# Controllable Synthesis of Conjugated Thiophenylethyne-based Compounds with Different Chain Lengths 

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Table S1 Summary of crystal data and reflective collection parameters for $\mathbf{2}$.


| Empirical formula | $\mathrm{C}_{16} \mathrm{H}_{8} \mathrm{~S}_{3}$ |
| :---: | :---: |
| Formula weight | 296.40 |
| Crystal size, mm | $0.26 \times 0.21 \times 0.17$ |
| Crystal system | Monoclinic, C2/c |
| space group | P2(1)/c |
| a, $\AA$ | 15.042(5) |
| $\mathrm{b}, \AA$ | 11.404(4) |
| c, $\AA$ | $\mathrm{c}=32.856$ (10) |
| a, deg | 90 |
| $\beta$, deg | 95.094(5) |
| $\gamma$, deg | 90 |
| $V, \AA^{3}$ | 5614(3) |
| Z | 16 |
| Calculated density, $\mathrm{Mg} / \mathrm{m}^{3}$ | 1.403 |
| F(000) | 2432 |
| Temperature, K | 296(2) |
| Wavelength, $\AA$ | 0.71073 |
| $\mu(\mathrm{Mo} \mathrm{Ka}), \mathrm{mm}^{-1}$ | 0.509 |
| $2 \theta_{\text {max }}$, deg (Completeness ) | 25.00 (98.5 \%) |
| no. of collected reflections | 13829 |
| no. of unique ref. $R_{\text {int }}$ ) | 4882 (0.0618) |
| Data/restraints/parameters | 4882 / 7 / 352 |
| $\mathrm{R}_{1}, \mathrm{wR}_{2}[\mathrm{obs} \mathrm{I}>2 \sigma(\mathrm{I})$ ] | $0.0881,0.1980$ |
| $\mathrm{R}_{1}, \mathrm{wR}_{2}$ (all data) | 0.1181, 0.2094 |
| residual peak/hole, e. $\AA^{-3}$ | $0.634 /-0.752$ |
| transmission ratio | 0.9185/ 0.8791 |
| Goodness-of-fit on $F^{2}$ | 1.067 |



Fig. S1 The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1}$.

| Parameter | Value |
| :---: | :---: |
| 1 Origin | Bruker BioSpin GabH |
| 2 Onner | root |
| 3 Spectrometer | spect |
| 4 Solvent | CD2C12 |
| 5 Temperature | 298.7 |
| 6 Pulse Sequence | zgpg |
| 7 Number of Scans | 1000 |
| 8 Receiver Gain | 195 |
| 9 Relaxation Delay | 3.0000 |
| 10 Pulse Width | 10.5200 |
| 11 Acquisition Time | 1. 3631 |
| 12 Acquisition Date | 2015-06-19T22:42:09 |
| 13 Modification Date | 2015-06-19T23:01:56 |
| 14 Spectrometer Frequency | 100.62 |
| 15 Spectral Width | 24038.5 |
| 16 Lowest Frequency | -951.8 |
| 17 Nucleus | ${ }^{13 C}$ |
| 18 Acquired Size | 32768 |
| 19 Spectral Size | 65536 |

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Fig. S3 The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2}$.

| Parameter | Value |
| :---: | :---: |
| 1 Origin | Bruker BioSpin GabH |
| 2 Oner | root |
| 3 Spectroneter | spect |
| 4 Solvent | CD2C12 |
| 5 Temperature | 298.2 |
| 6 Pulse Sequence | $z \mathrm{gpg}$ |
| 7 Number of Scans | 200 |
| 8 Receiver Gain | 195 |
| 9 Relazation Delay | 3.0000 |
| 10 Pulse Width | 10.5200 |
| 11 Acquisition Time | 1. 3631 |
| 12 Acquisition Date | 2015-06-19T23:11:00 |
| 13 Modification Date | 2015-06-19T23:24:57 |
| 14 Spectrometer | 100.62 |
| 15 Spectral Width | 24038.5 |
| 16 Lowest Frequency | -951. 8 |
| 17 Nucleus | ${ }^{13 C}$ |
| 18 Acquired Size | 32768 |
| 19 Spectral Size | 65536 |

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$\begin{array}{lllllllllllllllll}210 & 190 & 170 & 150 & 130 & \begin{array}{c}110 \\ \mathrm{f} 1(\mathrm{ppm})\end{array} & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$

Fig. S4 The ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2}$.


Fig. S5 The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3}$.

| Parameter | Value |
| :---: | :---: |
| 1 Origin | Bruker BioSpin GmbH |
| 2 Omer | root |
| 3 Spectrozeter | spect |
| 4 Solvent | CD2C12 |
| 5 Tenperature | 298.2 |
| 6 Pulse Sequence | zgpg |
| 7 Nurber of Scans | 1024 |
| 8 Receiver Gain | 195 |
| 9 Relaxation Delay | 3. 0000 |
| 10 Pulse Width | 10.5200 |
| 11 Acquisition Tize | 1. 3631 |
| 12 Acquisition Date | 2015-06-19T18:52:53 |
| 13 Yodification Date | 2015-06-19T20:07:17 |
| 14 Spectroneter Frequency | 100.62 |
| 15 Spectral Width | 24038.5 |
| 16 Lowest Frequency | -951.8 |
| 17 Nucleus | 13 C |
| 18 Acquired Size | 32768 |
| 19 Spectral Size | 65536 |

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Fig. S6 The ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{3}$.

| Parameter | Value |
| :---: | :---: |
| 1 Origin | Bruker BioSpin GabH |
| 2 muner | root |
| 3 Spectrometer | spect |
| 4 Solvent | CD2C12 |
| 5 Tenperature | 298.2 |
| 6 Pulse Sequence | zg |
| 7 Nurber of Scans | 16 |
| 8 Receiver Gain | 39 |
| 9 Relaxation Delay | 6. 0000 |
| 10 Pulse Width | 9. 5300 |
| 11 Acquisition Time | 2.7263 |
| 12 Acquisition Date | 2015-06-19T20:14:26 |
| 13 Modification Date | 2015-06-19T20:14:27 |
| 14 Spectrometer Frequency | 400. 13 |
| 15 Spectral Width | 6009.6 |
| 16 Lowest Frequency | -419.5 |
| 17 Nucleus | 1H |
| 18 Acquired Size | 16384 |
| 19 Spectral Size | 32768 |


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Fig. S7 The ${ }^{1} \mathrm{H}$ NMR spectrum of 4 .


Fig. S8 The ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{4}$.


Fig. S9 The ${ }^{1} \mathrm{H}$ NMR spectrum of PTE


Fig. S10 The MALDI-TOF of $\mathbf{1}$.


Fig. S11 The MALDI-TOF of $\mathbf{2}$.


Fig. S12 The MALDI-TOF of $\mathbf{3}$.


Fig. S13 The MALDI-TOF of 4.


Fig. S14 The GPC data of PTE.


Fig. S15 The fluorescence lifetime of 1-4 and PTE in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solutions.


Fig. S16 The CV curves of (a) 1, (b) 2, (c) 3, (d) 4 and (e) PTE in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution.


Fig. S17 The 2D-GIXRD patterns of $\mathbf{1}$. The inserted model is a schematic diagram of the orientations of the aggregation structure with respect to the substrate in the films.


Fig. S18 The 2D-GIXRD patterns of 2. The inserted model is a schematic diagram of the orientations of the aggregation structure with respect to the substrate in the films.


Fig. S19 The 2D-GIXRD patterns of 4. The inserted model is a schematic diagram of the orientations of the aggregation structure with respect to the substrate in the films.

## The detailed calculated procedures for the charge carrier mobility.

According to the obtained $V_{t h}$ values and the metal-oxide semiconductor FET formula for the saturation regime, $I_{D S}=\frac{\mu W C_{i}}{2 L}\left(V_{G}-V_{t h}\right)^{2}$, the calculations of the charge carrier mobility $(\mu)$ are below:

3
$I_{D S}=30.79 \times 10^{-6} \mathrm{~A}, V_{G}=-6.69 \mathrm{~V}, V_{D S}=1 \mathrm{~V}, C_{i}=20 \mu \mathrm{~F} / \mathrm{cm}^{2}, W=1 \mathrm{~mm}, L=1 \mathrm{~mm}, V_{t h}=$ - 1.81 V

$$
\begin{aligned}
\mu & =2 L I_{D S} /\left[W C_{i}\left(V_{G}-V_{t h}\right)^{2}\right]=2 I_{D S} /\left[C_{i}\left(V_{G}-V_{t h}\right)^{2}\right] \\
& =2 \times 30.79 \times 10^{-7} /\left[20 \times 10^{-6} \times(-6.69+1.81)^{2}\right] \\
& =0.13 \mathrm{~cm}^{2} V^{-1} s^{-1}
\end{aligned}
$$

4
$I_{D S}=35.93 \times 10^{-6} \mathrm{~A}, V_{G}=-6.23 \mathrm{~V}, V_{D S}=1 \mathrm{~V}, C_{i}=20 \mu \mathrm{~F} / \mathrm{cm}^{2}, W=1 \mathrm{~mm}, L=1 \mathrm{~mm}, V_{t h}=$ - 2.14 V

$$
\begin{aligned}
\mu & =2 L I_{D S} /\left[W C_{i}\left(V_{G}-V_{t h}\right)^{2}\right]=2 I_{D S} /\left[C_{i}\left(V_{G}-V_{t h}\right)^{2}\right] \\
& =2 \times 30.79 \times 10^{-7} /\left[20 \times 10^{-6} \times(-6.69+1.81)^{2}\right] \\
& =0.22 \mathrm{~cm}^{2} V^{-1} s^{-1}
\end{aligned}
$$

PTE

$$
\begin{aligned}
& I_{D S}=39.27 \times 10^{-6} \mathrm{~A}, V_{G}=-5.27 \mathrm{~V}, V_{D S}=1 \mathrm{~V}, C_{i}=20 \mu \mathrm{~F} / \mathrm{cm}^{2}, W=1 \mathrm{~mm}, L=1 \mathrm{~mm}, V_{t h}= \\
& \\
& -2.22 \mathrm{~V} \\
& \mu=2 L I_{D S} /\left[W C_{i}\left(V_{G}-V_{t h}\right)^{2}\right]=2 I_{D S} /\left[C_{i}\left(V_{G^{-}} V_{t h}\right)^{2}\right] \\
& =2 \times 30.79 \times 10^{-7} /\left[20 \times 10^{-6} \times(-6.69+1.81)^{2}\right] \\
& =0.42 \mathrm{~cm}^{2} V^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$



Fig. S20 The mobility plots versus gate voltages for (a) 3, (b) 4 and (c) PTE.

