6 g, 23 mmol) in 20 mL DMF was then added dropwise and the reaction mixture was kept at 80 °C overnight. DMF was removed under vacuum and the residue was dissolved in 100 mL CH₂Cl₂. The organic layer was washed twice with water and dried over Na₂SO₄. After removal of CH₂Cl₂ under reduced pressure, column chromatography with DCM/EtOAc (1/1, v/v) gave M5 as a white solid (2.54 g, 33.4%). ¹H NMR (300.13 MHz, $CDCl_3$, δ): 1.44-1.83 (m, 8H), 1.90 (s, 3H), 3.71 (t, 2H, J = 7.2 Hz), 4.04 (t, 2H, J = 6.0 Hz), 6.96 (d, 3H, J = 5.4 Hz), 7.83 (d, 2H, J =5.4 Hz), and 9.86 (s, 1H). ¹³C NMR (75.48 MHz, CDCl₃, δ): 190.9, 164.5, 164.2, 151.1, 140.4, 132.1, 129.9, 114.8, 110.8, 68.2, 48.5, 29.1, 29.0, 26.2, 25.8, and 12.4.

1-(1-Methylfulleropyrrolidin-2-yl)-4-((6-(5-methyl-2,4dioxo-3,4-dihydropyrimidin-1(2H)-yl)hexyl)oxy)benzene (F1)

The synthesis of **F1** is similar to reported procedures.^{38,39} A solution of C60 (436.4 mg, 0.606 mmol), N-methylglycine (81 mg, 0.909 mmol), and M5 (200 mg, 0.808 mmol) in toluene (100 mL) was heated at reflux for 15 h under nitrogen. After removal of solvent under reduced pressure, the crude product was purified by column chromatography using DCM/EtOAc (7/3, v/v) as a brownish powder (146 mg, 23%). ¹H NMR (300.13 MHz, CDCl₃, δ): 1.40–1.54 (m, 6H), 1.69-1.81 (m, 4H), 1.90 (s, 3H), 2.78 (s, 3H), 3.69 (t, 2H, J = 7.2 Hz), 3.96 (t, 2H, J = 6.3 Hz), 4.24 (d, 1H, J = 12.3 Hz), 4.88 (s, 1H), 4.98 (d, 1H, J = 9.3 Hz), 6.95 (t, 3H, J = 11.7 Hz), 7.70 (d, 2H, J = 5.7 Hz), 7.97 (s, 1H). HRMS (ESI): Calcd. for C₈₀H₂₇N₃O₃, 1078.2130 [M+], 1079.2163 for [M + H]; found, 1078.2111 [M+], 1079.2162 [M+H]. Cyclic voltammetry (0.1 M TBAPF₆ in THF, 100 mV/s, vs. Fc/Fc⁺): $E_{1/2}(1) =$ -1.04 V, $E_{1/2}(2) = -1.60$ V, and $E_{1/2}(3) = -2.21$ V.

N2,N4-dihexyl-6-(hexyloxy) pyrimidine-2,4-diamine (S5)

In a 25 mL flask added 200 mg **M3** (0.679 mmol), 0.08 mL bromohexane (0.543 mmol), 141 mg K_2CO_3 (1.102 mmol), and 5 mL anhydrous DMF. The solution was heated at 80 °C overnight and then poured into a large excess of water. The aqueous phase was extracted with 10 mL EtOAc for three times and the combined organic layer was washed with water and brine. The organic layer was then dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified via column chromatography (DCM/EtOAc = 10/1, v/v) to yield **S5** (146 mg, 71%) as the

small molecule model compound. ¹H NMR (300.13 MHz, CDCl₃, δ): 0.86–0.88 (m, 9H), 1.29–1.39 (m, 18H), 1.50–1.54 (m, 4 H), 1.65–1.74 (m, 2H), 3.12 (q, 2H, *J*1 = 6.3 Hz, *J*2 = 6.9 Hz), 3.31(q, 2H, *J*1 = 6.3 Hz, *J*2 = 6.9 Hz), 4.16 (t, 2H, *J* = 6.6), 4.61 (d, 1H, *J* = 5.1 Hz), 4.71 (t, 1H, *J* = 5.4 Hz), 5.05 (s, 1H). ¹³C NMR (75.48 MHz, CDCl₃, δ): 171.1, 165.3, 162.2, 74.9, 65.8, 41.8, 41.5, 31.7, 31.7, 30.0, 29.5, 29.2, 26.8, 25.8, 22.7, and 14.1.

Block copolymer P2

The precursor block copolymer P2 was prepared through modified procedures according to literature reports.⁴⁰⁻⁴³ Two three-necked round-bottomed flasks (250 and 50 mL) equipped with stopcock and septa were flamed dried under high vacuum and cooled to room temperature under N₂. Monomer M1 (1.482 g, 3.972 mmol) was placed in the 250 mL flask under N₂, and then evacuated under high vacuum to remove any residual water and oxygen. After adding dry THF (40 mL) into the flask via a syringe, the solution was cooled to 0 °C. A 2M solution of *i*-PrMgCl in THF (2 mL, 3.972 mmol) was added via syringe and the mixture was stirred at 0 °C for 30 min (solution 1). In the other 50 mL flask, 0.5 g (0.993 mmol) ((6-(2-bromo-5-iodothiophen-3yl)hexyl)oxy)(tert-butyl)dimethylsilane was first reacted with 0.5 mL i-PrMgCl in the presence of 42 mg LiCl (0.943 mmol) in 10 mL THF (solution 2) to yield M2. Solution 1 was heated up to 35 °C and Ni(dppp)Cl₂ catalyst (21.52 mg, 0.0397 mmol), which was suspended in 5 mL dry THF, was added in one portion. The reaction mixture was stirred at 35 °C for 15 min and an aliquot was withdrawn with a syringe and injected into a methanol solution to give P1 for SEC analysis (RI, CHCl₃, 1 mL/min: $M_{\rm n} = 23,645, M_{\rm w} = 25,082$, PDI = 1.07). Solution 2 containing M2 was then transferred to solution **1** via a cannula. The resulting red solution was stirred at 35 °C for 1 h before 0.5 mL EtMgCl solution (2 M in THF) was added. The polymer was isolated by precipitation into MeOH and successively washed by Soxhlet extraction using methanol, acetone, and chloroform. The polymer was recovered by precipitation of the chloroform solution into methanol and dried under high vacuum to give a black solid (0.8 g, 83%). ¹H NMR (300.13 MHz, CDCl₃, δ): 0.041 (s), 0.070 (s), 0.8-0.94 (m), 1.25-1.73 (m), 2.81(t), 3.61 (t), 6.98 (s). SEC (RI, CHCl₃ 1 mL/min): $M_{\rm n}$ = 36,683, $M_{\rm w}$ = 38,094, PDI = 1.04.

Block copolymer P3

In a 100 mL Schlenk flask was added 200 mg polymer **P2** and 20 mL THF under N₂. The solution became clear after stirring at 60 °C for about 30 min. Tetrabutylammonium fluoride (TBAF) solution (0.2 mL, 2M in THF) was then added dropwise via syringe. The reaction mixture was kept stirring at 60 °C for 8 h and concentrated under reduced pressure to about 5 mL. **P2** was recovered as a black solid by precipitation into a mixture of methanol and acetone (1/1, v/v) and dried under vacuum overnight (168 mg 95%). ¹H NMR (300.13 MHz, CDCl₃, δ): 0.915 (t), 1.25–1.73 (m), 2.04 (s), 2.81 (t), 3.66 (t), 6.98 (s). SEC (RI, CHCl₃ 1 mL/min): $M_n = 25,830$, $M_w = 29,572$, PDI = 1.15.





SCHEME 1 Synthesis of polymers and fullerene derivative.

Block copolymer P4

In a 50 mL Schlenk flask was added 100 mg P3 and 157 mg 2,6-bis(hexylamino)pyrimidin-4-ol M3 (0.532 mmol), 139 mg PPh₃ (0.532 mmol), and 20 mL THF under N₂. The mixture was stirred at 60 °C for about 30 min and became a clear solution. Diisopropyl azodicarboxylate (0.11 mL, 0.532 mmol) was then added dropwise via syringe. The reaction mixture was kept stirring at 60 °C for 24 h and concentrated under reduced pressure to about 5 mL. The crude polymer was isolated by precipitation into a methanol water mixture (4/1, v/ v) and successively Soxhlet extracted using methanol, acetone, and chloroform. The chloroform solution was concentrated and precipitated into MeOH to give P4 as a black solid (110 mg, 84%). ¹H NMR (300.13 MHz, CDCl₃, δ): 0.91 (t), 1.25– 1.71 (m), 2.80 (t), 3.12 (br), 3.32 (br), 3.49 (br), 3.64 (br), 4.19 (br), 4.92 (br), 5.04 (br), 6.98 (s). SEC (RI, CHCl₃ 1 mL/ min): $M_{\rm n} = 29,501$, $M_{\rm w} = 37,577$, and PDI = 1.27.

The synthesis of the random copolymer P4' bearing 20 mol % diaminopyrimidine functionality was similar to that of its

analogous block copolymer **P4** (Scheme 2). Yield: 80%. ¹H NMR (300.13 MHz, CDCl₃, δ): 0.85–0.91 (m), 1.25–1.71 (m), 2.57 (s), 2.81 (t), 3.12–3.14 (m), 3.28–3.34 (m), 3.66 (br), 4.18 (t), 4.49 (s), 4.61 (s), 5.05 (s), and 6.98 (s). SEC (RI, CHCl₃ 1 mL/min): M_n = 41,905, M_w = 95,007, PDI = 2.27.

RESULTS AND DISCUSSION

Synthesis and Characterization

Chemical synthesis of the diaminopyrimidine functionalized block copolymer (**P4**) and thymine tethered fullerene derivative (**F1**) is shown in Scheme 1; ¹H NMR spectra and SEC profiles of the polymers are shown in Figure 1.

Monomers **M1** and **M2** were sequentially polymerized using a typical Grignard metathesis polymerization protocol.⁴⁴ An **M1/M2** ratio of 4/1 was chosen in this study and **M2** was added at about 70% **M1** conversion during the polymerization to ensure complete chain extension. As a result, the longer block in **P2** has the structure of regio-regular poly(3-



SCHEME 2 Synthesis of model compound S5 and a random copolymer P4'.

hexylthiophene) (P3HT, i.e., **P1**) and the shorter block is expected to be a random copolymer of **M1** and **M2**. From ¹H NMR analysis, functional group concentration of **P2** is estimated to be about 16%. From SEC results (for **P1**, M_n = 23,645, M_w = 25,082; for **P2**, M_n = 36,683, M_w = 38,094) the block length ratio is calculated to be about 2.5 and the **M1/M2** ratio in the shorter random copolymer block is about 2/3. Controllability of the polymerization was confirmed by kinetic studies (Supporting Information Fig. S1) and SEC measurements. As seen in Figure 1 (insert), SEC traces of both **P1** and **P2** have symmetrical shapes and narrow polydispersities (PDIs). The lack of low molecular weight shoulder in the SEC profile of **P2** indicates quantitative chain extension of **P1** and the formation of block copolymers in the absence of homopolymers.

The hydroxyl functionalized block copolymer P3 was then obtained through deprotection of silvlether moieties in P2 using TBAF. Complete disappearance of ¹H NMR signals of the silvl groups at 0.04 and 0.89 ppm in the spectrum of P3 indicates quantitative chemical transformation. The SEC trace of P3 tails toward longer elution times and gives somewhat lower molecular weight than expected, which is possibly caused by interactions between the polar hydroxyl groups and column materials. Finally, diaminopyrimidine moieties were installed through Mitsunobu reaction between P3 and M3. ¹H NMR signals for the oxygen bound methylene groups in P4 downfield shifts to 4.19 ppm from 3.66 ppm as in P3, the integration of which gives about 15% functional group concentration, indicating nearly quantitative functionalization. To further elucidate the structure of P4, a similar random copolymer P4' containing 20% diaminopyrimidine

functionality and a small molecule model compound **S5**, the hexyloxy substituted **M3**, were synthesized (Scheme 2). Close match between ¹H NMR spectra of both the polymers and model compound (Fig. 2) unambiguously confirms the chemical structure of **P4**.

It was noticed that ¹H NMR signals of the diaminopyrimidine moieties in **P4** are broader and less resolved than those of **P4**['], which is presumably caused by interchain and intrachain hydrogen bonding between the functional groups and the much higher functional group concentration in **P4** (60% within the functionalized block). The SEC profile of **P4** also shows both a high molecular weight shoulder and low molecular weight tail (Fig. 1, insert), likely due to such hydrogen bonding interactions as well as interaction with column materials.

Powder X-ray scattering measurements (Supporting Information Fig. S2) were performed on **P4** to assess the influence of hydrogen bonding units on molecular packing of the P3HT main chain. Two major scattering peaks are clearly seen at 2θ values of 5.469 and 23.737°, corresponding to dspacings of 16.15 and 3.75 Å, respectively. These numbers are very similar to but slightly smaller than respective lamellar and π - π stacking distances observed in thin films and nanofibers of regioregular P3HT homopolymers.⁴⁵⁻⁴⁷ This indicates that the pyrimidine moieties on **P4** do not significantly change the main chain packing motif except slightly reducing intermolecular distances possibly caused by selfcomplementary hydrogen bonding interactions.

The thymine tethered fullerene derivative, **F1**, was prepared through a Prato-type addition reaction as shown in Scheme





FIGURE 1 ¹H NMR spectra of P1, P2, P3, and P4 in CDCl₃. Insert: SEC traces of P1, P2, P3, and P4 recorded by a refractive index detector, using chloroform (0.5% triethylamine) as the eluent (1 mL/min).

1 and fully characterized by NMR spectroscopy and HRMS. Cyclic voltammetry measurement of **F1** in THF solution reveals three quasi-reversible reduction peaks having $E_{1/2}$'s at -1.04, -1.60, and -2.21 V (ref. to Fc/Fc⁺ at -4.8 V), giving a LUMO energy level at about -3.8 eV, consistent with literature reported values for pyrrolidine functionalized fullerene derivatives.^{48,49}

Hydrogen Bonding Interactions in Solution ¹H NMR Study

The DAD-ADA "three-point" complementary hydrogen bonding between respective diaminopyrimidine units in **P4** and thymine moieties in **F1** was first studied by ¹H NMR spectroscopy. The **F1** imide-H signal was conveniently monitored since it experiences large downfield shift upon complexation and does not overlap with other proton signals. When **P4** was mixed in CDCl₃ with equimolar **F1** (based on diaminopyrimidine units, corresponding to a weight ratio of ca. 10/ 9), the imide-H signal experienced a downfield shift from 7.99 to 8.20 ppm (Fig. 3). However, no chemical shift changes were observed when P3HT and **F1** were mixed at the same ratio in CDCl₃ (Supporting Information Fig. S3).

To quantify the strength of such three-point hydrogen bonding, the solution binding constant was estimated through NMR titration experiments between **F1** and the model compound **S5** in CDCl₃ (Supporting Information Figs. S4 and S5). The small molecule model compound **S5** was used instead of **P4** to avoid complications commonly associated with polymers, including neighboring group effects and difficulties of preparing solutions with high polymer concentrations. As seen from the titration plot (Supporting Information Fig. S5), only one signal is observed for the imide-H with additions of **S5** up to 10 equivalents, which gradually shifts downfield and becomes broadened. A binding constant of 32.8 ± 1.1 M⁻¹ was obtained by fitting the imide-H chemical shifts versus **S5** equivalents using WinEQNMR program (Version 1.10).⁵⁰ This value is about 4–5 times lower than previously reported binding constants between similar diaminopyrimidine and uracil/thymine derivatives.^{33,51,52}

Fluorescence Quenching Studies

Figure 4 summarizes the fluorescence quenching experiments, in which fluorescence intensity of **P4** in



FIGURE 2 ¹H NMR (CDCl₃, 300.13 MHz) spectra of block copolymer **P4** (top), random copolymer **P4**' (middle) and model compound **S5** (bottom). The signals at about 0.08 ppm in all spectra are due to grease contaminants from air-free synthesis involving greased glass joints.



FIGURE 3 ¹H NMR (CDCl₃, 300.13 MHz) spectra of **P4** (bottom), **F1** (middle) and a 1:1 mixture of **P4** (30 mM based on diaminopyrimidine units) and **F1** (30 mM). The signals at about 0.08 ppm in all spectra are due to grease contaminants from air-free synthesis involving greased glass joints.

chlorobenzene $(10^{-5} \text{ M} \text{ based on total repeat units})$ was monitored with gradual addition of F1 (5 \times 10⁻⁴ M). For comparison, an in-house made P3HT ($M_n = 31,171, M_w =$ 32,504, and PDI = 1.04) polymer, which is not capable of complementary hydrogen bonding, was studied under the same quenching conditions. Both P4 and P3HT showed identical solution absorption and fluorescence emission spectra but distinct quenching behaviors with F1. In the case of P3HT, <10% fluorescence quenching was observed with the addition of up to 2 eq. of F1 and a linear fit of the Stern-Volmer plot gave a quenching constant of about 5.5 \times $10^{\rm \circ}$ M^{-1} . A much more pronounced quenching was observed for P4, in which over 40% fluorescence was quenched with the addition of 2 eq. of F1. This enhanced quenching is expected since P4 is capable of hydrogen bonding with F1 and form closely associated complexes that facilitate short-range electron transfer. Furthermore, the Stern-Volmer plot of P4 shows a two-step transition. The initial step has a large quenching constant of 1.2×10^5 M⁻¹ up to 0.2 eq. of F1, which is also the amount of F1 needed to fully complex all the diaminopyrimidine moieties in P4. After this point, the quenching constant is reduced to $8.0 \times 10^3 \text{ M}^{-1}$, similar to that of P3HT. Such sharp transition in quenching constant suggests strong complexation between P4 and F1 in chlorobenzene solution.53 The large Stern-Volmer constant in the first step of P4/F1 fluorescent quenching is also observed in silimar small molecule complementrary "multiple-point" hydrogen bonding systems.⁵⁴

Solid-State Morphology Stabilization

DSC measurements were performed on **P4**, P3HT, **F1**, and their blends to probe the effects of complementary hydrogen bonding on morphology stabilization. All samples (ca. 10 mg) were subjected to identical heating and cooling sequences (-50 °C-250 °C, 10 °C/min); blends were obtained by dissolving polymers and fullerene in a 10/9 weight ratio



followed by extensive drying. The first cooling and heating curves are shown in Supporting Information Figure S7. Both P3HT and **P4** show crystallization transitions at about 205 and 165 °C, respectively. The mixture of P3HT and **F1** shows distinct crystallization peak for the polymer, indicating phase separation of these two components to form pure polymer domains. This phenomenon is normally observed in BHJs involving conjugated polymers and fullerene derivatives where no interactions are present between the two materials. However, the melting and crystallization transitions of **P4** are mostly quenched by the addition of **F1**. This strongly suggests lack of macro-phase separation in the **P4/F1** blend caused by the complementary hydrogen bonding that is stable up to 250 °C.

To further confirm the phase stabilization effect, optical micrographs were taken on thin films (ca. 100 nm in thickness) of **P4**/PCBM, **P4/F1**, and P3HT/**F1** blends spin cast from chlorobenzene solutions. Polymer to fullerene ratio was kept at 10 to 9 by weight. Thin films were annealed at 150 °C for various times and representative optical graphs are shown in Figure 5. In the **P4**/PCBM films, thread-like PCBM crystals in starburst arrangement are observed after annealing for 15 min and become significant after 1 h. However, no observable change can be found in the **P4/F1** films. Furthermore, temperature-independent macrophase separation is found in the P3HT/**F1** film, suggesting incompatibility of these two materials presumably due to **F1** aggregation from self-complementary hydrogen bonding interactions.

P4/F1 Complexes as Solar Cell Active Layer

Solar cells employing P4/F1 complexes at different weight ratios were fabriacated using a common device geometry of ITO/MoO₃/polymer complexes/Al. The frequently applied PEDOT/PSS anode interfacial layer was avoided in this study due to its high acidity that can potentially disrupt the complementray hydrogen bonding interactions. Device

7



FIGURE 4 Fluorescence quenching measurements on **P4** (A) and P3HT (B) in chlorobenzene (10^{-5} M) excited at 458 nm with gradual addition of **F1** (5 × 10⁻⁴ M). The concentrations of polymers and equivalents of **F1** are calculated based on total number of repeating units in corresponding polymers. The inserts are Stern-Volmer plots and linear fits for calculations of quenching constants.

performaces under simulated AM 1.5G solar irradation are summarized in Table 1 and Supporting Information Figure S8.

Device performance was initially enhanced by reducing fullerene contents in the blends and reached an apparent maximum at a **P4/F1** weight ratio of 10/6. Further reduction in **F1** content led to decreased device performance. Such trend is quite different from the well-studied P3HT/PCBM systems that perform best at polymer-to-fullerene weight ratios around 10/10–10/8.⁵⁵ Furthermore, power conversion efficiency (PCE) differences in the **P4/F1** devices are mostly resulted from short circuit current (J_{sc}) changes, while little variations were observed for the other parameters. This is possibly due to thin film morphology differences, since J_{sc} is directly related to active layer morphologies that eventually determine exciton dissociation and charge collection efficiencies. Indeed, distinctly different morphologies were observed in AFM images for thin films of P4/F1 blends at different weight ratios, as seen in Figure 6. Large and disconnected aggregates are observed in the 10/10 blend film, which became smaller and more connected in the 10/8 film. A relatively rough film with no decernible aggregation was observed for the 10/6 blend film and the 10/4 blend gave a featureless and smooth morphology. Such morphology and $J_{\rm sc}$ differences are rationalized as follows. When P4 is complexed with F1, a "bottle-brush" type conjugated block copolymer is obtained. In a 10/10 complex, the relatively high fullerene contents lead to a large fullerene volume fraction. Phase separation of such "bottle-brush" complex is likely dominated by fullerene aggregation, which leads to large islands as seen in Figure 6(a). Domain discontinuity is detrimental for charge collection and thus leads to low J_{sc} . As fullerene contents decrease, its corresponding volume fraction



FIGURE 5 Thin film optical micrographs ($10 \times$ magnification) of **P4**/PCBM blends (10/9, wt/wt, A and B), **P4/F1** blends (10/9, wt/wt, C and D), and P3HT/**F1** blend (10/9 wt/wt, E and F) annealed at 150 °C for 15 min (A, C, and E) and for 60 min (B, D, and F).

reduces accordingly and thus aggregation between polymer and fullerene becomes more balanced, which leads to smaller aggregates and eventually to smooth films as normal BHJs. Charge separation and collection are thus facilitated by domain size reduction and interconnection. However, with decreasing F1 contents, a continuous fullerene path for electron transport becomes less likely, which can lead to imbalanced charge transport and inefficient exciton splitting. A clear S-type kink around V_{oc} in the I–V curve of the 10/4 device (Supporting Information Fig. S8) is likely resulted from space charge build-up due to inefficient electron transport.

In summary, device performance for the **P4/F1** block copolymer complexes depends on both domain sizes and interconnectivity, which can be tuned by varying fullerene loading percentages. For this system, a blend ratio of 10/6 was found to be optimal but not necessarily ideal due to the relatively low fullerence content. Changing block length ratios and functional group concentrations can provide opportunities for balanced phase separation as well as bicontinuous charge conducting pathways. Further investigations in blend morphologies and device performance by adjusting these structural parameters are currently underway.

TABLE 1 Device Performance of Solar Cells Fabricated Using

 P4/F1 at Different Weight Ratios as Active Layers^a

P4: F1 (wt:wt)	PCE ^b (%)	$J_{\rm sc}^{\rm \ b}$ (mA/cm ⁻²)	$V_{\rm oc}{}^{\rm b}$ (V)	FF^b
10:10	0.81	3.81	0.59	0.36
10:8	0.85	3.99	0.58	0.37
10:6	1.05	4.75	0.61	0.36
10:4	0.48	2.13	0.59	0.39

^a Thermal annealed at 150 °C for 15 min.

^b Averaged over five cells.





FIGURE 6 AFM height images (5 × 5 μ m²) of **P4/F1** complexes films spin cast from blend solutions at varied polymer-to-fullerene weight ratios of (A) 10:10; (B) 10:8; (C) 10:6; (D) 10:4. All films were annealed at 150 °C for 15 min.

P4/F1 Complex as Compatibilizers

Block copolymers based on polythiophene backbone having fullerene moieties selectively attached to one block have shown to improve performances and, more pronouncedly, thermal stability of P3HT/PCBM BHJ devices as compatibilizers.^{56,57} Such block copolymer systems can stabilize P3HT/ PCBM interfaces, which effectively reduces domain sizes and slows down macrophase separation. We have preliminarily investigated the stabilization effect of **P4/F1** complexes as phase compatibilizers in the benckmark P3HT/PCBM BHJ solar cells.

Table 2 and Supporting Information Figure S9 summarize the device performance of P3HT/PCBM (10:10, wt:wt) BHJ solar cells containing **P4/F1** (1:1 wt:wt) at various concentrations. By adding a few percent (2.5% and 5%) of the polymer complexes, device performance was slightly enhanced, as reflected by a small increase in fill factors (FFs). Such increase is likely due to polymer/fullerene interface stabilization by the compatibilizers, which leads to smaller domain sizes and better morphologies for charge generation and collection. Further increase of compatibilizer concentration up to 10% led to a decrease in device performance by reduction in all parameters, possibly due to more significant unfavorable aggregation effects as seen in the pure **P4/F1** blend films (Fig. 6).

Thermal stability of these compatibilized devices was evaluated at 110 °C for prolonged time intervals and the results are summarized in Figure 7 and Supporting Information Figure S10. Without **P4/F1** compatibilizers, the P3HT/PCBM BHJ device lost about 60% of its original performance after 150 h. The best stability was observed in the device containing 2.5% compatibilizer, for which up to 60% efficiency was retained. The stability differences were mainly caused by differences in FF changes as seen in Figure 7(b) and Supporting Information Figure S10. FFs dropped significantly for the noncompatibilized devices and a slight S-type kink was observed after annealing for 150 h. This indicates unfavorable phase separation leading to imbalanced charge transport. However, relatively small decreases in FFs were observed for the device containing 2.5% compatibilizer, indicating unfavorable phase separation to a lesser degree. Detailed morphological and electrical studies on these compatibilized solar cells are currently underway.

CONCLUSIONS

In conclusion, we have successfully prepared a novel conjugated block copolymer and a fullerene derivative capable of "three-point" complementary hydrogen bonding interactions. Strong complexation between these compounds leads to

TABLE 2 Device Performance of BHJ P3HT/PCBM Solar Cells

 Containing P4/F1 Complex (1:1, wt:wt) as Compatibilizers at

 Different Concentrations^a

P4/F1 ^b	PCE ^c (%)	$J_{\rm sc}^{\rm c}$ (mA/cm ⁻²)	$V_{\rm oc}{}^{\rm c}$ (V)	FF°
0	4.60	12.45	0.58	0.64
2.5%	4.83	12.30	0.58	0.68
5%	4.65	11.75	0.58	0.68
7.5%	4.55	12.13	0.58	0.64
10%	4.14	11.27	0.57	0.64

^a Thermal anneal at 150 °C for 15 min.

^b Based on the total weight of P3HT/PCBM.

^c Averaged over five cells.



FIGURE 7 Thermal stability test of P3HT/PCBM BHJ solar cells containing P4/F1 complexes as compatibilizers at different concentrations, annealed at 110 °C up to 150 h. (A) Normalized PCE vs. annealing time; (B) FF vs. annealing time.

stabilization of blend morphologies. Fullerene loading percentages can easily be adjusted by taking advantage of the noncovalent attachment, which significantly affects thin film morphologies and device performance. Preliminary results also demonstrated that these block copolymer complexes can be used as phase compatibilizers in BHJ solar cells in order to enhance device long-term stability. Our methodology provides a facile way of fine-tuning conjugated polymer–fullerene morphologies by adjusting block length ratios and fullerene loading. This strategy can be extended to other conjugated polymers possessing lower bandgaps for better device perfromances, which is currently carried out in our laboratory.

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