5,6-Difluorobenzothiadiazole and silafluorene based conjugated polymers for organic photovoltaic cells

Guangwu Li, a Chong Kang, a Xue Gong, a Jicheng Zhang, a Weiwei Li, a Cuihong Li, * a
Huanli Dong, b Wenping Hu, b Zhishan Bo**

a Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China
b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

E-mail: licuihong@bnu.edu.cn; zsbo@bnu.edu.cn

Experimental Part

Materials and Instruments. Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH₂. Chloroform (CF) was distilled before use. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The gel permeation chromatography (GPC)
measurements were performed at 150 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with 1,2,4-trichlorobenzene as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X’Pert PRO MPD diffractometer with Cu KR radiation (wave length: 1.5406 Å). The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu$_4$NPF$_6$ solution in CH$_3$CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO$_3$ (0.01 M in CH$_3$CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium ($F_c$) redox system and assumption that the energy level of $F_c$ is 4.8 eV below vacuum.

**Fabrication and Characterization of Organic Field-Effect Transistors (OFETs)**

Bottom-contact devices were fabricated based on Si/SiO$_2$ substrates (the back low resistance Si as gate, SiO$_2$ (500 nm) as gate insulator). Polymer thin films were spin-coated on the OTS-modified Si/SiO$_2$ substrate from 1, 2-dichlorobenzene (o-DCB) saturated solution. Electrodes of Au (25 nm) were vacuum deposited before depositing on the polymer thin films.

**Fabrication and Characterization of SCLC devices**

Space charge limited current (SCLC) devices were fabricated with the configuration of ITO/PEDOT:PSS/Polymer:PC$_{71}$BM/Au. The conductivity of ITO was 20 Ω·cm. PEDOT:PSS is Baytron Al 4083 from H.C.Starck and was filtered with a 0.45 μm polyethersulfone (PES) film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC$_{71}$BM was dissolved in 1,2-dichlorobenzene (DCB) and heated at 120 °C for overnight to ensure
the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated, with a 100 nm of gold at a pressure of $10^{-4}$ Pa through a shadow mask. The measurement of devices was conducted in air without encapsulation. Dark Current-voltage characteristics were recorded using an Agilent B2902A Source in a dark circumstance with a range of 1.0 V to 5.0 V. The temperature while measuring the dark $J-V$ curves was approximately 25 °C. The hole mobilities were calculated according to the Mott-Gurney equation:

$$\mu = \frac{8d^3}{9\varepsilon_r\varepsilon_0} \left( \frac{\sqrt{J}}{V} \right)^2,$$

which $d$ was the thickness of active layer, $\varepsilon_0$ is the vacuum dielectric constant, $\varepsilon_r$ is the relative dielectric constant of polymer.

**Polymer Solar Cell Fabrication and Characterization.** PSCs were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC$_{71}$BM /LiF /Al. The conductivity of ITO was 20 $\Omega \square$. PEDOT:PSS is Baytron Al 4083 from H.C. Starck and was filtered with a 0.45 µm polyvinylidene difluoride (PVDF) film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC$_{71}$BM was dissolved in 1,2-dichlorobenzene (o-DCB) and heated at 100 °C for overnight to ensure the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, then followed by 100 nm of aluminum at a pressure of $10^{-4}$ Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm$^2$. The measurement of devices was conducted in air without encapsulation. Current-voltage characteristics were recorded using an Agilent B2902A Source Meter under an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mWcm$^{-2}$ as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the $J-V$ curves was approximately 25 °C.

**Synthesis of monomers and polymers**

**Synthesis of 5,6-difluorobenzo[c][1,2,5]thiadiazole (2)**
To a solution of aniline (19.5 g, 0.21 mol) in 300 mL anhydrous toluene, SOCl$_2$ (27.3 g, 0.22 mol) was added drop wise at 0 °C. After the addition of SOCl$_2$, the mixture was heated at 100 °C for one hour, 4,5-difluorobenzene-1,2-diamine (28.8 g, 0.2 mol) was then added to the solution in one portion, and the mixture was stirred at 100 °C overnight. The reaction mixture was allowed to cool to room temperature and poured into water (300 mL), the organic phase was separated, washed with water and aqueous NaHCO$_3$ three times, and dried over anhydrous MgSO$_4$. After removal of the solvent under reduced pressure, the residue was chromatographically purified on silica gel column eluting with petroleum ether:DCM (4:1, by volume) to afford 5 as a colorless crystal (23.6 g, 68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (t, $J$ = 8.7 Hz, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 153.79, 150.81, 106.10. Anal. Calcd for C$_6$H$_2$F$_2$N$_2$S: C 41.86, H 1.17, N 16.27. Found: C 41.76, H 1.34, N 16.09.

**Synthesis of 5,6-difluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (3)**

To a solution of 5,6-difluorobenzo[c][1,2,5]thiadiazole (1.0 g, 5.8 mmol) in H$_2$SO$_4$ (98%, 60 mL) and HOAc (12 mL) was added NIS (5.22 g, 23.2 mmol) was added in several portions. The reaction mixture was stirred at room temperature for 24 hours and poured into crashed ice; the mixture was extracted with DCM; and the organic phase was washed with water and then aqueous NaHCO$_3$ three times, dried over anhydrous MgSO$_4$, and recrystallization from ethanol. Compound 6 was obtained as a slight yellow crystal (1.2 g, 49%) and used for next step without further purification.

**Synthesis of 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (4)**

A mixture of 5,6-difluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (1.00 g, 2.36 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (1.24 g, 5.9 mmol), NaHCO$_3$ (1.20 g, 14 mmol ), THF (30 mL), and H$_2$O (4 mL) was degassed and recharged with N$_2$ before and after the addition of Pd$_2$(dba)$_3$ (108 mg, 0.12 mmol) and P(o-tol)$_3$ (340 mg, 1.2 mmol). The mixture was heated to 90 °C and stirred for three days; water and DCM were added; and the organic phase was separated, dried over anhydrous MgSO$_4$, and evaporated to dryness. The residue was chromatographically purified on silica gel eluting petroleum ether:toluene (1:1, by volume) to afford 7 as a yellow solid (590 mg, 74%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.29 (d, $J$ = 7.6 Hz, 2H),
7.62 (dd, $J = 5.1$ Hz, $J = 1.0$ Hz, 2H), 7.27 (m, 2H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 149.82, 148.90, 131.51, 130.90, 128.88, 127.40, 111.82. Anal. Calcd for C$_{22}$H$_{23}$FN$_2$OS$_3$: C 59.16, H 5.19, N 6.27. Found: C 59.06, H 5.39, N 6.07.

**Synthesis of 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (M-1)**

To a solution of 5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1.0 g, 3 mmol) in 200 mL CH$_2$Cl$_2$, Br$_2$ (1 mL) in CH$_2$Cl$_2$ (1 mL) solution was added drop wise, after 1 minute, the solution of Na$_2$S$_2$O$_4$ was added to quench the reaction, the organic phase was separated, and the water phase was washed with DCM three times, the organic phase was dried with MgSO$_4$ and the solvent was removed under reduced pressure, the crude products was purified by recrystallization from chloroform after a short column to give the final products as a yellow solid. (1.15 g, 78%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (d, $J = 4.1$ Hz, 2H), 7.22 (d, $J = 4.2$ Hz, 2H). Anal. Calcd for C$_{22}$H$_{23}$FN$_2$OS$_3$: C 34.03, H 0.82, N 5.67. Found: C 33.84, H 1.18, N 5.68.

**Synthesis of 5,6-difluoro-4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (5)**

A mixture of 5,6-difluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (1.0 g, 2.36 mmol), 4,4,5,5-tetramethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborolane (1.9 g, 5.9 mmol), NaHCO$_3$ (1.19 g,14 mmol ),THF (30 mL) and H$_2$O (4 mL) was gassed and degassed carefully before and after Pd$_2$(dba)$_3$ (108 mg, 0.12 mmol) and P($\alpha$-tol)$_3$ (340 mg, 1.2 mmol) was added, then the reaction solution was heated at 90 °C for three days, water was added to the solution for extracted with dichloromethane, the organic phase was dried with anhydrous MgSO$_4$, removing the solvents and column purification using petroleum ester and dichloromethane as eluents to get the products as a yellow solid. (1.1 g, 84%)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (s, 2H), 7.20 (s, 2H), 2.72 (t, $J = 7.6$ Hz, 4H), 1.63-1.80 (m, 4H), 1.21-1.48 (m, 20H), 0.89 (t, $J = 6.6$ Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 149.73, 148.88, 143.68, 132.22, 131.18, 123.92, 111.62, 31.90, 30.55, 30.47, 29.46, 29.37, 29.30, 22.69, 14.13. Anal. Calcd for C$_{22}$H$_{23}$FN$_2$OS$_3$: C 64.25, H
6.83, N 5.00. Found: C 64.18, H 7.22, N 4.95.

**Synthesis of 4,7-bis(5-bromo-4-octylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (M-2)**

To a solution of 5,6-difluoro-4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (1.0 g, 1.8 mmol) in 100 mL CH₂Cl₂, Br₂ (1 mL) in CH₂Cl₂ (1 mL) solution was added drop wise, after 1 minute, the solution of Na₂S₂O₄ was added to quench the reaction, the organic phase was separated, and the water phase was washed with DCM three times, the organic phase was dried with MgSO₄ and the solvent was removed under reduced pressure, the crude products was purified by column chromatography to afford a yellow solid. (1.1 g, 86%)

¹H NMR (400 MHz, CDCl₃): δ 7.95 (s, 2H), 2.65 (t, J = 7.7 Hz, 4H), 1.61-1.75 (m, 4H), 1.20-1.47 (m, 20H), 0.88 (t, J = 5.9 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): δ 149.65, 148.26, 142.57, 131.70, 131.35, 114.47, 110.92, 31.89, 39.75, 29.54, 29.40, 29.29, 22.85, 22.69, 14.12. Anal. Calcd for C₃₀H₃₆F₂N₂S₃Br₂: C 50.14, H 5.05, N 3.90. Found: C 50.06, H 5.64, N 3.84

**Synthesis of 5,6-difluoro-4,7-bis(4-octyl-5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (6)**

4,7-bis(5-bromo-4-octylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (1.0 g, 1.4 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (731 mg, 3.5 mmol), NaHCO₃ (1.4 g, 16.6 mmol), H₂O (5 mL) and THF (50 mL) was carefully degas before and after Pd₂(dbca)₃ (65 mg, 0.07 mmol) and P(o-tol)₃ (270 mg, 0.7 mmol) was added, the reaction mixture was refluxed for 3 days, water was added, the organic phase was separated and the water was extracted with DCM (100 mL) three times, the combined organic layer was dried and the organic solvents was removed under reduced pressure, the crude products was purified by column chromatography as a brick red solid. (760 mg, 75%)

¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 2H), 7.37 (dd, J = 5.2 Hz, J = 1.1 Hz, 2H), 7.26 (dd, J = 3.5 Hz, J = 1.2 Hz, 2H), 7.11 (dd, J = 5.2 Hz, J = 3.6 Hz, 2H), 2.84 (t, J = 7.8 Hz, 4H), 1.63-1.85 (m, 4H), 1.24-1.58 (m, 20H), 0.89 (t, J = 6.7 Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): δ 149.77, 148.77, 139.83, 135.54, 134.59, 133.93, 129.41,
Anal. Calcd for C_{22}H_{23}FN_{2}OS_{3}: C 62.95, H 5.84, N 5.00. Found: C 63.23, H 6.30, N 3.79.

**Synthesis of 4,7-bis(5-(5-bromothiophen-2-yl)-4-octylthiophen-2-yl)-5,6-difluoro-benzoc[1,2,5]thiadiazole (M-3)**

To a solution of 5,6-difluoro-4,7-bis(4-octyl-5-(thiophen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1.0 g, 1.4 mmol) in 200 mL CHCl_{3}, NBS (503 mg, 2.8 mmol) was added in one portion, and a few drops of DMF was added, after 12 hours at room temperature, the solvents was removed and the crude products was purified by column chromatography to afford a brick red solid (1.07 g, 88%).

{^1}H NMR (400 MHz, CDCl_{3}): δ 8.10 (s, 2H), 7.06 (d, J = 3.9 Hz, 2H), 7.01 (d, J = 3.8 Hz, 2H), 2.81 (t, J = 7.6 Hz, 4H), 1.63-1.79 (m, 4H), 1.23-1.48 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H). {^13}C NMR (400 MHz, CDCl_{3}): δ 149.70, 148.53, 140.13, 137.12, 133.73, 133.57, 130.34, 129.73, 126.34, 112.55, 110.95, 31.89, 30.54, 29.58, 29.41, 29.29, 22.69, 14.12. Anal. Calcd for C_{38}H_{40}F_{2}N_{2}S_{5}: C 51.70, H 4.57, N 3.17. Found: C 51.69, H 4.90, N 3.11.

**Synthesis of 2,7-dibromo-9,9-dioctyl-3,6-bis(octyloxy)-silafluorene (8)**

4,4-dibromo-5,5′-bis(octyloxy)-2,2′-diiodobiphenyl (1.0 g, 1.2 mmol) was dissolved in 30 mL dry THF, then 2.5 M n-BuLi (1.1 mL, 2.7 mmol) was added drop wise at -100 °C under nitrogen atmosphere, after 1 h, dichlorodiocetyl silane (875 mg, 2.7 mmol) was added, then reacted overnight, water was added and the organic phase was separated, dried, filtered and removed under reduced pressure, the crude product was purified by column chromatography as a colorless oil (690 mg, 69%).

{^1}H NMR (400 MHz, CDCl_{3}): δ 7.68 (s, 2H), 7.22 (s, 2H), 4.14 (t, J = 6.0 Hz, 4H), 1.82-1.95 (m, 4H), 1.15-1.46 (m, 40H), 0.81-0.99 (m, 16H). {^13}C NMR (100 MHz, C_{6}D_{6}): δ 157.19, 148.41, 137.37, 131.09, 112.42, 105.95, 69.22, 33.30, 31.83, 39.34, 39.26, 29.20, 29.06, 26.08, 23.82, 22.69, 22.66, 14.12, 14.11, 12.35. Anal. Calcd for C_{44}H_{72}Br_{2}O_{2}Si: C 64.37, H 8.84. Found: C 64.21, H 8.70.

**Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-3,6-bis(octyloxy)silafluorene (M-4)**
A solution of 2,7-dibromo-9,9-dioctyl-3,6-bis(octyloxy)-silafluorene (1.0 g, 1.2 mmol), NEt₃ (1.5 mL), pinacolborane (1.25 g, 9.7 mmol) and 1,2-dichloroethane (30 mL) was carefully gas and degas before and after Pd(PPh₃)₂Cl₂ (86 mg, 0.12 mmol) was added, then reacted at 80 °C for 24 h, the solvents was removed under reduced pressure and the crude product was purified by column chromatography (660 mg, 59%).

¹H NMR (400 MHz, C₆D₆): δ 8.62 (s, 2H), 7.55 (s, 2H), 3.92 (t, J = 6.0 Hz, 4H), 1.72-1.82 (m, 4H), 1.55-1.66 (m, 4H), 1.36-1.45 (m, 4H), 1.00-1.45 (m, 60H), 0.82-0.99 (m, 16H). ¹³C NMR (100 MHz, CDCl₃): δ 166.17, 152.48, 141.33, 128.64, 103.89, 81.74, 32.35, 30.92, 30.88, 28.59, 28.52, 28.28, 28.07, 25.08, 23.73, 23.12, 21.75, 21.66, 12.99, 12.97, 11.73. Anal. Calcd for C₅₆H₉₆B₂O₆Si: C 73.50, H 10.57. Found: C 73.00, H 10.51.

**General procedures for synthesis the polymers**

Above mentioned benzo[c][1,2,5]thiadiazole containing monomers (0.3 mmol), silafluorene containing monomers (0.3 mmol), NaHCO₃ (500 mg, 6.0 mmol), toluene (20 mL) and H₂O (3 mL) was carefully gas and degas before and after Pd(PPh₃)₄ (0.006 mmol, 7 mg) was added, after copolymerization for three days, the polymer was end-capped by phenyl boric acid and bromobenzene, respectively. Then the polymer was afforded according to our previous reported procedures.

**PDOSiF-DTDFBT** was obtained as a dark red solid (210 mg, 73%)

¹H NMR (400 MHz, C₆D₄Cl₂): δ 8.51-8.73 (br, 2H), 8.06-8.50 (br, 4H), 7.70-8.05 (br, 2H), 3.00-3.51 (br, 4H), 2.0-2.3 (br, 4H), 1.31-2.03 (br, 48H), 0.92-1.26 (br, 12H).


**PSiF-TTDFBT** was obtained as a black solid (271 mg, 80%)

¹H NMR (400 MHz, C₆D₄Cl₂): δ 8.19-8.45 (br, 2H), 7.95-8.15 (br, 2H), 7.65-7.79 (br, 2H), 7.26-7.40 (br, 2H), 7.15-7.26 (br, 2H), 2.78-3.10 (br, 4H), 1.75-1.89 (br, 4H), 0.95-1.61 (br, 44H), 0.73-0.92 (br, 4H), 0.73-0.92 (br, 16H). Anal. Calcd for C₆₆H₆₂F₂N₂S₅Si: C 70.16, H 7.32, N 2.48. Found: C 71.62, H 8.36, N 2.48.

**PSiD(OT)DFBT** was obtained as a blue solid (265 mg, 88%)
$^1$H NMR (400 MHz, C$_6$D$_4$Cl$_2$): δ 8.40-8.60 (br, 2H), 8.20-8.40 (br, 2H), 7.70-8.00 (br, 2H), 7.60-7.80 (br, 2H), 3.80-4.40 (m, 4H), 1.80-2.10 (br, 4H), 0.95-1.82 (m, 44H), 0.72-0.91 (br, 16H). Anal. Calcd for C$_{58}$H$_{78}$F$_2$N$_2$O$_2$S$_3$: C 69.83, H 7.88, N 2.81. Found: C 68.49, H 8.02, N 2.44.

Table S1. Photovoltaic cells performance of three polymers

<table>
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<th>J$_{sc}$</th>
<th>V$_{oc}$</th>
<th>FF</th>
<th>PCE</th>
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<tr>
<td>PSiF-D(OT)DFBT:PC$_{71}$BM (1:3) (2% CN)</td>
<td>1.71</td>
<td>1.00</td>
<td>0.35</td>
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<td>PSiF-TTDFBT:PC$_{71}$BM (1:3) (2% DIO)</td>
<td>4.18</td>
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<tr>
<td>PDOSiF-DTDFBT:PC$_{71}$BM (1:1) (2.5% DIO)</td>
<td>7.41</td>
<td>0.62</td>
<td>0.61</td>
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Figure S1. UV-visible absorption coefficients of PSiF-D(OT)DFBT:PC$_{71}$BM (1:3), PSiF-TTDFBT:PC$_{71}$BM (1:3), and PDOSiF-DTDFBT:PC$_{71}$BM (1:1) blend films fabricated under optimized conditions. The absorption coefficient was calculated by film absorbance/film thickness (nm)