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# Effect of linear side-chain length on the photovoltaic performance of benzodithiophene-*alt*-dicarboxylic ester terthiophene polymers

Kangqiao Ma,[a,b] Tao Zhang,[b] Pan Wan,[b] Bowei Xu,[b] Pengxin Zhou[a]* and Cunbin An[b]*

[a]College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

[b]Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

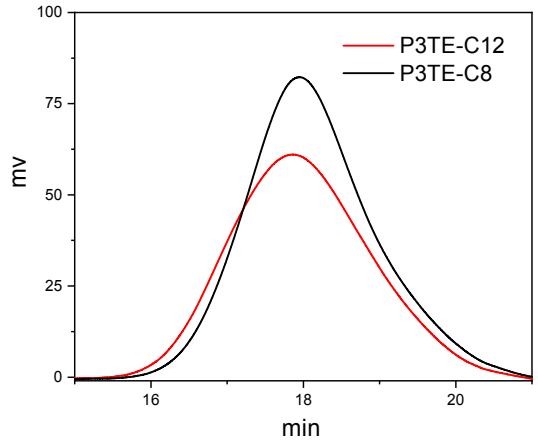


**Figure S1**. GPC curves for P3TE-C8 and P3TE-C12 measured at 145 °C.

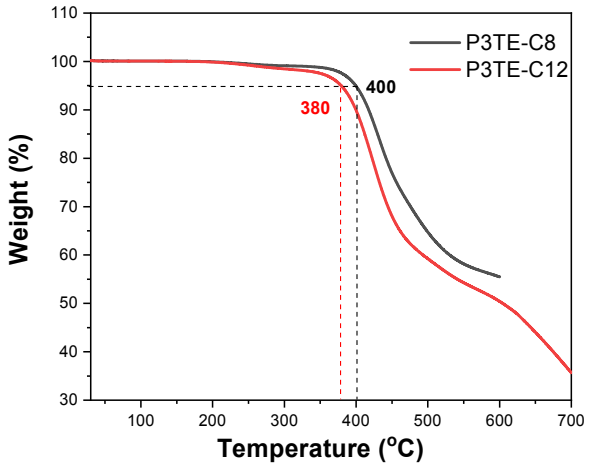


**Figure S2**. TGA curves for P3TE-C8 and P3TE-C12 measured under a nitrogen atmosphere at a heating rate of 10 ºC/min.

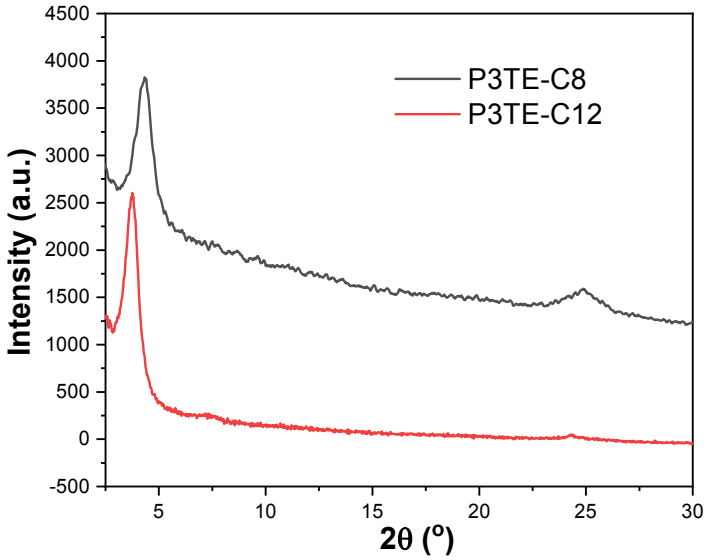


**Figure S3**. The XRD profiles of P3TE-C8 and P3TE-C12.

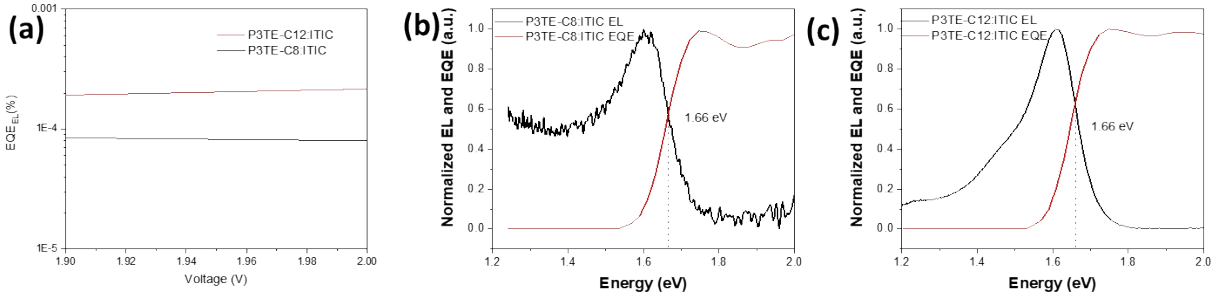


**Figure S4**. (a) The $EQE_{EL}$ of P3TE-C8:ITIC and P3TE-C12:ITIC The band gap of P3TE-C8:IITIC(b) and P3TE-C12:ITIC (c).

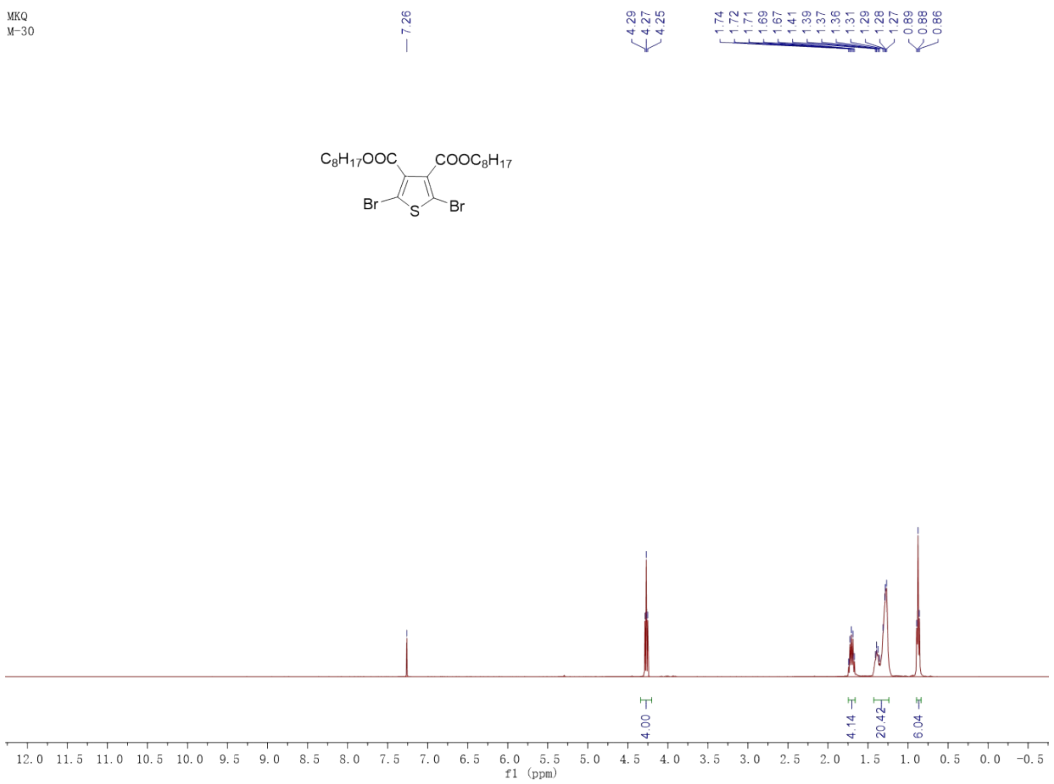


**Figure S5.** The $^{1}$H-NMR spectra of compound **2a** in $CDCl_3$.

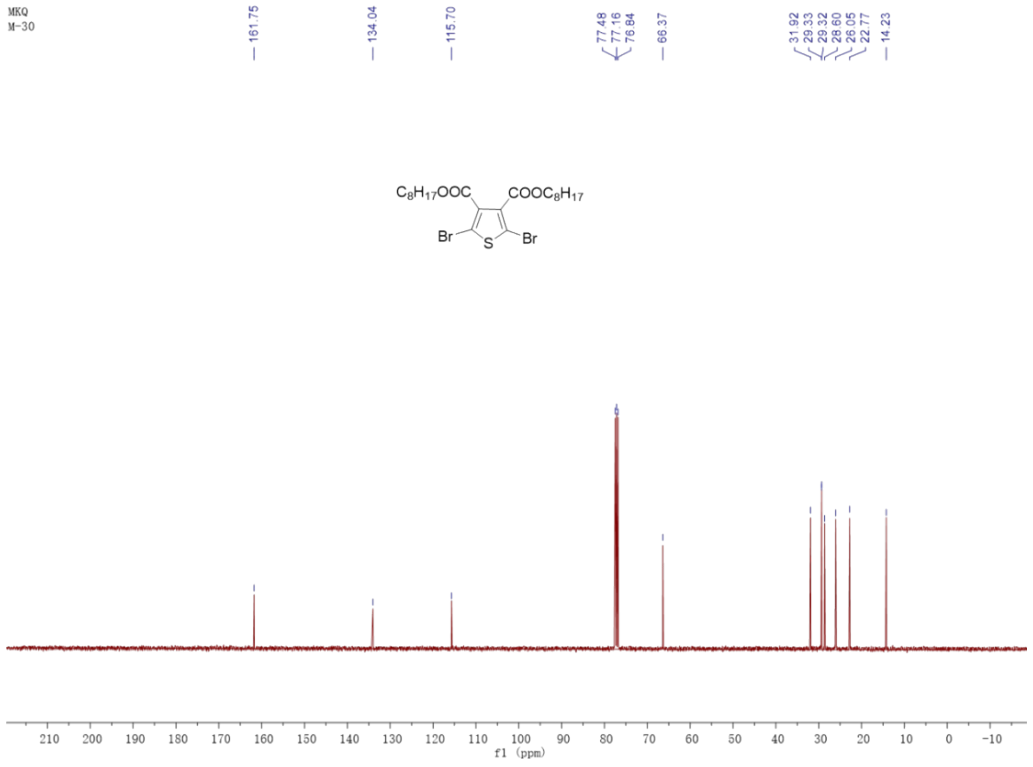


**Figure S6.** The $^{13}$C-NMR spectra of compound **2a** in $CDCl_3$.

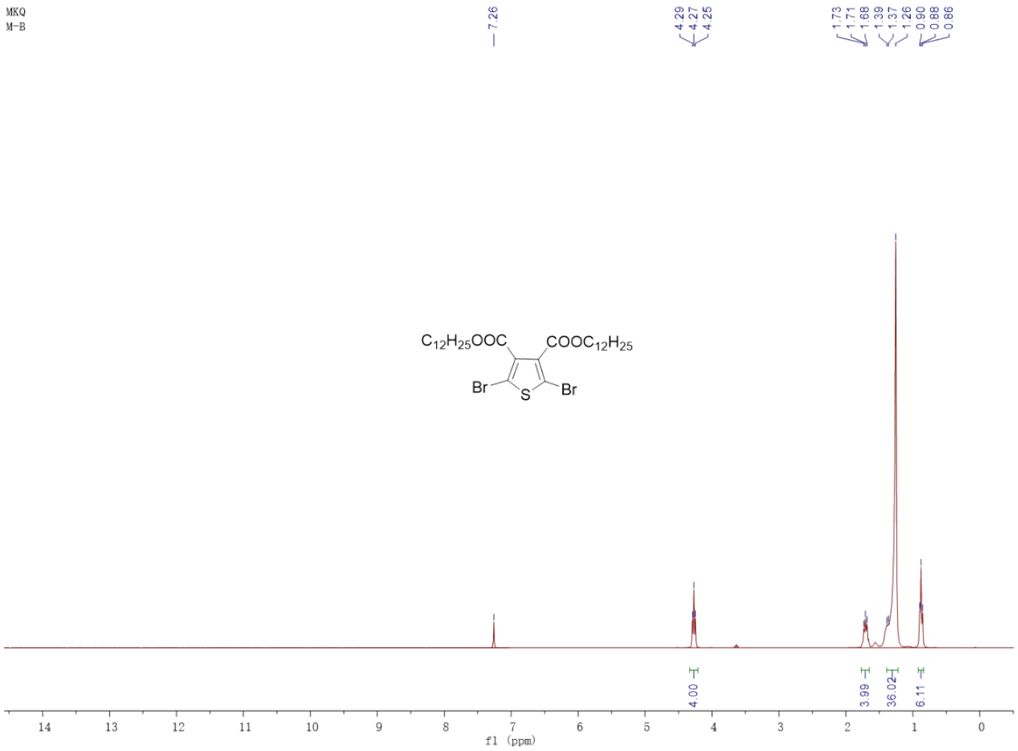


**Figure S7.** The $^{1}$H-NMR spectra of compound **2b** in $CDCl_3$.

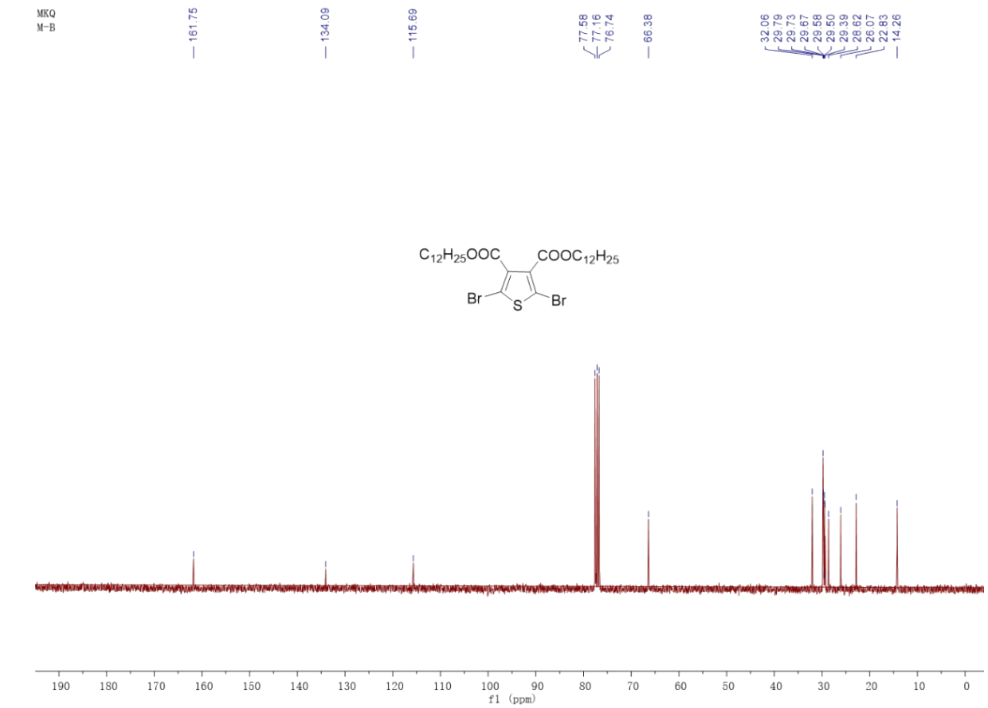


**Figure S8.** The $^{13}$C-NMR spectra of compound **2b** in $CDCl_3$.

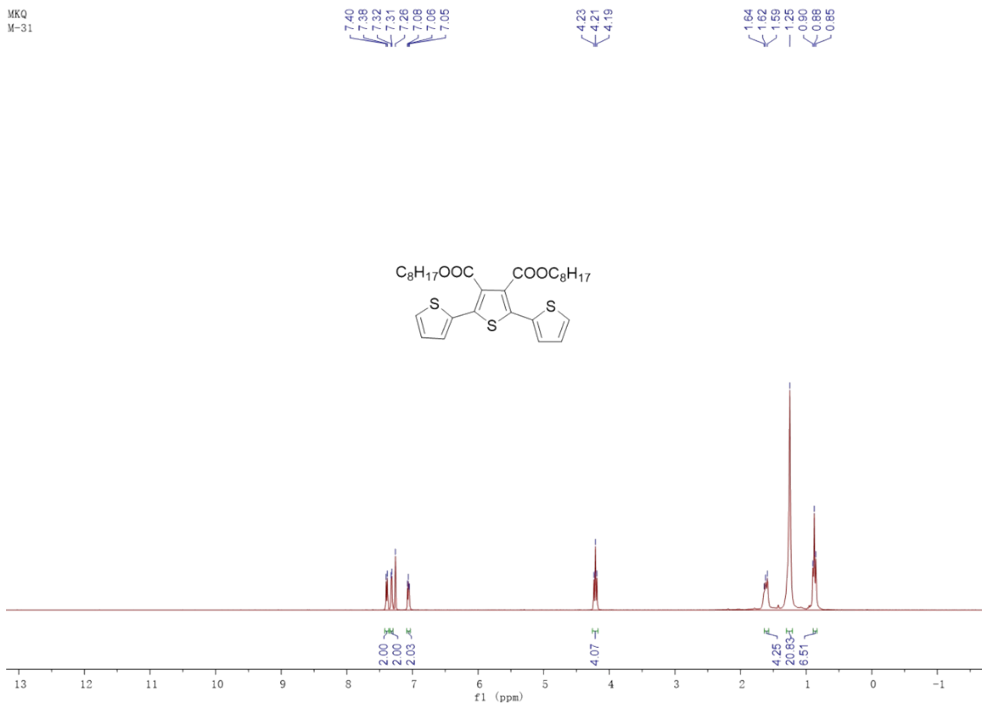


**Figure S9.** The $^{1}$H-NMR spectra of compound **3a** in $CDCl_3$.

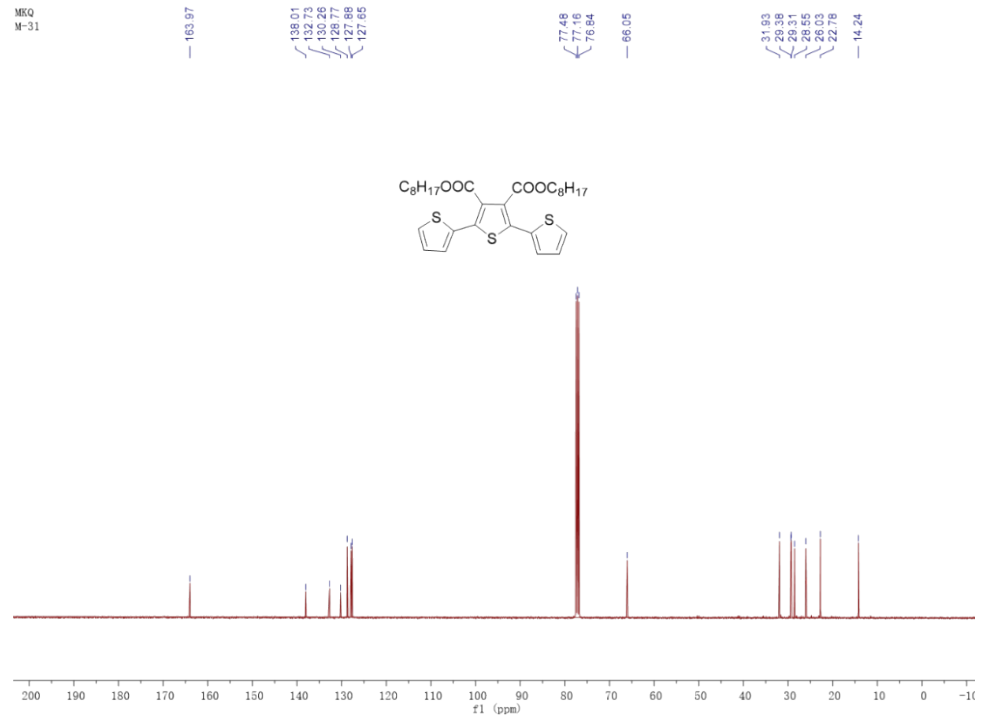


**Figure S10.** The $^{13}$C-NMR spectra of compound **3a** in $CDCl_3$.

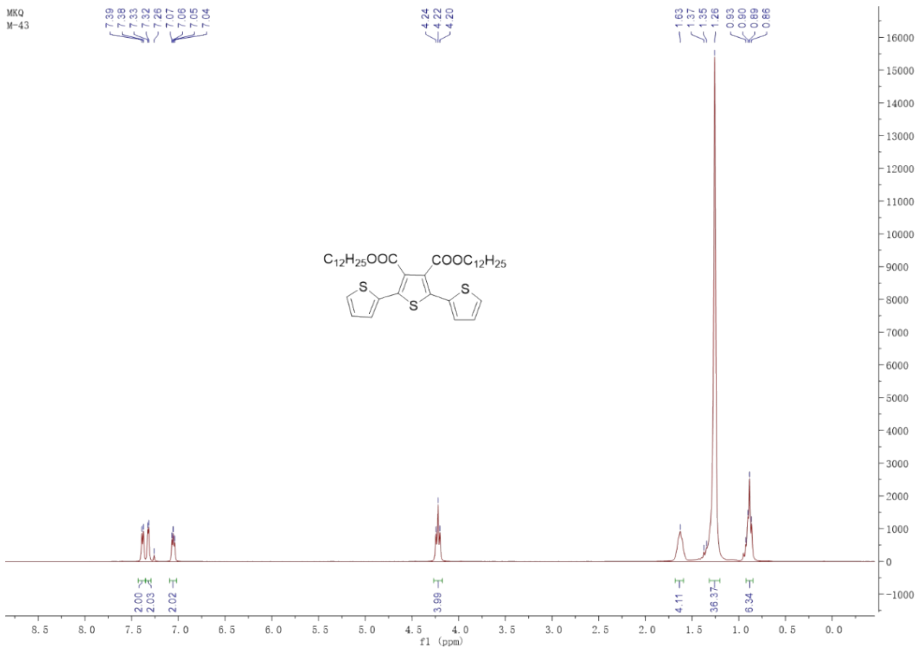


**Figure S11.** The $^{1}$H-NMR spectra of compound **3b** in $CDCl_3$.

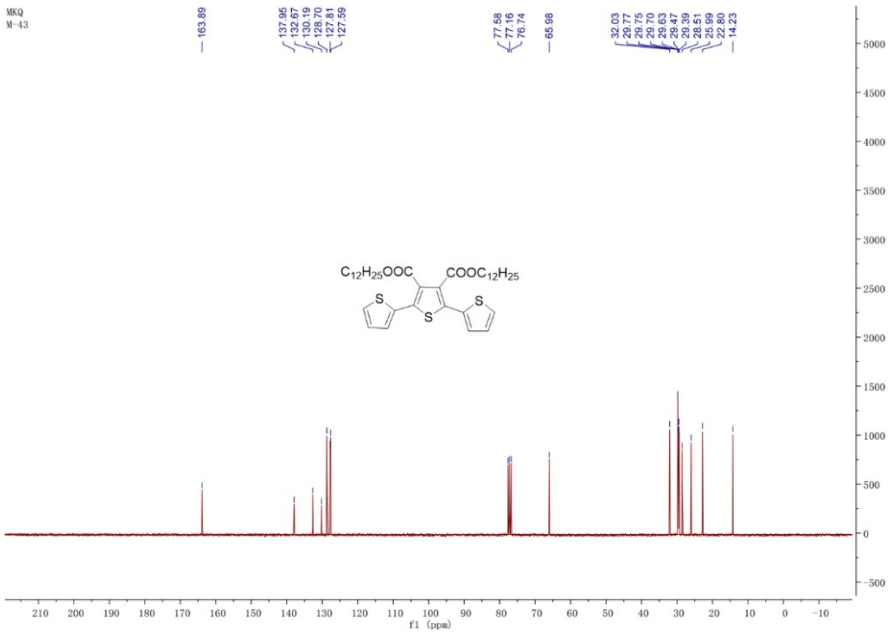


**Figure S12.** The $^{13}$C-NMR spectra of compound **3b** in $CDCl_3$.

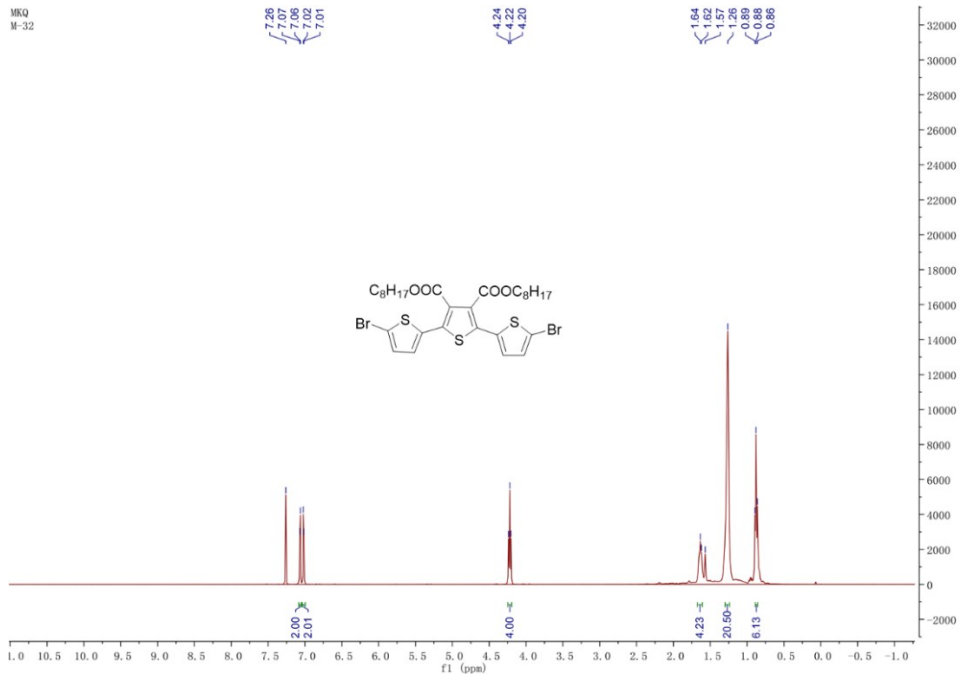


**Figure S13.** The $^{1}$H-NMR spectra of compound **4a** in $CDCl_3$.

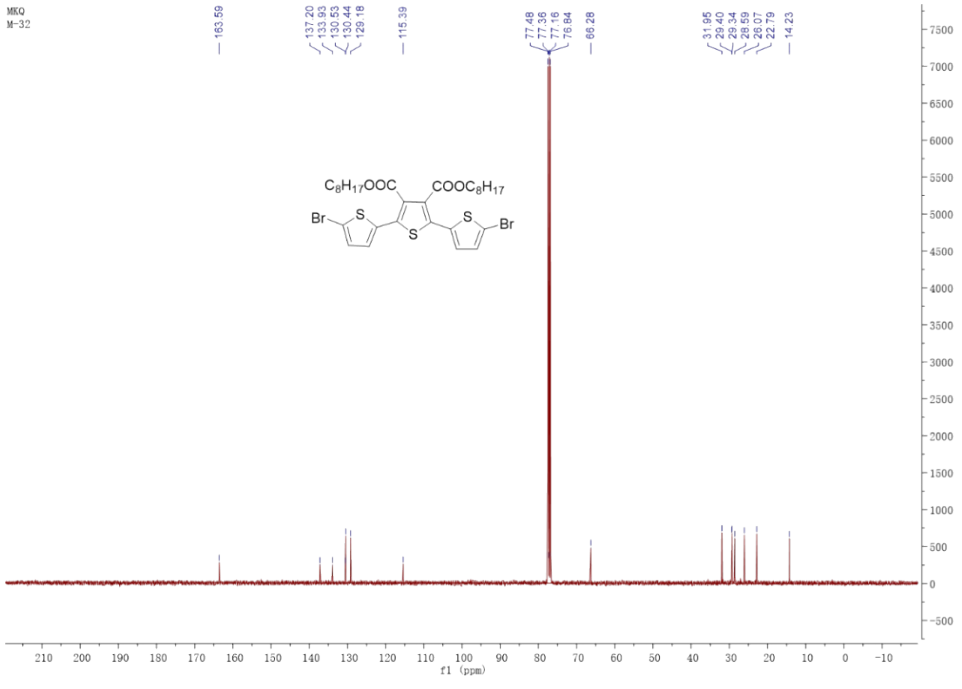


**Figure S14.** The $^{13}$C-NMR spectra of compound **4a** in $CDCl_3$.

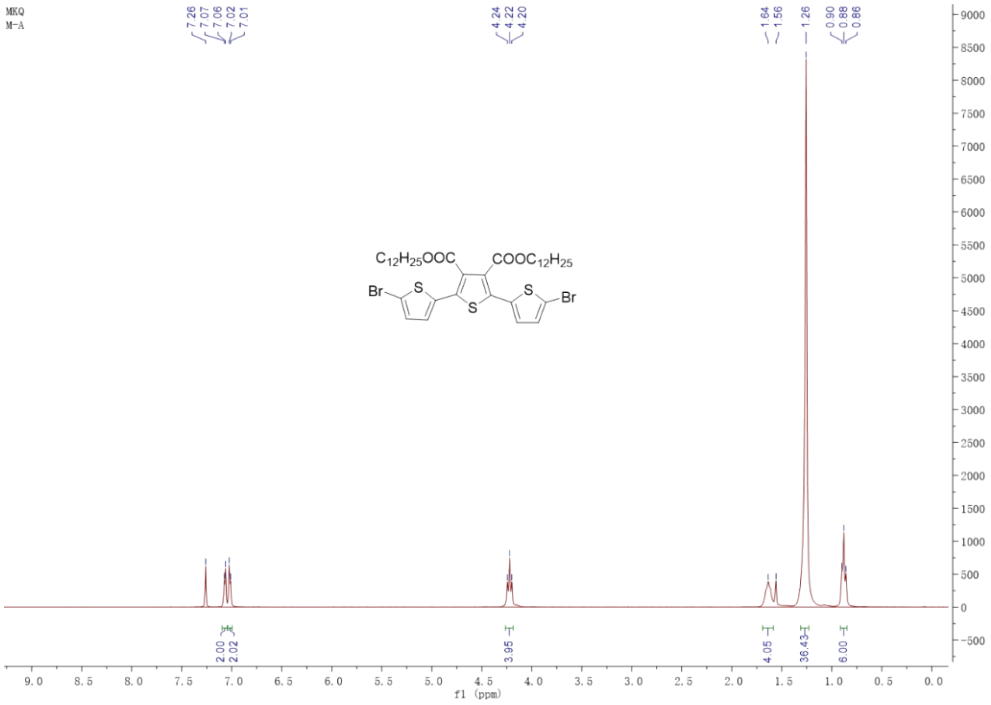


**Figure S15.** The $^{1}$H-NMR spectra of compound **4b** in $CDCl_3$.

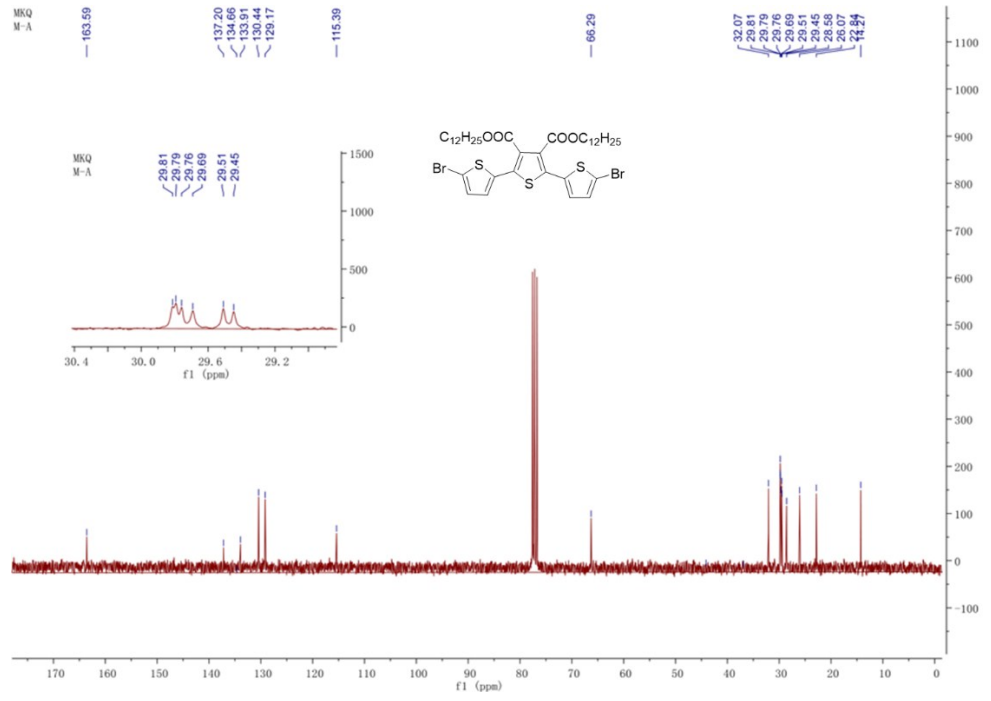


**Figure S16.** The $^{13}$C-NMR spectra of compound **4b** in $CDCl_3$.

**Table S1**. The best photovoltaic parameters of P3TE-C8:ITIC with different D:A weight ratios (w/w).

| D:A ratio | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 1.5:1 | 0.797 | 12.70 | 45.29 | 4.58 |
| 1:1 | 0.777 | 13.52 | 42.38 | 4.45 |
| 1:1.5 | 0.769 | 13.52 | 40.66 | 4.23 |

P3TE-C8:ITIC was dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 $^{o}$C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1500-2000 r.m.p. Subsequently, the active layer was annealed at 100 $^{o}$C for 10 min.

**Table S2.** The best photovoltaic parameters of P3TE-C8:ITIC with different DIO ratios.

| DIO ratio | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 0 | 0.797 | 12.70 | 45.29 | 4.58 |
| 0.5% | 0.814 | 12.80 | 52.48 | 5.47 |
| 1% | 0.809 | 12.24 | 44.57 | 4.42 |
| 2% | 0.815 | 9.96 | 39.44 | 3.20 |

P3TE-C8:ITIC (1.5:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 $^{o}$C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1500 r.m.p. Subsequently, the active layer was annealed at 100 $^{o}$C for 10 min.

**Table S3.** The best photovoltaic parameters of P3TE-C8:ITIC with different annealing temperatures.

| Annealing temperature (°C) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 80 | 0.827 | 12.13 | 49.25 | 4.94 |
| 100 | 0.814 | 12.86 | 52.48 | 5.47 |
| 120 | 0.825 | 12.71 | 50.61 | 5.31 |
| 140 | 0.828 | 11.59 | 52.21 | 5.30 |
| 160 | 0.829 | 11.40 | 51.78 | 4.89 |

P3TE-C8:ITIC (1.5:1 w/w)were dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 °C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1500 r.m.p. Subsequently, the active layer was annealed at 80-160 °C for 10 min.

**Table S4**. The best photovoltaic parameters of P3TE-C12:ITIC with different D:A weight ratios (w/w).

| D:A ratio | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 1.5:1 | 0.917 | 10.15 | 57.54 | 5.36 |
| 1:1 | 0.916 | 12.83 | 52.06 | 6.12 |
| 1:1.5 | 0.907 | 12.46 | 49.48 | 5.59 |

P3TE-C12:ITIC was dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 °C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1500-2000 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

**Table S5.** The best photovoltaic parameters of P3TE-C12:ITIC with different DIO ratios.

| DIO ratio | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 0 | 0.916 | 12.83 | 52.06 | 6.12 |
| 0.5% | 0.904 | 13.81 | 55.96 | 6.99 |
| 1% | 0.885 | 11.56 | 42.86 | 4.39 |
| 2% | 0.888 | 10.14 | 37.26 | 3.35 |

P3TE-C12:ITIC (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 $^{o}$C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1700 r.m.p. Subsequently, the active layer was annealed at 100 $^{o}$C for 10 min.

**Table S6.** The best photovoltaic parameters of P3TE-C12:ITIC with different annealing temperatures.

| Annealing temperature ($^{o}$C) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| 80 | 0.903 | 14.25 | 53.99 | 6.95 |
| 100 | 0.904 | 13.81 | 55.96 | 6.99 |
| 120 | 0.909 | 13.50 | 58.09 | 7.13 |
| 140 | 0.906 | 14.20 | 59.36 | 7.64 |
| 160 | 0.890 | 12.57 | 60.25 | 6.74 |

P3TE-C12:ITIC (1:1 w/w)were dissolved in chlorobenzene solution with a concentration of 10 mg mL$^{-1}$. The solution was heated to 40 $^{o}$C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1700 r.m.p. Subsequently, the active layer was annealed at 80-160 $^{o}$C for 10 min.

**Table S7.** The detailed energy losses of P3TE-C8:ITIC and P3TE-C12:ITIC-based devices.

| | $E_{gap}$ (eV) | $qV_{oc}$ (eV) | $q\Delta V$ (eV) | $\Delta E_1$ (eV) | $\Delta E_2$ (eV) | $EQE_{EL}$ | $\Delta E_3$ (eV) |
|---|---|---|---|---|---|---|---|
| P3TE-C8:ITIC | 1.66 | 0.814 | 0.846 | 0.276 | 0.207 | 7.97E-7 | 0.363 |
| P3TE-C12:ITIC | 1.66 | 0.906 | 0.754 | 0.276 | 0.141 | 2.18E-6 | 0.337 |