Novel Unsymmetrical Squaraine-Based Small Molecules for Organic Solar Cells

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Synthesis

Compound 13 was prepared according to the procedures described in the literature.^{1, 2} *n*-Butanol and toluene were distilled freshly from sodium prior to use. All the other chemicals were obtained from commercial sources and used as-received without further purification.



N-octylindole (4)³: A solution of indole (4.00 g, 3.42 mmol) (1) in anhydrous DMF (15 mL) was added dropwise at 0 °C to a suspension of NaH (50% suspension in mineral oil, 3.28 g, 6.84 mmol) in the same solvent. The resulting suspension was stirred at 0 °C for 30 min, and a solution of 1-bromooctane (9.90 g, 5.13 mmol) in anhydrous DMF (15 mL) was added dropwise. The suspension was stirred overnight at room temperature and then poured into 100 ml water and extracted with $CH_2Cl_2(3 \times 30 \text{ ml})$. The organic phase was washed with water, dried over anhydrous Na₂SO₄ and filtered, and the solvent was removed under reduced pressure to give a yellow oil. The product was purified by column chromatography (silica gel, hexane/ DCM=2:1) to give a yellow oil, 6.5 g (83%). ¹H NMR (CDCl₃, 400 MHz, ppm): 7.62 (d, 1H, *J* = 8.0 Hz, ArH), 7.34 (d, 1H, *J* = 8.4 Hz, ArH), 7.20 (t, 1H, *J* = 7.6 Hz, ArH), 7.11-7.07 (m, 2H, ArH), 6.47 (d, 1H, *J* = 2.8 Hz, ArH), 4.11 (t, 2H, *J* = 7.2 Hz, CH₂), 1.87-1.81 (m, 2H, CH₂), 1.31-1.28 (m, 10H, CH₂), 0.87 (t, 3H, *J* = 7.2 Hz, CH₃).

N-octyl-5-fluoroindole (5)⁴: the same procedure as 4, 87%.¹H NMR (CDCl₃, 400 MHz, ppm):7.27-7.23 (m, 1H, ArH), 7.24-7.21 (m, 1H, ArH), 7.12 (d, 1H, *J* = 3.2 Hz, ArH), 6.97-6.92 (m, 1H, ArH), 6.42 (d, 1H, *J* = 4.8 Hz, ArH), 4.08 (t, 2H, *J* = 7.2 Hz, CH₂), 1.83-1.79 (m, 2H, CH₂), 1.29-1.24 (m, 10H, CH₂), 0.87 (t, 3H, *J* = 7.2 Hz, CH₃).

N-octyl-6-fluoroindole (6)⁴: the same procedure as 4, 87%. ¹H NMR (CDCl₃, 400 MHz, ppm):7.51-7.49 (m, 1H, ArH), 7.06 (d, 1H, J = 3.2 Hz, ArH), 7.01 (dd, 1H, J = 2.0 Hz, J = 10.0

Hz ArH), 6.88-6.83 (m, 1H, ArH), 6.45 (d, 1H, *J* = 3.2 Hz, ArH), 4.03 (t, 2H, *J* = 7.2 Hz, CH₂), 1.85-1.78 (m, 2H, CH₂), 1.30-1.25 (m, 10H, CH₂), 0.88 (t, 3H, *J* = 7.2 Hz, CH₃).

3-hydroxy-4-(1-octyl-1H-indol-3-yl)cyclobut-3-ene-1,2-dione (10)⁵: To a solution of compound **4** (1.00 g, 4.37 mmol) in dry toluene (25 mL) a solution of squaryl chloride (0.66 g, 4.37 mmol) in 15 ml toluene was added dropwise. The resulting mixture was stirred at 80 °C for 4 h during which time the color changed red. The solvent was removed under vacuum to afford hydroxy(3-chloro-4-(1-octyl-1H-indol-3-yl)cyclobut-3-ene-1,2-dione (7)), which was used for the next step without purification. A solution of compound **7** in a mixture of acetic acid (10 mL), water (5 mL), and 2M HCl (10 ml) was refluxed for 12 h. After being cooled to room temperature, 50 mL of H₂O was added and the resulting solid was collected by filtration, washed with hexane to afford the product **10** as yellow solid (0.85 g, 61%).¹H NMR (DMSO-*d*⁶, 400 MHz, ppm): 8.37 (d, 1H, *J* = 7.8 Hz, ArH), 8.20 (s, 1H, ArH), 7.58 (d, 1H, *J* = 8.0 Hz, ArH), 7.29-7.25 (m, 1H, ArH), 7.22-7.18 (m, 1H, ArH), 5.83 (br, 2H, OH), 4.30 (t, 2H, *J* = 7.2 Hz, CH₂), 1.81-1.75 (m, 2H, CH₂), 1.24-1.20 (m, 10H, CH₂), 0.83 (t, 3H, *J* = 6.8 Hz, CH₃).

3-(5-fluoro-1-octyl-1H-indol-3-yl)-4-hydroxycyclobut-3-ene-1,2-dione (11): The same procedure as the **10** (yellow solid, 60%).¹H NMR (DMSO- d^6 , 400 MHz, ppm): 8.24 (s, 1H, ArH), 8.09 (dd, 1H, J = 9.6Hz, ArH), 7.65-7.62 (m, 1H, ArH), 7.12 (t, 1H, J = 9.2 Hz, ArH), 4.30 (t, 2H, J = 6.8 Hz, CH₂), 1.79-1.75 (m, 2H, CH₂), 1.24-1.99 (m, 10H, CH₂), 0.83 (t, 3H, J = 6.8 Hz, CH₃).

3-(6-fluoro-1-octyl-1H-indol-3-yl)-4-hydroxycyclobut-3-ene-1,2-dione: The same procedure as the **10** (yellow solid, 63%).¹H NMR (DMSO-*d*⁶, 400 MHz, ppm): 8.38-8.34 (m, 1H, ArH), 8.18 (s, 1H, ArH), 7.50 (d, 1H, *J* = 10.0 Hz, ArH), 7.08 (t, 1H, *J* = 7.2 Hz, ArH), 4.26 (t, 2H, *J* = 6.8 Hz, CH₂), 1.77-1.73 (m, 2H, CH₂), 1.25-1.20(m, 10H, CH₂), 0.83 (t, 3H, *J* = 6.8 Hz, CH₃).

2-(2,6-dihydroxy-4-(8,9,10,10a-tetrahydrobenzo[e]cyclopenta[b]indol-7(7aH)-yl)phenyl)-4-(1-octyl-1H-indol-3-yl)-3-oxocyclobutanolate (YSQY): A mixture of compound 10 (0.19 g, 0.63 mmol) and 13 (0.20 g, 0.63 mmol) in n-butanol (10 mL) and toluene (10 mL) was refluxed for 12 h (equipped with a Dean-Stark apparatus). After cooling the mixture to room temperature, the solvent was removed under reduced pressure to leave a crude product, which was purified by column chromatography (silica gel, hexane/ $CH_2Cl_2 = 1:5$, v/v) to afford **YSQY** as a green solid. The solid was further purified by crystallization from a mixture of CH_2Cl_2 and methanol (1:4, v/v) to afford the pure **YSQY** (0.16 g, 49 %). Mp:154.0-155.1 °C. ¹H NMR (CDCl₃, 400 MHz, ppm):12.67 (s, 2H, OH), 8.60-8.57 (m, 1H, ArH), 8.23 (s, 1H, ArH), 7.80 (d, 1H, J=8.0 Hz, ArH), 7.75-7.66(m, 3H, ArH), 7.45 (t, 1H, J=7.2 Hz, ArH), 7.38-7.33 (m, 4H, ArH), 6.36 (s, 2H, ArH), 4.90-4.85 (m, 1H, CH), 4.29-4.24 (m, 1H, CH), 4.15 (t, 2H, J=7.8 Hz, CH₂), 2.31-2.18 (m, 2H, CH), 2.06-1.96 (m, 2H, CH₂), 1.94-1.87 (m, 2H, CH₂), 1.73-1.64 (m, 1H, CH), 1.54-1.43 (m, 1H, CH), 1.33-1.26 (m, 10H, CH₂), 0.87 (t, 3H, J=7.2 Hz, CH₃).¹³C NMR (CDCl₃, 100 MHz, ppm):181.39, 178.40, 164.75, 155.43, 140.00, 137.40, 135.85, 130.95, 130.92, 130.11, 128.82, 128.63, 126.87, 126.42, 124.59, 124.58, 124.43, 123.64, 123.32, 115.32, 110.53, 109.95, 107.89, 97.00, 69.71, 47.86, 44.68, 35.13, 33.33, 31.73, 29.63, 29.11, 29.09, 26.88, 24.83, 22.61, 14.08. HR-MS (ESI): m/z [M+H]⁺ calculated, 625.3061; found, 625.3055.

2-(2,6-dihydroxy-4-(8,9,10,10a-tetrahydrobenzo[e]cyclopenta[b]indol-7(7aH)-yl)phenyl)-4-(5-fluoro-1-octyl-1H-indol-3-yl)-3-oxocyclobutanolate(5FYSQY): the same procedure as **YSQY**, green solid, 50 %, Mp:160.6-161.5 °C. ¹H NMR (CDCl₃, 400 MHz, ppm):12.64 (s, 2H, OH), 8.26 (dd, 1H, *J*=2.4 Hz, *J*=9.2 Hz, ArH), 8.19 (s, 1H, ArH), 7.79 (d, 1H, *J*=8.0 Hz, ArH), 7.75-7.64 (m, 3H, ArH), 7.44 (t, 1H, *J*=6.8 Hz, ArH), 7.34 (t, 1H, *J*=6.8 Hz, ArH), 7.25-7.23 (m, 1H, ArH), 7.08-7.02 (m, 1H, ArH), 6.34 (s, 2H, ArH), 4.89-4.84 (m, 1H, CH), 4.29-4.24 (m, 1H, CH), 4.13 (t, 2H, *J* = 7.2 Hz, CH₂), 2.35-2.21 (m, 2H, CH₂), 2.05-1.98 (m, 2H, CH₂), 1.96-1.86 (m, 2H, CH₂), 1.72-1.65 (m, 1H, CH₂), 1.51-1.44 (m, 1H, CH), 1.34-1.26 (m, 10H, CH₂), 0.86 (t, 3H, *J*=7.2 Hz, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm):181.11, 178.63, 164.89, 163.76, 160.94, 158.55, 155.65, 139.85, 136.22, 133.76, 131.15, 130.98, 130.07, 128.80, 128.65, 127.33, 127.22, 126.96, 124.65, 123.35, 115.36, 112.82, 112.56, 111.38, 111.28, 110.09, 109.84, 109.66, 109.62, 108.15, 97.00, 69.72, 48.07, 44.68, 35.12, 33.30, 31.73, 29.61, 20.09, 26.87, 24.83, 22.61, 14.08. HR-MS (ESI): m/z [M+H]⁺ calculated, 643.2967; found, 625.2929.

2-(2,6-dihydroxy-4-(8,9,10,10a-tetrahydrobenzo[e]cyclopenta[b]indol-7(7aH)-yl)phenyl)-4-(6-fluoro-1-octyl-1H-indol-3-yl)-3-oxocyclobutanolate(6FYSQY): the same procedure as YSQY, green solid, 45%, Mp:205.1-206.1°C. ¹H NMR (CDCl₃, 400 MHz, ppm): 12.64 (s, 2H, OH), 8.53-8.49 (m, 1H, ArH), 8.15 (s, 1H, ArH), 7.79 (d, 1H, *J* = 8.0 Hz, ArH), 7.73 (t, 2H, *J* = 8.8 Hz, ArH), 7.65 (d, 1H, *J* = 8.8 Hz, ArH), 7.45 (t, 1H, *J* = 7.2 Hz, ArH), 7.36 (t, 1H, *J* = 6.8 Hz, ArH), 7.06 (t, 1H, *J* = 6.8 Hz, ArH), 7.00 (d, 1H, *J* = 7.2 Hz, ArH), 6.36 (s, 2H, ArH), 4.88-4.84 (m, 1H, CH), 4.29-4.24 (m, 1H, CH), 4.07 (t, 2H, *J* = 6.8 Hz, CH₂), 2.32-2.18 (m, 2H, CH), 2.05-1.96 (m, 2H, CH₂), 1.91-1.85 (m, 2H, CH₂), 1.74-1.64 (m, 1H, CH), 1.51-1.43 (m, 1H, CH), 1.34 -1.26 (m, 10H, CH₂), 0.87 (t, 3H, *J* = 7.2 Hz, CH₃). ¹³C NMR (CDCl₃, 100 MHz, ppm): 181.25, 178.64, 164.90, 163.48, 162.19, 159.77, 155.71, 139.80, 137.68, 137.56, 135.71, 131.20, 131.01, 130.06, 128.80, 128.66, 126.89, 125.55, 125.45, 124.70, 123.36, 122.66, 115.38, 111.87, 111.63, 109.70, 108.25, 97.48, 97.21, 96.98, 69.73, 47.91, 44.69, 35.12, 33.28, 31.73, 29.50, 29.09, 26.86, 24.83, 22.61, 14.08. HR-MS (ESI): m/z [M+H]⁺ calculated, 643.2967; found, 643.2964.

Donor	Ratio (D: A)	$V_{\rm oc}({ m V})$	$J_{\rm sc}({\rm mA/cm^2})$	FF	PCE (%)
YSQY	1:1	0.84 ± 0.01	5.94±0.10	0.31±0.01	1.52±0.03
	1:3	0.85 ± 0.01	10.5±0.10	0.39 ± 0.02	3.45±0.13
	1:5	0.87 ± 0.01	11.7±0.26	0.41 ± 0.01	4.18±0.12
	1:7	0.86 ± 0.01	9.71±0.54	0.44 ± 0.01	3.68±0.12
5FYSQY	1:1	0.92 ± 0.01	7.53±0.25	0.37±0.01	2.54±0.12
	1:3	0.92 ± 0.01	11.05±0.24	0.46 ± 0.02	4.67±0.26
	1:5	0.92 ± 0.01	12.08±0.17	0.42 ± 0.10	4.65±0.07
	1:7	0.89 ± 0.01	9.82±0.27	0.41 ± 0.01	3.60±0.21
6FYSQY	1:1	0.91±0.01	4.94±0.22	0.31±0.01	1.41±0.06
	1:3	0.91±0.01	10.25±0.36	0.43 ± 0.01	4.01±0.13
	1:5	0.92±0.01	11.2±0.31	0.44 ± 0.02	4.66±0.18
	1:7	0.90 ± 0.01	9.73±0.16	0.40 ± 0.01	3.56±0.11

Table S1. Photovoltaic performance of BHJ-OSCs based on **YSQY**, **5FYSQY** and **6FYSQY** and PC₇₁BM blends.



Figure S1. J-V characteristics (a) and EQE characteristics (b) of the indicated OSC devices.



Figure S2. AFM height (top)/phase (bottom) images (a) and TEM images (b) of blend films (D:A = 1:5 weigh ratios) spin-coated from $CHCl_3$ solutions. The scale bar in the TEM images is 100 nm.



Figure S3. J-V characteristic of USQ/blend hole-only (left) and electron-only (right) devices.

Table S2. Woolinty data of the indicated donois and blends.					
	$\mu_{\rm h}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{\rm e}$ (cm ² V ⁻¹ s ⁻¹)			
YSQY	6.46×10 ⁻⁵	9.33×10 ⁻⁶			
YSQY: PC71BM	1.10×10 ⁻⁵	2.34×10 ⁻⁵			
5FYSQY	8.13×10 ⁻⁵	1.74×10^{-6}			
5FYSQY: PC ₇₁ BM	5.50×10 ⁻⁵	6.61×10 ⁻⁵			
6FYSQY	8.91×10 ⁻⁵	1.44×10 ⁻⁵			

5.25×10-5

Table S2. Mobility data of the indicated donors and blends

6FYSQY: PC71BM



2.95×10-5

Figure S4. Normalized efficiency *vs.* storage time for devices stored (a) in a glove box and (b) in the air (humidity, 30%; 25 °C) without any encapsulation.

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