Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A heptacyclic acceptor unit developed for D-A copolymers used in polymer solar cells

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1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 series GPC coupled with UV-vis detector by using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done by using a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode. PBDTTTP was coated onto glassy carbon electrode and all potentials were corrected against Fc/Fc^+. AFM was performed on a Dimension 3100 microscope (Veeco) by using tapping mode. X-ray diffraction (XRD) of thin films was performed on a Rigaku D/max-2500 X-ray diffractometer in the reflection mode by using Cu Kα radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Lyntech Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

***N*-(2-octyldodecyl)thieno[3,2-*b*]thiophen-3-amine (2).** Compound **1** (2.27 g, 10.36 mmol), 2-octyldodecan-1-amine (4.62 g, 15.53 mmol), copper (0.1 g, 1.57 mmol), copper(I) iodide (0.3 g, 1.58 mmol) and potassium phosphate tribasic (5.0 g, 23.6 mmol) were stirred in 30 mL N,N-dimethylethanolamine at 80 °C for 48 h. Then the mixture was filtered and the solvent was removed under reduced pressure. The crude product was then purified via column chromatography over silica gel by using petroleum ether/CH_2Cl_2 (3:1) as eluent to give compound **2** (1.6 g, 35%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.32 (d, *J* = 5.0 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 6.02 (s, 1H), 3.52 (s, 1H), 3.10 (d, *J* = 6.1 Hz, 2H), 1.68-1.64 (m, 1H), 1.39-1.18 (m, 32H), 0.90-0.86 (m, 6H).

2,5-Dibromo-*N*^{1},*N*^{4}-bis(2-octyldodecyl)-*N*^{1},*N*^{4}-bis(thieno[3,2-*b*]thiophen-3-yl)terephthalamide (3). To a solution of 2,5-dibromoterephthalic acid (0.51 g, 1.59 mmol) in dry CH_2Cl_2 (30 mL) were added oxalyl chloride (2 mL, 22.8 mmol) and 2 drops DMF. The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure to obtain 2,5-dibromoterephthaloyl dichloride, which was used in next step without purification. To the solution of 2,5-dibromoterephthaloyl dichloride in dry CH_2Cl_2 (20 mL) was added slowly a solution of compound **2** (1.52 g, 3.49 mmol) and Et_3N (1 mL) in dry CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with $CHCl_3$ for three times. The collected organic solution was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with CH_2Cl_2 to give compound **3** as a yellow oil (0.6 g, 33%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.39 (d, *J* = 5.1 Hz, 2H), 7.19 (d, *J* = 5.2 Hz, 2H), 7.10 (s, 2H), 6.88 (s, 2H), 3.83 (br, 4H), 2.06 (br, 2H), 1.53-1.20 (m, 64H), 0.90-0.85 (m, 12H).

2,9-Bis(2-octyldodecyl)thieno[2'',3'':4',5']thieno[2',3':5,6]pyrido[3,4-*g*]thieno[2',3':4,5]thieno[3,2-*c*]isoquinoline-1,8(2*H*,9*H*)-dione (TTP). To a solution of compound **3** (0.3 g, 0.26 mmol) in N,N-dimethylacetamide (40 mL) were added $PCy_3{\cdot}HBF_4$ (150 mg, 0.41 mmol), Cs_2CO_3 (1.5 g, 4.6 mmol) and $Pd(OAc)_2$ (70 mg, 0.32 mmol) under Ar. The mixture was stirred at 120 °C overnight and then cooled to room temperature. The mixture was poured into water and extracted with $CHCl_3$ for three times. The combined organic solution was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH_2Cl_2 (3:2) as eluent to give **TTP** as a yellow solid (97 mg, 38%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.83 (s, 2H), 7.52 (d, *J* = 5.3 Hz, 2H), 7.37 (d, *J* = 5.3 Hz, 2H), 4.46 (d, *J* = 7.3 Hz, 4H), 2.24 (br, 2H), 1.48-1.19 (m, 64H), 0.86-0.81 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 161.48, 138.62, 133.11, 130.66, 128.69, 128.56, 126.34, 123.31, 120.49, 119.34, 50.66, 37.58, 31.90, 31.85, 31.16, 30.01, 29.61, 29.55, 29.49, 29.33, 29.24, 26.43, 22.67, 22.63, 14.08, 14.07.

4,11-Dibromo-2,9-bis(2-octyldodecyl)thieno[2'',3'':4',5']thieno[2',3':5,6]pyrido[3,4-*g*]thieno[2',3':4,5]thieno[3,2-*c*]isoquinoline-1,8(2*H*,9*H*)-dione (TTP-Br). To a solution of **TTP** (87 mg, 0.09 mmol) in a mixed solvent of $CHCl_3$ (30 mL) and DMF (5 mL) was added NBS (33 mg, 0.18 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into 120 mL methanol. The precipitate was filtered and purified through a silica gel column with petroleum ether/CH_2Cl_2 (3:2) as eluent to give **TTP-Br** as a yellow solid (78 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.70 (s, 2H), 7.35 (s, 2H), 4.31 (br, 4H), 2.15 (br, 2H), 1.45-1.19 (m, 64H), 0.86-0.81 (m, 12H). MALDI-TOF MS (m/z): 1156.1 (M^+). Elemental analysis (%) calcd for $C_{60}H_{86}Br_2N_2O_2S_4$: C, 62.37; H, 7.50; N, 2.42. Found: C, 62.31; H, 7.37; N, 2.59.

Poly{2,6-(4,8-bis(2-ethylhexyloxy))benzo[1,2-*b*:4,5-*b'*]dithiophene-alt-4,11-(2,9-bis(2-octyldodecyl))thieno[2'',3'':4',5']thieno[2',3':5,6]pyrido[3,4-*g*]thieno[2',3':4,5]thieno[3,2-*c*]isoquinoline-1,8(2*H*,9*H*)-dione}(PBDTTTP). TTP-Br (70 mg, 0.061 mmol) and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (47 mg, 0.061 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 8 mg $Pd(PPh_3)_4$ was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise into 150 mL methanol. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. The precipitate was collected and dried under vacuum overnight to give **PBDTTTP** as a dark red solid (84 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.62 (br, 2H), 7.52-

6.51 (br, 4H), 4.99 (br, 4H), 4.21 (br, 4H), 2.03-0.82 (br, 108H). Elemental analysis (%) calcd for $C_{86}H_{122}N_2O_4S_6$: C, 71.72; H, 8.54; N, 1.94. Found: C, 71.73; H, 8.49; N, 2.00.

3. ^{1}H NMR

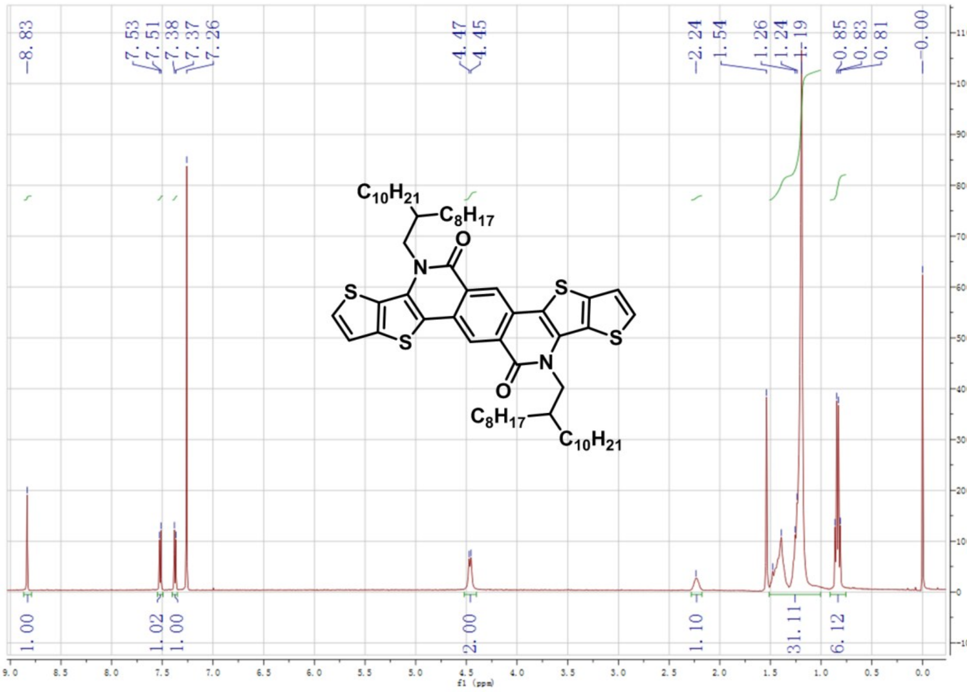

Fig. S1 ^{1}H NMR spectrum of **TTP**.

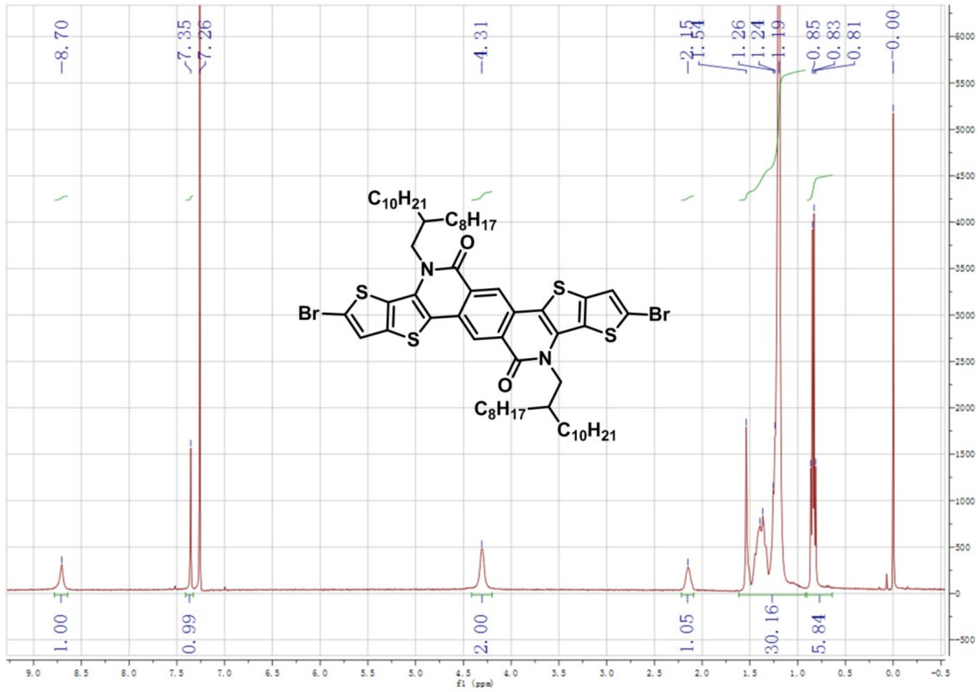

Fig. S2 ^{1}H NMR spectrum of **TTP-Br**.

4. TGA

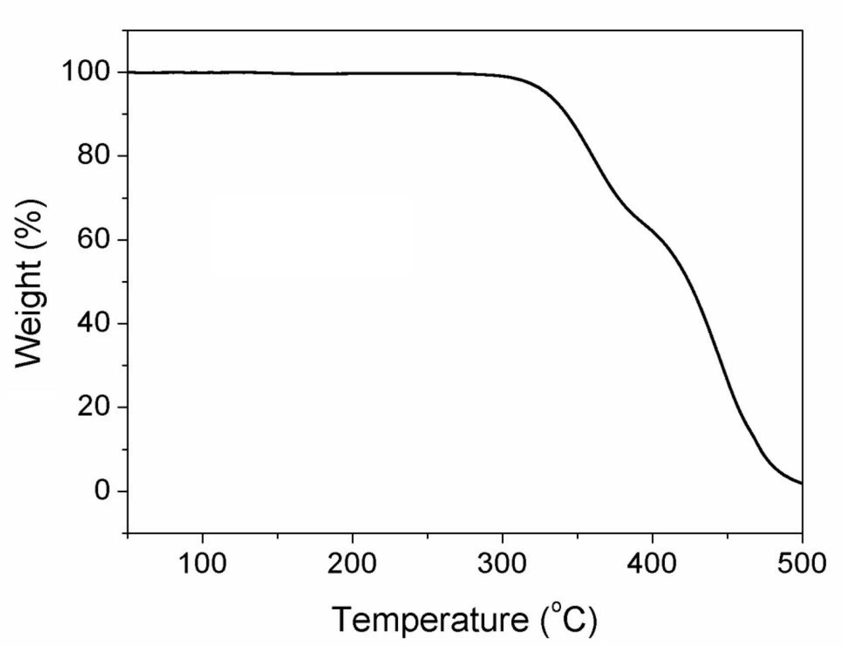

Fig. S3 TGA curve for PBDTTTP.

5. CV

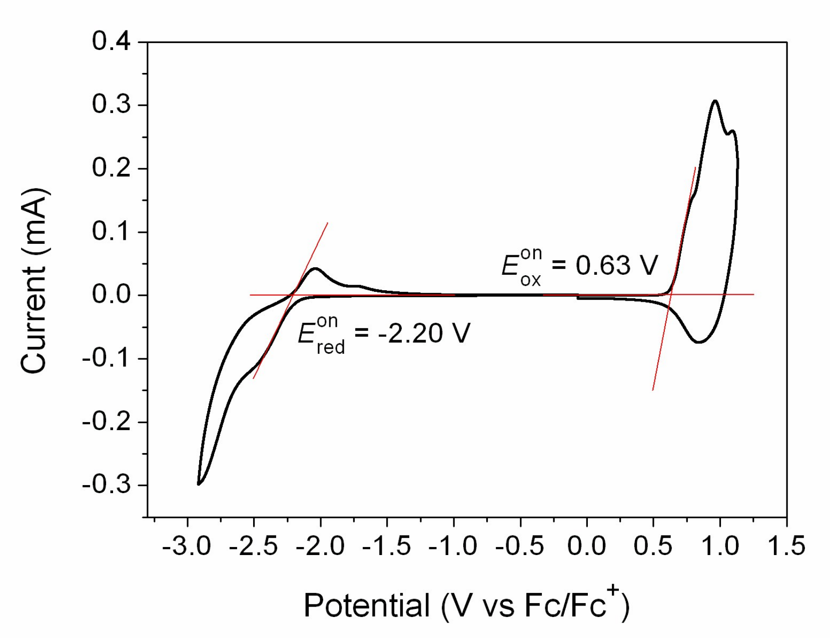

Fig. S4 Cyclic voltammogram for PBDTTTP.

6. Device fabrication and measurements

Conventional solar cells

Patterned ITO glass with a sheet resistance of 15 Ω sq^{-1} was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT:PSS, Clevios^{TM} P VP AI 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A PBDTTTP:PC$_{71}$BM blend in chlorobenzene with DIO additive (0~5 vol%) was spin-coated onto PEDOT:PSS layer. Finally, Ca (~10 nm) and Al (~100 nm) were successively evaporated under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. The thicknesses of the active layers were measured by a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2420 SourceMeter and a Xenon-lamp-based solar simulator (Newport, Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Oriel 91150, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO$_3$/Al. A 30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A PBDTTTP:PC$_{71}$BM blend in chlorobenzene (16 mg/mL) without or with 3 vol% DIO additive was spin-coated onto PEDOT: PSS layer. Finally, MoO$_3$ (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2420 SourceMeter in the dark.

Electron-only devices

The structure of electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was first evaporated onto a glass substrate. A PBDTTTP:$PC_{71}BM$ blend in chlorobenzene (16 mg/mL) without or with 3 vol% DIO additive was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated under a shadow mask (pressure ca. 10^{-4} Pa). *J*-*V* curves were measured by using a computerized Keithley 2420 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PBDTTTP:$PC_{71}BM$ solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:0.6	0.98	6.69	62.6	4.10
1:0.8	0.97	7.76	65.1	4.88
1:1.0	0.96	8.07	67.2	5.23
1:1.2	0.95	8.33	65.4	5.20
1:1.4	0.95	7.94	66.4	5.03

[a] Blend solution: 16 mg/mL in CB with 3 vol% DIO; spin coating: 800 rpm for 60 s.

Table S2 Optimization of the active layer thickness for PBDTTTP:$PC_{71}BM$ solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
109	0.97	8.01	68.5	5.33
121	0.98	8.06	67.6	5.33
134	0.98	8.03	67.7	5.34
149	0.98	8.22	67.9	5.44
157	0.97	8.20	66.0	5.27

[a] D/A ratio: 1:1 (w/w); blend solution: 16 mg/mL in CB with 3 vol% DIO.

Table S3 Optimization of the additive content for PBDTTTP:$PC_{71}BM$ solar cells.[a]

DIO [v/v, %]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.97	1.58	52.1	0.80
1	0.96	7.88	68.3	5.18
2	0.98	8.11	66.6	5.31
3	0.98	8.12	69.5	5.53
4	0.99	8.09	65.8	5.26
5	1.00	7.92	65.8	5.22

[a] D/A ratio: 1:1 (w/w); blend solution: 16 mg/mL in CB; spin coating: 1200 rpm for 60s.

Table S4 Optimization of solvent for PBDTTTP:$PC_{71}BM$ solar cells.[a]

Solvent	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
CB	0.98	8.12	69.5	5.53
CB:$CHCl_3$ (2:1)	0.99	7.60	68.6	4.90
ODCB	0.99	7.67	69.0	5.22

[a] D/A ratio: 1:1 (w/w); blend solution: 16 mg/mL with 3 vol% DIO; spin coating: 1200 rpm for 60s.

8. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_h) or electron (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. The mobility was calculated from the slope of $J^{1/2}$-V plots.

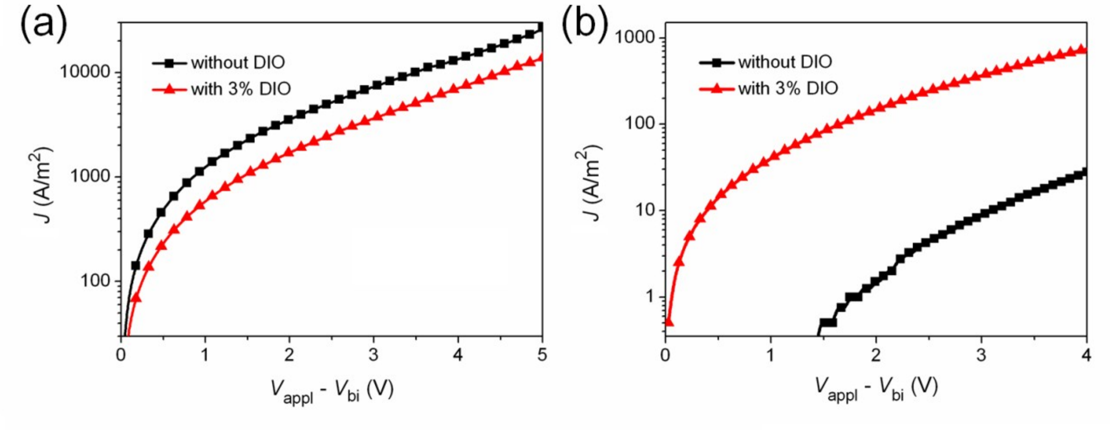

Fig. S5 *J*-*V* curves for hole-only (a) and electron-only (b) devices based on PBDTTTP/PC$_{71}$BM blend films without or with 3 vol% DIO (in dark). The thicknesses for the blend films are 125 and 134 nm, respectively.