Aromatic end-capped acceptor effects on molecular stacking and photovoltaic performance of solution-processable small molecules

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1: Characterization method

(1) Molecular structure/properties characterization and calculation (NMR, MS spectra, DFT).

¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were obtained on a Bruker DMX–400 NMR Spectrometer and using tetramethylsilane as internal standard. MS spectra (MALDI–TOF–MS) were determined on a Micromass GCT–MS spectrometer. The HOMO and LUMO levels of the four end-capped acceptor units were optimized by density functional theory (DFT)/time-dependent density functional theory (TDDFT) at the B3LYP/6-31G (d, p) level. All calculations were performed in the gas phase and with Gaussian 09 program.¹⁻³ UV-Vis spectra were obtained with a JASCO–V570 spectrophotometer. Electrochemical cyclic voltammetry was conducted on an electrochemical work station (VMP3 Biologic, France), with a Pt disk coated with a

molecular film, a Pt plate, and an Ag/Ag^+ electrode as working, counter, and reference electrodes, respectively, in a 0.1 mol L⁻¹ tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆) acetonitrile solution.

(2) Morphology characterization

All films for characterization are prepared under identical optimized conditions of device fabrication in the absence of special emphasis. GIXRD measurements were performed at the beam line of 7.3.3 at the Advanced Light Source (ALS).⁴ Samples were prepared on Si/PEDOT: PSS substrates. The 10 keV X-ray beam was incident at a grazing angle of 0.12°–0.15° and selected to maximize the scattering intensity from the samples. Scattered X-rays were detected by using a Dectris Pilatus 2M photon counting detector. The calculations of face on: edge on ratios are according to literature.⁵ The AFM images of the blended films on PEDOT: PSS substrates were obtained on a Nanoscope Ia AFM (Digital Instruments) in tapping mode. The TEM images of the blended films were prepared under the same conditions as AFM, and the samples on the ITO/PEDOT: PSS substrate were transferred by floating in water.

(3) Solar cell fabrication and measurements

Devices were fabricated with a structure of glass/ITO/PEDOT: PSS/ Ca/Al. The ITOcoated glass substrates were cleaned by the same procedure with inverted devices. A thin layer of PEDOT: PSS was spin-coated at 4,000 r.p.m onto the ITO surface. After being baked at 150 °C for 15min, the substrates were transferred into a nitrogen-filled glove box. The mixture of small molecules and PC₇₁BM with total concentration *ca*. 16.7 mg mL⁻¹ with or without additives stirred at 60 °C in chloroform for *ca*. 0.5 hour until they intensively dissolved. Subsequently, the active layer was spin-coated from blend chloroform solutions of small molecules and $PC_{71}BM$ with or without additives. Finally, a layer of ~20 nm Ca and then 100 nm Al layer was evaporated under high vacuum (<1 × 10⁻⁴ Pa).

Device *J–V* characteristics was measured under AM 1.5G (100 mWcm⁻²) using a Newport Thermal Oriel 91159A solar simulator. Light intensity is calibrated with a Newport Oriel PN 91150 V Si-based solar cell. *J–V* characteristics were recorded using a Keithley 2400 source-measure unit. Typical cells have device areas of approximately 4 mm². EQEs were performed in air with an Oriel Newport system (Model 66902) equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source. Mobility measurements of pristine films and blend films were characterized by a hole-only space-charge limited current (SCLC) method with the following diode structures: ITO/PEDOT: PSS/active layer/Au for hole (Al/active layer/Al for electrons) by taking current–voltage current in the range of 0–5 V and fitting the results to a space–charge-limited form. ^{6–7} Charge carrier motilities were calculated by using the SCLC model considering electric-field dependence, as described by:

$$J = \frac{9}{8} \varepsilon_r \varepsilon \mu V^2 \exp\left(0.89 \sqrt{\frac{V}{E_0 L}}\right) / L^3$$

where J is the current density (mA cm⁻²), L is the film thickness of the active layer (cm), μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10⁻¹⁴ F cm⁻¹), and V is the internal voltage in the device. V = V_{appl} – V_{bi}, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage owing to the relative work function difference of the two electrodes.

2 Materials and synthesis

All reagents and chemicals were purchased from Aldrich, Alfa and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Toluene, chloroform and THF were freshly distilled prior to use. Other materials were used without further purification. The compound **1**, compound **2** and molecule **BT-ID** were synthesized according to our previous work.⁸



Scheme S1 Synthesis routes of small molecules

Under Ar protection, five drops of piperidine was added into the mixture of compound 1 (180 mg, 0.12 mmol) and 3-ethyl-2-thioxothiazolidin-4-one (193.2 mg, 1.2 mmol). After being stirred for 24 h at ambient temperature, the mixture was poured into water and extracted by CHCl₃. The organic layer was washed with brine and water and then dried over MgSO₄. After being concentrated, the crude product was purified by using column chromatography on silica gel, with a mixture of $CHCl_3$ and petroleum (2:3) as eluent, and then recrystallized with chloroform and methanol to yield the target compound (125 mg, 61.0 %) as a dark solid. MALDI-TOF MS calcd for C₉₁H₁₁₂N₂O₂S₁₄ 1712.5 found 1712.9, ¹H NMR (400 MHz, CHCl₃): 7.96 (s, 2H), 7.91 (s, 2H), 7.68–7.80 (m, 4H), 7.22-7.24 (d, 2H), 6.89-6.90 (d, 2H), 4.21-4.41 (m, 4H), 3.05-3.14 (t, 4H), 2.66–2.88 (m, 8H), 1.71–1.89 (m, 12H), 1.30–1.49 (m, 48H), 0.84– 0.98 (m, 24H). 13C NMR (101 MHz, CDCl₃) δ 192.09, 167.36, 146.22, 142.65, 141.75, 139.68, 137.94, 137.46, 137.04, 136.91, 136.55, 135.99, 133.75, 133.01, 127.96, 125.56, 124.72, 123.70, 122.28, 121.17, 119.26, 41.67, 40.36, 39.99, 35.98, 34.49, 33.33, 32.74, 32.29, 31.66, 31.64, 30.67, 30.34, 30.12, 29.49, 29.37, 29.22, 29.09, 28.23, 25.94, 23.96, 23.10, 22.82, 22.68, 22.63, 21.97, 14.18, 14.10, 14.05, 13.46, 12.31, 11.73, 10.99, 9.93.

BT-BA

Under Ar protection, five drops of triethylamine was added into the mixture of compound **1** (160 mg, 0.11 mmol) and 1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (171.7 mg, 1.1 mmol). After being stirred for 24 h at ambient temperature, the

mixture was poured into water and extracted by CHCl₃. The organic layer was washed with brine and water and then dried over MgSO₄. After being concentrated, the crude product was purified by using column chromatography on silica gel, with a mixture of CHCl₃ and petroleum (1:2) as eluent, and then recrystallized with chloroform and hexane to yield the target compound (90 mg, 60.4%) as a dark solid. MALDI–TOF MS calcd for $C_{93}H_{114}N_4O_6S_{10}$ 1702.6 found 1703.2, ¹H NMR (400 MHz, CHCl3): 8.59 (s, 2H), 7.75 (s, 2H), 7.70 (s, 2H), 7.57 (s, 2H), 7.37-7.38 (d, 2H), 6.93-6.94 (d, 2H), 3.43-3.44 (d, 12H), 2.99–3.03 (t, 4H), 2.87-2.90 (m, 8H), 1.70–1.82 (m, 12H), 1.34–1.53 (m, 42H), 0.89–0.98 (m, 24H). (Notes: the ¹³C NMR is difficult to obtain defined data for its lower solubility, and we have tried several times.)

BT-RCN

Under Ar protection, five drops of piperidine was added into the mixture of compound **2** (160 mg, 0.105 mmol) and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (202.8 mg, 1.05 mmol). After being stirred for 24h at ambient temperature, the mixture was poured into water and extracted by CHCl₃. The organic layer was washed with brine and water and then dried over MgSO₄. After being concentrated, the crude product was purified by using column chromatography on silica gel, with a mixture of CHCl₃ and petroleum (2:5) as eluent, and then recrystallized with chloroform and methanol to yield the target compound (95 mg, 47.0%) as a dark solid. MALDI–TOF MS calcd for $C_{105}H_{128}N_6O_2S_{12}$ 1888.7 found 1889.6, ¹H NMR (400 MHz, CHCl3): 7.97(s, 2H), 7.73 (s, 2H), 7.42 (s, 2H), 7.37-7.38 (d, 2H), 7.30 (s, 2H), 6.92-6.93 (d, 2H), 4.28-4.34 (m, 4H), 2.98–3.02 (t, 4H), 2.84-2.90 (m, 8H), 1.68–1.82 (m, 12H), 1.29–1.41 (m, 64H),

0.85–0.91 (m, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 165.86, 165.48, 146.12, 142.94, 141.78, 141.02, 139.23, 138.52, 137.84, 137.24, 136.85, 136.71, 135.88, 134.37, 134.12, 132.82, 128.42, 127.89, 125.55, 123.55, 122.17, 119.67, 113.73, 113.25, 112.27, 55.73, 40.67, 40.07, 34.73, 33.45, 33.05, 31.95, 31.59, 30.23, 29.74, 29.46, 29.20, 29.03, 28.92, 26.69, 23.08, 22.72, 22.67, 22.61, 14.22, 14.15, 14.13, 14.08.



Fig. S1 The calculated dipole moment of the D- π -A



Fig. S2 The calculated HOMO and LUMO of four molecules





Fig. S3 a) The CV plots of the four molecules b) The enlarged reduction parts of CV plots based on the four molecules.



Fig. S4 Electron mobility images based on the optimized condition



Fig. S5 AFM phase (size: $2\mu m \times 2\mu m$) images and TEM images

Table S1 The calculated HOMO and LUMO of the four end-capped acceptors

Acceptor Units	НОМО	LUMO	Acceptor Units	НОМО	LUMO
BA	-7.26 eV	-2.50 eV	ID	-6.76 eV	-2.47 eV
RA	-6.47 eV	-2.51 eV	RCN	-6.88 eV	-2.83 eV

Table S2 Calculated dipole moment of the four small molecules based on ground state and excited states.

Molecules	ground state				(excited state				
	$\mu_{ m gx}$	$\mu_{ m gy}$	$\mu_{ m gz}$	$\mu_{ m g}$	μ_{ex}	$\mu_{ m ey}$	$\mu_{ m ez}$	$\mu_{ m e}$	$\Delta \mu_{\rm ge}$	
BT-RCN	-0.46	0.24	0.59	0.79	-1.10	0.35	0.63	1.32	0.65	
BT-RA	0.04	0.83	0.98	1.28	0.06	0.36	-0.68	0.77	1.72	
BT-BA	0.01	0.90	-1.54	1.79	0.40	0.73	-1.36	1.59	0.48	
BT-ID	0.00	0.09	0.06	0.11	0.00	0.00	0.00	0.00	0.11	

Table S3 Detailed parameters of absorption and energy levels based on small molecules

Molecules	λ _{solution} (nm)	λ_{film}^{max} (nm)	ε _{solution} (g mL ⁻¹)	ε _{film} (cm ⁻¹)	λ _{edge} (nm)	E^{opt}_{g} (eV)	HOMO (eV)	LUMO (eV)	Energy Loss (eV)
BT-RCN	534	583/623	5.78×10 ⁴	5.01×10 ⁴	716	1.73	-5.49	-3.71	0.72
BT-RA	514	574/618	6.25×10 ⁴	5.31×10 ⁴	691	1.79	-5.30	-3.58	0.8
BT-BA	538	589/641	6.25×10 ⁴	6.71×10 ⁴	711	1.74	-5.25	-3.50	0.75
BT-ID	544	591/643	7.00×10 ⁴	7.20×10 ⁴	712	1.74	-5.19	-3.48	0.79

Table S4 Detailed device optimization based on BT-RA

Conc	Rotation	Conditions		V _{oc}	J _{sc}	FF	PCE _{max}
a	speed(r/s)	Conditions	ratios	[V]	[mA cm ⁻²]	[%]	(PCE _{ave}) ^c [%]
10	2500	None	1:1	1.03	7.21	29.07	2.17 (2.05±0.12)

10	2500	None	1.5:1	1.06	9.42	38.24	3.81 (3.70±0.11)
10	2500	None	2:1	1.05	8.60	34.68	3.14 (3.09±0.05)
10	2500	0.2%DIO	1.5:1	0.99	12.51	70.06	8.93(8.84±0 .09)
10	2500	annealing ^b	1.5:1	1.00	13.16	58.06	7.66 (7.60±0.06)
10	3000	0.2%DIO	1.5:1	0.99	13.13	71.06	9.42 (9.35±0.07)
10	3200	0.2%DIO	1.5:1	0.99	13.07	70.17	9.25 (9.21 \pm 0.04)
10	3500	0.2%DIO	1.5:1	0.99	13.39	70.89	9.64 (9.57±0.07)
12	3500	0.2%DIO	1.5:1	0.98	13.51	71.09	9.64 (9.52±0.12)
15	3500	0.2%DIO	1.5:1	0.98	12.71	70.39	8.96 (8.89±0.07)

^a Concentration for donors (mg/ml); ^b heating temperature is 110 °C, and time is 10 minutes; ^c the average PCEs are obtained over 12 devices.

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Conc a	Rotation speed(r/s)	Conditions	ratios	$V_{ m oc}$ [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE _{max} (PCE _{ave}) ^d [%]
10	2500	None	1:1	1.00	12.1	60.8	7.37 (7.31±0.06)
10	2500	None	1.5:1	1.01	12.7	62.3	8.00 (7.91±0.09)
10	2500	None	2:1	1.00	12.0	58.8	7.03 (6.92±0.11)
10	2500	0.2%DIO	1.5:1	1.00	12.2	54.57	6.68 (6.60±0.08)
10	2500	0.4%CP	1.5:1	1.00	13.0	60.76	7.90 (7.81 ± 0.09)
10	2500	Heat annealing ^b	1.5:1	1.02	11.0	51.74	5.80 (5.70±0.10)
10	2500	0.2%DPE	1.5:1	0.99	12.5	63.77	7.86 (7.80±0.06)
9	2000	None	1.5:1	0.99	14.1	61.0	8.51 (8.33±0.18)
9	2000	CF annealing ^c	1.5:1	1.00	13.5	62.8	8.49 (8.41±0.08)

Table S5 Detailed device optimization based on BT-BA

a Concentration for donors (mg/ml); b heating temperature is 110 oC, and time is 10 minutes; c annealing time is 60s; d the average PCEs are obtained over 12 devices.

Conc a	Rotation speed(r/s)	Conditions	ratios	$V_{\rm oc}$ [V]	$\frac{J_{\rm sc}}{[\rm mA} cm^{-2}]$	FF [%]	PCE _{max} (PCE ave) ^c
10	2500	None	1.5:1	1.04	9.42	38.99	3.64

Table S6 Detailed device optimization based on BT-RCN

							(3.32 ± 0.32)
10	2500	0.3%DIO	1.5:1	1.00	11.3 7	49.11	5.57 (5.50±0.07)
10	2500	0.3%CN	1.5:1	0.88	6.97	40.93	2.51 (2.30±0.21)
10	2500	0.4%CP	1.5:1	0.84	8.36	41.03	2.90 (2.85±0.05)
10	2500	0.3% DPE	1.5:1	0.92	9.33	44.60	3.83 (3.71±0.12)
10	2500	annealing ^b	1.5:1	0.97	8.89	51.85	4.47 (4.21±0.26)
10	2500	0.2%DIO	1.5:1	1.01	11.4	51.4	5.85 (5.79±0.06)
10	3000	0.2%DIO	1.5:1	1.01	11.7	51.5	6.10 (6.02+0.08)

^a Concentration for donors (mg/ml); ^b heating temperature is 110 °C, and time is 10 minutes; ^c the average PCEs are obtained over 12 devices.

Donors	D-sp (010	acing) (Å)	M (10 ⁻⁴	Mobility (10 ⁻⁴ cm ² V ⁻¹ s - ¹)		Crystal size (Å)	
	Pa	B ^b	Pa	B ^b	Pa	B ^b	Bp
BT-RCN	3.71	3.74	0.24	0.07	40.3	54.6	1:2.54
BT-RA	3.72	3.74	12.1	3.11	47.1	49.3	1:1.59
BT-BA	3.83	3.83	1.74	0.22	70.2	38.3	1:2.87
BT-ID	3.65	3.69	12.9	2.23	51.0	44.3	1:3.63

Table S7 Detailed parameters of GIXRD and hole mobility

^a P is shortened for pristine; ^b B is shortened for blends; ^c F:E is shortened for face on: edge on.

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