[Supporting Information]

Effective modulation of conjugated aryl acetylenic molecular system
based on dithienyldiketopyrrolopyrrole for organic solar cells

Chun-Hui Zhang, a Li-Ping Wang, a Wan-Yi Tan, a Si-Ping Wu, a Xue-Ping Liu, b Pan-Pan Yu, a Ju Huang, a Xu-Hui Zhu, a* Hong-Bin Wu, a Cun-Yuan Zhao, b Jun-Biao Peng, a and Yong Cao a

a State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices South China University of Technology (SCUT) Guangzhou (China);
b MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China.

*E-mail: Xu-Hui Zhu, xuhuizhu@scut.edu.cn

This electronic supplementary information contains the following data:
1. 1H NMR spectra of An-1 and An-2 as well as the reaction intermediates
2. Mass spectra and microanalysis data of An-1 and An-2
3. Table S1. The optimized geometry of An-1 and An-2 involving various dihedral angles
4. Thermogravimetric diagrams of An-1 and An-2
5. The J-V characteristics of the photovoltaic devices based on different weight ratios of An-1 or An-2 with PC_{61}BM
6. Topographic atomic force microscopy (AFM) images (5 μm × 5 μm) of the as-cast (a, c, e, g) and thermally annealed thin films (b, d, f, h) of An-1, An-2 and their blends with PC_{61}BM on ITO/PEDOT:PSS.
Fig. S1  $^1$H NMR spectrum of compound 2

Fig. S2  $^1$H NMR spectrum of compound 3

Fig. S3  $^1$H NMR spectrum of compound 4
Fig. S4  $^1$H NMR spectrum of An-1

Fig. S5  $^1$H NMR spectrum of An-2
Fig. S6  Mass spectrum of An-1

![Mass spectrum of An-1](image1.png)

Fig. S7  Mass spectrum of An-2

![Mass spectrum of An-2](image2.png)
Fig. S8  Microanalysis data of An-1


CHNS元素含量测定
vario EL cube 元素分析仪

<table>
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<th>No.</th>
<th>Name</th>
<th>Weight [mg]</th>
<th>C [%]</th>
<th>H [%]</th>
<th>N [%]</th>
<th>S [%]</th>
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Fig. S9  Microanalysis data of An-2

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CHNS元素含量测定
vario EL cube 元素分析仪

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<th>Name</th>
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<th>CH ratio</th>
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1 The microanalysis data provided by the Instrumental Analysis & Research Center, Sun Yat-Sen University, Guangzhou, China
Table S1. The optimized geometry of An-1 and An-2 involving various dihedral angles

![Image of molecular geometries](image)

<table>
<thead>
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<th>An-1</th>
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<td>( \angle 1 )</td>
<td>( \angle 2 )</td>
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<td>11.10°</td>
<td>0.59°</td>
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The geometries of molecules An-1 and An-2 were optimized at the level of B3LYP/6-31G(d) via density functional theory (DFT). All the alkyl-groups were replaced by methyl group for convenience.
Fig. S10  Thermogravimetric (TG) diagrams of An-1 and An-2.
Fig. S11  $J-V$ characteristics of photovoltaic devices (ITO/PEDOT:PSS/An-1 or AN-2:PC$_{61}$BM/Al), under simulated AM1.5G with an illumination intensity of 100 mW cm$^{-2}$. Device area: 0.16 cm$^2$.

The active layer involving different D/A weight ratios were spin-cast from chloroform solution (total concentration, 20 mg mL$^{-1}$) with (W) or without (w/o) thermal annealing (TA) at 50 °C for 10 min.
Fig. S12  Topographic atomic force microscopy (AFM) images (5 µm × 5 µm) of the as-cast (a, c, e, g) and thermally annealed thin films (b, d, f, h) of An-1, An-2 and their blends with PC_{61}BM on ITO/PEDOT:PSS. (a, b) An-1. (c, d) An-2. (e, f) An-1:PC_{61}BM = 2:3 w/w. (g, h) An-2:PC_{61}BM = 1:1 w/w. Concentration: 20 mg mL^{-1} CHCl_{3} solution, spin speed: 3000 rpm. Thermal annealing (TA) was performed at 50 °C for 10 min.

(a) An-1, w/o TA
(b) An-1, w TA
(c) An-2, w/o TA
(d) An-2, w TA

\[ R_{\text{rms}} = 1.07 \text{ nm} \]
\[ R_{\text{rms}} = 1.08 \text{ nm} \]
\[ R_{\text{rms}} = 3.70 \text{ nm} \]
\[ R_{\text{rms}} = 3.73 \text{ nm} \]

(e) An-1:PC_{61}BM = 2:3, w/o TA
(f) An-1:PC_{61}BM = 2:3, w TA
(g) An-2:PC_{61}BM = 1:1, w/o TA
(h) An-2:PC_{61}BM = 1:1, w TA

\[ R_{\text{rms}} = 2.06 \text{ nm} \]
\[ R_{\text{rms}} = 2.22 \text{ nm} \]
\[ R_{\text{rms}} = 1.91 \text{ nm} \]
\[ R_{\text{rms}} = 1.99 \text{ nm} \]