Electronic Supplementary Information

Energy Transfer Within Small Molecule/Conjugated Polymer Blends Enhances Photovoltaic Efficiency

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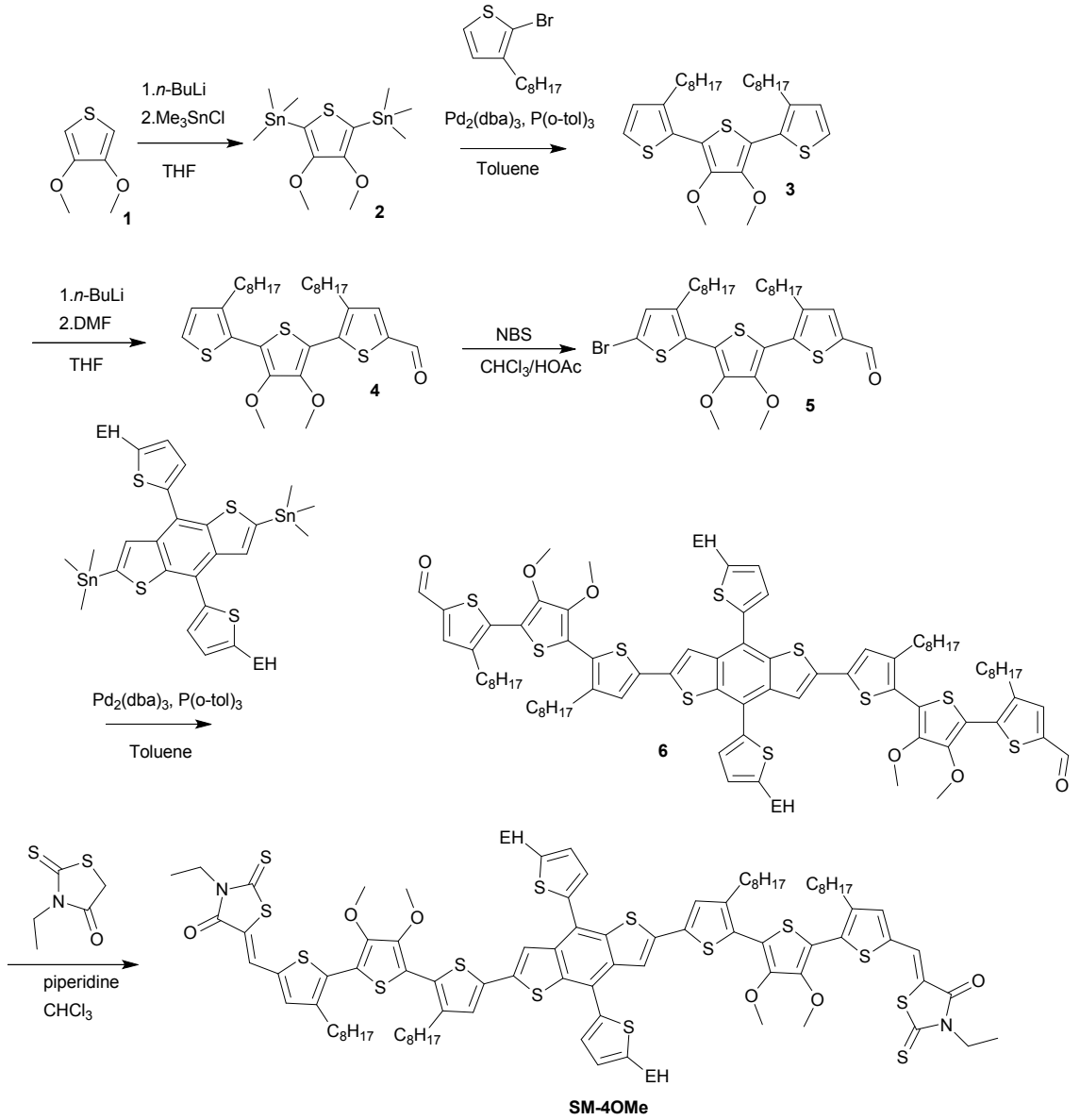

Scheme S1 Synthesis of SM-4OMe

Stnthesis of (3,4-dimethoxythiophene-2,5-diyl)bis(trimethylstannane) (Compound 2) ***:*** *n*-Butyllithium (2.50 M in THF, 29.2 mL, 72.9 mmol) was added dropwise to a stirred solution of 3,4-dimethoxythiophene (5.00 g, 34.7 mmol) in dry THF (60 mL) under N_2 at –78 °C. The mixture was stirred at –78 °C for 1 h before trimethyltin chloride (1.00 M in THF, 76.4 mL, 76.4 mmol) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched by pouring into water. The aqueous phase was extracted three times with hexane. The combined organic phases were dried ($MgSO_4$) and concentrated. The crude compound was used in the next step without purification.

Stnthesis of 3',4'-dimethoxy-3,3''-dioctyl-2,2':5',2''-terthiophene (Compound 3) : A solution of $Pd_2(dba)_3$ (0.54 g, 0.58 mmol, 0.02 eq) in toluene (15 mL) was added dropwise to a solution of (3,4-dimethoxythiophene-2,5-diyl)bis(trimethylstannane) (13.7 g, 29.03 mmol), 2-bromo-3-octylthiophene (73.8 mmol, 2.5 eq), and tri-*o*-tolylphosphine (0.72 g, 2.4 mmol, 0.08 eq) in toluene (150 mL) under N_2. The mixture was then heated at 115 °C for 2 days. The solvent was evaporated and the residue partitioned between water and CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified through gradient column chromatography (SiO_2; CH_2Cl_2/hexane) to yield a yellow oil (9.1g, 59%). MS (MALDI-TOF): m/z 532.23 (M+). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm):7.26(d, 2H, Ar H), 6.92 (d, 2H, Ar H), 3.79 (s, 6H, CH_3), 2.70 (t, 4H, CH_2), 1.60 (m, 4H, CH_2), 1.31 (m, 20H, CH_2), 0.84 (t, 6H, CH_3).

Stnthesis of 3',4'-dimethoxy-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (Compound 4) : *n*-Butyllithium (2.50 M in THF, 8.30 mL, 20.7 mmol, 1.1 eq) was added dropwise to a stirred solution of 3',4'-dimethoxy-3,3''-dioctyl-2,2':5',2''-terthiophene (10.0 g, 18.8 mmol) in dry THF under N_2 at to –78 °C. The mixture was stirred at –78 °C for 1 h before *N*,*N*-dimethylformamide (1.68ml, 21.7mmol, 1.15eq) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by gradient column chromatography (SiO_2; CH_2Cl_2/hexane) to yield a dark-yellow oil (7.4g, 70%). MS (MALDI-TOF): m/z 560.3 (M+). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm):9.84(s, 1H, COH), 7.56(s, 1H, Ar H), 7.03 (d, 1H, Ar H), 6.94 (d, 1H, Ar H), 3.91 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 2.79 (t, 2H, CH_2), 2.70 (t, 2H, CH_2), 1.61 (m, 4H, CH_2), 1.23 (m, 20H, CH_2), 0.84 (m, 6H, CH_3).

Stnthesis of 5''-bromo-3',4'-dimethoxy-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (Compound 5) : NBS (1.67g, 9.37 mmol, 1.05 eq) was added in one portion to a solution of 3',4'-dimethoxy-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5g, 8.92 mmol) in $CHCl_3$/acetic acid (1:1, 150 mL) at 0 °C. The mixture was stirred in the dark overnight and then poured into saturated $NaHCO_3$. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified through gradient column chromatography (SiO_2; CH_2Cl_2/hexane) to yield a dark-brown oil (5.20g, 91%). MS (MALDI-TOF): m/z 638.02 (M+). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm):9.85(s, 1H, COH), 7.56(s, 1H, Ar H), 6.88 (s, 1H, Ar H), 3.89 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 2.78 (t, 2H, CH_2), 2.66 (t, 2H, CH_2), 1.61 (m, 4H, CH_2), 1.23 (m, 20H, CH_2), 0.84 (m, 6H, CH_3).

Stnthesis of 5'',5''''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',4'-dimethoxy-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (Compound 6) : A solution of $Pd_2(dba)_3$ (10.1mg, 0.01 mmol, 2mol%) in toluene (2 mL) was added dropwise to a solution of {4,8-bis[5-(2-ethylhexyl)thien-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}bis-(trimethylstannane) (500 mg, 0.55 mmol), 5''-bromo-3',4'-dimethoxy-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (879 mg, 1.38 mmol, 2.5eq), and tri-*o*-

tolylphosphine (13.4 mg, 0.04 mmol, 8mol%) in toluene (20 mL) under N_2 and then the mixture was heated at 115 °C for 2 days. The solvent was evaporated and the residue partitioned between water and CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified through gradient column chromatography (SiO_2; CH_2Cl_2/hexane) to yield a dark-red solid (765mg, 82%). MS (MALDI-TOF): m/z 1694.31 (M+). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm):9.8(s, 2H, COH), 7.63(s, 2H, Ar H), 7.58(s, 2H, Ar H), 7.30(d, 2H, Ar H), 7.16(d, 2H, Ar H), 7.12(s, 2H, Ar H), 6.92 (d, 2H, Ar H), 3.92 (s, 6H, CH_3), 3.87 (s, 6H, CH_3), 2.87(d, 4H, CH_2), 2.80 (t, 4H, CH_2), 2.74 (t, 4H, CH_2), 2.60 (t, 2H, CH), 1.61 (m, 12H, CH_2), 1.23-1.40 (m, 56H, CH_2), 0.82-0.91 (m, 24H, CH_3).

Stnthesis of SM-4OMe: Piperidine (2 drops) was added to a solution of 5",5""-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',4'-dimethoxy-3,3"-dioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde) (500 mg, 0.29 mmol) and 3-ethylrhodanine (475 mg, 2.9 mmol, 10eq) in $CHCl_3$ (20 mL) and then the mixture was stirred at room temperature overnight. The mixture was poured into MeOH to precipitate a dark purple solid, which was filtered off and purified through gradient column chromatography (SiO_2; CH_2Cl_2/hexane) to yield a black solid. MS (MALDI-TOF) m/z: calcd for $C_{106}H_{136}N_2O_6S_{14}$, [M]+, 1980.6532; found, 1980.6515. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm):7.8(s, 2H, Ar H), 7.63(s, 2H, Ar H), 7.31(d, 2H, Ar H), 7.21(s, 2H, Ar H), 7.12(s, 2H, Ar H), 6.92 (d, 2H, Ar H), 4.19 (q, 4H, CH_2), 3.95 (s, 6H, CH_3), 3.88 (s, 6H, CH_3), 2.89(d, 4H, CH_2), 2.80 (t, 4H, CH_2), 2.72 (t, 4H, CH_2), 1.65 (m, 12H, CH_2), 1.27-1.42 (m, 56H, CH_2), 0.84-0.91 (m, 30H, CH_3). Elemental Analysis: calcd for $C_{106}H_{136}N_2O_6S_{14,}$ C, 64.20; H, 6.91; N, 1.41; found, C, 64.25; H, 6.93; N, 1.40.

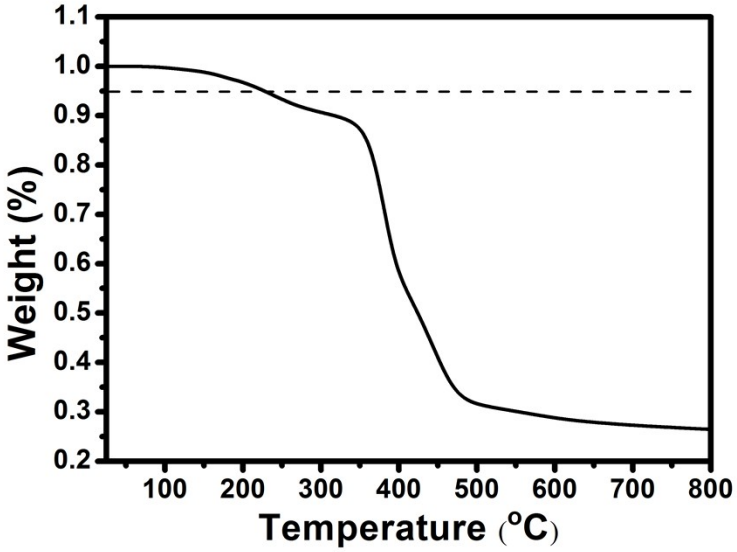

Fig. S1 TGA thermogram of SM-4OMe, recorded at a heating rate of 10 °C min^{-1} under a N_2 atmosphere (T_d: 227 °C).

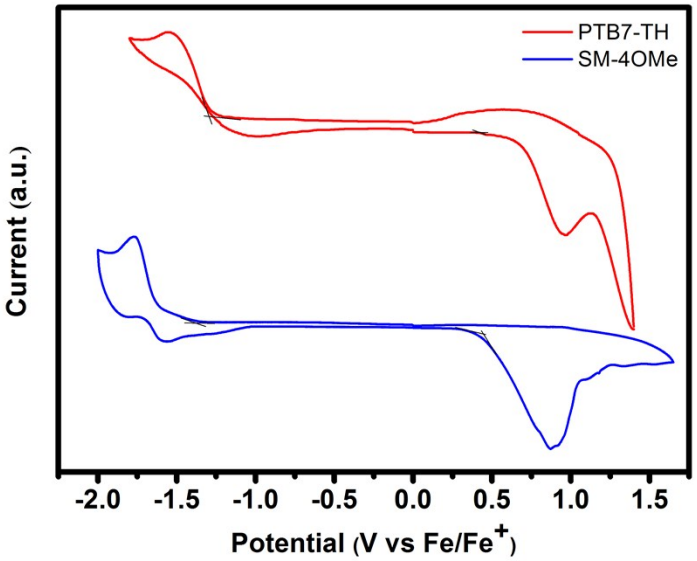

Fig. S2 Cyclic voltammograms of SM-4OMe and PTB7-TH as solid films.

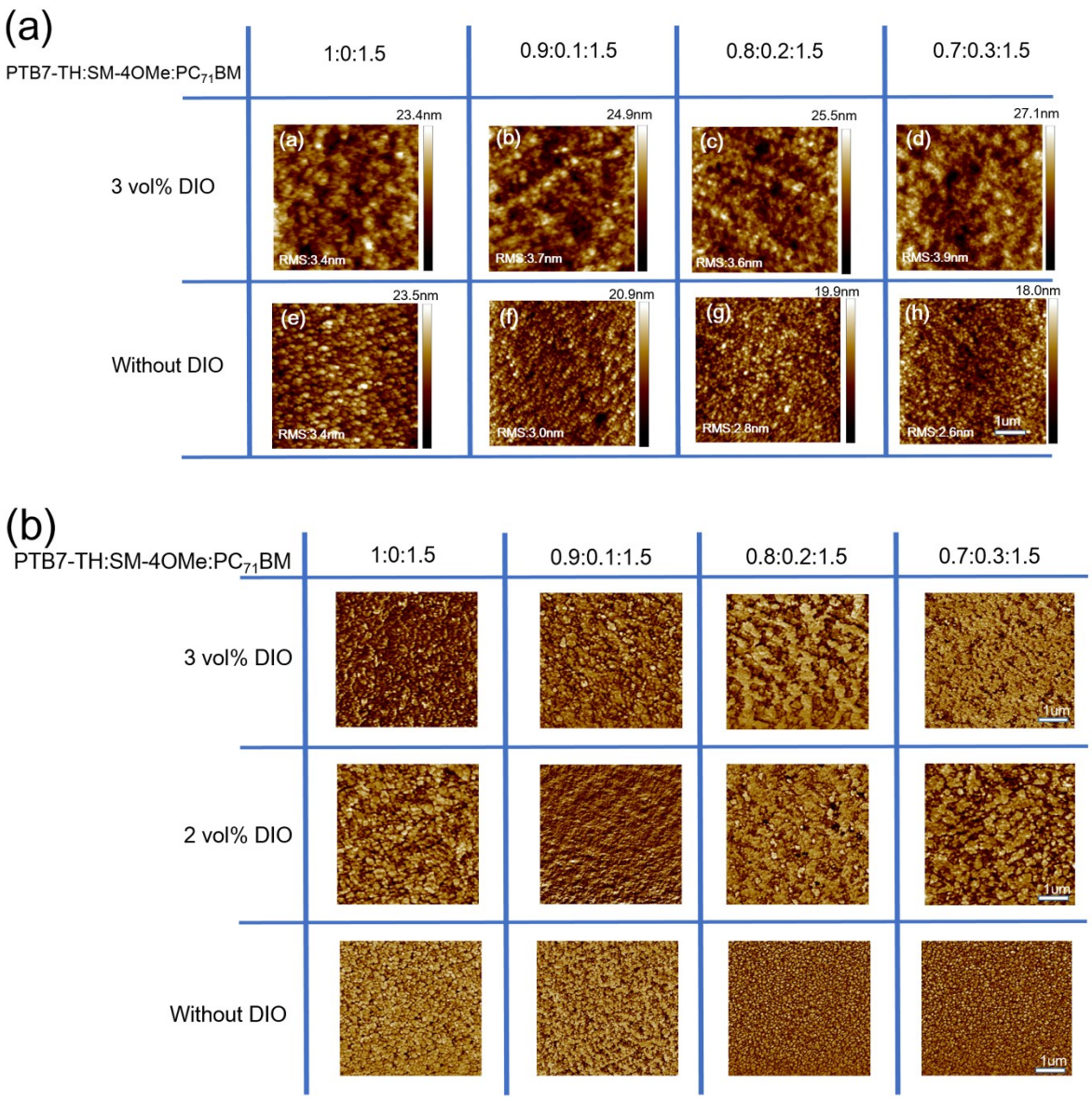

Figure S3. AFM (a) height and (b) phase images (5 × 5 μm) of ternary blend films incorporating various weight ratios of SM-4OMe.

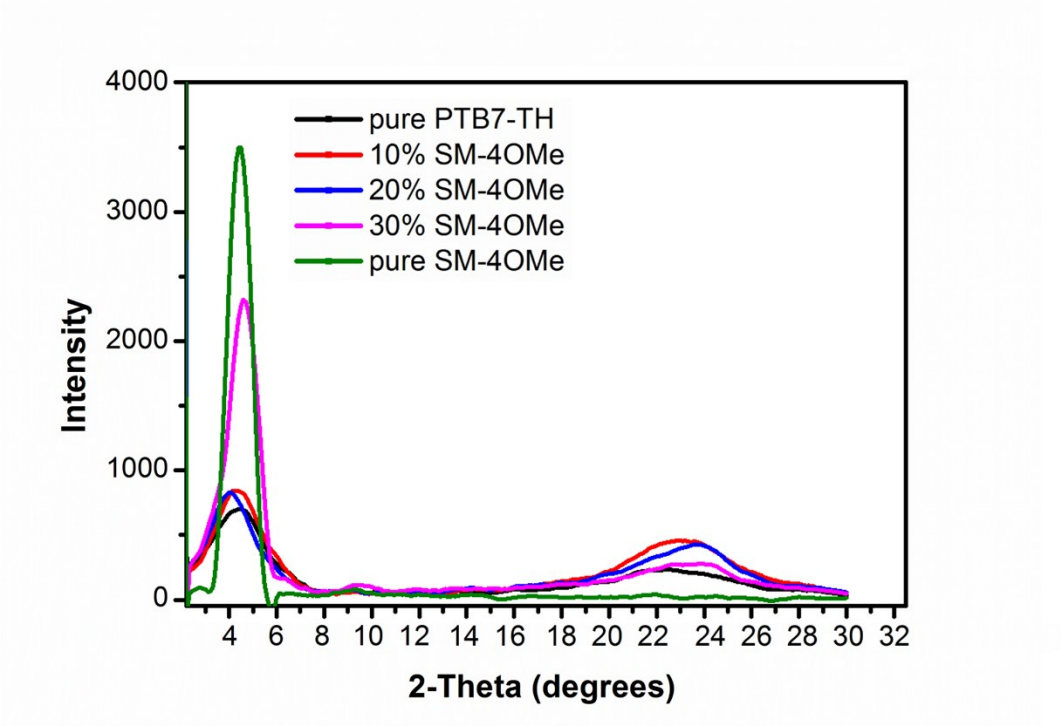

Figure S4. X-ray diffraction patterns of pristine films incorporating various weight ratios of SM-4OMe.

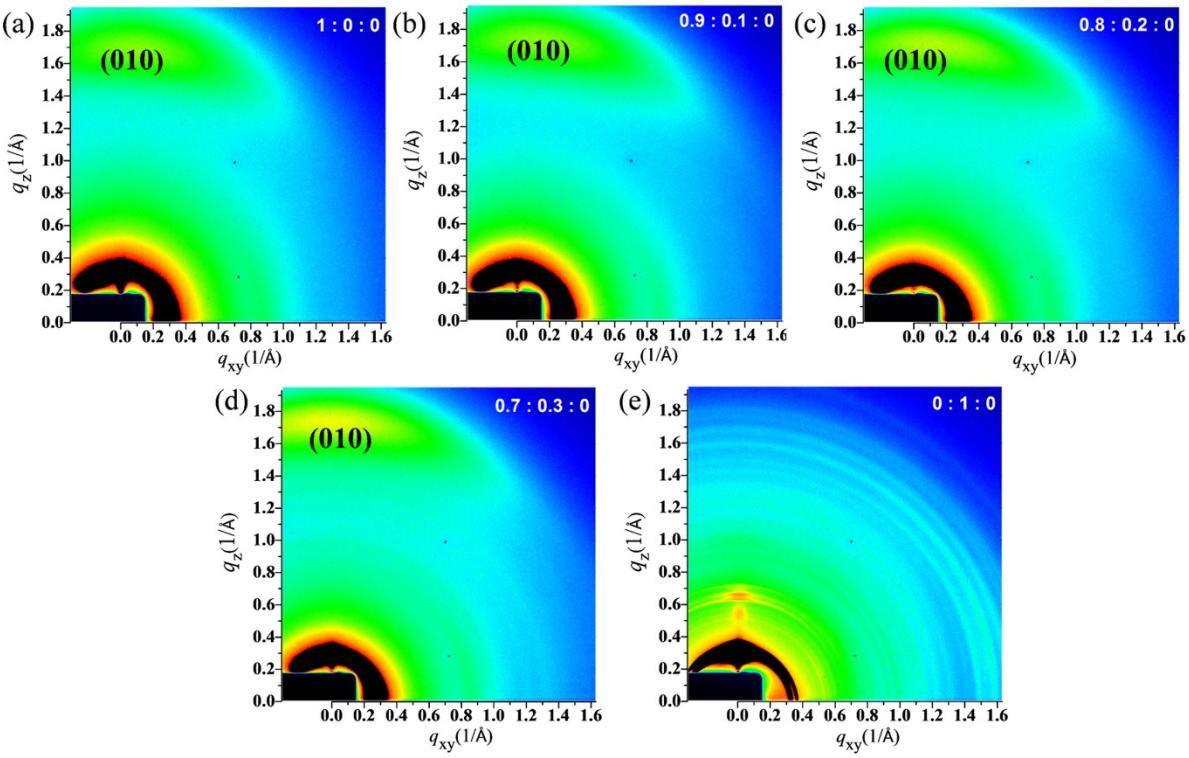

Figure S5. 2-D GIWAXS patterns of PTB7-TH:SM-4OMe blend films having composition ratios of (a) 1:0:1.5, (b) 0.9:0.1:1.5, (c) 0.8:0.2:1.5, (d) 0.7:0.3:1.5, and (e) 0:1:1.5.

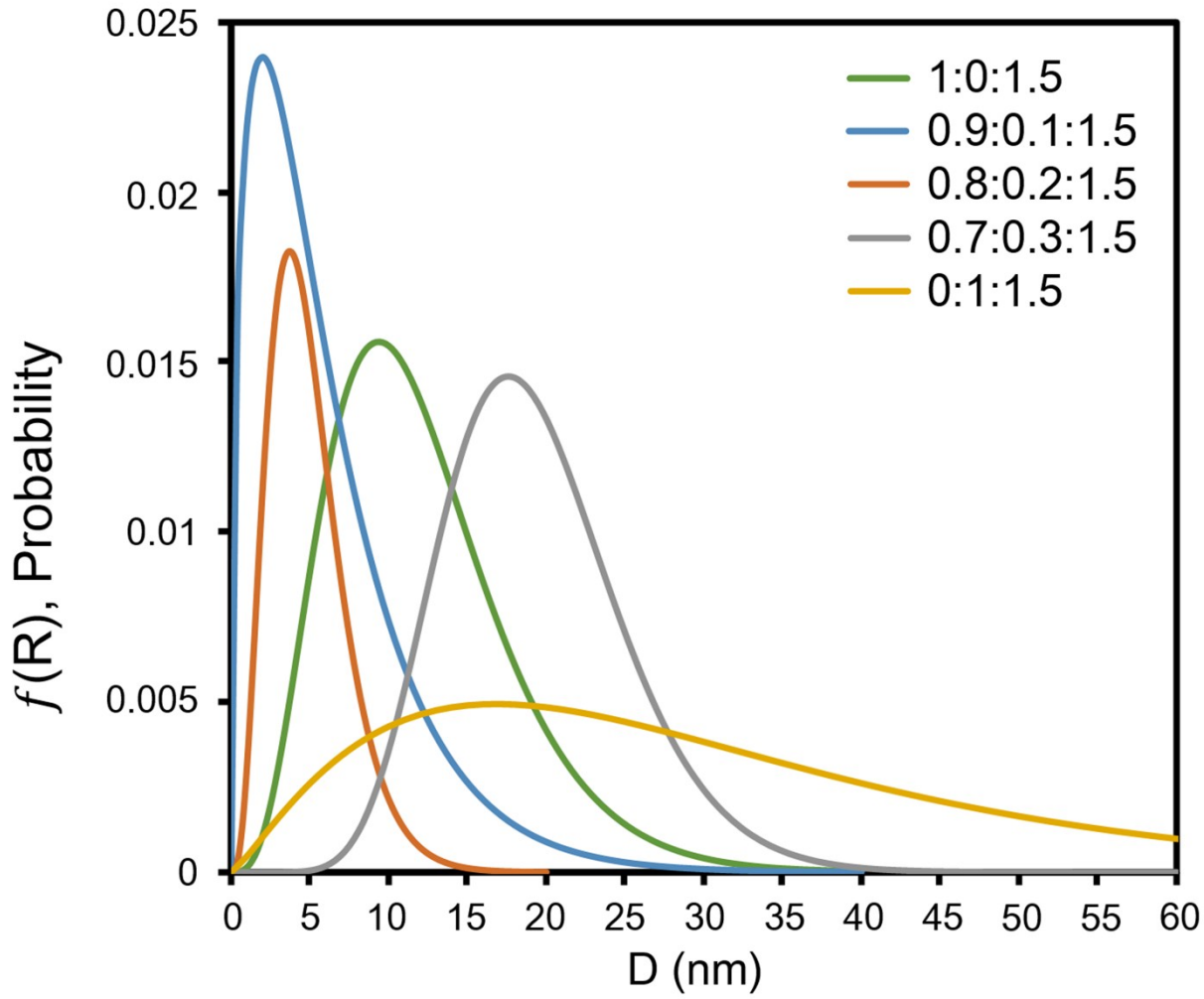

Figure S6. The Schultz distributions of $PC_{71}BM$ cluster sizes is plotted according to the equation 3 and the parameter *p* is from the fitted polydispersity values.

Table S1. Optical and Electronic Properties of SM-4OMe and PTB7-TH.

	E^{ox} (eV)	HOMO (eV)	E_g^{opt} (eV)	$LUMO^{opt}$ (eV)	λ_{onset} (nm)	E_g^{cv} (eV)	$LUMO^{cv}$ (eV)
SM-4OMe	0.45	–5.25	1.76	–3.49	703	1.83	–3.42
PTB7-TH	0.42	–5.22	1.58	–3.64	787	1.71	–3.51

Table S2. Photovoltaic properties of PSCs incorporating various weight ratios of SM-4OMe in the ternary blends (processed without DIO)

PTB7-TH:SM-4OMe: $PC_{71}BM$	PCE_{avg}[a] (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)
1:0:1.5	5.61 ± 0.20	0.81 ± 0.01	15.2 ± 0.3	45.9 ± 0.08
0.9:0.1:1.5	6.52 ± 0.12	0.80 ± 0.01	14.5 ± 0.3	55.8 ± 0.1
0.8:0.2:1.5	6.38 ± 0.20	0.81 ± 0.01	13.8 ± 0.4	57.2 ± 0.07
0.7:0.3:1.5	6.31 ± 0.10	0.83 ± 0.01	13.4 ± 0.5	60.1 ± 0.05
0:1:1.5	0.54 ± 0.10	0.65 ± 0.03	2.6 ± 0.1	31.6 ± 0.5

a: 20 devices were fabricated.

Table S3. Photovoltaic properties of PSCs incorporating various weight ratios of SM-4OMe in the ternary blends (processed with 3% DIO)

PTB7-TH:SM-4OMe:$PC_{71}BM$	PCE_{avg}[a] (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)
1:0:1.5	9.45 ± 0.12	0.79 ± 0.01	17.6 ± 0.1	66.7 ± 0.05
0.9:0.1:1.5	9.11 ± 0.17	0.79 ± 0.01	17.4 ± 0.2	65.5 ± 0.07
0.8:0.2:1.5	9.10 ± 0.20	0.78 ± 0.01	16.6 ± 0.4	70.3 ± 0.05
0.7:0.3:1.5	7.80 ± 0.10	0.79 ± 0.01	14.6 ± 0.2	66.1 ± 0.03
0:1:1.5	0.80 ± 0.10	0.80 ± 0.01	2.3 ± 0.1	44.3 ± 0.05

a: 20 devices were fabricated.

Table S4. Values of μ determined from dark *J–V* curves for the hole and electron-dominated carrier devices incorporating different weight ratios of SM-4OMe in the ternary blends.

Device μ ($cm^2\ V^{-1}\ s^{-1}$)	μ_h without DIO	μ_e without DIO	μ_h/μ_e	μ_h with 2 vol% DIO	μ_e with 2 vol% DIO	μ_h/μ_e
control	1.34×10^{-4}	3.40×10^{-4}	0.38	9.66×10^{-5}	1.85×10^{-4}	0.52
10% SM-4OMe	1.53×10^{-4}	1.80×10^{-4}	0.85	1.24×10^{-4}	1.84×10^{-4}	0.67
20% SM-4OMe	1.99×10^{-4}	2.17×10^{-4}	0.91	1.40×10^{-4}	4.36×10^{-4}	0.32
30% SM-4OMe	1.55×10^{-4}	2.09×10^{-4}	0.74	1.38×10^{-4}	5.97×10^{-4}	0.23

Table S5. Fitting parameters from the GISAXS curves of PTB7-TH:SM-4OMe:PC71BM (DIO) blend films.

Composition (PTB7-TH:SM-4OMe:PC71BM)	1:0:1.5	0.9:0.1:1.5	0.8:0.2:1.5	0.7:0.3:1.5	0:1:1.5
Coefficient	3.05×10^{-7}	3.40×10^{-10}	5.69×10^{-8}	2.34×10^{-8}	N/A
(-)Power	2.145	2.98	2.73	2.89	N/A
Volume fraction (scale)	1.18×10^{-5}	1.14×10^{-5}	8.36×10^{-6}	2.71×10^{-6}	3.94×10^{-6}
Mean cluster size (nm)	12.0	6.1	9.9	19.3	30.3
polydispersity (sig/avg)	0.471	0.821	0.497	0.295	0.667
SLD sphere ($Å^{-2}$)	3.00×10^{-6}	3.00×10^{-6}	3.00×10^{-6}	3.00×10^{-6}	3.00×10^{-6}
SLD solvent ($Å^{-2}$)	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}	1.00×10^{-6}
bkg ($cm^{-1}\ sr^{-1}$)	0.001	0.001	0.0008	0.001	8.00×10^{-4}

Table S6. The integrated and measured photocurrent from EQE curves incorporating different weight ratios of SM-4OMe in the ternary blends.

Device active layer	Integrated photocurrent/measured photocurrent ($mAcm^{-2}$)
binary blend (control)	14.5/15.8
10% SM-4OMe ternary blend	17.2/18.2
20% SM-4OMe ternary blend	15.7/16.9
30% SM-4OMe ternary blend	13.3/14.8