Supporting Information

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Thiophene Rings Improve the Device Performance of Conjugated Polymers in Polymer Solar Cells with Thick Active Layers

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1. Synthesis

General information: All synthetic procedures were performed under argon atmosphere. All reactants and reagents are commercially available and used as received, unless otherwise specified. [70]PCBM was purchased from Solenne BV. 2,6-Bis(trimethyltin)-4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophene (C10-BDT),and 5,6-difluoro-4,7-dibromobenzo[2,1,3]thiadiazole (ffBT) were purchased from SunaTech Inc. 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (DTffBT) was synthesized according to our previous method [1].

Synthesis of polymers: Tris(dibenzylideneacetone)-dipalladium(0) (2.47 mg, 0.0027 mmol) and tri(o-tolylphosphine) (6.57 mg, 0.0216 mmol) were added to a degassed solution of the C10-BDT monomer (0.09 mmol), and the dibrominated monomer(s) (DTffBT or/and ffBT) (total 0.09 mmol) with the desired feeding ratio in anhydrous o-xylene (1.6 mL) and anhydrous N,N-dimethylformamide (DMF) (0.2 mL). The mixture was stirred at 115 °C overnight, after which 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added to the reaction mixture with 2 h interval. After another 2 h, the reaction mixture was diluted with ortho-dichlorobenzene (o-DCB), and refluxed with ethylenediaminetetraacetic acid dipotassium salt dihydrate (EDTA) (100 mg) for 2 h. Upon cooling, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with acetone, hexane, dichloromethane, and chloroform under argon protection. The residue in Soxhlet thimble was dissolved in hot o-DCB and filtered.
afterward. Chloroform fractions were collected for C10-Th00 and C10-Th25, while the \( o\)-DCB fractions were collected for C10-Th50, C10-Th75, and C10-Th100. All collected solutions were then concentrated under reduced pressure and precipitated in methanol to obtain the resulting polymers.

C10-Th00: Yield (65%). GPC: \( M_n = 33.8 \) kDa, PDI = 3.1.

C10-Th25: Yield (69%). GPC: \( M_n = 46.3 \) kDa, PDI = 3.2.

C10-Th50: Yield (45%). GPC: \( M_n = 69.4 \) kDa, PDI = 3.7.

C10-Th75: Yield (46%). GPC: \( M_n = 67.2 \) kDa, PDI = 3.0.

C10-Th100: Yield (85%). GPC: \( M_n = 65.2 \) kDa, PDI = 2.1.

2. Measurements and characterization

**Gel permeation chromatography (GPC):** Molecular weights and polydispersity index (PDI) were determined with gel permeation chromatography at 140 °C on a PL-GPC 120 system using a PL-GEL 10 \( \mu \)m MIXED-B column and \( o\)-DCB as the eluent against polystyrene standards. All the polymer samples were dissolved in \( o\)-DCB at 140 °C overnight and the solutions were filtered through PTFE filters (0.2 \( \mu \)m) prior to injection.

**Differential scanning calorimetry (DSC):** DSC measurements were carried out on a DSC Q2000 differential scanning calorimeter from \( -80 \) to 300 °C at a heating and cooling rate of 10 °C min\(^{-1}\) under N\(_2\) flow.

**UV-visible spectra:** UV-visible spectra were recorded on a PekinElmer Lambda 900 UV/vis/near IR spectrophotometer at room temperature unless otherwise noted. All solution UV-vis experiments were performed in \( o\)-DCB with sample concentration of 0.05 mg mL\(^{-1}\). Films were prepared by spin coating \( o\)-DCB solutions on glass substrates.

**Cyclic voltammetry (CV):** Cyclic voltammetry studies were performed with a scan rate of 0.1 V s\(^{-1}\) under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte. The working electrode was indium tin oxide (ITO) bar and the
counter electrode was a silver electrode. A silver wire coated with silver chloride (Ag/AgCl) was used as quasi-reference electrode in combination with Fe/Fe\(^+\) as an internal standard. The samples were spin coated on top of ITO work electrode to form ~10 nm thick films.

**Transmission electron microscopy (TEM):** Transmission electron microscopy was performed on a Tecnai G\(^2\) Sphera transmission electron microscope (FEI) operated at 200 kV.

**Grazing incidence X-ray diffraction (GIXD):** Grazing incidence X-ray diffraction characterization of the thin films was performed at the Advanced Light Source on beamline 7.3.3, Lawrence Berkeley National Lab (LBNL). Thin film samples were prepared on wafer substrates. The scattering signal was recorded on a 2D detector (Pilatus 2M) with a pixel size of 0.172 mm by 0.172 mm. The samples were ~15 mm long in the direction of the beam path, and the detector was located at a distance of ~300 mm from the sample center (distance calibrated using a silver behenate standard). The incidence angle of 0.16\(^\circ\) was chosen which gave the optimized signal-to-background ratio. The beam energy was 10 keV, operating at top-off mode. Typically, 5 seconds exposure time was used to collect diffraction signals. All GIXD experiments were done in helium atmosphere. The data was processed and analyzed using Nika software package.

**Resonant soft X-ray scattering (RSoXS):** Resonant soft X-ray scattering was performed at beamline 11.0.1.2 Advanced Light Source, LBNL. Thin film samples were spin-casted on top of the PEDOT:PSS covered Si wafers under exactly the same condition as those for the fabrication of solar cell devices. Then BHJ thin films were floated and transferred onto silicon nitride membrane windows. The scattering was done in transmission mode and signals were collected in vacuum using Princeton Instrument PI-MTE CCD camera.

**Charge-only devices:** Space-charge-limited-current hole and electron mobilities were acquired through the hole-only devices with a configuration of ITO/PEDOT:PSS (40 nm)/C10-Thx:[70]PCBM/MoO\(_x\) (10 nm)/Ag (100 nm) or electron-only devices with a configuration ITO/ZnO (30 nm)/C10-Thx:[70]PCBM/LiF (1 nm)/Al (100 nm). At least three different
thickness of C10-Thx:[70]PCBM blend films were tested for each polymer. The dark current densities of C10-Thx:[70]PCBM blends were measured by applying a voltage between 0 and 6 V using a computer-controlled Keithley 2400 source meter in N2 atmosphere. These data were analyzed according to the Mott-Gurney laws that includes a Poole-Frenkel-type dependence of mobility on the electric field: 

\[ J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 (V^2/d^3) \exp(0.89 \gamma \sqrt{V/d}) \],  

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the dielectric constant of the polymer which is assumed to be around 3 for the conjugated polymers, \( \mu_0 \) is the zero-field mobility, \( V \) is the voltage drop across the device, \( d \) is the film thickness of active layer, and \( \gamma \) is a parameter that describes the strength of the field-dependence effect. The applied voltage is used without correcting from series resistance or built-in voltage, which offers the best fitting of the experimental data following the protocol reported in literature.\(^2\) The mobilities are extracted with the fit parameters at an electric field (\( E \)) of \( 1.5 \times 10^5 \) V cm\(^{-1} \) by the Murgatroyd equation 

\[ \mu = \mu_0 \exp(\gamma \sqrt{E}) \].

**Time resolved fluorescence:** Time resolved fluorescence measurement were performance on an Edinburgh Instruments LifeSpec-PS spectrometer using a 405 nm (3.06 eV) pulsed laser (PicoQuant PDL 800B) operated at 2.5 MHz. For detection a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-50) was used. Lifetimes were obtained by fitting a mono-exponential function convoluted with the instrument response function (IRF) to the measured intensity decay curve, using a non-linear least squares algorithm.

### 3. Fabrication and characterization of solar cells

**Fabrication of polymer solar cells:** Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP AI 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates in air (14 \( \Omega \) per square) (Naranjo Substrates). The polymer-fullerene photoactive layers were deposited by spin coating in air from the solutions containing corresponding C10-Thx polymers and [70]PCBM with optimal
weight ratio. The active layer films of C10-Th00 and C10-Th25 were deposited from their solution in chloroform containing 3\% 1,8-diiodooctane (DIO) at room temperature, while the films of C10-Th50, C10-Th75, and C10-Th100 were deposited from hot (120 °C) solutions in chlorobenzene/1-chloronaphthalene (CB/CN) (7/3), CB/CN (7/3), and CB/CN (9/1) respectively. The optimal C10-Th}\_\text{x}:\text{PCBM ratio is 1:1.5 (w/w) for C10-Th100, while the optimal ratio is 1:2 (w/w) for the other polymers. No thermal annealing was applied to the resulting films. The thickness of active layer films was controlled by solution concentration and spin speed. Finally, LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at $\sim 3 \times 10^{-7}$ mbar as the back electrode. The active area of the cells was 0.09 or 0.16 cm$^2$, which provided similar results.

**Current density–voltage ($J$–$V$) characteristics:** $J$–$V$ curves were measured under simulated solar light (100 mW cm$^{-2}$) from a tungsten–halogen lamp filtered by a Hoya LB100 daylight using a Keithley 2400 source meter. No mismatch correction was done. All measurements were conducted in nitrogen-filled glove box. The accurate short-circuit current density ($J_{sc}$) was determined from the external quantum efficiency by integration with the AM1.5G solar spectrum.

**External quantum efficiency (EQE):** EQE measurements were performed in a homebuilt set-up, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm, 30 mW). The intensity of the bias laser light was adjusted using a variable-neutral density filter. The response was recorded using a lock-in amplifier (Stanford Research Systems SR 830). For all devices, the measurement was carried out under representative illumination intensity (AM1.5G equivalent, provided by the 532 nm laser).
4. Additional figures and tables

**Table S1.** Conjugated polymers reported in literatures that show \( \text{FF} \geq 0.6 \) and \( \text{PCE} \geq 7.0\% \) simultaneously at active layer thickness larger than 200 nm.

| Conjugated Polymers | FF, PCE | Thickness (nm) |
|---------------------|---------|----------------|
| FF = 0.75, PCE = 7.4\% @ 200 nm | X. Guo, C. Cui, M. Zhang, L. Huo, Y. Huang, J. Hou, Y. Li, *Energy Environ. Sci.*, 2012, 5, 7943. |
| FF = 0.71, PCE = 7.7\% @ 250 nm | K. Li, Z. Li, K. Feng, X. Xu, L. Wang, Q. Peng, *J. Am. Chem. Soc.*, 2013, 135, 13549. |
| FF = 0.69, PCE = 7.5\% @ 250 nm | Z. Li, H. Lin, K. Jiang, J. Carpenter, Y. Li, Y. Liu, H. Hu, J. Zhao, W. Ma, H. Ade, H. Yan, *Nano Energy*, 2015, 15, 607. |
| FF = 0.65, PCE = 7.3\% @ 206 nm | N. Wang, Z. Chen, W. Wie, Z. Jiang, *J. Am. Chem. Soc.*, 2013, 135, 17060. |
| FF = 0.69, PCE = 7.7\% @ 250 nm | T. L. Nguyen, H. Choi, S. J. Ko, M. A. Uddin, B. Walker, S. Yum, J. E. Jeong, M. H. Yun, T. J. Shin, S. Hwang, J. Y. Kim, H. Y. Woo, *Energy Environ. Sci.*, 2014, 7, 3040. |
| FF = 0.62, PCE = 7.6\% @ 250 nm | Z. Chen, P. Cai, J. Chen, X. Liu, L. Zhang, L. Lan, J. Peng, Y. Ma, Y. Cao, *Adv. Mater.*, 2014, 26, 2586. |
FF = 0.75, PCE = 10.8% @ 300 nm
Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, Nat. Commun., 2014, 5, 5293.

FF = 0.73, PCE = 11.7% @ 350–400 nm
J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma, H. Yan, Nat. Energy, 2016, 1, 15027.

FF = 0.74, PCE = 10.4% @ 300 nm
Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, Nat. Commun., 2014, 5, 5293.

FF = 0.66, PCE = 9.4% @ 250 nm
J. Zhao, Y. Li, A. Hunt, J. Zhang, H. Yao, Z. Li, J. Zhang, F. Huang, H. Ade, H. Yan, Adv. Mater., 2016, 28, 1868.

FF = 0.69, PCE = 10.7% @ 250 nm
H. Hu, K. Jiang, G. Yang, J. Liu, Z. Li, H. Lin, Y. Liu, J. Zhao, J. Zhang, F. Huang, Y. Qu, W. Ma and H. Yan, J. Am. Chem. Soc., 2015, 137, 14149.

FF = 0.65, PCE = 10.0% @ 250 nm
H. Hu, K. Jiang, G. Yang, J. Liu, Z. Li, H. Lin, Y. Liu, J. Zhao, J. Zhang, F. Huang, Y. Qu, W. Ma and H. Yan, J. Am. Chem. Soc., 2015, 137, 14149.

FF = 0.66, PCE = 8.6% @ 280 nm
X. Hu, C. Yi, M. Wang, C.-H. Hsu, S. Liu, K. Zhang, C. Zhong, F. Huang, X. Gong, Y. Cao, Adv. Energy Mater., 2014, 4, 1400378.

FF = 0.66, PCE = 8.6% @ 280 nm
X. Hu, C. Yi, M. Wang, C.-H. Hsu, S. Liu, K. Zhang, C. Zhong, F. Huang, X. Gong, Y. Cao, Adv. Energy Mater., 2014, 4, 1400378.

FF = 0.68, PCE = 10.1% @ 300 nm
Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, Nat. Commun., 2014, 5, 5293.

FF = 0.73, PCE = 10.1% @ 290 nm
V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, Nat. Photonics, 2015, 9, 403.

FF = 0.67, PCE = 10.5% @ 230 nm
K. Kawashima, T. Fukuhara, Y. Suda, Y. Suzuki, T. Koganezawa, H. Yoshida, H. Ohkita, I. Osaka, K. Takimiya, J. Am. Chem. Soc., 2016, 138, 10265.

FF = 0.73, PCE = 10.3% @ 300 nm
Y. Jin, Z. Chen, S. Dong, N. Zheng, L. Ying, X. Jiang, F. Liu, F. Huang, Y. Cao, Adv. Mater., 2016, 28, 9811.
FF = 0.64, PCE = 8.9% @ 225 nm  
K. Kawashima, Y. Tamai, H. Ohkita, I. Osaka, K. Takimiya, *Nat. Commun.*, 2015, 6, 10085.

FF = 0.68, PCE = 7.3% @ 250 nm  
Q. Fan, W. Su, X. Guo, B. Guo, W. Li, Y. Zhang, K. Wang, M. Zhang, Y. Li, *Adv. Energy Mater.*, 2016, 6, 1600430.

FF = 0.68, PCE = 7.5% @ 203 nm  
X. Zhu, J. Fang, K. Lu, J. Zhang, L. Zhu, Y. Zhao, Z. Shuai, Z. Wei, *Chem. Mater.*, 2014, 26, 6947.

FF = 0.70, PCE = 9.4% @ 340 nm  
H. Choi, S.-J. Ko, T. Kim, P.-O. Morin, B. Walker, B. H. Lee, M. Leclerc, J. Y. Kim, A. J. Heeger, *Adv. Mater.*, 2015, 27, 3318.

FF = 0.63, PCE = 8.0% @ 270 nm  
Y. Li, S.-J. Ko, S. Y. Park, H. Choi, T. L. Nguyen, M. A. Uddin, T. Kim, S. Hwang, J. Y. Kim, H. Y. Woo, *J. Mater. Chem. A*, 2016, 4, 9967.

FF = 0.71, PCE = 9.8% @ 210 nm  
S. Shi, Q. Liao, Y. Tang, H. Guo, X. Zhou, Y. Wang, T. Yang, Y. Liang, X. Cheng, F. Liu, X. Guo, *Adv. Mater.*, 2016,28, 9969.

FF = 0.65, PCE = 7.5% @ 330 nm  
I. Osaka, M. Saito, T. Koganezawa, K. Takimiya, *Adv. Mater.*, 2014, 26, 331.

FF = 0.65, PCE = 7.1% @ 235 nm  
X. Dong, Y. Deng, H. Tian, Z. Xie, Y. Geng, F. Wang, *J. Mater. Chem. A*, 2015, 3, 19928.

FF = 0.74, PCE = 9.3% @ 310 nm  
S. Berny, N. Blouin, A. Dister, H.-J. Egelhaaf, M. Krompiec, A. Lohr, W. R. Lozman, G. E. Morse, L. Nansin, A. Pron, T. Sauermann, N. Seider, S. Tierney, P. Tiwana, M. Wagner, H. Wilson, *Adv. Sci.*, 2016, 3, 1500342.
**Table S2.** Conjugated polymers reported in literatures that show PCE ≥ 8.0% with optimal active layer thickness of ~100 nm but no efficient thick-film (≥ 200 nm) devices reported.

| Compound | FF   | PCE  | Active Layer Thickness (nm) | Reference  |
|----------|------|------|-----------------------------|------------|
| FF = 0.72, PCE = 9.2% @ ~80 nm | Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, Nat. Photonics 2012, 6, 591. |
| FF = 0.74, PCE = 10.6% @ 80–100 nm | Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, Nat. Photonics 2015, 9, 174. |
| FF = 0.69, PCE = 10.2% @ ~100 nm | S. Zhang, L. Ye, W. Zhao, B. Yang, Q. Wang, J. Hou, Sci. China Chem., 2015, 58, 248. |
| FF = 0.70, PCE = 8.5% @ 100–120 nm | C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGeehe, P. M. Beaulieu, J. Am. Chem. Soc., 2013, 135, 4656. |
| FF = 0.67, PCE = 8.5% @ 105 nm | C. E. Small, S. Chen, J. Subbiah, C. M. Amb, S.-W. Tsang, T.-H. Lai, J. R. Reynolds, F. So, Nat. Photonics, 2012, 6, 115. |
| FF = 0.69, PCE = 8.2% @ 139 nm | Y. Deng, J. Liu, J. Wang, L. Liu, W. Li, H. Tian, X. Zhang, Z. Xie, Y. Geng, F. Wang, Adv. Mater., 2014, 26, 471. |
| FF = 0.66, PCE = 9.4% @ ~90 nm | J. Subbiah, B. Purushothaman, M. Chen, T. Qin, M. Gao, D. Vak, F. H. Scholes, X. Chen, S. E. Watkins, G. J. Wilson, A. B. Holmes, W. W. H. Wong, D. J. Jones, Adv. Mater., 2015, 27, 702. |
| FF = 0.63, PCE = 8.0% @ 100 nm | L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard, Y. Yang, Macromolecules, 2013, 46, 3384. |
| FF = 0.70, PCE = 8.4% @ 90–115 nm | Z. Zhang, F. Lin, H.-C. Chen, H.-C. Wu, C.-L. Chung, C. Lu, S.-H. Liu, S.-H. Tung, W.-C. Chen, K.-T. Wong, P.-T. Chou, Energy Environ. Sci., 2015, 8, 552. |
Figure S1. GPC traces of the polymers acquired with o-DCB as eluent at 140 °C.

Figure S2. DSC thermograms of pure polymers measured with a scan rate of 10 °C min⁻¹.

Table S3. The theoretical mass fractions (wt%) of the characteristic elements F, N, and S of the polymers.

| Polymer     | wt % F | wt% N | wt % S |
|-------------|--------|-------|--------|
| C10-Th00    | 3.506  | 2.585 | 14.794 |
| C10-Th25    | 3.378  | 2.491 | 15.680 |
| C10-Th50    | 3.259  | 2.403 | 16.503 |
| C10-Th75    | 3.148  | 2.321 | 17.270 |
| C10-Th100   | 3.045  | 2.244 | 17.986 |
Figure S3. UV-vis absorption spectra of the polymers in o-DCB solutions with concentration of 0.05 mg mL\(^{-1}\).

Figure S4. Cyclic voltammograms of the polymers and ferrocene measured in acetonitrile.
Table S4. Device statistics of C10-Thx:[70]PCBM solar cells at ~250 nm active layer thickness.\(^{a)}\)

| Polymer     | \(J_{sc}\) (mA cm\(^{-2}\)) | \(J_{sc}(\text{EQE})\)\(^{b)}\) (mA cm\(^{-2}\)) | \(V_{oc}\) (V) | FF (-) | \(P_{max}\) (mW cm\(^{-2}\)) | PCE\(^{c)}\) (%) |
|-------------|-------------------------------|---------------------------------|--------------|--------|----------------------------|-----------------|
| C10-Th00    | 10.0                          | 9.8                             | 0.93         | 0.45   | 4.2                        | 4.1             |
|             | 9.7 ± 0.2                     |                                 | 0.93 ± 0.001 | 0.45 ± 0.00 | 4.1 ± 0.1                 |                 |
| C10-Th25    | 12.7                          | 12.3                            | 0.89         | 0.47   | 5.3                        | 5.1             |
|             | 12.7 ± 0.2                    |                                 | 0.89 ± 0.002 | 0.46 ± 0.01 | 5.2 ± 0.1                 |                 |
| C10-Th50    | 12.9                          | 13.5                            | 0.88         | 0.55   | 6.2                        | 6.5             |
|             | 12.6 ± 0.3                    |                                 | 0.88 ± 0.001 | 0.55 ± 0.01 | 6.0 ± 0.2                 |                 |
| C10-Th75    | 12.8                          | 13.9                            | 0.84         | 0.56   | 6.0                        | 6.5             |
|             | 12.4 ± 0.4                    |                                 | 0.84 ± 0.002 | 0.56 ± 0.01 | 5.8 ± 0.2                 |                 |
| C10-Th100   | 14.7                          | 14.9                            | 0.84         | 0.61   | 7.5                        | 7.7             |
|             | 14.3 ± 0.6                    |                                 | 0.84 ± 0.005 | 0.62 ± 0.2 | 7.4 ± 0.2                 |                 |

\(^{a)}\) Measured with white light (100 mW cm\(^{-2}\)) in a ITO/PEDOT:PSS/C10-Thx:[70]PCBM/LiF (1 nm)/Al(100 nm) device configuration. Both maximum and device statistics from four devices are given. \(^{b)}\) Determined by integrating the EQE with the AM1.5G solar spectrum. \(^{c)}\) Calculated using \(J_{sc}(\text{EQE})\).

Figure S5. \(J-V\) curves (a) and EQE (b) spectra of C10-Thx:[70]PCBM PSCs with 100 nm active layer thickness. And change of \(J_{sc}\) and \(V_{oc}\) (c) and of FF and PCE (d) with \(x\) for C10-Thx polymers for the PSCs with 100 nm active layer thickness.
Table S5. Device parameters and statistics of C10-Thx:[70]PCBM solar cells at ~100 nm active layer thickness.a)

| Polymer   | \(J_{sc}\) (mA cm\(^{-2}\)) | \(J_{sc}(\text{EQE})\) (mA cm\(^{-2}\)) | \(V_{oc}\) (V) | FF  | \(P_{max}\) (mW cm\(^{-2}\)) | PCE\(^c\) (%) |
|-----------|-------------------------------|------------------------------------------|--------------|-----|----------------|---------------|
| C10-Th00  | 8.6                           | 8.5 ± 0.2                                | 0.94         | 0.66| 5.3            | 5.4           |
| C10-Th25  | 9.6                           | 9.5 ± 0.1                                | 0.91         | 0.69| 6.0            | 6.7           |
| C10-Th50  | 10.3                          | 10.2 ± 0.1                               | 0.89         | 0.68| 6.3            | 6.5           |
| C10-Th75  | 10.7                          | 10.6 ± 0.1                               | 0.85         | 0.64| 5.8            | 6.7           |
| C10-Th100 | 12.7                          | 12.8 ± 0.2                               | 0.85         | 0.68| 7.4            | 7.7           |

a) Measured with white light (100 mW cm\(^{-2}\)) in a ITO/PEDOT:PSS/C10-Thx:[70]PCBM/LiF (1 nm)/Al(100 nm) device configuration. Both maximum and device statistics from four devices are given. b) Determined by integrating the EQE with the AM1.5G solar spectrum. c) Calculated using \(J_{sc}(\text{EQE})\).

Figure S6. Chemical structures of C8-Th00 and C8-Th25.

Table S6. Performance parameter comparison of PSCs based on C8-Th00, C8-Th25, C10-Th50, C10-Th75, and C10-Th100 at ~250 nm active layer thickness.

| Polymer   | Solvent | Thickness (nm) | \(J_{sc}\) (mA cm\(^{-2}\)) | \(V_{oc}\) (V) | FF  | PCE (%) | EQE\(_{max}\) |
|-----------|---------|----------------|-----------------------------|--------------|-----|---------|--------------|
| C8-Th00   | CF (3% DIO) | 240          | 7.7                         | 0.92         | 0.44| 3.1     | 0.40         |
| C8-Th25   | CB (3% DIO) | 247          | 13.3                        | 0.90         | 0.50| 6.0     | 0.66         |
| C10-Th50  | CB/CN (7/3) | 245          | 13.5                        | 0.88         | 0.55| 6.5     | 0.68         |
| C10-Th75  | CB/CN (7/3) | 240          | 13.9                        | 0.84         | 0.56| 6.5     | 0.69         |
| C10-Th100 | CB/CN (9/1) | 246          | 14.9                        | 0.84         | 0.61| 7.7     | 0.76         |
Figure S7. (a) $J-V$ curves of the PSCs based on C8-Th00, C8-Th25, C10-Th50, C10-Th75, and C10-Th100 at ~250 nm thickness of active layer under dark and under AM1.5G illumination. (b) EQE spectra of the corresponding devices. (c) The change of $J_{sc}$ and $V_{oc}$ with increased amount of thiophene ring. (d) The change of FF and PCE with increased amount of thiophene ring.

Table S7. Time-resolved photoluminescence parameters of the films.a)

| Sample                     | $\tau_1$ (ps) | $\tau_2$ (ps) | $k_{\text{dec,blend}}$ (ns$^{-1}$) | $k_{\text{CT}}$ (ns$^{-1}$) | $\eta_{\text{CT}}$ (%) |
|---------------------------|---------------|---------------|-----------------------------------|-----------------------------|-----------------------|
| C10-Th00                  | 463           | -             | -                                 | -                           | -                     |
| C10-Th00:[70]PCBM         | 161 (65%)$^b$ | 950 (35%)$^b$ | 6.21                              | 4.05                        | 65.2                  |
| C10-Th25                  | 718           | -             | -                                 | -                           | -                     |
| C10-Th25:[70]PCBM         | 102 (64%)$^b$ | 985 (36%)$^b$ | 9.80                              | 8.41                        | 85.8                  |
| C10-Th50                  | 687           | -             | -                                 | -                           | -                     |
| C10-Th50:[70]PCBM         | 106 (73%)$^b$ | 1016 (27%)$^b$| 9.43                              | 7.98                        | 84.6                  |
| C10-Th75                  | 762           | -             | -                                 | -                           | -                     |
| C10-Th75:[70]PCBM         | 102 (74%)$^b$ | 1154 (26%)$^b$| 9.80                              | 8.49                        | 86.6                  |
| C10-Th100                 | 738           | -             | -                                 | -                           | -                     |
| C10-Th100:[70]PCBM        | 68 (78%)$^b$  | 887 (22%)$^b$ | 14.71                             | 13.35                       | 90.8                  |

a)The fluorescence decay traces of the samples were recorded at 720 nm with the wavelength of the excitation light at 400 nm. $^b$The number in bracket is the percentage of corresponding decay component relative to the total decay. These data show that the fast component (τ) is the major decay pathway in all blend films. $^c k_{\text{dec,blend}} = \tau_1,\text{blend}^{-1}$. $^d k_{\text{CT}} = \tau_1,\text{blend}^{-1} - \tau_1,\text{pure}^{-1}$. $^e \eta_{\text{CT}} = k_{\text{CT}}/k_{\text{dec,blend}}$. 
**Figure S8.** Average $\text{EQE}_{\text{bias}}/\text{EQE}_{\text{no bias}}$ values for C10-Thx:[70]PCBM solar cells at ~100 nm active layer thickness.

**Figure S9.** EQEs measured with and without light bias of the polymer:[70]PCBM solar cells at ~250 nm active layer thickness: (a) C10-Th00; (b) C10-Th25; (c) C10-Th50; (d) C10-Th75; and (e) C10-Th100.
Figure S10. EQEs measured with and without light bias of the polymer:[70]PCBM solar cells at ~100 nm active layer thickness: (a) C10-Th00; (b) C10-Th25; (c) C10-Th50; (d) C10-Th75; and (e) C10-Th100.
Figure S11. Bright field TEM images of the C10-Thx:[70]PCBM blend films at ~100 nm thickness formed under the same conditions as solar cell fabrications for C10-Th00 (a), C10-Th25 (b), C10-Th50 (c), C10-Th75 (d), and C10-Th100 (e). Image size: 1.5 × 1.5 μm²; scale bar: 0.2 μm.

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