# **Electronic supplementary information**

A low bandgap asymmetrical squaraine for solutionprocessed small molecule organic solar cells with highperformance

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## **Experimental details**

### Instruments and characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured using a Bruker Avance AV II-400 MHz spectrometer, and the chemical shifts were recorded in units of ppm with TMS as the internal standard. High resolution MS spectra were obtained from a Shimadzu LCMS-IT-TOF. Single crystal X-ray diffraction data of the target molecules were obtained on a Xcalibur E X-ray single crystal diffractometer equipped with graphite monochromator Mo-Ka ( $\lambda$ = 0.71073 Å) radiation. The data collection was executed using CrysAlisPro program. The structures were determined using direct method and successive Fourier difference syntheses (SHELXS-97) and refined using full-matrix leastsquares procedure on F2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Single crystal X-ray structures were obtained for a metallic yellow crystals of ASQ-5 obtained from CH<sub>2</sub>Cl<sub>2</sub>/ hexane (CCDC: 986049) and ASQ-6 obtained from CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>OH (CCDC: 986050).

Electronic absorption spectra of both solution and thin-film of the small molecules were recorded using a Perkin Elmer Lamdba 950 UV-Vis scanning spectrophotometer. The solution samples were prepared in chloroform solution at a concentration of  $2.00 \times 10^{-6}$  mol L<sup>-1</sup>, while the film samples were obtained by spin-coating from chloroform solution (5.0 mg mL<sup>-1</sup>, 1400 rpm/ 30 s) on quartz substrates. Cyclic voltammetry measurements were carried out in  $2.50 \times 10^{-4}$  mol L<sup>-1</sup> anhydrous dichloromethane with tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) under an argon atmosphere at a scan rate of 50 mV s<sup>-1</sup> using a LK 2006A electrochemical workstation. The CV system was constructed using a Pt disk, a Pt wire, and a Ag/AgNO<sub>3</sub> (0.1 mol L<sup>-1</sup> in acetonitrile) electrode as the working electrode, counter electrode and reference electrode, respectively, and the potential of the Ag/AgNO<sub>3</sub> reference was internally calibrated using the ferrocene/ ferrocenium redox couple (Fc/ Fc<sup>+</sup>), which has a known reduction potential of -4.80 eV relative to vacuum level. The morphologies of the active layers were analyzed through atomic force microscopy (AFM) in tapping mode under ambient conditions using a MFP 3D Asylum

Research instrument.

#### Fabrication and characterization of organic solar cells devices

Small molecules bulk-heterojunction organic solar cells were fabricated using indium-tin-oxide (ITO) coated glass as substrate. The thickness of ITO is 190 nm and sheet resistance is 15  $\Omega$ /sq. The substrate was cleaned consecutively in ultrasonic baths containing detergent, deionized water, acetone and ethanol for 10 min each, and finally blow-dried by high purity nitrogen. The substrate was treated by UV-ozone for 5 min, then immediately transferred into a high vacuum chamber for deposition of 80 Å MoO<sub>3</sub> at pressures of less than  $3 \times 10^{-4}$  Pa with a rate of 0.5 Å s<sup>-1</sup>. Subsequently, photoactive layers were fabricated by spin-coating a blend of the target molecules and PC<sub>71</sub>BM in chloroform with total concentration of 20 mg mL<sup>-1</sup> (1500 rpm, 30 s) under a N<sub>2</sub>-filling glovebox at 25 °C. The solution mixtures were stirred for 12 h at room temperature. Then the substrates were loaded into a vacuum chamber to finish the deposit LiF (8 Å) and Al (1000 Å) at pressures of less than  $3 \times 10^{-4}$  Pa with a rate of 0.05 Å s<sup>-1</sup> and 1.5 Å s<sup>-1</sup> <sup>1</sup>, respectively. Deposition rate and film thickness were in situ monitored using a quartz crystal oscillator mounted to the substrate holder. The active area of OPV cells is 6 mm<sup>2</sup>. The current-voltage curves under illumination were measured using an Abet solar simulator with a Keithley 4200 source measurement unit under AM 1.5G illumination (100 mW cm<sup>-2</sup>), after spectral mismatch correction under an ambient atmosphere at 25 °C. The EQE measurements were performed in air using a QE/IPCE Measurements Solar Cell Scan 100 (ZOLIX) system.

## **Synthesis**

Compound 3a <sup>[1]</sup> was prepared according to the procedures described in the literature. *n*-Butanol and toluene were distilled from sodium freshly prior to use. All other chemicals were obtained from commercial sources and used as-received without further purification.



**Scheme 1**. Synthetic routes to the target molecules. 1) NaOBu-*t*, Pd(OAc)<sub>2</sub>, P(*t*-Bu)<sub>3</sub> HBF<sub>4</sub>, reflux 10 h. 2) BBr<sub>3</sub>, DCM, room temperature, 12 h. 3) *n*-butanol and toluene (1:1), 140 °C, 36 h.

### N-(3,5-Dimethoxyphenyl)-indoline (1a)

A mixture of indoline (1.10 g, 9.22 mmol), 1-bromo-3,5- dimethoxybenzene (2.00 g, 9.22 mmol), NaOBu-*t*[Sodium tert-butoxide] (1.77 g, 18.44 mmol), Pd(OAc)<sub>2</sub> [Palladium (II) acetate] (62 mg, 3%), and P(*t*-Bu)<sub>3</sub> HBF<sub>4</sub> [Tri-tert-butyl phosphine tetrafluoroborate] (160 mg, 6%) were dissolved in 100 mL of toluene and refluxed under Ar for 10 h. The reaction mixture was cooled down and passed through a filter paper to remove insoluble material, then the solvents were removed under reduced pressure. The crude product was purified by silica gel chromatography (eluent, hexane/ethyl acetate = 15:1) to afford compound **1a** as a colorless oil (2.00 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 7.20 (d, 1H, *J*=8.0 Hz, Ar), 7.17 (d, 1H, *J*=7.6 Hz, Ar), 7.09 (t, 1H, *J*=7.6 Hz, Ar), 6.77 (t, 1H, *J*=7.6 Hz, Ar), 6.41 (d, 2H, <sup>3</sup>*J*=2.0 Hz, Ar), 6.12 (t,

1H, <sup>3</sup>*J*=2.0 Hz, Ar), 3.96 (t, 2H, *J*=8.4 Hz, -NCH<sub>2</sub>-), 3.80 (s, 6H, -OCH<sub>3</sub>), 3.13 (t, 2H, *J*=8.4 Hz, -CH<sub>2</sub>-).

#### N-(3,5-Dihydroxyphenyl)-indoline (1b)

Compound **1a** (1.00 g, 3.91 mmol) was added to 40 mL of anhydrous  $CH_2Cl_2$ , boron tribromide (40 mL of 1 M solution in  $CH_2Cl_2$ , 39.1 mmol) was added dropwise slowly at ice bath, then the solution was stirred under room temperature for 24 h. The solution was then decanted to 160 mL of ice water to remove any excess of BBr<sub>3</sub>, the organic phase was separated, and the aqueous phase was extracted with  $CH_2Cl_2$  for three times. The combined organic phases were washed with saturation aqueous NaHCO<sub>3</sub> solution and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then the solvents were removed under reduced pressure. The crude product was purified by silica gel chromatography (eluent, dichloromethane/methanol = 50:1) to afford compound **1b** as a colorless viscous liquid (0.65 g, 71%).

#### N-(3,5-Dimethoxyphenyl)-1,2,3,4-tetrahydroquinoline (2a)

Compound **2a** was obtained as a colorless oil (2.01 g, 81%) from the reaction of 1,2,3,4-tetrahydroquinoline (1.23 g, 9.22 mmol) and 1-bromo-3,5-dimethoxybenzene (2.00 g, 9.22 mmol) according to the procedure described for the synthesis of Compound **1a**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 7.05 (d, 1H, *J*=7.2 Hz, Ar), 6.97 (t, 1H, *J*=8.0 Hz, Ar), 6.87 (d, 1H, *J*=8.0 Hz, Ar), 6.74 (t, 1H, *J*=7.6 Hz, Ar), 6.40 (d, 2H, <sup>3</sup>*J*=2.4 Hz, Ar), 6.22 (t, 1H, <sup>3</sup>*J*=2.0 Hz, Ar), 3.76 (s, 6H, -OCH<sub>3</sub>), 3.62 (t, 2H, *J*=5.6 Hz, -NCH<sub>2</sub>-), 2.84 (t, 2H, *J*=6.4 Hz, -CH<sub>2</sub>-), 2.05-1.99 (m, 2H, -CH<sub>2</sub>-).

#### N-(3,5-Dihydroxyphenyl)-1,2,3,4-tetrahydroquinoline (2b)

Compound **2b** was obtained as a colorless viscous liquid (0.78 g, 86%) from the reaction of Compound **2a** (1.00 g, 3.70 mmol) and boron tribromide (50 mL of 0.6 M solution in  $CH_2Cl_2$ , 29.6 mmol) according to the procedure described for the synthesis of Compound **1b**.

## 2-[(3-Butyl-1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)methyl]-4-[(4-indoline-2,6-dihydroxyphenyl)-2,5-dien-1-ylidene]-3-oxocyclobut-1-en-1-olate (ASQ-5)

A mixture of compound **3a** (700 mg, 1.94 mmol) and **1b** (500 mg, 2.16 mmol) in nbutanol (50 mL) and toluene (50 mL) were added into a round bottom flask. The mixture was refluxed with a Dean-Stark apparatus for 36 h. After reaction was cooled down, the solvents were removed under reduced pressure. This crude product was purified by silica gel chromatography using dichloromethane/ methanol (50:1, v/v) as the eluent to afford green solid. The solid was recrystallized from a 1:6 volume ratio of dichloromethane and methanol mixture to afford green crystals with metallic lustre of ASQ-5 (873 mg, 78%), mp 229-230 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ:12.37 (s, 2H, -OH), 8.23 (d, 1H, J=8.4 Hz, Ar), 7.96 (d, 1H, J=8.0 Hz, Ar), 7.95 (d, 1H, J=8.8 Hz, Ar), 7.65 (t, 1H, J=8.0 Hz, Ar), 7.53 (t, 1H, J=8.0 Hz, Ar), 7.44 (d, 1H, J=8.0 Hz, Ar), 7.39 (d, 1H, J=8.8 Hz, Ar), 7.22 (d, 1H, J=7.2 Hz, Ar), 7.19 (t, 1H, J=8.0 Hz, Ar), 6.92 (t, 1H, J=7.2 Hz, Ar), 6.29 (s, 2H, Ar), 5.99 (s, 1H, =CH-), 4.24 (t, 2H, J=7.6 Hz, -NCH<sub>2</sub>-), 4.07 (t, 2H, J=7.6 Hz, -NCH<sub>2</sub>-), 3.17 (t, 2H, J=8.4 Hz, -CH<sub>2</sub>-), 2.04 (s, 6H, -CH<sub>3</sub>), 1.92-1.84 (m, 2H, -CH<sub>2</sub>-), 1.56-1.46 (m, 2H, -CH<sub>2</sub>-), 1.04 (t, 3H, *J*=7.6 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ: 175.59, 169.24, 168.46, 162.88, 152.43, 144.10, 138.63, 136.12, 133.14, 132.09, 130.33, 129.86, 128.26, 127.87, 127.41, 125.56, 125.31, 122.77, 121.82, 113.05, 110.51, 104.29, 96.46, 87.78, 52.23, 52.00, 44.58, 29.83, 27.97, 26.38, 20.31, 13.85. HR-MS (ESI): m/z [M+H] 571.2592, calcd.: 571.2597

# 2-[(3-Butyl-1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene)methyl]-4-[(4-(1,2,3,4tetrahydroquinoline)-2,6-dihydroxyphenyl)-2,5-dien-1-ylidene]-3-oxocyclobut-1en-1-olate (ASQ-6)

**ASQ-6** was obtained from the reaction of compound **3a** (925 mg, 2.56 mmol) and **2b** (700 mg, 2.84 mmol) according to the procedure described for the synthesis of ASQ-5. The solid was recrystallized from a 1:8 volume ratio of dichloromethane and methanol mixture to afford golden crystals with metallic lustre of **ASQ-6** (1210 mg, 80%), mp 245-246 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 8.22 (d, 1H, *J*=8.4 Hz, Ar), 7.96 (d, 1H, *J*=8.0 Hz, Ar), 7.95 (d, 1H, *J*=8.8 Hz, Ar), 7.65 (t, 1H, *J*=8.0 Hz, Ar), 7.52 (t, 1H,

*J*=7.6 Hz, Ar), 7.39 (d, 1H, *J*=8.8 Hz, Ar), 7.34 (d, 1H, *J*=8.4 Hz, Ar), 7.15-7.12 (m, 2H, Ar), 7.00 (t, 1H, *J*=7.6 Hz, Ar), 6.22 (s, 2H, Ar), 5.98 (s, 1H, =CH-), 4.23 (t, 2H, *J*=7.6 Hz, -NCH<sub>2</sub>-), 3.72 (t, 2H, *J*=6.4 Hz, -NCH<sub>2</sub>-), 2.73 (t, 2H, *J*=6.4 Hz, -CH<sub>2</sub>-), 2.03 (s, 6H, -CH<sub>3</sub>), 2.03-1.97 (m, 2H, -CH<sub>2</sub>-), 1.91-1.84 (m, 2H, -CH<sub>2</sub>-), 1.55-1.46 (m, 2H, -CH<sub>2</sub>-), 1.04 (t, 3H, *J*=7.2 Hz, -CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ: 175.49, 169.70, 168.98, 162.46, 156.66, 140.19, 138.66, 136.04, 132.06, 132.04, 130.30, 129.86, 128.73, 128.28, 127.85, 126.44, 125.52, 123.40, 122.76, 110.49, 104.60, 98.09, 87.67, 52.21, 48.36, 44.53, 29.80, 27.12, 26.39, 24.28, 20.31, 13.85. HR-MS (ESI): *m*/*z* [M+H] 585.2736, calcd.: 585.2753

**Table S1** Summary of crystal data, data collection and refinement parameters for ASQ-5 CCDC: 986049 and ASQ-6 CCDC: 986050 )

Compound	ASQ-5	ASQ-6
Empirical formula	$C_{37}H_{34}N_2O_4$	$C_{38}H_{36}N_2O_4$
Formula weight	570.66	584.69
Temperature	173.15 K	143.05 K
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	8.978(2)	14.0820(6)
b/Å	10.664(2)	14.0978(4)
c/Å	15.890(4)	16.5453(5)
$\alpha/^{\circ}$	104.914(3)	90
β/°	94.754(4)	112.969(4)
$\gamma/^{\circ}$	100.900(4)	90
Volume/Å <sup>3</sup>	1429.7(6)	3024.2(2)
Ζ	2	4
$ ho_{calc}mg/mm^3$	1.326	1.284
m/mm <sup>-1</sup>	0.086	0.083
F(000)	604.0	1240.0
Crystal size/mm <sup>3</sup>	$0.211\times0.131\times0.089$	$0.3\times0.3\times0.2$
$2\theta$ range for data collection	4.186 to 50.992°	5.806 to 52.742°
Index ranges	$-10 \le h \le 10, -11 \le k \le 12,$	$-17 \le h \le 17, -17 \le k \le 17,$

	$-19 \le 1 \le 19$	$-20 \le l \le 18$
Reflections collected	9718	13824
Independent reflections	5269 [R(int) = 0.0483]	6180 [R(int) = 0.0180]
Data/restraints/parameters	5269/0/393	6180/0/416
Goodness-of-fit on F <sup>2</sup>	1.020	1.032
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0745, wR_2 = 0.2092$	$R_1 = 0.0619, wR_2 = 0.1577$
Final R indexes [all data]	$R_1 = 0.1293, wR_2 = 0.2579$	$R_1 = 0.0875, wR_2 = 0.1753$
Largest diff.peak/hole/e Å-3	1.57/-0.26	1.59/-0.22



Fig. S1 Crystal packing diagrams for ASQ-5 (left) and ASQ-6 (right).



Fig. S2 Cyclic voltammogram of the two target molecules.

## Charge carrier mobilities

The hole mobility of ASQ-5 and ASQ-6 neat films were measured by the space charge limited current (SCLC) method with the hole-only device structure of ITO/ MoO<sub>3</sub> (80 Å)/ASQ (500 Å)/Au. The hole mobility of ASQ-5/PC<sub>71</sub>BM and ASQ-6/PC<sub>71</sub>BM blend films were measured by the hole-only device structure of ITO/MoO<sub>3</sub> (80 Å)/ASQ: PC<sub>71</sub>BM (1:5) (800 Å)/Au. We plot the *J-V* characterisitcs of a hole-only device, with the top cathode biased positive with respect to the anode. The data follow  $J \propto V^2$ , and hence are fit to a trap-free space charge limited model to extract the zero-field hole mobility, as shown in **Fig. S3, S4**.



**Fig. S3** *J-V* characteristic of ASQ-5 neat film (left) and ASQ-6 neat film (right) single carrier devices used for hole mobility measurement.



**Fig. S4** *J-V* characteristic of ASQ-5: PC<sub>71</sub>BM (left) and ASQ-6: PC<sub>71</sub>BM (right) single carrier devices used for hole mobility measurement.

Table S2 The photovoltaic performances of the organic solar cells based on ASQ:

Active layer (w/w)	V <sub>oc</sub>	$J_{ m sc}$	FF	PCE
	(V)	(mA cm <sup>-2</sup> )		(%)
$ASQ-5 : PC_{71}BM = 1 : 3$	0.82	9.75	0.45	3.60
ASQ-5 : PC <sub>71</sub> BM =1 : 5	0.82	10.29	0.45	3.80
ASQ-5 : PC <sub>71</sub> BM =1 : 8	0.83	9.60	0.44	3.51
ASQ-6 : PC <sub>71</sub> BM =1 : 3	0.83	7.83	0.46	3.00
ASQ-6 : PC <sub>71</sub> BM =1 : 5	0.83	8.97	0.46	3.42
ASQ-6 : PC <sub>71</sub> BM =1 : 8	0.83	8.81	0.44	3.21

PC<sub>71</sub>BM blend films with different weight ratios.



**Fig. S5** *J-V* curve of the devices based on ASQ:  $PC_{71}BM$  blend films with different weight ratios.

**Table S3** The photovoltaic performances of the organic solar cells based on ASQ-5:  $PC_{71}BM=1$ : 5 blend films with different thermo-annealing time.

Active layer (w/w)	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	(V)	(mA cm <sup>-2</sup> )		(%)
Un-annealed	0.82	10.29	0.45	3.80
Annealed at 70° C for 10 min	0.81	10.62	0.47	4.04
Annealed at 70° C for 20 min	0.81	11.03	0.48	4.29
Annealed at 70° C for 30 min	0.81	10.69	0.47	4.07



**Fig. S6** *J-V* curve of the devices based on ASQ-5:  $PC_{71}BM=1$ : 5 blend films with different thermo-annealing time.



**Fig. S7** 3D image obtained by tapping-mode AFM showing the morphology of ASQ-5:  $PC_{71}BM$  (1: 5) blend film (size 2×2 µm) for root-mean-square (RMS) roughness is 0.24 nm (left) and ASQ-6:  $PC_{71}BM$  (1: 5) blend film for RMS roughness is 0.22 nm (right).

## References

[1] D. Yang, Q. Yang, L. Yang, Q. Luo, Y. Huang, Z. Lu and S. Zhao, *Chem. Commun.*, 2013, 49, 10465-10467.









