Supporting Information

# A hexacyclic ladder-type building block for high-performance D-A copolymers

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#### 1. General characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 1515 series GPC coupled with UV-vis detector using tetrahydrofuran as eluent and polystyrenes as standards. Thermogravimetric analysis was done using a Perkin-Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag<sup>+</sup> electrode was used as the reference electrode. Polymers were coated onto glassy carbon electrode and all potentials were corrected against Fc/Fc<sup>+</sup>. AFM was performed on a Dimension 3100 microscope (Veeco) using tapping mode. X-ray diffraction (XRD) of thin films was performed in reflection mode using Cu Ka radiation (40 kV, 200 mA) on a Rigaku D/max-2500 X-ray diffractometer.

### 2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. 2,6-Dibromonaphthalene-1,5-dicarboxylic acid (1)<sup>1</sup> and N-(2-octyldodecyl)thiophen-3-amine<sup>2</sup> were prepared according to literatures.

### 2,6-Dibromo-N<sup>1</sup>,N<sup>5</sup>-bis(2-octyldodecyl)-N<sup>1</sup>,N<sup>5</sup>-di(thiophen-3-yl)naphthalene-1,5-

**dicarboxamide (2).** To a solution of compound **1** (0.90 g, 2.4 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) were added oxalyl chloride (2 mL, 23.4 mmol) and 2 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure to obtain 2,6-dibromonaphthalene-1,5-dicarbonyl dichloride, which was used in next step without purification. To the solution of 2,6-dibromonaphthalene-1,5-dicarbonyl dichloride in dry

CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was slowly added a solution of *N*-(2-octyldodecyl)thiophen-3-amine (2.74 g, 7.2 mmol) and Et<sub>3</sub>N (2 mL) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with CHCl<sub>3</sub> three times. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified through a silica gel column with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (1:1) as eluent to give compound **2** as a light brown solid (0.90 g, 34%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.57 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H), 6.94-6.90 (m, 2H), 6.84 (br, 2H), 6.67 (d, *J* = 5.1 Hz, 2H), 4.00-3.82 (m, 4H), 1.63-1.57 (m, 2H), 1.37-1.26 (m, 64H), 0.90-0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm): 167.53, 138.85, 136.92, 130.95, 129.59, 126.58, 125.12, 124.83, 120.20, 118.18., 52.26, 36.18, 31.92, 31.45, 31.24, 30.10, 30.05, 29.70, 29.65, 29.61, 29.57, 29.35, 29.33, 26.29, 22.69, 14.12.

### 7,14-Bis(2-octyldodecyl)thieno[3',2':3,4]isoquinolino[8,7-h]thieno[3,2-c]isoquinoline-

**6,13(7***H***,14***H***)-dione (TITI). To a solution of compound <b>2** (0.70 g, 0.64 mmol) in N,N-dimethylacetamide (50 mL) were added PCy<sub>3</sub>·HBF<sub>4</sub> (250 mg, 0.68 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.5 g, 7.7 mmol) and Pd(OAc)<sub>2</sub> (150 mg, 0.65 mmol) under Ar. The mixture was stirred at 120 °C overnight and then cooled to room temperature. The mixture was poured into water and extracted with CHCl<sub>3</sub> three times. The combined organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (3:2) as eluent to give **TITI** as a yellow solid (396 mg, 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 10.78 (d, *J* = 9.3 Hz, 2H), 7.98 (d, *J* = 9.3 Hz, 2H), 7.56 (d, *J* = 5.4 Hz, 2H), 7.15 (d, *J* = 5.4 Hz, 2H), 4.35 (br, 4H), 2.12 (br, 2H), 1.40-1.21 (m, 64H), 0.87-0.82 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm): 162.80, 140.70, 132.82, 132.64, 132.52, 126.91, 123.02, 117.79, 117.58, 116.64, 50.08, 37.17, 31.91, 31.87, 31.80, 30.02, 29.62, 29.60, 29.55, 29.50, 29.31, 29.27, 26.67, 22.66, 22.63, 14.04.

2,9-Dibromo-7,14-bis(2-octyldodecyl)thieno[3',2':3,4]isoquinolino[8,7-*h*]thieno[3,2*c*]isoquinoline-6,13(7*H*,14*H*)-dione (TITI-Br). To a solution of TITI (166 mg, 0.18 mmol) in a mixed solvent of CHCl<sub>3</sub> (10 mL) and DMF (5 mL) was added NBS (66 mg, 0.37 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into 100 mL methanol. The precipitate was filtered and purified through a silica gel column with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (2:1) as eluent to give **TITI-Br** as a yellow solid (172 mg, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 10.70 (d, *J* = 9.3 Hz, 2H), 7.79 (d, *J* = 9.3 Hz, 2H), 7.12 (s, 2H), 4.25 (br, 4H), 2.07 (br, 2H), 1.38-1.21 (m, 64H), 0.87-0.82 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm):162.16, 139.98, 132.72, 132.24, 131.96, 122.58, 120.63, 118.67, 116.56, 116.03, 50.08, 37.05, 31.91, 31.87, 31.67, 30.01, 29.63, 29.61, 29.56, 29.51, 29.32, 29.27, 26.57, 22.66, 22.63, 14.04. MALDI-TOF MS (m/z): 1094.0 (M<sup>+</sup>).

**PThTITI. TITI-Br** (86 mg, 0.079 mmol) and 2,5-bis(trimethylstannyl)thiophene (33 mg, 0.079 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 7 mg Pd(PPh<sub>3</sub>)<sub>4</sub> was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise into 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitate was collected and dried under vacuum overnight to give **PThTITI** as a dark-yellow metallic solid (76 mg, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 10.45 (br, 2H), 8.02-6.08 (br, 6H), 4.96 (br, 4H), 2.11-0.84 (br, 78H). Elemental analysis (%) calcd for C<sub>64</sub>H<sub>90</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 75.69; H, 8.93; N, 2.76. Found: C, 75.37; H, 8.86; N, 2.68.

**PSeTITI. PSeTITI** was synthesized by following similar procedures for **PThTITI. TITI-Br** (104 mg, 0.095 mmol) and 2,5-bis(trimethylstannyl)selenophene (44 mg, 0.095 mmol) were used as starting materials. **PSeTITI** was obtained as a dark-yellow metallic solid (97 mg, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 10.46 (br, 2H), 8.05-6.29 (br, 6H), 4.95 (br, 4H), 2.10-0.88 (br, 78H). Elemental analysis (%) calcd for C<sub>64</sub>H<sub>90</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Se: C, 72.35; H, 8.54; N, 2.64. Found: C, 72.12; H, 8.42; N, 2.59.

# 3.<sup>1</sup>H NMR



Fig. S1 <sup>1</sup>H NMR spectrum of TITI.



Fig. S2 <sup>1</sup>H NMR spectrum of TITI-Br.

4. TGA

![](_page_5_Figure_1.jpeg)

Fig. S3 TGA curves for PThTITI and PSeTITI.

5. CV

![](_page_5_Figure_4.jpeg)

Fig. S4 Cyclic voltammograms for PThTITI and PSeTITI.

#### 6. Device fabrication and measurements

#### **Conventional solar cells**

Patterned ITO glass with a sheet resistance of 15  $\Omega$  sq<sup>-1</sup> was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone thick poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate treatment. А 30 nm (PEDOT:PSS, Clevios<sup>TM</sup> P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A polymer:PC<sub>71</sub>BM blend in CB (16 mg/mL) was spincoated onto PEDOT:PSS layer. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10<sup>-4</sup> Pa). The effective area for the devices is 4 mm<sup>2</sup>. The thicknesses for the active layers were measured by KLA Tencor D-120 profilometer. J-V curves were measured in air using a computerized Keithley 2420 SourceMeter and a Xenon-lamp-based solar simulator (Newport, Oriel 91159A, 150 W, AM 1.5G, 100 mW/cm<sup>2</sup>). The illumination intensity of solar simulator was determined using a monocrystalline silicon solar cell (Oriel 91150, 2×2 cm) calibrated by NREL. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech.).

#### **Hole-only devices**

The structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al. A 30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A polymer:PC<sub>71</sub>BM blend in CB (16 mg/mL) with DIO additive was spin-coated onto PEDOT: PSS layer. Finally, MoO<sub>3</sub> (~6 nm) and Al (~100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10<sup>-4</sup> Pa). *J-V* curves were measured with a computerized Keithley 2420 SourceMeter in the dark.

# 7. Optimization of device performance

D:A	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
1:0.8	0.94	7.46	69.0	$4.86(4.43)^b$
1:1.0	0.92	7.84	67.6	4.88 (4.67)
1:1.2	0.94	7.69	68.9	4.95 (4.73)
1:1.5	0.94	7.74	68.7	5.00 (4.87)
1:1.8	0.95	7.52	68.7	4.89 (4.79)
1:2.0	0.92	7.34	66.1	4.49 (4.28)

Table S1 Optimization of D/A ratio for PThTITI:PC71BM solar cells.<sup>a</sup>

<sup>*a*</sup>Blend solution: 16 mg/mL in CB with 3 vol% DIO; spin coating: 1000 rpm for 60 s. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for PThTITI:PC71BM solar cells.<sup>a</sup>

Thickness	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
95	0.94	7.43	66.0	$4.63 (4.55)^b$
109	0.94	7.73	65.7	4.79 (4.60)
119	0.94	7.83	65.5	4.82 (4.63)
128	0.95	7.93	66.9	5.04 (4.90)
145	0.93	7.87	65.0	4.78 (4.67)

<sup>&</sup>lt;sup>*a*</sup>D/A ratio: 1:1.5 (w/w); blend solution: 16 mg/mL in CB with 3 vol% DIO. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

DIO	V <sub>oc</sub>	$\overline{J}_{ m sc}$	FF	PCE
[V/V, %]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
0	0.92	2.39	61.6	1.35 (1.23) <sup>b</sup>
1	0.96	5.97	68.2	3.89 (3.72)
2	0.95	7.59	70.0	5.02 (4.79)
3	0.95	7.88	67.3	5.04 (4.86)
4	0.96	7.90	67.6	5.11 (4.92)
5	0.95	7.90	66.3	4.89 (4.82)

Table S3 Optimization of the additive content for PThTITI:PC71BM solar cells.<sup>a</sup>

<sup>*a*</sup>D/A ratio: 1:1.5 (w/w); blend solution: 16 mg/mL in CB; spin coating:1200 rpm for 60 s. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

Salvant	$V_{ m oc}$	$J_{ m sc}$	FF	PCE
Solvent	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
CB:CHCl <sub>3</sub> (1:1)	0.94	7.63	68.2	$4.89 (4.68)^b$
CB:CHCl <sub>3</sub> (2:1)	0.97	8.14	67.9	5.35 (5.19)
CB:CHCl <sub>3</sub> (3:1)	0.95	7.65	66.2	4.84 (4.59)
CB	0.96	8.28	69.8	5.53 (5.28)
ODCB	0.94	7.42	68.7	4.77 (4.49)

Table S4 Optimization of solvent for PThTITI:PC71BM solar cells.<sup>a</sup>

<sup>*a*</sup>D/A ratio: 1:1.5 (w/w); blend solution: 16 mg/mL with 4 vol% DIO; spin coating: 1200 rpm for 60 s. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

D:A	V <sub>oc</sub>	$J_{ m sc}$	FF	PCE
[w/w]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
1:0.6	0.94	7.68	64.7	$4.69(4.38)^b$
1:0.8	0.94	8.49	66.6	5.29 (5.22)
1:1.0	0.92	8.79	66.6	5.40 (5.28)
1:1.2	0.93	8.51	62.7	4.96 (4.85)
1:1.4	0.91	8.02	67.6	4.96 (4.81)

Table S5 Optimization of D/A ratio for PSeTITI:PC71BM solar cells.<sup>a</sup>

<sup>*a*</sup>Blend solution: 16 mg/mL in CB with 3 vol% DIO; spin coating: 1000 rpm for 60 s. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of the active layer thickness for PSeTITI:PC71BM solar cells.<sup>a</sup>

Thickness	V <sub>oc</sub>	$J_{ m sc}$	FF	PCE
[nm]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
88	0.92	8.95	69.1	5.67 (5.55) <sup>b</sup>
100	0.92	9.41	68.6	5.93 (5.79)
111	0.92	9.01	68.8	5.67 (5.65)
123	0.91	9.01	68.9	5.65 (5.43)
146	0.91	9.02	68.3	5.59 (5.32)

<sup>*a*</sup>D/A ratio: 1:1 (w/w); blend solution: 16 mg/mL in CB with 3 vol% DIO. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

-	DIO	V <sub>oc</sub>	$J_{ m sc}$	FF	PCE
	[v/v, %]	[V]	[mA/cm <sup>2</sup> ]	[%]	[%]
	0	0.93	1.98	65.4	1.20 (1.01) <sup>b</sup>
	1	0.92	9.18	69.4	5.85 (5.72)
	2	0.93	9.47	69.2	6.11 (6.03)
	3	0.94	9.35	70.5	6.17 (6.09)
	4	0.93	9.57	67.2	5.97 (5.88)
	5	0.93	9.41	66.7	5.84 (5.69)

Table S7 Optimization of the additive content for PSeTITI:PC71BM solar cells.<sup>a</sup>

<sup>*a*</sup>D/A ratio: 1:1 (w/w); blend solution: 16 mg/mL in CB; spin coating:1400 rpm for 45 s. <sup>*b*</sup>Data in parentheses stand for the average PCEs for 10 cells.

## 8. AFM

![](_page_10_Figure_4.jpeg)

**Fig. S5** AFM height images for PThTITI:PC<sub>71</sub>BM blend films without DIO (a) and with 4% DIO (b); PSeTITI:PC<sub>71</sub>BM blend films without DIO (c) and with 3% DIO (d).

### 9. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$9_{J=\overline{8}_{\mathcal{E}_0\mathcal{E}_r\mu}}\frac{V^2}{d^3}$$

where J is the current density,  $\mu$  is the zero-field mobility of holes ( $\mu_h$ ),  $\varepsilon_0$  is the permittivity of the vacuum,  $\varepsilon_r$  is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage,  $V = V_{appl} - V_{bi}$ , where  $V_{appl}$  is the applied voltage, and  $V_{bi}$ is the built-in potential determined by electrode workfunction difference. Fig. S6 shows J-V curves for the hole-only devices. The mobilities were calculated from the slope of  $J^{1/2}-V$ lines.

![](_page_11_Figure_4.jpeg)

Fig. S6 J-V curves (a) and the corresponding J<sup>1/2</sup>-V lines (b) for hole-only devices based on PThTITI:PC<sub>71</sub>BM blend and PSeTITI:PC<sub>71</sub>BM blend containing DIO (in dark). The thicknesses for the blend films are 118 and 110 nm, respectively.

# References

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[2] R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939.