

Supporting Information

Indacenodithiophene-Based N-Type Conjugated Polymers Provide Highly Thermally Stable Ternary Organic Photovoltaics Displaying a Performance of 17.5%

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Experimental Section

General methods: All chemical reagents were purchased from Sigma–Aldrich used as received (unless noted otherwise). PM6 and Y6 (Solarmer) were used without further treatment. The following steps were used to fabricate OPV devices having the inverted structural configuration ITO/ZnO/active layers/MoO₃/Ag. ITO glass substrates [Sanyo, Japan (6.4 Ω square⁻¹)] were patterned lithographically to determine the effective area, then washed with detergent, treated ultrasonically with acetone, water, and isopropyl alcohol (IPA), dried at 140 °C for 10 min, and cleaned with oxygen plasma for 5 min. Zinc acetate (3.15 g), ethanolamine (0.9 mL), and 2-methoxyethanol (29.1 mL) were used to prepare the sol–gel ZnO precursor solution, which was stirred at room temperature for 3 day. The sol–gel ZnO precursor was passed through a 0.45-μm polytetrafluoroethylene (PTFE) filter before being deposited through spin-coating (3000 rpm) in air onto the ITO substrate, then dried at 180 °C for 20 min in air (thickness: ca. 30 nm). The binary and ternary blends of PM6:Y6:PITIC- were prepared at various ratios. Each mixture was dissolved in CF (7.3 mg/mL for the D component), with or without 0.5% CN as an additive, and stirred overnight. The active layer solution was spin-coated onto the ZnO layer at 4000 rpm for 30 s (thickness: ca. 100 nm). Finally, MoO₃ (thickness: 3 nm) and the Ag electrode (thickness: 100 nm) were deposited onto the active layer under a pressure of less than 10⁻⁶ torr. The effective area of the ternary OPV device was 0.1 cm².

Characterization

UV-Vis absorption spectra were recorded using a Jasco V-650 UV-Vis spectrophotometer. PL spectra were recorded using a FluoroMax-4 spectrofluorometer (HORIBA Jobin Yvon inc.). The current density-voltage ($J-V$) curves (PCE and $J_{\text{ph}}-V_{\text{eff}}$ curves) of the devices inside a glove box were determined using a computer-controlled Keithley 2400 source measurement unit and an Enlitech simulator (AAA Class Solar Simulators) under AM 1.5 illumination (1000 W m^{-2}). The illumination intensity of the EQE was calibrated using a standard Si reference cell cover with a KG-5 filter, and matched using an integration system combining a monochromator (Newport 74100), a lock-in amplifier (Stanford Research Systems SR 830), and a chopper to measure the EQE spectra. The surface morphology of the ternary blend films was measured using a Bruker Dimension Edge atomic force microscope, operated in tapping mode at room temperature. GIWAXS was performed at the TLS-BL23A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan (X-ray wavelength: 0.83 \AA ; incident angle: 0.12°). The scattering intensities are reported as intensity versus Q [where $Q = (4\pi/\lambda)\sin(\theta/2)$], along with the scattering angles in these patterns; calibration was performed using silver behenate.

Synthesis procedures

Synthesis of compound 3 (5-bromo-1H-indene-1,3(2H)-dione). Compound 1 (4-bromophthalic anhydride) (5 g, 22 mmol), acetic anhydride (12 mL) and triethylamine (6.5 mL) was added to two-necked round bottom flask under a nitrogen atmosphere, then the compound 2 (ethyl acetoacetate) (3.15 mL) was added quickly under argon. The solution color will be changed from orange to red after addition of compound 2. The mixture was stirred at room temperature for 22 h, then ice-water (8.5 g) and concentrated HCl (8 mL) were added to the mixture followed by

addition of 5M HCl (35 mL). After that, the mixture was stirred at 80 °C for 15 min. After the crude product was cooled to room temperature, water was added, and the mixture was extracted with dichloromethane (DCM). The organic phase was taken, and the solvent evaporated under reduced pressure. The dried solid was dissolved in a minimum volume of acetone and cooled to – 20 °C. The product was collected by filtration and then dried under high vacuum to give a material which obtained as a brown solid. ¹H-NMR (500 MHz, CD₂Cl₂): δ 8.1(s, 1H), 7.94 (d, 1H), 7.83 (d, 1H), 3.23(s, 2H).

Synthesis of compound 5 (IC-Br) (2-(5(6)-bromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile). Compound 3 (2.33 g, 10.35 mmol) and malononitrile (1.37 g, 20.7 mmol) were mixed in 40 mL ethanol in a 250 mL single neck round bottom flask and stirred for 30 min at room temperature. Then, anhydrous sodium acetate (1.28 g, 15.52 mmol) was added to the reaction, and the mixture was stirred at room temperature for 2 h. After the reaction 40 mL water was added, and the mixture was stirred at room temperature for half an hour. Then, concentrated HCl dropped in mixture to acidify the mixture with PH = 2. The precipitate was filtered and washed with water many times. The crude product was further purified by flash column chromatography to afford title compound 3 as yellow solid (0.38 g, yield: 29.4%). ¹H NMR (500 MHz, CDCl₃) δ 8.75 (s, 1H), 8.49 (d, 1H), 8.1 (s, 1H), 7.97 (m, 1H), 7.82 (d, 1H), 3.72 (d, 2H).

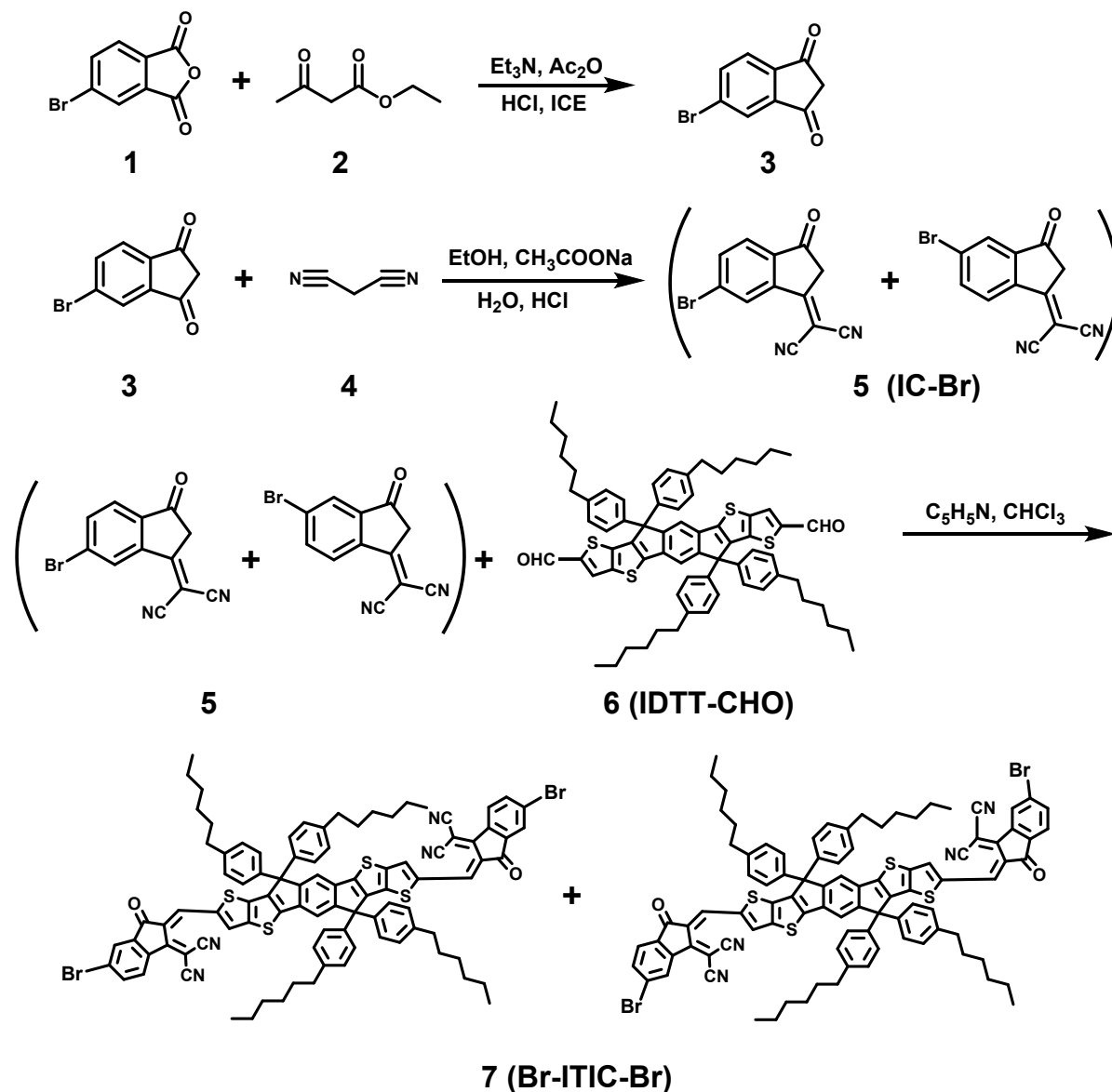
Synthesis of compound 7 (Br-ITIC-Br). Compound 5 (558 mg, 2.04 mmol) and Compound 6 (400 mg, 0.38 mmol) were added to a 250 ml two-necked round bottom flask, after being rinsed with a mild stream of nitrogen for ten minutes, then anhydrous chloroform (100 mL) was added to the flask. Finally, pyridine (2 mL) was added to reaction, the mixture turned green gradually. Then, the reaction was placed in an oil bath at 65 °C stirred and refluxed for 12 hours. After the reaction was completed, it was cooled to room temperature. The crude product was poured to methanol

(400 mL), then the precipitate filtered and purified by flash column (DCM/Hexane (1:1)). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.85 (d, 1H), 8.79 (dd, 0.5H), 8.52 (dd, 0.5H), 8.21 (d, 1H), 7.99 (dd, 0.5H), 7.85-7.82 (m, 1H), 7.74 (dd, 0.5H), 7.62 (m, 1H), 7.19-7.10 (dd, 8H), 2.56-2.53 (m, 4H), 1.60-1.52 (m, 4H), 1.32 (dq, 12H), 0.84 (t, 6H).

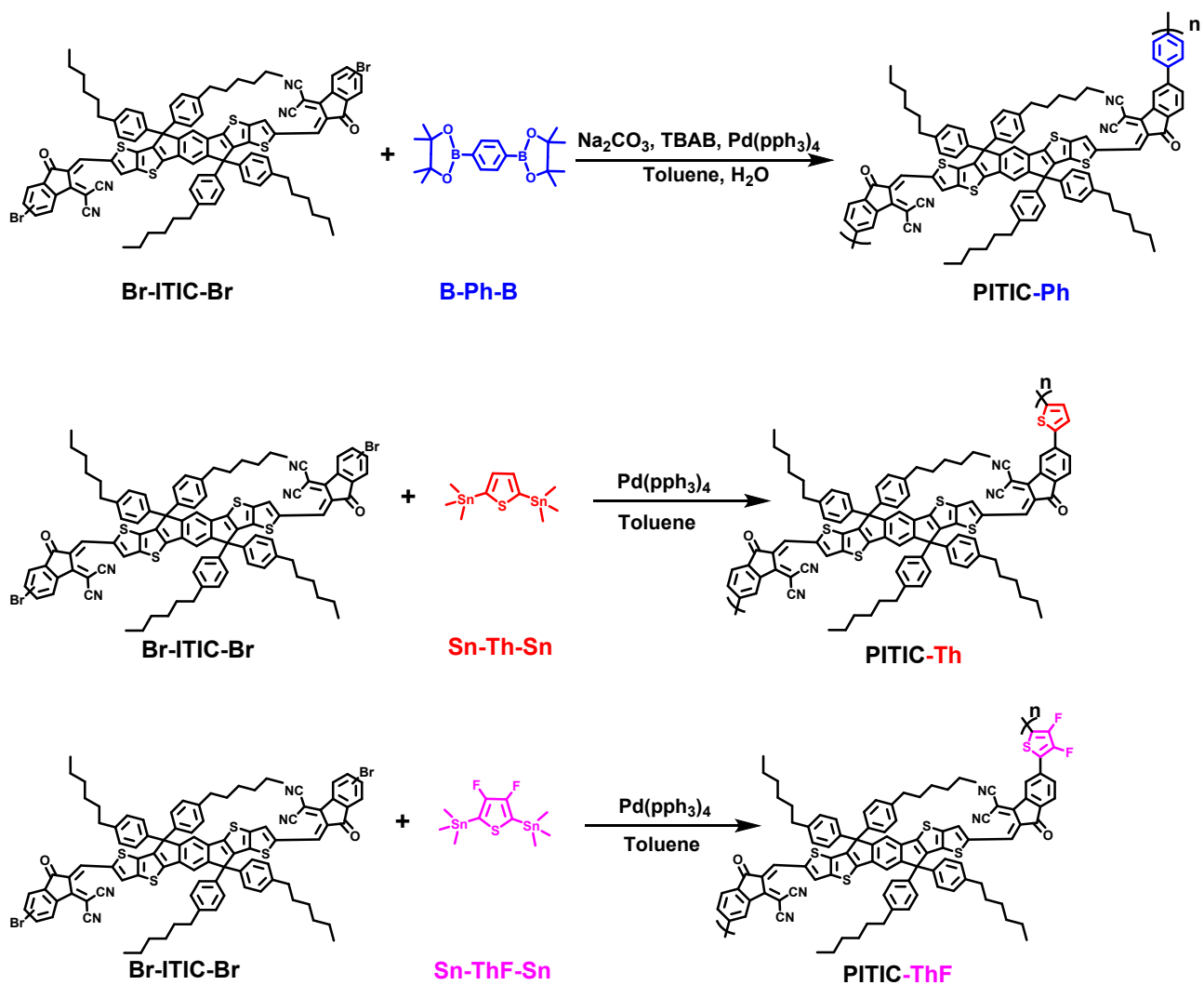
Synthesis of PITIC-Ph polymer: PITIC-Ph prepared by Suzuki–Miyaura coupling polymerization. Monomer Br-ITIC-Br (152 mg 0.1 mmol), monomer B-Ph-B (33 mg, 0.1 mmol), Na_2CO_3 (79 mg, 0.75 mmol), tetra-*n*-butylammonium bromide (1.6 mg, 0.005 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (9.0 mg, 0.008 mmol), toluene (10 mL), and water (2.5 mL) were injected into a sealed tube. The mixture was degassed by bubbling with N_2 for 30 min and then heated at 120 °C for 72 h. After cooling to room temperature, bromobenzene was added and then the sealed tube was heated at 120 °C for 6 h, followed by addition of phenyl boronic acid and heating at 120 °C for another 6 h. The mixture was cooled to room temperature and poured into MeOH. The precipitate was collected through membrane filtration. Purification of the polymer was performed through Soxhlet extraction with MeOH and hexane. Finally, the polymer was dissolved in hot CHCl_3 , concentrated, and then precipitated in MeOH. The polymer was collected and dried under vacuum.

Synthesis of PITIC-Th polymer: PITIC-Th prepared by Stille coupling polymerization. Monomer Br-ITIC-Br (152 mg 0.1 mmol), monomer Sn-Th-Sn (41 mg, 0.1 mmol), $\text{Pd}(\text{PPh}_3)_4$ (9.0 mg, 0.008 mmol), and anhydrous toluene (10 mL) were added to a sealed tube. The mixture was degassed by bubbling with N_2 for 30 min and then stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was poured into MeOH. The precipitate was collected through membrane filtration. Purification of the polymer was performed through Soxhlet extraction with MeOH and hexane. Finally, the polymer was dissolved in hot CHCl_3 , concentrated, and then precipitated in MeOH. The polymer was collected and dried under vacuum.

Synthesis of PITIC-ThF polymer: PITIC-Th prepared by the same synthetic method of PITIC-Th mentioned above. Monomer Br-ITIC-Br (152 mg 0.1 mmol), monomer Sn-ThF-Sn (44.6 mg, 0.1 mmol), Pd(PPh₃)₄ (9.0 mg, 0.008 mmol), and anhydrous toluene (10 mL) were added to a sealed tube. Then follow the same procedure above.



Scheme S1. Synthesis of IC-Br (isomers containing the Br atom at either the 5- or 6-position) and the monomer Br-ITIC-Br (isomers containing the Br atom at either the 5- or 6-position).



Scheme S2. Synthesis of the polymers PITIC-Ph, PITIC-Th, and PITIC-ThF.

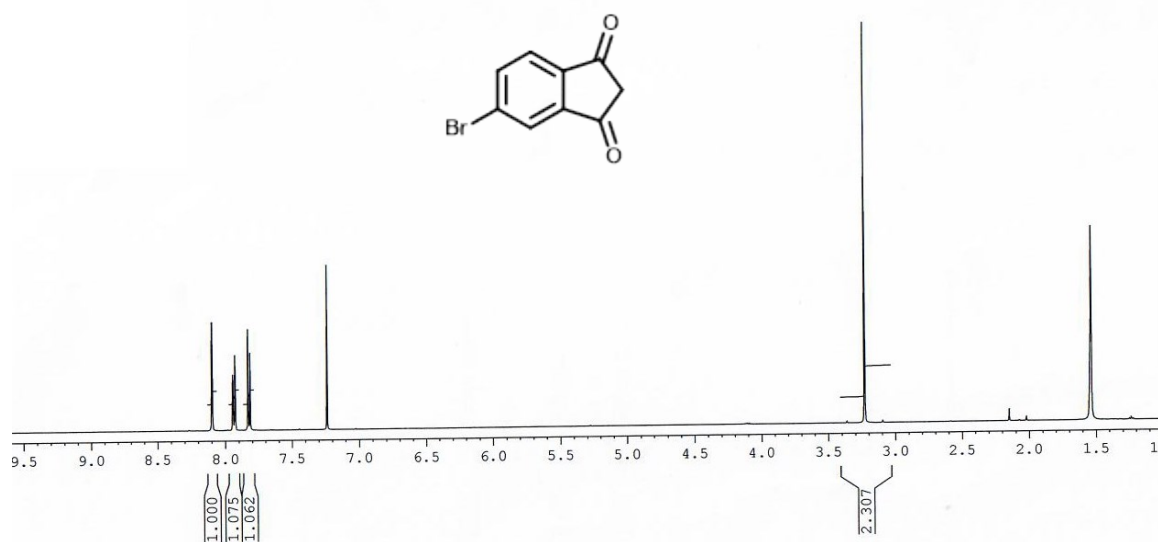


Figure S1. ^1H NMR spectrum of 5-bromo-1*H*-indene-1,3(2*H*)-dione in CDCl_3 .



Figure S2. ^1H NMR spectrum of 2-(5(6)-bromo-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile in CDCl_3 .

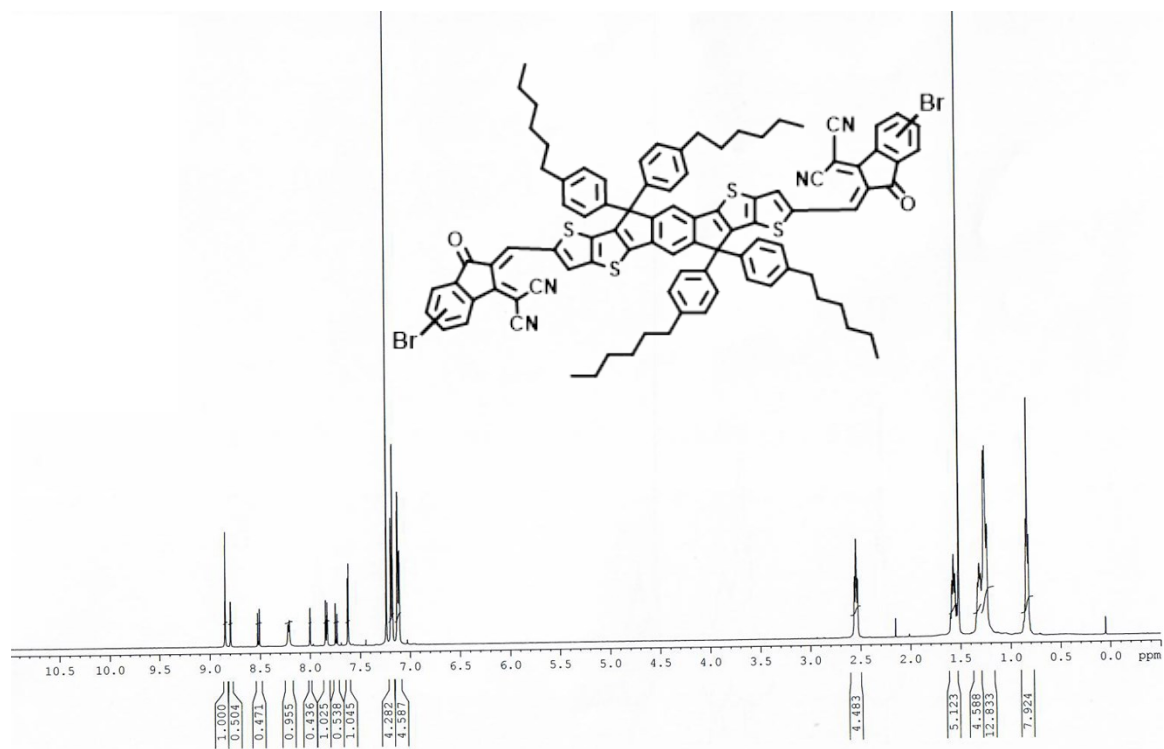


Figure S3. ^1H NMR spectrum of Br-ITIC-Br in CDCl_3 .

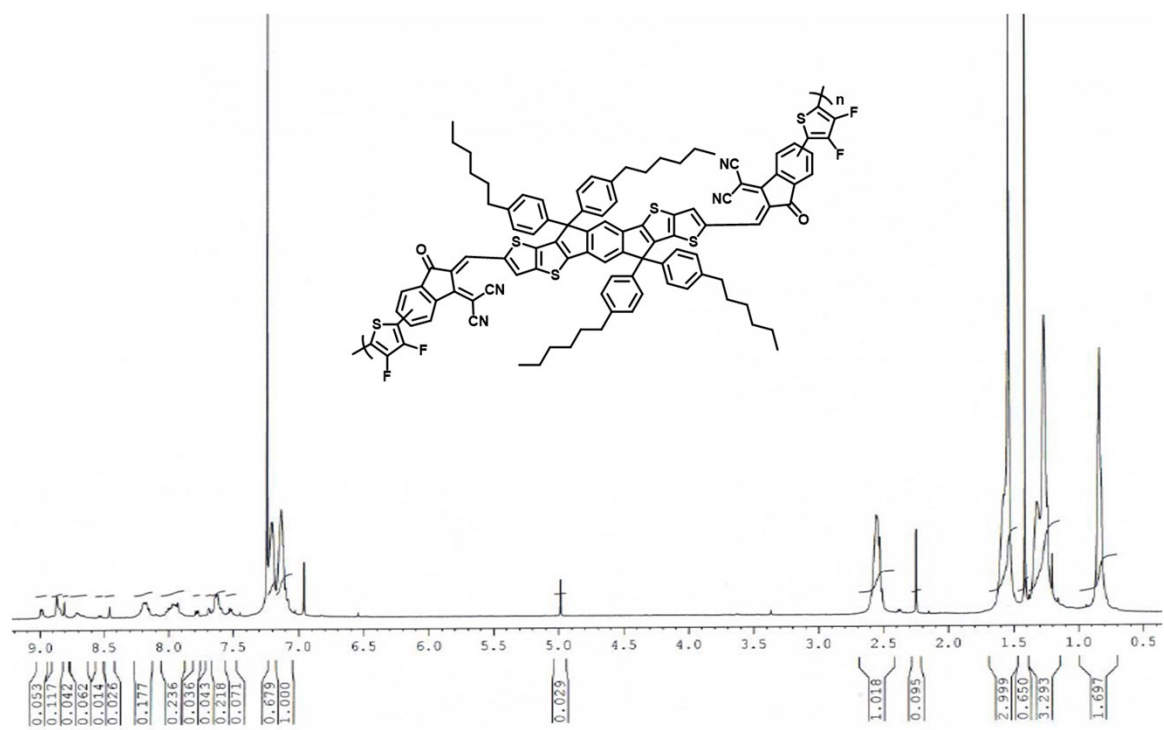


Figure S4. ^1H NMR spectrum of PITIC-ThF in CDCl_3 .

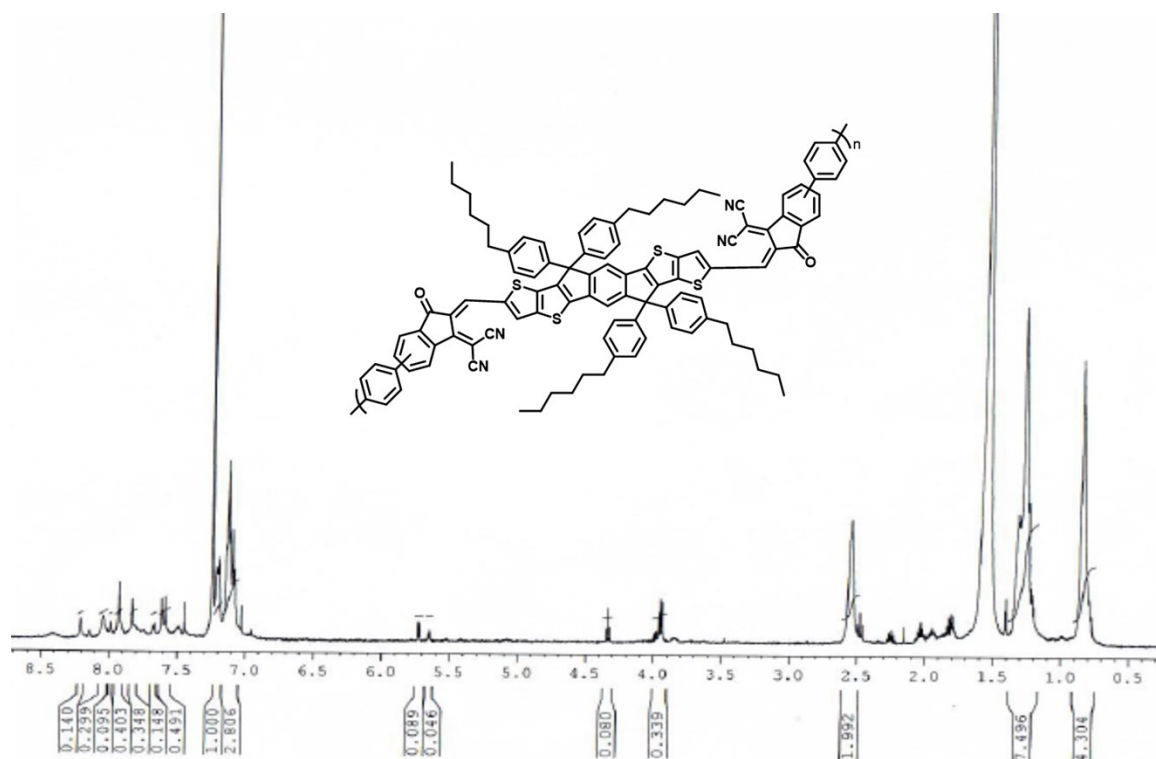


Figure S5. ¹H NMR spectrum of PITIC-Ph in CDCl₃.

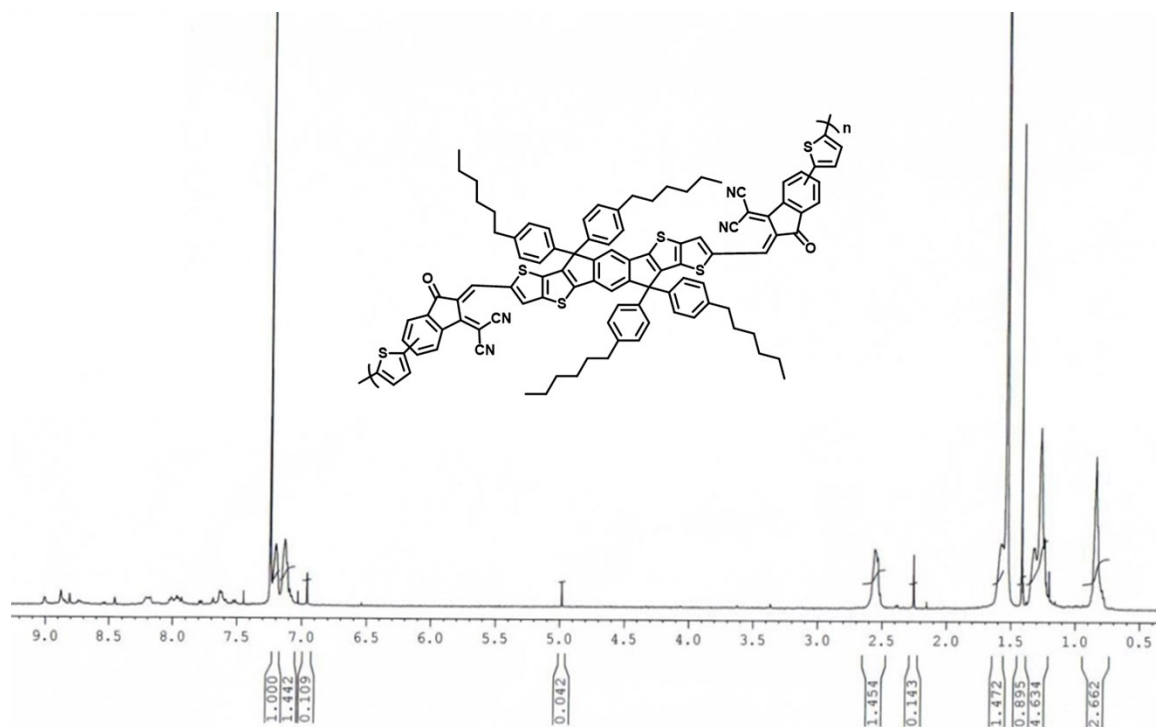
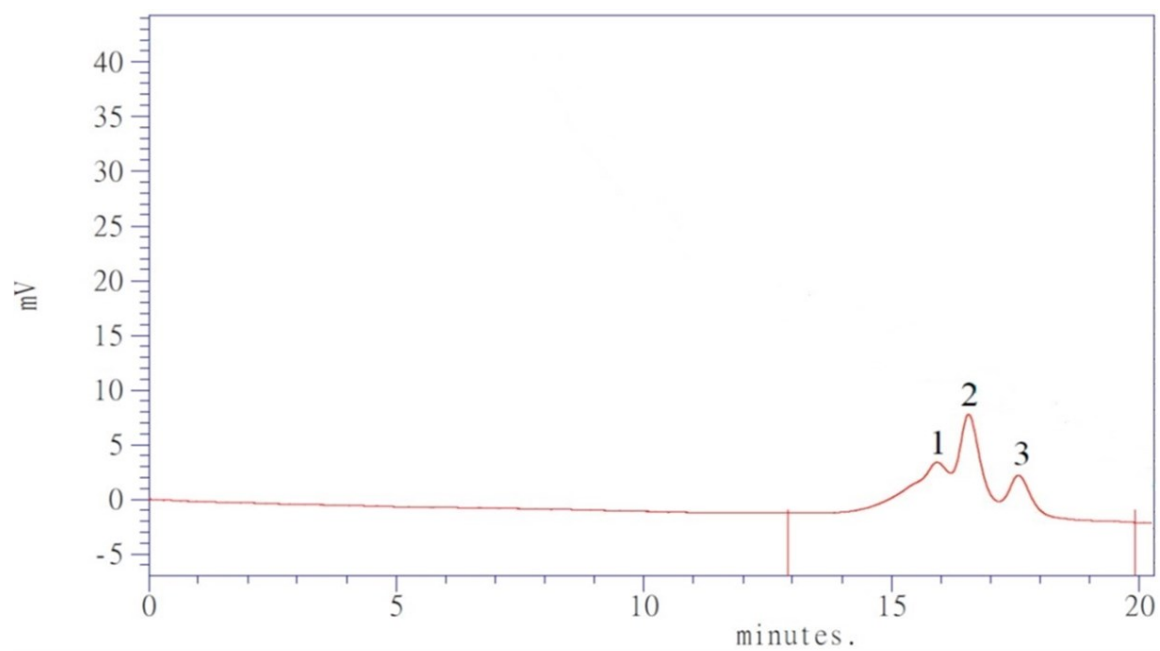
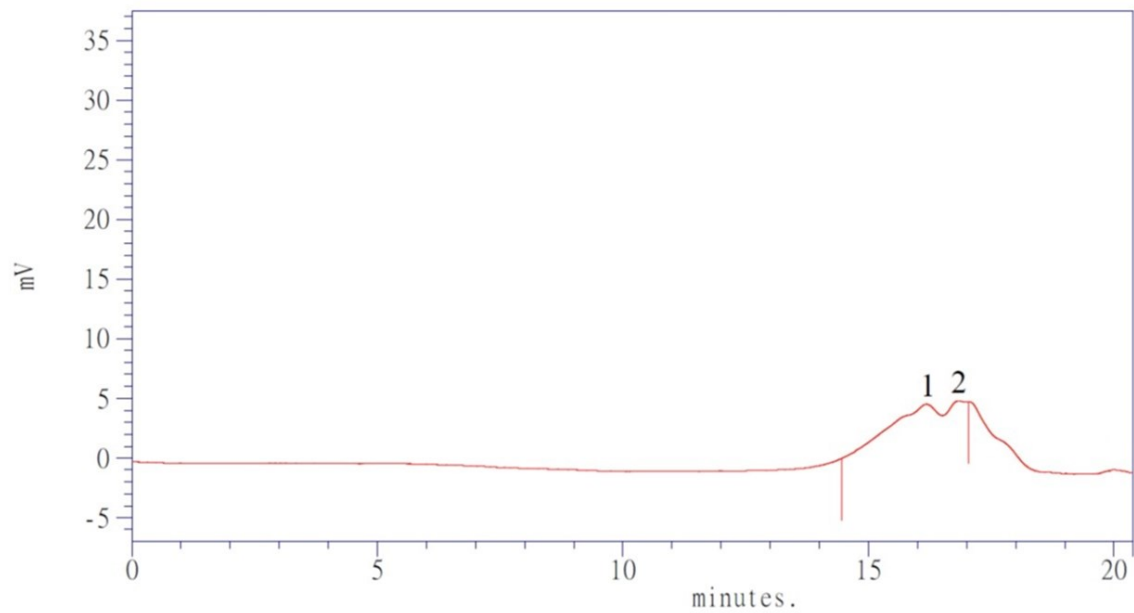


Figure S6. ¹H NMR spectrum of PITIC-Th in CDCl₃.



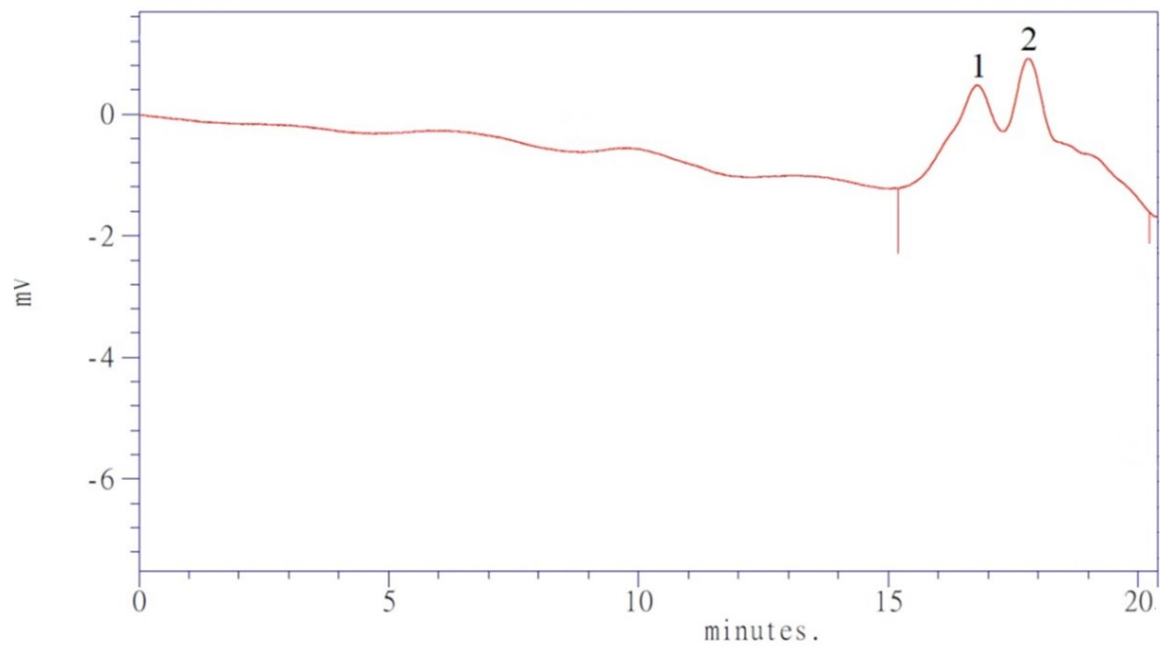
	Mn	Mw	Mw/Mn
1	7649	11092	1.45
2	4568	5117	1.12
3	2300	3035	1.32
Average	5536	9910	1.79

Figure S7. GPC curves of PITIC-Ph.



	Mn	Mw	Mw/Mn
1	6920	10589	1.53
2	3531	4379	1.24
Average	6325	10184	1.61

Figure S8. GPC curves of PITIC-Th.



	Mn	Mw	Mw/Mn
1	4072	5415	1.33
2	3071	3379	1.10
Average	3367	4761	1.41

Figure S9. GPC curves of PITIC-ThF.

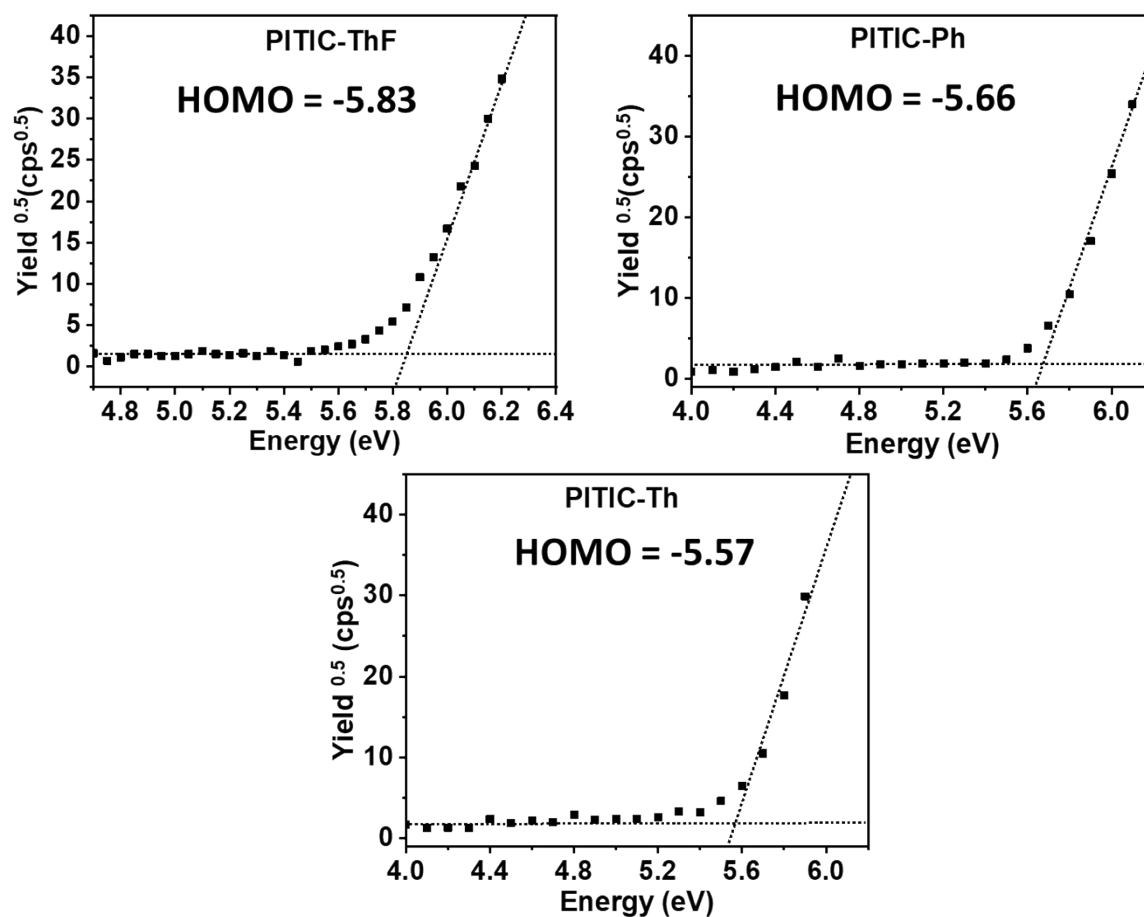


Figure S10. HOMO energy levels of the conjugated polymers, determined using photoelectron spectroscopy.

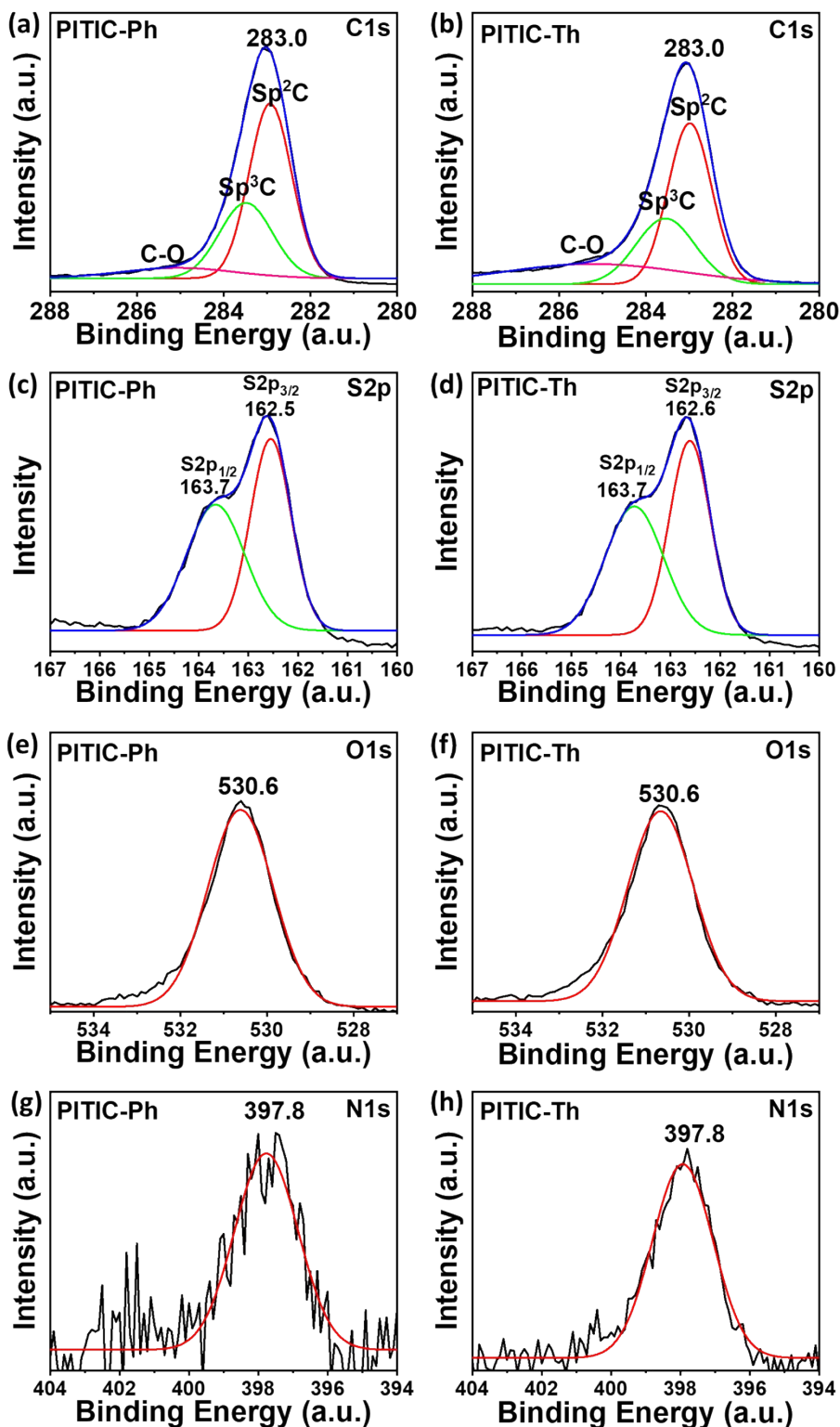


Figure S11. High-resolution XPS spectra of the C 1s, S 2p, O 1s, and N 1s binding energies of PITIC-Ph and PITIC-Th.

	PITIC-Ph	PITIC-Th	PITIC-ThF
LUMO+2			
LUMO+1			
LUMO			
HOMO			
HOMO-1			
HOMO-2			
Dihedral angle	 34.8° 34.28°	 23.72° 21.69°	 22.46° 18.4°

Figure S12. Distributions of the HOMOs and LUMOs of the polymers, calculated using DFT.

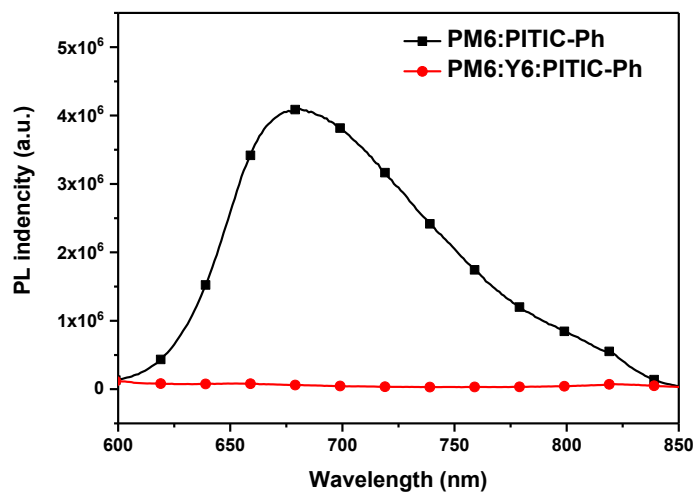


Figure S13. PL spectra of PM6:PITIC-Ph (1:1.2) and PM6:Y6:PITIC-Ph (1:1.2:0.1).

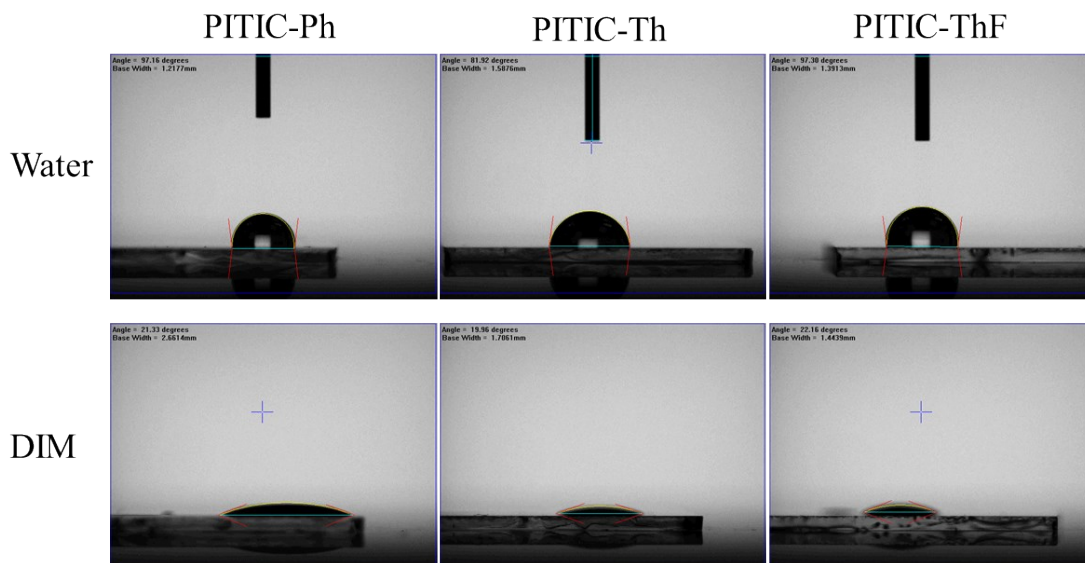


Figure S14. Contact angles of the PITIC-containing thin films.

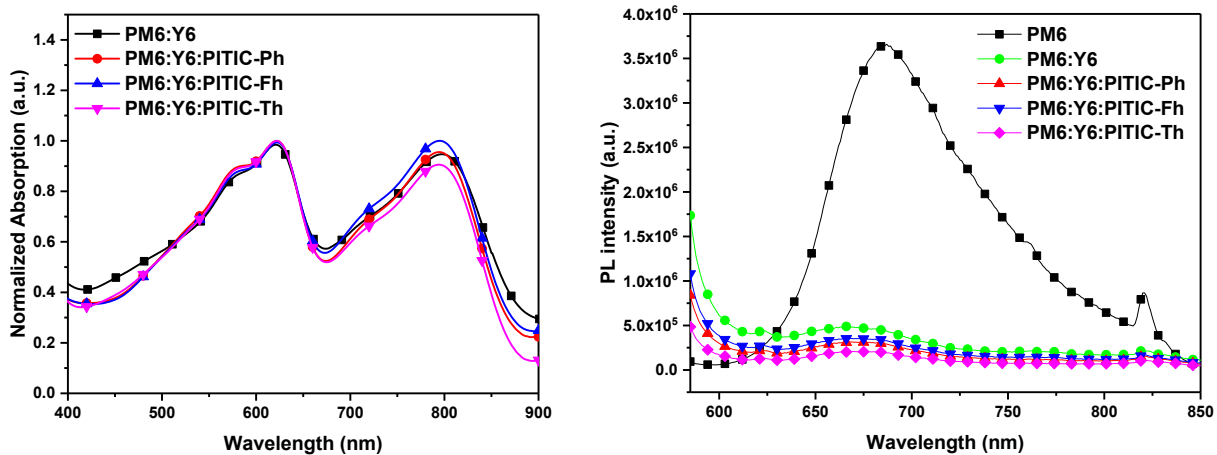


Figure S15. UV–Vis and PL spectra of PM6:Y6 and blend films containing the PITIC derivatives.

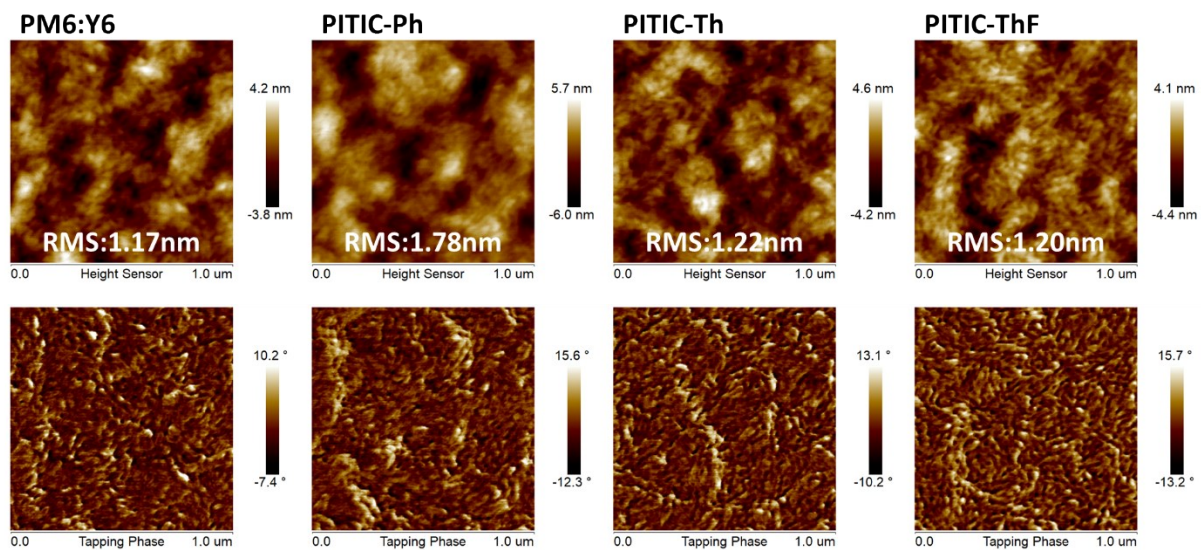


Figure S16. AFM topographic and phase images of PM6:Y6 blend films in the presence of the PITIC derivatives as additives.

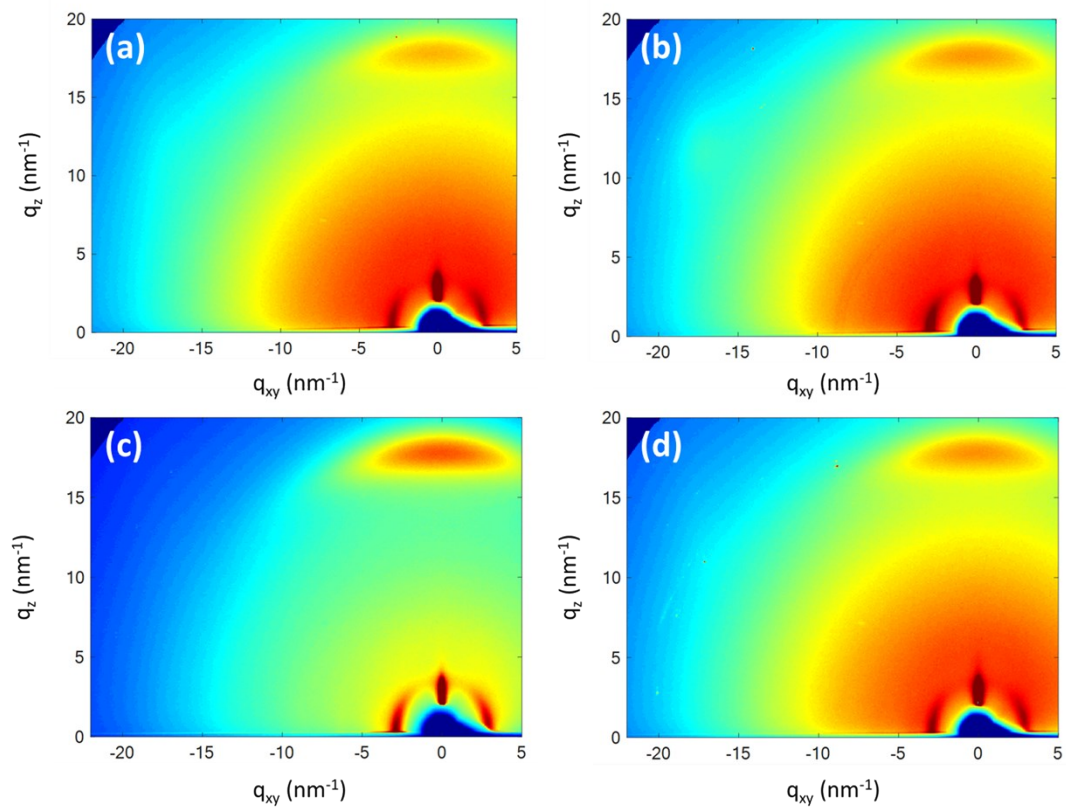


Figure S17. 2D-GIWAXS patterns of a) PM6:Y6, b) PM6:Y6 + PITIC-Ph, c) PM6:Y6 + PITIC-Th, and d) PM6:Y6 + PITIC-ThF films.

Table S1. OPV parameters of binary devices (PM6:PITIC-Ph=1:1.2).

BHJ	Additive	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)
PM6:PITIC-Ph	w/o	0.97	1.02	31.8	0.315
	DIO 2%	0.94	1.03	33.1	0.323
PM6:PITIC-Th	w/o	3.54	0.84	39.5	1.177
	DIO 2%	3.20	0.90	35.8	1.034

Table S2. Contact angles, surface energies, and Flory–Huggins interaction parameters (χ) of the various films.

	θ_{water} [°]	θ_{DIM} [°]	γ_{polar} [mN m ⁻¹]	$\gamma_{dispersive}$ [mN m ⁻¹]	γ_{total} [mN m ⁻¹]	$\chi_{PM6:A}$	$\chi_{Y6:A}$
PITIC-Ph	93.48	23.19	2.32	46.86	49.17	0.36	0.03
PITIC-Th	81.37	23.61	6.89	46.72	53.60	0.82	0.02
PITIC-ThF	97.82	27.14	1.01	45.50	46.50	0.16	0.13
PM6*	-	-	-	-	41.15	-	0.54
Y6*	-	-	-	-	51.49	0.54	-

* data obtained from ACS Applied Materials & Interfaces 2021 DOI: 10.1021/acsami.0c19198.

Table S3. OPV parameters of the ternary devices

	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF (%)	PCE (%)
PM6:Y6:PITIC- Ph_1:1.2:0.1	25.2±1.11	0.90±0.01	61.7±4.72	14.0±1.54
w/ PITIC-Ph_0.03	25.2±0.35	0.87±0.01	74.6±0.75	16.4±0.19
w/ PITIC-Ph_0.04	26.5±0.70	0.87±0.01	74.0±1.50	17.0±0.35
w/ PITIC-Ph_0.05	26.0±0.24	0.88±0.01	67.6±0.82	15.4±0.22

Table S4. GIWAXS data of the PM6:Y6 blend and PITIC polymers.

sample	Lamellar (nm)	$\pi - \pi$ stacking (nm)
PM6:Y6	2.106	0.362
PITIC-Ph	2.106	0.364
PITIC-Th	2.130	0.362
PITIC-ThF	2.106	0.358

Table S5. Optoelectronic parameters of the devices, calculated from $J_{\text{ph}}-V_{\text{eff}}$ curves.

Active layer	J_{sat} (mA cm ⁻²)	J_{ph}^* (mA cm ⁻²)	G_{max} (m ⁻³ s ⁻¹)	P(E,T) (%)
PM6:Y6	28.41	24.98	$1.77*10^{28}$	87.92%
PITIC-Ph	28.26	27.07	$1.76*10^{28}$	95.76%
PITIC-Th	25.88	24.90	$1.61*10^{28}$	96.21%
PITIC-ThF	26.80	25.41	$1.67*10^{28}$	94.81%