

Supplementary Information

**Thienoisindigo (TIIG)-Based Small Molecules for Understanding of
Structure–Property–Device Performance Correlations**

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Table S1. Photovoltaic device performance at various blending ratios between small molecule and PC₆₁BM and at fixed ratio between small molecule and PC₇₁BM using DIO and CN as additives.

Active layer	Small molecule :PCBM (w/w)	T _A , time (°C, min)	J _{sc} (mAcm ⁻²)	V _{oc} (V)	FF	PCE (%)
THG-Bz:PC₆₁BM	3:7	-	2.23	0.66	0.29	0.42
		(80, 10)	2.35	0.71	0.30	0.50
	4:6	-	1.97	0.65	0.24	0.30
		(80, 10)	2.56	0.65	0.35	0.58
	5:5	-	1.86	0.68	0.26	0.33
		(80, 10)	3.48	0.61	0.44	0.93
	6:4	-	1.32	0.72	0.25	0.23
		(80, 10)	4.48	0.63	0.42	1.18
	7:3	-	0.87	0.64	0.25	0.14
		(80, 10)	5.33	0.64	0.41	1.40
THG-Np:PC₆₁BM	3:7	-	3.21	0.58	0.29	0.55
		(100, 10)	3.18	0.62	0.48	0.96
	4:6	-	3.10	0.62	0.30	0.58
		(100, 10)	3.34	0.62	0.45	0.93
	5:5	-	2.55	0.57	0.28	0.41
		(100, 10)	5.26	0.61	0.43	1.36
	6:4	-	1.72	0.62	0.26	0.28
		(100, 10)	6.49	0.62	0.45	1.83
	7:3	-	1.00	0.40	0.29	0.12
		(100, 10)	5.55	0.62	0.46	1.56
THG-Bf:PC₆₁BM	3:7	-	4.20	0.65	0.32	0.88
		(80, 10)	3.81	0.65	0.32	0.79
	4:6	-	4.23	0.69	0.35	1.02
		(80, 10)	3.26	0.67	0.33	0.73
	5:5	-	3.58	0.68	0.30	0.74
		(80, 10)	5.03	0.68	0.39	1.32
	6:4	-	1.86	0.65	0.28	0.33
		(80, 10)	5.70	0.67	0.43	1.65
	7:3	-	0.61	0.57	0.27	0.09
		(80, 10)	4.90	0.65	0.38	1.21
THG-Bz:PC₇₁BM + 0.4% DIO	7:3	-	3.52	0.51	0.49	0.88
THG-Bz:PC₇₁BM + 0.4% CN		-	3.65	0.58	0.43	0.91
THG-Np:PC₇₁BM + 0.4% DIO	6:4	-	3.98	0.58	0.46	1.07
THG-Np:PC₇₁BM + 0.4% CN		-	4.66	0.60	0.48	1.32
THG-Bf:PC₇₁BM + 0.4% DIO	6:4	-	1.53	0.50	0.41	0.31
THG-Bf:PC₇₁BM + 0.4% CN		-	2.32	0.49	0.49	0.55

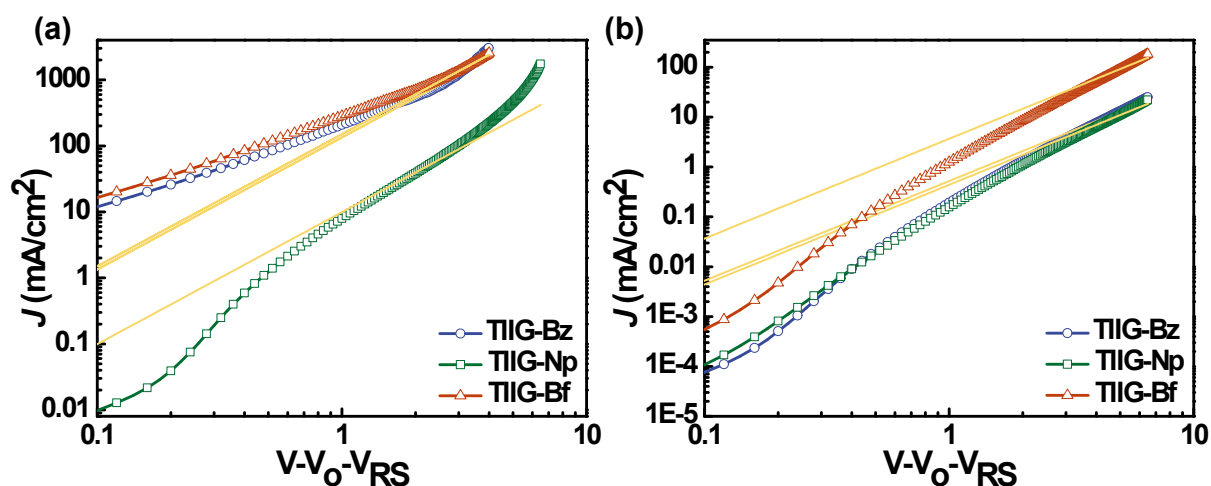


Fig. S1. J – V characteristics of (a) electron- and (b) hole-only devices based on small molecule:PC₇₁BM blend films. Yellow lines represent fits of the curves using the Mott-Gurney relationship. All devices were measured after thermal annealing at 100 °C.

Table S2. Calculated electron and hole mobility values for small molecule:PC₇₁BM devices for **TIIG-Bz**, **TIIG-Np**, and **TIIG-Bf**, respectively, prepared using optimized processing conditions identified for OPV devices.

Small Molecule	Thickness _{electron} (nm)	Electron mobility (cm ² V ⁻¹ s ⁻¹)	Thickness _{hole} (nm)	Hole mobility (cm ² V ⁻¹ s ⁻¹)	μ_e/μ_{hole}
TIIG-Bz	88.5	3.11×10^{-4}	146.5	5.50×10^{-6}	56.54
TIIG-Np	107.3	4.10×10^{-5}	239.5	2.02×10^{-5}	2.03
TIIG-Bf	125.75	1.00×10^{-3}	261	2.19×10^{-4}	4.57

Table S3. Detailed GIWAXS profiles of pristine small molecules and small molecule:PC₇₁BM blend films before and after thermal annealing at 100 °C for **TIIG-Bz**, **TIIG-Np**, and **TIIG-Bf**, respectively.

Type	Direction	Scattering vector (q) of π - π stacking [$\text{\AA}^{-1}$]	d -spacing [$\text{\AA}$]	Lamella interaction (h00)	Scattering vector (q) of lamella peak [$\text{\AA}^{-1}$]	Lamella interaction distance [$\text{\AA}$]
Pristine TIIG-Bz	In-plane (q_{xy})	1.73	3.63	(100)	0.43	14.77
	Out-of-plane (q_z)	1.73	3.63	(100)	0.42	14.82
TIIG-Bz :PC ₇₁ BM	In-plane (q_{xy})	-	-	(100)	0.48	13.00
	Out-of-plane (q_z)	-	-	(100)	0.45	13.97
TIIG-Bz :PC ₇₁ BM annealed at 100 °C	In-plane (q_{xy})	1.74	3.61	(100)	0.43	14.50
	Out-of-plane (q_z)	1.75	3.60	(100)	0.44	14.22
Pristine TIIG-Np	In-plane (q_{xy})	1.73	3.63	(100)	0.40	15.55
	Out-of-plane (q_z)	1.74	3.61	(100)	0.42	15.10
TIIG-Np :PC ₇₁ BM	In-plane (q_{xy})	-	-	(100)	0.45	14.04
	Out-of-plane (q_z)	-	-	(100)	0.41	15.26
TIIG-Np :PC ₇₁ BM annealed at 100 °C	In-plane (q_{xy})	1.74	3.60	(100)	0.43	14.70
	Out-of- plane (q_z)	1.73	3.62	(100)	0.42	15.26
Pristine TIIG-Bf	In-plane (q_{xy})	1.73	3.63	(100)	0.40	15.63
	Out-of-plane (q_z)	-	-	(100)	0.39	16.00
TIIG-Bf :PC ₇₁ BM	In-plane (q_{xy})	-	-	(100)	0.45	13.98
	Out-of-plane (q_z)	-	-	(100)	0.43	14.69
TIIG-Bf :PC ₇₁ BM annealed at 100 °C	In-plane (q_{xy})	1.77	3.56	(100)	0.42	15.13
	Out-of-plane (q_z)	1.76	3.57	(100)	0.42	14.90

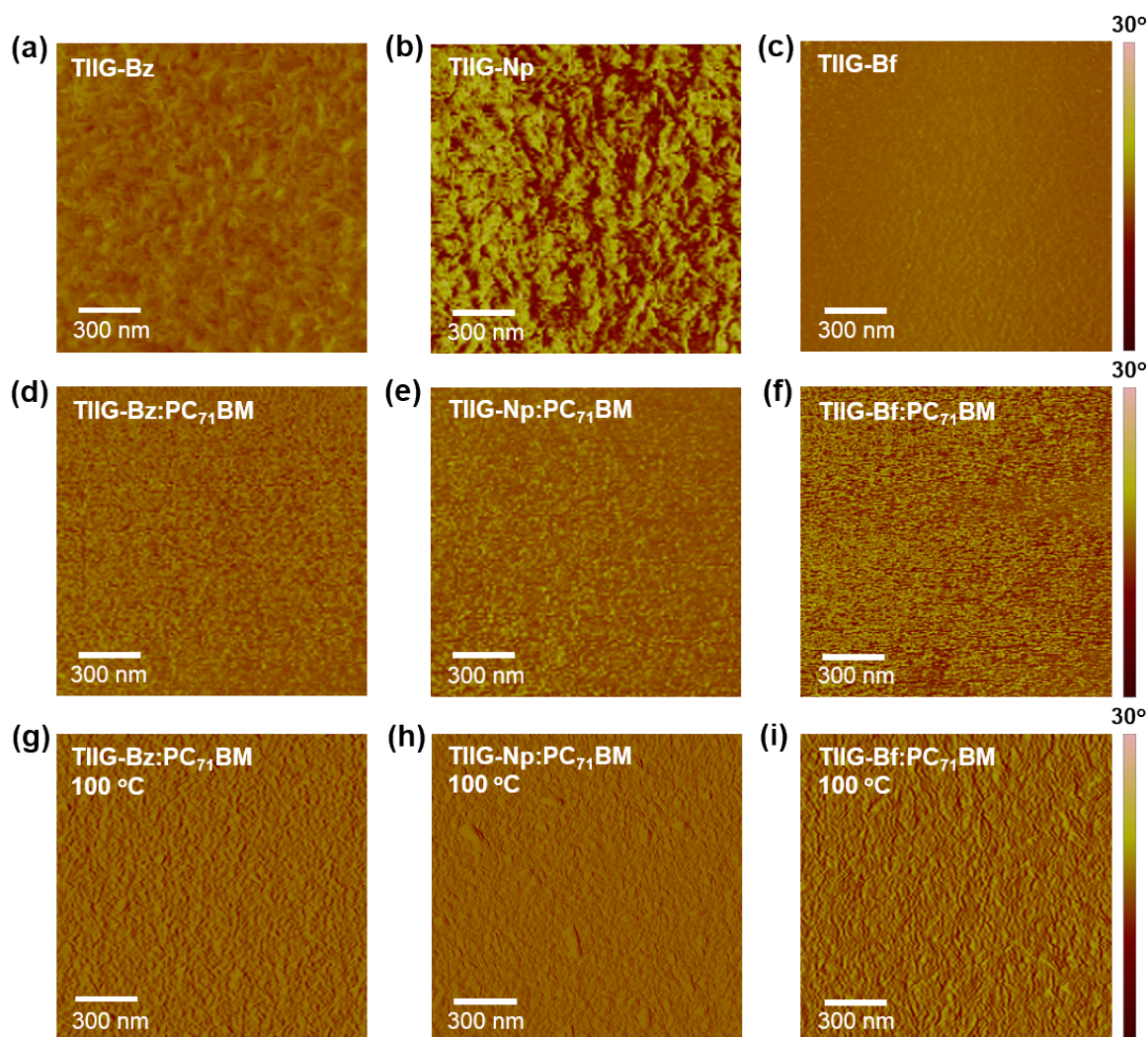


Fig. S2. AFM phase images of (a–c) pristine small molecules, small molecule:PC₇₁BM blend films (d–f) without and (g–i) with thermal annealing at 100 °C. Left, middle, and right columns show images corresponding to **TIIG-Bz**, **TIIG-Np**, and **TIIG-Bf**, respectively. Each film was prepared on glass/ITO/PEDOT:PSS substrates. The size of all images is 1.5 $\mu\text{m} \times 1.5 \mu\text{m}$.