Supporting Information for

Trifluoromethylated thieno[3,4-\textit{b}]thiophene-2-ethyl carboxylate as building block for conjugated polymers

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1. TGA and DSC thermograms of polymers

Fig. S1. TGA thermograms of polymers at temperature ramp of 20 °C min⁻¹ under a N₂ atmosphere.

Fig. S2. DSC thermograms of first cooling and second heating scan of polymers at temperature ramp of 10 °C/min.
2. NMR spectra

**Fig. S3.** $^1$H NMR spectrum of compound 1.
Fig. S4. $^1$H NMR spectrum of compound 2.

Fig. S5. $^1$H NMR spectrum of compound 3.

Fig. S6. $^1$H NMR spectrum of polymer PBDT-TTCF$_3$. 

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**Fig. S7.** $^1$H NMR spectrum of polymer PPDA-TTCF$_3$.

**Fig. S8.** $^1$H NMR spectrum of polymer PPDA-TT.
3. GPC curves of polymers

**Fig. S9.** GPC curve of PBDT-TTCF$_3$.

**Fig. S10.** GPC curve of PPDA-TT
Fig. S11. GPC curve of PPDA-TTCF₃

4. UV-vis absorption spectra of polymer thin-films

Fig. S12. UV-vis absorption spectra of thieno[3,4-b]thiophene-based polymer thin-films
5. The $J-V$ characteristics of devices based on the polymer/PC$_{61}$BM blends (w/w=1:1, without 1 vol % DIO).

![Graph](image)

**Fig. S13.** The $J-V$ characteristics of devices based on the polymer/PC$_{61}$BM blends with weight ratio of 1:1 fabricated from CB solutions without 1 vol % DIO.

6. **Hole mobilities of polymers investigated by the space charge limited current (SCLC) method**

The hole-only device structure is ITO/PEDOT:PSS/polymer/MoO$_3$/Al, which is fabricated to investigate the hole mobility using the space charge limited current (SCLC) method. The hole mobility is determined by fitting the dark J-V curves for single carrier devices to SCLC model at low voltages, where the current is given by $J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8d^3$, where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the polymer, $\mu_h$ is the zero-field mobility, and $d$ is the thickness of polymer film. In this measurement, the film thicknesses are 35 nm, 40 nm, 40 nm for PBDT-TTCF$_3$, PPDA-TT and PPDA-TTCF$_3$ respectively. The applied bias voltage is corrected for the built-in potential so that $V = V_{\text{app}} - V_{\text{bi}}$. 

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7. AFM study of polymers/PC$_{61}$BM blend morphologies

Fig. S14. AFM images (1×1 μm$^2$) of polymer/PC$_{61}$BM blends at 1:1 ratio by weight: (a) PBDT-TT/PC$_{61}$BM film with DIO; (b) PPDA-TT/PC$_{61}$BM with DIO; (c) PPDA-TTCF$_3$/PC$_{61}$BM with DIO; (d) PPDA-TTCF$_3$/PC$_{61}$BM without DIO.