Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2021

Supporting Information

Efficient wide-bandgap copolymer donors with reduced synthesis

cost

Jingui Xu^{a,b,‡}, Anxin Sun^{b,c,‡}, Zuo Xiao^{b,*}, Ergang Wang^a, Bin Zhang^{a,*}, Yong Hua^{c,*} and Liming Ding^{b,*}

^a Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, School of Materials Science and Engineering, Changzhou University, Changzhou 213164, China. E-mail: msbinzhang@outlook.com
^b Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China. E-mail: xiaoz@nanoctr.cn, ding@nanoctr.cn
^c Yunnan Key Laboratory for Micro/Nano Materials & Technology, School of Materials and Energy, Yunnan University, Kunming 650091, China. E-mail: huayong@ynu.edu.cn

[‡] J. Xu and A. Sun contributed equally to this work.

1. General characterization

¹H and ¹³C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry was done by using 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⁺ electrode was used as the reference electrode. Polymers were coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc⁺. AFM was performed on a Multimode microscope (Veeco) by using tapping mode.

2. Synthesis

All reagents were purchased from Bidepharm Co., J&K Co., Aladdin Co., Innochem Co., Derthon Co. and other commercial suppliers. Y6 was purchased from eFlexPV Co. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques.

M1. To a solution of 5,5'-(2,3-difluoro-1,4-phenylene)bis(2-bromothiophene) (500 mg, 1.15 mmol) and NaH (138 mg, 5.75 mmol) in DMF (10 mL) was added 2-octyldodecan-1-ol (376 mg, 1.26 mmol) dropwise at 0 °C under N₂. The mixture was heated to reflux and stirred overnight. After cooling to room temperature, the mixture was poured into water and extracted with petroleum ether. The combined organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:5) as eluent. Further recrystallization in CHCl₃:methanol gave **M1** as a white solid (300 mg, 37%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.33 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 4.0 Hz, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 3.96 (d, *J* = 6.0 Hz, 2H), 1.90-1.84 (m, 1H), 1.41-1.20 (m, 32H), 0.92-0.84 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 153.95, 151.45, 144.24, 139.11, 138.02, 130.47, 129.62, 127.54, 126.51, 125.75, 122.48, 121.86, 113.92, 113.23, 77.65, 77.60, 77.20, 38.92, 31.93, 31.03, 30.04, 29.71, 29.67, 29.64, 29.37, 26.74, 22.70, 14.13. MALDI-TOF MS (m/z): 714.3 (M⁺).

M2. To a solution of 5,5'-(2,5-difluoro-1,4-phenylene)bis(2-bromothiophene) (150 mg, 0.34 mmol) and NaH (41 mg, 1.72 mmol) in DMF (5 mL) was added 2-octyldodecan-1-ol (154 mg, 0.52 mmol) dropwise at 0 °C under N₂. The mixture was heated to reflux

and stirred overnight. After cooling to room temperature, the mixture was poured into water and extracted with petroleum ether. The combined organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified via column chromatography (silica gel) by using CH₂Cl₂:petroleum ether (1:5) as eluent to give **M2** as an oil (87 mg, 35%). ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.38 (d, *J* = 12.0 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 4.4 Hz, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 7.02 (d, *J* = 6.4 Hz, 1H), 3.97 (d, *J* = 6.0 Hz, 2H), 1.96-1.90 (m, 1H), 1.41-1.20 (m, 32H), 0.92-0.84 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 154.23, 151.81, 151.10, 138.93, 138.44, 130.53, 129.31, 126.45, 125.12, 122.97, 120.42, 114.12, 113.05, 110.79, 72.60, 38.02, 31.92, 31.91, 31.45, 29.99, 29.68, 29.65, 29.60, 29.36, 29.34, 26.92, 22.69, 14.12. MALDI-TOF MS (m/z): 714.3 (M⁺).

W4. To a mixture of M1 (34.5 mg, 0.048 mmol), FBDT-Sn (46.4 mg, 0.049 mmol), Pd(PPh₃)₄ (3.4 mg, 0.0029 mmol) in a Schlenk flask was added toluene (0.7 mL) and DMF (0.1 mL) under argon. The mixture was heated to reflux for 24 h. Then, 5 mL chlorobenzene was added and the mixture was stirred for 10 min. The solution was added into 100 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH₂Cl₂, CH₂Cl₂:CHCl₃ (1:1), CHCl₃ in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and further by using CH₂Cl₂, CH₂Cl₂:CHCl₃ (1:1), CHCl₃ in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **W4** as a brown solid (36 mg, 77%). The M_n for W4 is 53.4 kDa, with a PDI of 1.77. ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 6.84 (br, aromatic protons), 2.86 (br, aliphatic protons).

W5. To a mixture of M2 (62.9 mg, 0.088 mmol), FBDT-Sn (82.8 mg, 0.088 mmol), Pd(PPh₃)₄ (6.1 mg, 0.0053 mmol) in a Schlenk flask was added toluene (1.2 mL) and DMF (0.2 mL) under argon. The mixture was heated to reflux for 24 h. Then, 8 mL chlorobenzene was added and the mixture was stirred for 10 min. The solution was added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using CH₂Cl₂, CH₂Cl₂:CHCl₃ (1:1), CHCl₃ in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **W5** as a brown solid (43 mg, 52%). The M_n for W5 is 64.9 kDa, with a PDI of 2.03. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 6.84 (br, aromatic protons), 2.89 (br, aliphatic protons).

3. The synthesis costs estimation for W1, W4 and W5

Synthetic route for W1 [Sci. Bull., 2020, 65, 179]:



W1 (1 g)					
Reagent	Quantity	Price (source)	Cost (Y)		
FBDT-Sn	1.36 g	¥6000/5 g (Derthon)	1632.00		
Pd(PPh ₃) ₄	100 mg	¥117/g (Bidepharm)	11.70		
NBS	1.11 g	¥36/100 g (Bidepharm)	0.40		
SnBu ₃	2.79 g	¥777/100 g (Bidepharm)	21.68		
Pd(PPh ₃) ₄	216 mg	¥117/g (Bidepharm)	25.27		
NBS	2.30 g	¥36/100 g (Bidepharm)	0.83		
C ₈ H ₁₇ Br	5.05 g	¥ 50/100 g (Bidepharm)	2.53		
NaH	1.57 g	¥43/100 g (Bidepharm)	0.68		
HO OH F F	481 mg	¥2333/g (Bidepharm)	1122.17		
Total Cost			2817.26		

Synthetic route for W4:



W4 (1 g)						
Reagent	Quantity	Price (source)	Cost (Y)			
FBDT-Sn	1.29 g	¥6000/5 g (Derthon)	1548.00			
Pd(PPh ₃) ₄	94 mg	¥117/g (Bidepharm)	11.00			
NaH	441 mg	¥43/100 g (Bidepharm)	0.19			
C ₈ H ₁₇ C ₁₀ H ₂₁ OH	1.20 g	¥377/500 g (Bidepharm)	0.90			
NBS	1.43 g	¥36/100 g (Bidepharm)	0.51			
SnBu ₃	3.82 g	¥777/100 g (Bidepharm)	29.68			
Pd(PPh ₃) ₄	321 mg	¥117/g (Bidepharm)	37.56			
Br Br	1.26 g	¥48/g (Bidepharm)	60.48			
Total Cost	·		1688.32			

Synthetic route for W5:



W5 (1 g)					
Reagent	Quantity	Price (source)	Cost (Y)		
FBDT-Sn	1.92 g	¥ 6000/5 g (Derthon)	2304.00		
Pd(PPh ₃) ₄	142 mg	¥117/g (Bidepharm)	16.61		
NaH	689 mg	¥43/100 g (Bidepharm)	0.30		
C ₈ H ₁₇ C ₁₀ H ₂₁ OH	2.59 g	¥377/500 g (Bidepharm)	1.95		
NBS	2.37 g	¥36/100 g (Bidepharm)	0.85		
SnBu₃	5.74 g	¥777/100 g (Bidepharm)	44.60		
Pd(PPh ₃) ₄	485 mg	¥117/g (Bidepharm)	56.75		
Br - Br	1.90 g	¥6/g (Bidepharm)	11.40		
Total Cost			2436.46		

4. NMR



Fig. S1 ¹H NMR spectrum of M1.



Fig. S2 ¹³C NMR spectrum of M1.







Fig. S4 ¹³C NMR spectrum of M2.



Fig. S6 ¹H NMR spectrum of W5.

5. FT-IR



Fig. S7 FT-IR spectra of W4 and W5.

6. TGA



Fig. S8 TGA curves for W4 and W5.

7. DSC



Fig. S9 DSC curves for W4 and W5.



Fig. S10 Cyclic voltammogram for W4 and W5.

9. DFT



Fig. S11 Four possible conformers of the FAB unit of W4 and their relative energies.



Fig. S12 Four possible conformers of the FAB unit of W5 and their relative energies.

10. Device fabrication and measurements

Conventional solar cells

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 substrates were dried at 150 °C for 10 min. A W4:Y6 (or W5:Y6) blend in chloroform (CF) was spin-coated onto PEDOT:PSS. PDIN (2 mg/mL) in MeOH:AcOH (1000:3) was spin-coated onto active layer (5000 rpm for 30 s). Ag (~80 nm) was evaporated onto PDIN through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm². The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm²). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/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 substrates were dried at 150 °C for 10 min. A pure W4 (or W5) in CF or a W4:Y6 (or W5:Y6) blend in CF was spin-coated onto PEDOT:PSS. Finally, MoO₃ (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10⁻⁴ Pa). J-V curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

Electron-only devices

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. a W4:Y6 (or W5:Y6) blend in CF was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

11. Optimization of device performance

D/A [w/w]	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.8	0.87	23.49	68.2	$13.90 (13.87 \pm 0.02)^b$
1:1.2	0.88	23.90	71.7	15.02 (14.87±0.11)
1:1.6	0.87	23.31	71.7	14.54 (14.48±0.05)
1:2	0.87	22.07	71.6	13.80 (13.71±0.07)

Table S1 Optimization of D/A ratio for W4:Y6 solar cells.^a

^{*a*}Blend solution: 14.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s. ^{*b*}Data in parentheses are averages for 8 cells.

Table S2 Optimization of active layer thickness for W4:Y6 solar cells.^a

Thickness [nm]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
155	0.86	22.66	66.7	$12.95 (12.74 \pm 0.15)^b$
130	0.87	23.77	69.2	14.27 (14.07±0.14)
115	0.88	23.90	71.7	15.02 (14.87±0.11)
100	0.88	23.84	71.2	14.85 (14.71±0.09)

^{*a*}D/A ratio: 1:1.2 (w/w); blend solution: 14.5 mg/mL in CF.

^bData in parentheses are averages for 8 cells.

DPE [vol%]	$V_{ m oc}$ [V]	$J_{ m sc}$ [mA/cm ²]	FF [%]	PCE [%]
0	0.88	23.90	71.7	15.02 (14.87±0.11) ^b
0.1	0.86	24.75	71.0	15.05 (14.89±0.14)
0.3	0.86	25.05	71.0	15.25 (15.14±0.08)
0.5	0.83	25.52	70.8	14.99 (14.91±0.07)

Table S3 Optimization of DPE content for W4:Y6 solar cells.^a

^{*a*}D/A ratio: 1:1.2 (w/w); blend solution: 14.5 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses are averages for 8 cells.

Table S4 Optimization of D/A ratio for W5:Y6 solar cells.^a

D/A [w/w]	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
1:0.8	0.83	24.56	57.7	$11.77 (11.42 \pm 0.29)^b$
1:1.2	0.83	24.94	62.4	12.87 (12.73±0.11)
1:1.6	0.83	23.90	63.6	12.59 (12.47±0.09)
1:2	0.83	22.17	66.9	12.32 (12.18±0.11)

^{*a*}Blend solution: 16 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses are averages for 8 cells.

Thickness [nm]	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
140	0.81	24.21	54.2	$10.68 (10.59 \pm 0.06)^{b}$
125	0.82	24.99	58.4	11.98 (11.79±0.18)
110	0.83	24.94	62.4	12.87 (12.73±0.11)
90	0.83	23.95	64.1	12.75 (12.48±0.19)

Table S5 Optimization of active layer thickness for W5:Y6 solar cells.^a

^{*a*}D/A ratio: 1:1.2 (w/w); blend solution: 16 mg/mL in CF. ^{*b*}Data in parentheses are averages for 8 cells.

Table S6 Optimization of DPE content for W5:Y6 solar cells.^a

DPE [vol%]	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
0	0.83	24.94	62.4	$12.87 (12.73 \pm 0.11)^b$
0.1	0.82	25.33	62.2	13.00 (12.87±0.10)
0.3	0.79	25.78	63.2	12.90 (12.75±0.13)
0.5	0.78	25.30	63.0	12.41 (12.34±0.09)

^{*a*}D/A ratio: 1:1.2 (w/w); blend solution: 16 mg/mL in CF; spin-coating: 4000 rpm for 30 s.

^bData in parentheses are averages for 8 cells.

12. SCLC

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:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where *J* is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_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 work function difference). Here, $V_{bi} = 0.1$ V for hole-only devices, $V_{bi} = 0$ V for electrononly devices.^[1] The mobility was calculated from the slope of $J^{1/2}$ -*V* plot.



Fig. S8 *J-V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the hole-only devices (in dark). The thicknesses for W4 and W5 pure films are 101 nm and 98 nm, respectively.



Fig. S9 *J-V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the hole-only devices (in dark). The thicknesses for W4:Y6 and W5:Y6 films are 108 nm and 105 nm, respectively.



Fig. S10 *J*-*V* curves (a) and corresponding $J^{1/2}$ -*V* plots (b) for the electron-only devices (in dark). The thicknesses for W4:Y6 and W5:Y6 films are 110 and 107 nm, respectively.

Films	μ _h [×10 ⁻⁴ cm ² /Vs]	μ _e [×10 ⁻⁴ cm ² /Vs]	$\mu_{ m h}/\mu_{ m e}$
W4	$7.47(6.92\pm0.29)^a$	-	-
W5	4.98 (4.80±0.14)	-	-
W4:Y6 (1:1.2)	4.85 (4.39±0.18)	$2.58(2.45\pm0.07)$	1.87
W5:Y6 (1:1.2)	$2.95(2.81\pm0.13)$	$1.03~(0.92\pm0.08)$	2.86

Table S7 Hole and electron mobilities.

^bData in parentheses are averages of 8 measurements.

13. Bimolecular recombination



Fig. S16 J_{sc} - P_{light} plots.



Fig. S17 AFM height (left) and phase (right) images for the blend films. (a) and (b), W4:Y6 film ($R_{\rm rms} = 1.59$ nm); (c) and (d), W5:Y6 film ($R_{\rm rms} = 1.09$ nm). $R_{\rm rms}$: root-mean-square roughness.

Reference

[1] C. Duan, W. Cai, B. B. Y. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A. J. Heeger and Y. Cao, Toward green solvent processable photovoltaic materials for polymer solar cells: the role of highly polar pendant groups in charge carrier transport and photovoltaic behavior, *Energy Environ. Sci.*, 2013, 6, 3022-3034.