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**Supplementary Information for**

# Triad-Type, Multi-Functional Compatibilizers for Enhancing Efficiency, Stability and Mechanical Robustness of Polymer Solar Cells

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## Experimental Section

### Materials

Phenyl-C61 (or C71)-butyric acid methyl ester, $PC_{61}BM$ ($PC_{71}BM$) and regio-regular (>99%) poly(3-hexylthiophene-2,5-diyl) (P3HT) were purchased from Nano-C and TCI. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was obtained from Clevios. Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b′*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carbo-xylate-2-6-diyl)] (PTB7-Th) and poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T) were purchased from 1-Materials, and other solvents and additives were purchased from Sigma Aldrich.

### Synthesis

**5TRh-OH.** The formyl-functionalized oligothiophene core (1), 3-(6-hydroxyhexyl)rhodanine (2) and phenyl-$C_{61}$-butyric acid ($PC_{61}BA$) were synthesized by following previous procedures.[1-3] Pyridine (1mL) and piperidine (0.1 mL) were added to a mixture of compound (1) (0.5 g, 0.54 mmol) and compound (2) in anhydrous 1,2-dichloroethane (20 mL) and the resulting mixture was heated under reflux for 12 h. The reaction solution was cooled down to room temperature, and poured into methanol. The precipitated solid was filtered and washed with methanol several times. After silica gel column chromatography (eluent: $CH_2Cl_2$/MeOH=98/2, v/v), 5TRh-OH (0.7 g, 95 %) was obtained as a dark red solid. $^1H$ NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76 (s, 2H), 7.14 (s, 2H), 7.11 (s, 2H), 7.11 (s, 2H), 4.11 (t, 4H), 3.65 (t, 8H), 2.81 (t, 4H), 1.74-1.66 (m, 16H), 1.41-1.27 (m, 48H), 0.86 (m, 12H); 13C NMR (125MHz, CDCl3): δ (ppm) 192.28, 167.58, 141.10, 140.50, 139.64, 137.46, 135.77, 135.10, 132.95, 132.23, 129.95, 126.43, 125.02, 120.39, 62.78, 44.64, 32.55, 31.9, 31.8, 30.6, 30.2, 29.56, 29.52, 29.47, 29.42, 29.40, 29.32, 29.26, 26.93, 26.46, 25.23, 22.69, 22.68, 14.13.

**5TRh-PCBM.** 4-Dimethylaminopyridine (DMAP) (0.135 g, 1.11 mmol) was added to a mixture of 5TRh-OH (0.3 g, 0.22 mmol), $PC_{61}BA$ (0.499 g, 0.56 mmol), and 1,3-dicyclohexylcarbodiimide-4-dimethylaminopyridine (DCC) (0.230 g, 1.11 mmol) in 10 mL o-dichloromethane (o-DCB). The resulting mixture was stirred at room temperature for 36 h. The reaction solution was poured into 200 mL of methanol, and the precipitated solid was filtered and washed with methanol. The crude solid purified *via* silica gel column chromatography with chloroform as eluent. 5TRh-PCBM (0.18 g, 40.8%) was obtained as a dark black solid. $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 7.92 (m, 4H), 7.76 (s, 2H), 7.54 (m, 4H), 7.48 (m, 2H), 7.22 (s, 2H), 7.15 (s, 2H), 7.11 (s, 2H), 4.09 (m, 8H), 2.91 (m, 4H), 2.81 (m, 8H), 2.52 (m, 4H), 2.18 (m, 4H), 1.70 (br, 16H), 1.40-1.25 (br, 48), 0.86 (m,12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ (ppm) 192.22, 173.12, 167.49, 148.83, 147.81, 145.84, 145.16, 145.12, 145.08, 144.99, 144.75, 144.66, 144.63, 144.46, 144.39, 143.98, 143.73, 143.10, 142.99, 142.95, 192.94, 142.89, 142.87, 142.21, 142.15, 142.09, 141.18, 140.96, 140.71, 140.57, 139.70, 138.05, 137.54, 137.52, 136.78, 135.81, 135.21, 132.99, 132.30, 132.13, 130.00, 128.43, 128.24, 126.53, 125.16, 120.41, 79.88, 64.57, 51.89, 44.58, 34.20, 33.65, 31.93, 31.90, 30.62, 30.30, 29.68, 29.54, 29.51, 29.43, 29.41, 29.34, 29.29, 28.42, 26.90, 26.35, 25.69, 22.71, 22.70, 22.48, 14.16.

## Characterization

UV-vis absorption spectra were measured in solution (0.02 mg mL$^{-1}$, chloroform) and in film using a UV-1800 spectrophotometer (Shimadzu Scientific Instruments) at room temperature. Polymer films on glass substrates were prepared by spin-coating at 3000 rpm for 40 s. Cyclic voltammetry (CV) measurements were conducted with a Versa STAT3 electrochemical analyzer from AMETE using a conventional three electrodes system (Pt disk as a working electrode, Pt wire as a counter electrode, and Ag/Ag$^+$ electrode as a quasi-reference electrode). The CV measurements were carried out in anhydrous acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate ($Bu_4BF_4$) and calibrated against a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple (potential scan rate: 50 mV s$^{-1}$) as an internal standard, assuming that the absolute energy level of Fc/Fc$^+$ was −4.80 eV. The *J-V* characteristics of the polymer solar cells were measured using a Keithley 2400 SMU digital source meter under a simulated AM 1.5G solar irradiation at 100 mW cm$^{-2}$ (K201 LAB55, McScience). Light intensity was calibrated by a Si reference cell (K801S-K302, McScience). External quantum efficiency (EQE) spectra were measured using K3100 IQX instrument (McScience Inc.) with a monochromatic light produced by a xenon arc lamp at 300 W, which was filtered by a monochromator (Newport) and an optical chopper (MC 200 Thorlabs) under ambient conditions. The blend morphologies of the donor polymers: $PC_{61}BM$ (or $PC_{71}BM$) were characterized by optical microscopy (OM) (Nikon, Eclipse 80i). Resonant soft X-ray scattering (RSoXS) measurements were performed at BL 11.0.1.2 in the Advanced Light Source in Lawrence Berkeley National Laboratory (USA). Before the RSoXS measurement, the optimized and annealed blend films for RSoXS samples were prepared on a polystyrene sulfonate (PSS)/bare glass substrate. The active layers were floated on water and transferred to a 1.0 mm × 1.0 mm, 100 nm thick $Si_3N_4$ membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). Grazing incidence X-ray scattering (GIXS) was performed at the beamline 3C in the Pohang Accelerator Laboratory (South Korea) and the GIXS samples were prepared on bare Si substrates/PEDOT:PSS. The wavelength of X-ray was 1.2301 Å and the incidence angle was about 0.12° − 0.14° (wavelength= 1.1179 Å). The heating rate of the thermogravimetric analysis (TGA) (SCINCO TGA N-1000) was 10 °C min$^{-1}$ and heating range was from 25 to 800 °C. Differential scanning calorimetry (DSC) was performed by DSC 4000 (PerkinElmer) with a heating and cooling rate of 10 °C min$^{-1}$ under nitrogen (purity, 99.999%).

**Fabrication of bulk-heterojunction (BHJ) PSCs**

PSCs were fabricated with a conventional-type device structure of ITO/PEDOT:PSS (AI4083)/active layer (P3HT:PC$_{61}$BM)/Al and an inverted-type architecture of ITO/ZnO/active layer (PTB7-Th:PC$_{71}$BM) or (PBDB-T:PC$_{71}$BM)/MoO$_3$/Ag. First, indium tin oxide (ITO) covered glasses were ultrasonicated for 20 min each in detergent, acetone, deionized water, and isopropyl alcohol (IPA). Then, UV-ozone plasma treatment on ITO substrates was performed for 15 min. For conventional-type PSCs, PEDOT:PSS (AI4083) was filtered through a 0.2-um PTFE filter and spin-coated on ITO at 3000 rpm for 40 s, followed by thermal annealing at 165 °C for 20 min in air. After that, the devices were moved to a N$_2$-filled glove box. The blend solutions of P3HT:PC$_{61}$BM (blend ratio = 1:0.8 by weight) in chlorobenzene (total concentration: 23.4 mg/mL) were prepared with varying the amount of 5TRh-PCBM as compatibilizers (0 wt%, 10 wt%, and 20 wt%). The blend solution kept at 85°C, was spin-coated on PEDOT:PSS at 1250 rpm for 60 s. Before deposition of top electrode, solvent vapor annealing (SVA) with IPA was done for 20 min. Then, Al was thermally evaporated as the top electrode with thickness of 100 nm under 3x10$^{-6}$ torr. For inverted-type devices, the ZnO layer was prepared using a sol–gel procedure, dissolving zinc acetate dihydrate

($(CH_3CO_2)_2Zn·(H_2O)_2$, 99.9%, 1.5g) and ethanolamine ($HOCH_2CH_2NH_2$, 99.5%, 0.405 mL) in anhydrous 2-methoxy ethanol ($CH_3OCH_2CH_2OH$, > 99.8%, 15 mL) under vigorous stirring for more than 24 hr to allow the hydrolysis reaction and aging to proceed. The ZnO solution was spin-coated on top of the ITO substrates at 4000 rpm for 40 s to produce a 30 nm-thick ZnO layer, followed by thermal annealing at 215 °C for 20 min in air. After the films were baked, the devices were moved to a $N_2$-filled glove box. The blend solutions of PTB7-Th:$PC_{71}BM$ (1:1.5 by weight) in chlorobenzene (total concentration: 25 mg/mL) with 5 vol% of 1,8-diiodooctane (DIO) as the additive were stirred on a 95 °C hot-plate and spin cast onto the ITO/ZnO substrate at 2000 rpm for 60 s. The blend solutions of PBDB-T:$PC_{71}BM$ (1:1 by weight) in o-DCB (total concentration: 20 mg/mL) with 3 vol% of DIO additive were stirred at 90 °C and spin-coated at 2000 rpm for 60 s. Finally, 10 nm-thick $MoO_3$ and 120 nm-thick Ag were deposited under high vacuum using thermal evaporation. The active area of the devices is 0.164 $cm^2$. For the thermal stability comparison, the PCEs of PTB7-Th:$PC_{71}BM$ and PBDB-T:$PC_{71}BM$ PSCs with different amounts of 5TRh-PCBM (i.e. from 0 to 20 wt%) were tested by annealing at 80 °C for different times in the $N_2$ filled glove box. For the P3HT:$PC_{61}BM$ PSC, annealing was performed at higher temperature of 150 °C to accelerate the degradation. The BHJ active layers were spin-coated, and the devices were stored under high vacuum ($< 10^{-7}$ Torr) for more than 2 h to remove residual solvent in the film. The films were then heated for different times (at 80 ˚C for the PTB7-Th:$PC_{71}BM$ and PBDB-T:$PC_{71}BM$ PSCs and at 150 ˚C for the P3HT:$PC_{61}BM$ PSC) in $N_2$ atmosphere prior to deposition of top electrode to exclude the influence of other factors on the thermal stability of the active layer morphology, such as interlayer degradation.

**Double cantilever beam (DCB) test**

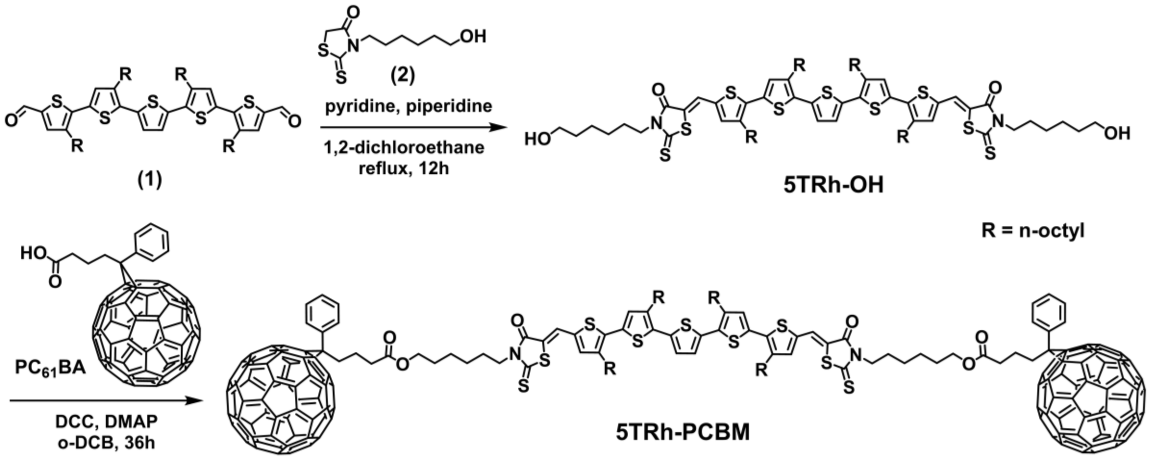
For measuring fracture toughness of PSCs by DCB test, samples with a structure of ITO glass/Active layer/Au were fabricated. The 25 mm × 25 mm square samples were cut into 8 mm × 25 mm size, followed by Au deposition. Identical ITO glass substrates were attached to films on ITO glass substrates by using epoxy (Epo-Tek 353ND, Epoxy Technology). Under ambient condition at ~25 ºC and ~30% RH, the epoxy between the glasses were cured for 72 hr. Next, by using a high-precision micromechanical test system (Delaminator Adhesion Test System, DTS Company, Menlo Park, USA), load-displacement data under repetitive loading and unloading were recorded to calculate the cohesion energy values. The critical strain energy release rate, $G_c$ value for each debonded length ($a$) was calculated by following equations:

$$G_c = \frac{12P_c^2a^2}{E'B^2h^3}\left(1+\frac{0.64h}{a}\right)^2$$

$$a = \left(\frac{CE'Bh^3}{8}\right)^{\frac{1}{3}} - 0.64h$$

where C is the specimen compliance ($d\delta/dP$), $\delta$ is the displacement of the beam ends, and $P_c$ is the critical load where the load decreases during the crack-growth, $E'$ is the plain strain modulus of ITO glass substrates (= 76 GPa), $B$ is the specimen width (= 8 mm), and $h$ is the half height of each specimen.

## Supplementary Figures



**Scheme S1**. Synthetic routes for 5TRh-PCBM.

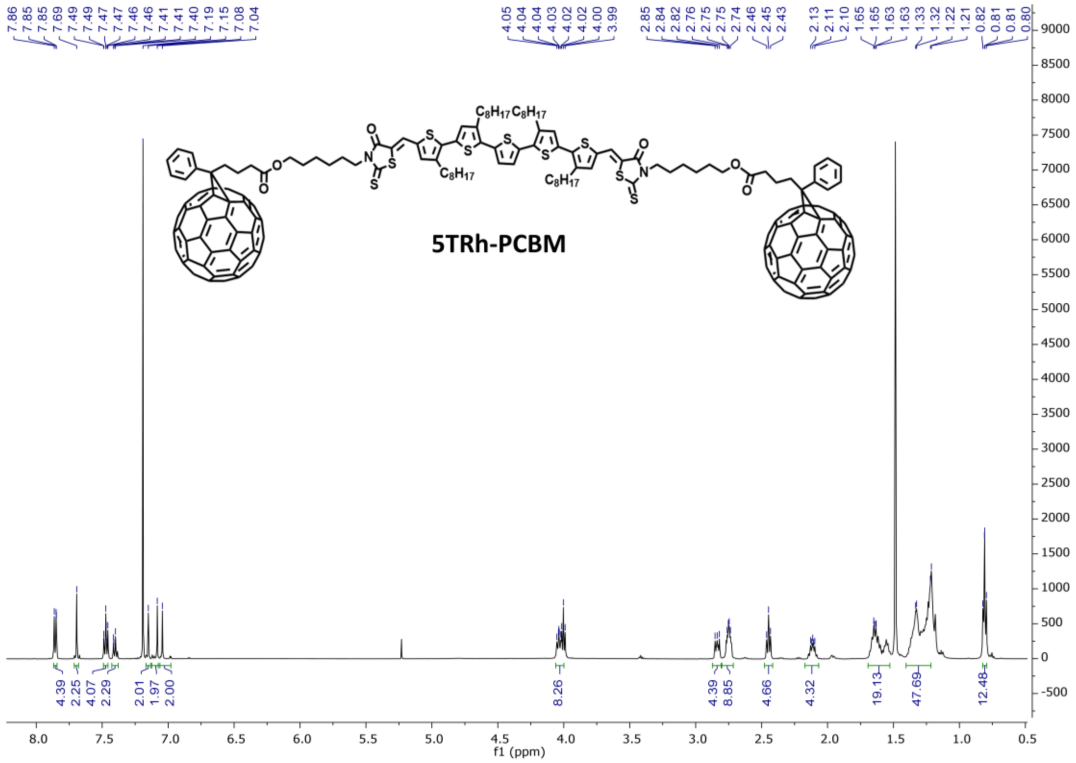


**Fig. S1**. $^1$H NMR spectrum of 5TRh-PCBM.

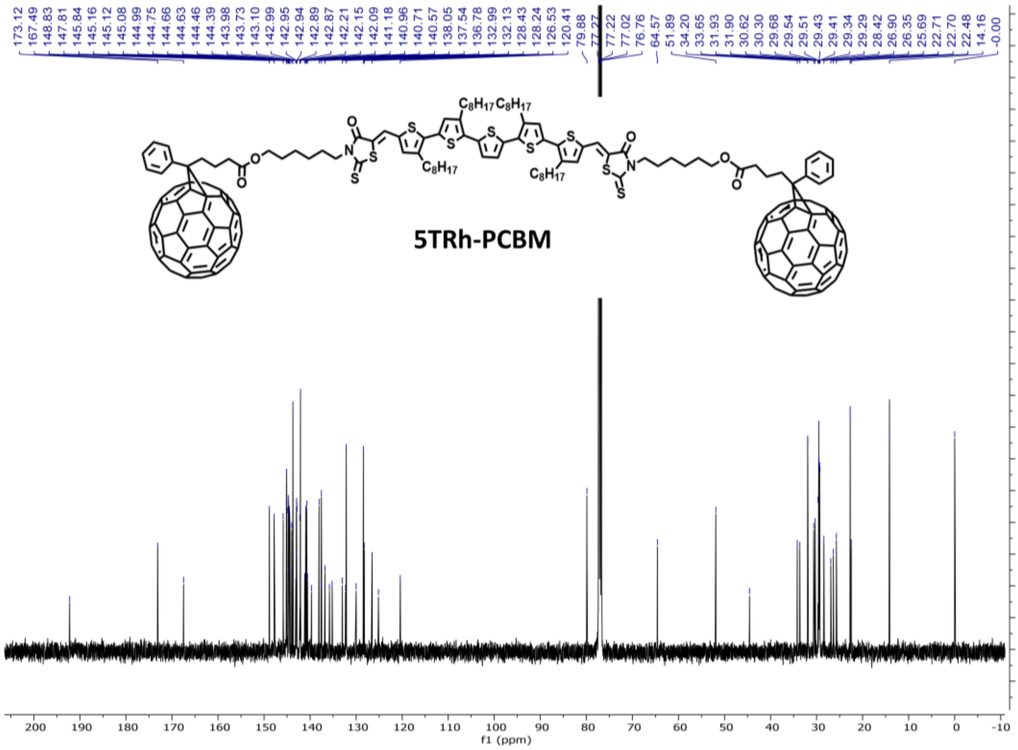


**Fig. S2**. $^{13}$C NMR spectrum of 5TRh-PCBM**.**

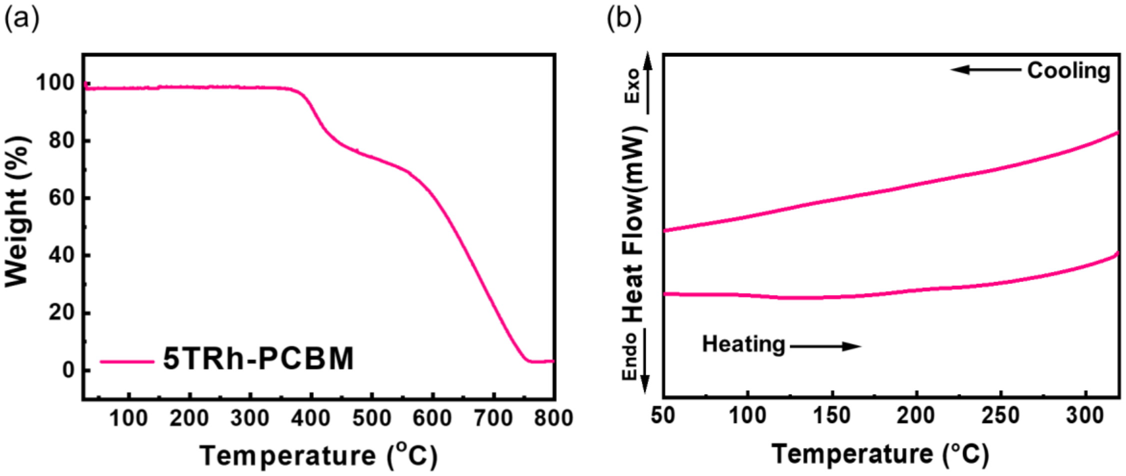


**Fig. S3.** (a) TGA and (b) DSC thermograms of 5TRh-PCBM.

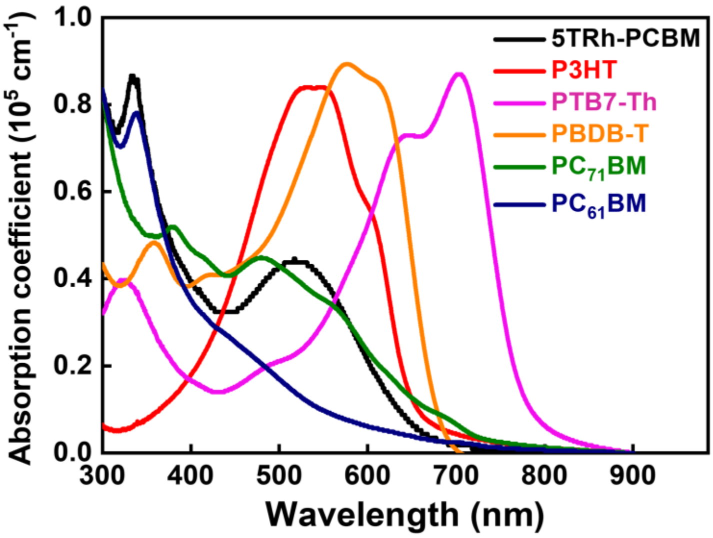


**Fig. S4.** Absorption coefficient (cm$^{-1}$) of polymer donors (PTB7-Th, PBDB-T, and P3HT), fullerene derivative acceptors ($PC_{61}BM$ and $PC_{71}BM$), and 5TRh-PCBM.

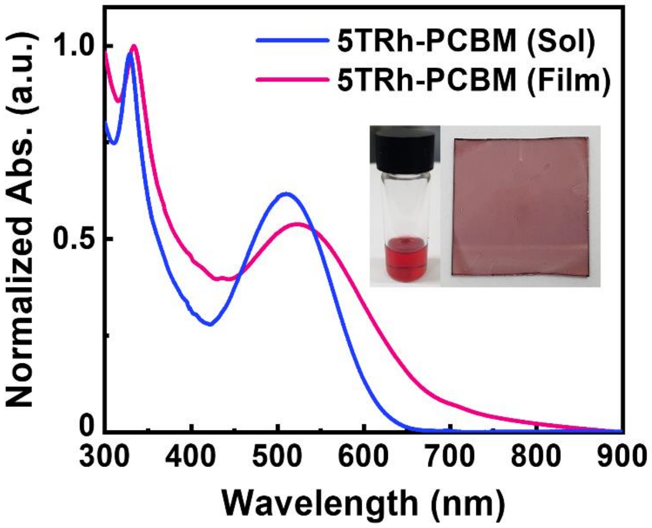


**Fig. S5.** Normalized UV-vis absorption spectra and photographs of 5TRh-PCBM in solution and in film.

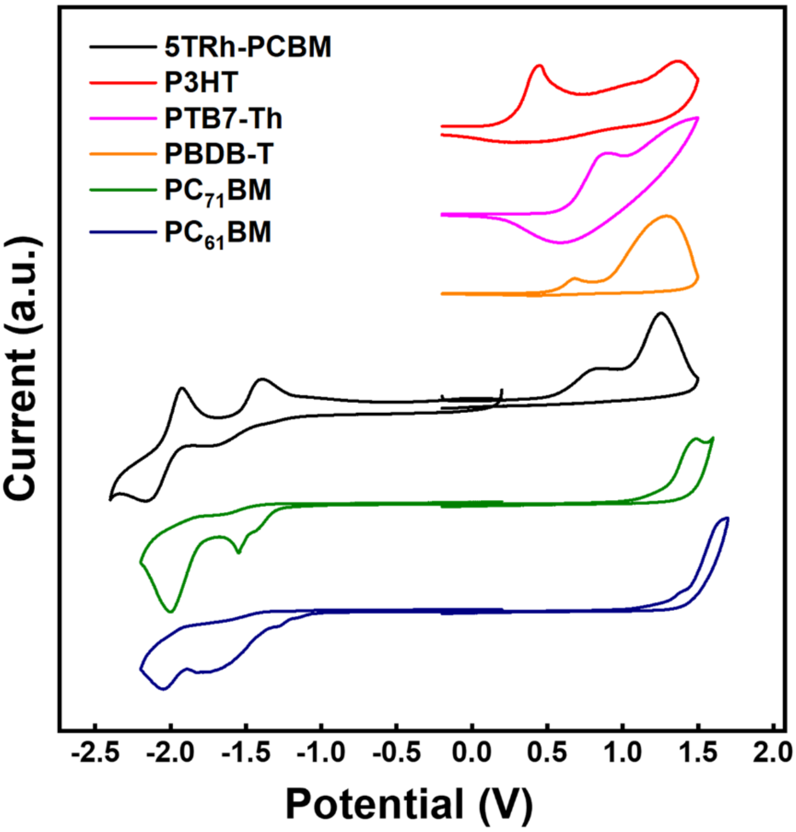


**Fig. S6.** Cyclic voltammograms of polymer donors (PTB7-Th, PBDB-T, and P3HT), fullerene derivative acceptors ($PC_{61}BM$ and $PC_{71}BM$), and 5TRh-PCBM.

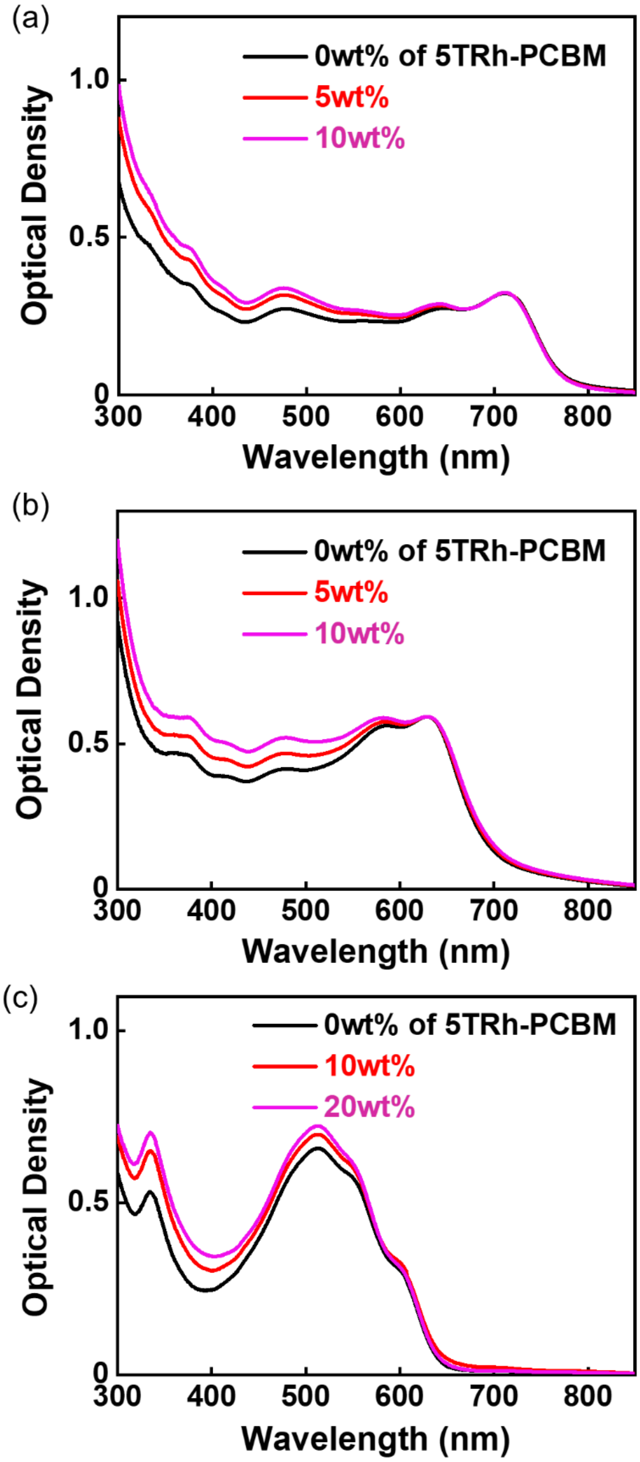


**Fig. S7.** UV-vis absorption spectra of (a) PTB7-Th:$PC_{71}BM$, (b) PBDB-T:$PC_{71}BM$, and (c) P3HT: $PC_{61}BM$ by varying the content of 5TRh-PCBM in blend films.

**Table S1.** Photovoltaic characteristics of the PTB7-Th:$PC_{71}BM$ PSCs with different content of 5TRh-PCBM. The devices were annealed at 80 °C for different times.

| PTB7-Th:$PC_{71}BM$ :5TRh-PCBM | $V_{oc}$ (V) | $J_{sc}$ (mA $cm^{-2}$) | FF | $PCE_{max}$ ($PCE_{avg}$) [a] (%) |
|---|---|---|---|---|
| 0 wt%, 0 hr | 0.80 ± 0.01 | 15.99 ± 0.18 | 0.65 ± 0.01 | 8.38 (8.30 ± 0.08) |
| 6 hr | 0.79 ± 0.02 | 15.05 ± 0.33 | 0.54 ± 0.02 | 6.67 (6.41 ± 0.18) |
| 12 hr | 0.78 ± 0.02 | 14.31 ± 0.48 | 0.52 ± 0.03 | 5.98 (5.80 ± 0.20) |
| 24 hr | 0.77 ± 0.02 | 12.64 ± 0.52 | 0.48 ± 0.02 | 5.26 (4.66 ± 0.37) |
| 48 hr | 0.76 ± 0.03 | 12.29 ± 0.43 | 0.43 ± 0.03 | 4.33 (3.97 ± 0.29) |
| 72 hr | 0.76 ± 0.03 | 12.19 ± 0.34 | 0.40 ± 0.03 | 3.84 (3.68 ± 0.17) |
| 120 hr | 0.75 ± 0.03 | 11.06 ± 0.56 | 0.39 ± 0.03 | 3.28 (3.20 ± 0.09) |
| 5 wt% (1:1.5:0.125), 0 hr | 0.80 ± 0.01 | 16.75 ± 0.18 | 0.65 ± 0.01 | 8.89 (8.72 ± 0.13) |
| 6 hr | 0.78 ± 0.01 | 16.06 ± 0.28 | 0.58 ± 0.01 | 7.46 (7.32 ± 0.13) |
| 12 hr | 0.79 ± 0.01 | 15.82 ± 0.12 | 0.57 ± 0.01 | 7.24 (7.14 ± 0.12) |
| 24 hr | 0.80 ± 0.01 | 14.50 ± 0.33 | 0.59 ± 0.02 | 7.19 (6.98 ± 0.19) |
| 48 hr | 0.79 ± 0.02 | 14.60 ± 0.40 | 0.57 ± 0.02 | 6.77 (6.68 ± 0.09) |
| 72 hr | 0.79 ± 0.02 | 14.53 ± 0.47 | 0.56 ± 0.03 | 6.59 (6.51 ± 0.11) |
| 120 hr | 0.78 ± 0.02 | 14.70 ± 0.45 | 0.51 ± 0.02 | 6.18 (5.86 ± 0.27) |
| 10 wt% (1:1.5:0.25), 0 hr | 0.80 ± 0.01 | 16.68 ± 0.20 | 0.64 ± 0.01 | 8.70 (8.40 ± 0.21) |
| 6 hr | 0.80 ± 0.01 | 16.35 ± 0.38 | 0.63 ± 0.01 | 8.41 (8.16 ± 0.24) |
| 12 hr | 0.79 ± 0.01 | 16.17 ± 0.16 | 0.62 ± 0.01 | 8.06 (7.91 ± 0.15) |
| 24 hr | 0.80 ± 0.01 | 16.38 ± 0.26 | 0.60 ± 0.02 | 7.97 (7.83 ± 0.13) |
| 48 hr | 0.79 ± 0.01 | 16.23 ± 0.47 | 0.60 ± 0.01 | 7.82 (7.77 ± 0.07) |
| 72 hr | 0.78 ± 0.02 | 15.96 ± 0.36 | 0.59 ± 0.02 | 7.62 (7.52 ± 0.11) |
| 120 hr | 0.79 ± 0.02 | 15.37 ± 0.34 | 0.58 ± 0.02 | 7.33 (7.11 ± 0.23) |

[a] Average values and standard deviations were derived from more than 10 devices.

**Table S2.** Photovoltaic charateristics of the PBDB-T:PC$_{71}$BM PSCs with different content of 5TRh-PCBM. The devices were annealed at 80 °C for different times.

| PBDB-T: PC$_{71}$BM :5TRh-PCBM | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE$_{max}$ (PCE$_{avg}$) [a] (%) |
|---|---|---|---|---|
| 0 wt%, 0 hr | 0.85 ± 0.01 | 12.69 ± 0.08 | 0.67 ± 0.01 | 7.39 (7.33 ± 0.09) |
| 6 hr | 0.84 ± 0.01 | 12.03 ± 0.24 | 0.65 ± 0.02 | 6.69 (6.50 ± 0.18) |
| 12 hr | 0.85 ± 0.02 | 11.36 ± 0.23 | 0.56 ± 0.01 | 5.62 (5.41 ± 0.20) |
| 24 hr | 0.84 ± 0.02 | 11.02 ± 0.31 | 0.50 ± 0.03 | 4.95 (4.69 ± 0.23) |
| 48 hr | 0.83 ± 0.02 | 9.90 ± 0.47 | 0.48 ± 0.03 | 4.98 (3.91 ± 0.09) |
| 72 hr | 0.84 ± 0.02 | 9.94 ± 0.41 | 0.42 ± 0.02 | 3.86 (3.54 ± 0.12) |
| 120 hr | 0.83 ± 0.02 | 9.61 ± 0.35 | 0.42 ± 0.03 | 3.78 (3.44 ± 0.33) |
| 5 wt% (1:1:0.1), 0 hr | 0.86 ± 0.01 | 12.95 ± 0.30 | 0.67 ± 0.01 | 7.50 (7.39 ± 0.11) |
| 6 hr | 0.85 ± 0.01 | 12.71 ± 0.34 | 0.64 ± 0.01 | 6.99 (6.86 ± 0.16) |
| 12 hr | 0.84 ± 0.02 | 12.13 ± 0.32 | 0.57 ± 0.02 | 6.10 (5.80 ± 0.27) |
| 24 hr | 0.84 ± 0.02 | 10.80 ± 0.20 | 0.59 ± 0.03 | 5.51 (5.37 ± 0.14) |
| 48 hr | 0.83 ± 0.01 | 10.54 ± 0.25 | 0.57 ± 0.02 | 5.27 (4.98 ± 0.24) |
| 72 hr | 0.84 ± 0.01 | 10.03 ± 0.18 | 0.59 ± 0.03 | 5.19 (5.02 ± 0.19) |
| 120 hr | 0.83 ± 0.02 | 10.60 ± 0.50 | 0.54 ± 0.03 | 4.88 (4.66 ± 0.23) |
| 10 wt% (1:1:0.2), 0 hr | 0.86 ± 0.01 | 13.01 ± 0.19 | 0.64 ± 0.01 | 7.25 (7.14 ± 0.09) |
| 6 hr | 0.85 ± 0.01 | 12.59 ± 0.21 | 0.63 ± 0.01 | 6.87 (6.75 ± 0.14) |
| 12 hr | 0.85 ± 0.01 | 12.47 ± 0.24 | 0.62 ± 0.02 | 6.63 (6.57 ± 0.07) |
| 24 hr | 0.84 ± 0.01 | 11.75 ± 0.42 | 0.63 ± 0.02 | 6.48 (6.30 ± 0.15) |
| 48 hr | 0.85 ± 0.01 | 11.61 ± 0.33 | 0.60 ± 0.02 | 6.00 (5.93 ± 0.08) |
| 72 hr | 0.84 ± 0.02 | 11.43 ± 0.32 | 0.61 ± 0.02 | 6.35 (5.92 ± 0.36) |
| 120 hr | 0.83 ± 0.02 | 11.35 ± 0.50 | 0.60 ± 0.02 | 5.83 (5.77 ± 0.15) |

[a] Average values and standard deviations were derived from more than 10 devices.

**Table S3.** Photovoltaic characeristics of the P3HT:PC$_{61}$BM PSCs with different content of 5TRh-PCBM. The devices were annealed at 150 °C for different times.

| P3HT:PC$_{61}$BM :5TRh-PCBM | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF | PCE$_{max}$ (PCE$_{avg}$) [a] (%) |
|---|---|---|---|---|
| 0 wt%, 0 hr | 0.60 ± 0.01 | 9.06 ± 0.17 | 0.59 ± 0.01 | 3.34 (3.24 ± 0.06) |
| 6 hr | 0.59 ± 0.01 | 8.77 ± 0.29 | 0.54 ± 0.02 | 2.86 (2.78 ± 0.07) |
| 12 hr | 0.58 ± 0.02 | 8.05 ± 0.23 | 0.46 ± 0.02 | 2.47 (2.33 ± 0.12) |
| 24 hr | 0.58 ± 0.01 | 7.59 ± 0.21 | 0.46 ± 0.03 | 2.25 (2.02 ± 0.24) |
| 48 hr | 0.58 ± 0.01 | 7.24 ± 0.35 | 0.43 ± 0.02 | 1.94 (1.61 ± 0.34) |
| 72 hr | 0.57 ± 0.02 | 7.15 ± 0.33 | 0.40 ± 0.02 | 1.72 (1.37 ± 0.33) |
| 120 hr | 0.55 ± 0.02 | 6.14 ± 0.63 | 0.37 ± 0.04 | 1.50 (1.17 ± 0.35) |
| 10 wt% (1:0.8:0.18), 0 hr | 0.61 ± 0.01 | 9.39 ± 0.28 | 0.61 ± 0.01 | 3.51 (3.36 ± 0.11) |
| 6 hr | 0.60 ± 0.01 | 9.29 ± 0.15 | 0.61 ± 0.01 | 3.39 (3.28 ± 0.12) |
| 12 hr | 0.61 ± 0.01 | 9.03 ± 0.23 | 0.60 ± 0.01 | 3.24 (3.14 ± 0.09) |
| 24 hr | 0.60 ± 0.01 | 9.16 ± 0.27 | 0.55 ± 0.02 | 3.18 (3.01 ± 0.19) |
| 48 hr | 0.60 ± 0.01 | 9.08 ± 0.15 | 0.56 ± 0.01 | 3.08 (2.87 ± 0.20) |
| 72 hr | 0.59 ± 0.01 | 9.04 ± 0.24 | 0.54 ± 0.02 | 3.05 (2.85 ± 0.21) |
| 120 hr | 0.58 ± 0.02 | 8.52 ± 0.25 | 0.52 ± 0.03 | 2.73 (2.63 ± 0.10) |
| 20 wt% (1:0.8:0.36), 0 hr | 0.61 ± 0.01 | 9.21 ± 0.37 | 0.61 ± 0.01 | 3.45 (3.37 ± 0.07) |
| 6 hr | 0.61 ± 0.01 | 9.07 ± 0.21 | 0.61 ± 0.01 | 3.38 (3.27 ± 0.08) |
| 12 hr | 0.60 ± 0.02 | 9.05 ± 0.29 | 0.60 ± 0.01 | 3.44 (3.35 ± 0.10) |
| 24 hr | 0.60 ± 0.01 | 8.96 ± 0.31 | 0.59 ± 0.02 | 3.30 (3.23 ± 0.07) |
| 48 hr | 0.60 ± 0.01 | 8.85 ± 0.17 | 0.58 ± 0.02 | 3.28 (3.20 ± 0.13) |
| 72 hr | 0.59 ± 0.02 | 8.90 ± 0.27 | 0.59 ± 0.01 | 3.22 (3.16 ± 0.05) |
| 120 hr | 0.59 ± 0.01 | 8.92 ± 0.19 | 0.58 ± 0.02 | 3.20 (3.16 ± 0.06) |

[a] Average values and standard deviations were derived from more than 10 devices.

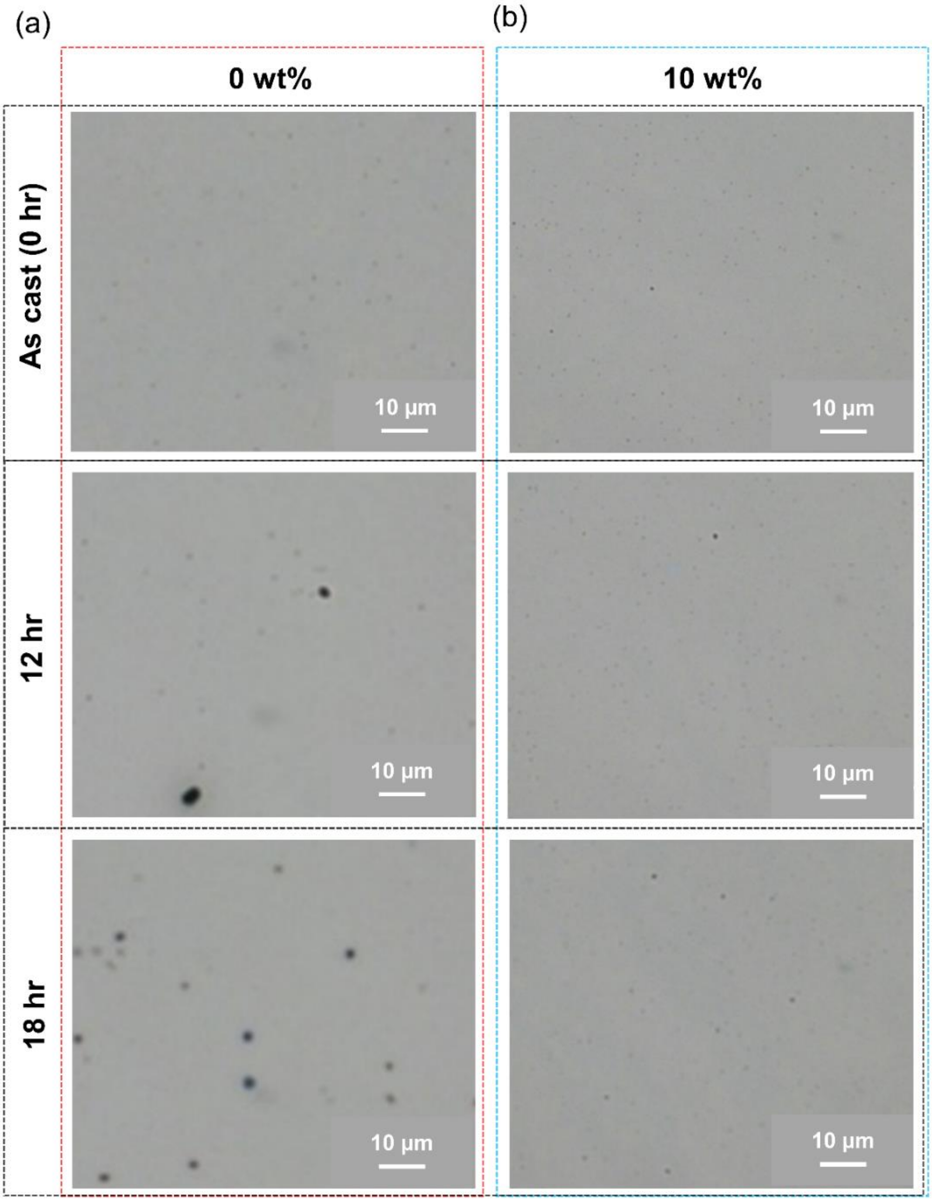


**Fig. S8.** OM images of the PTB7-Th:PC$_{71}$BM blends (a) without and (b) with 10 wt% compatibilizer. The films were annealed at 80 °C.

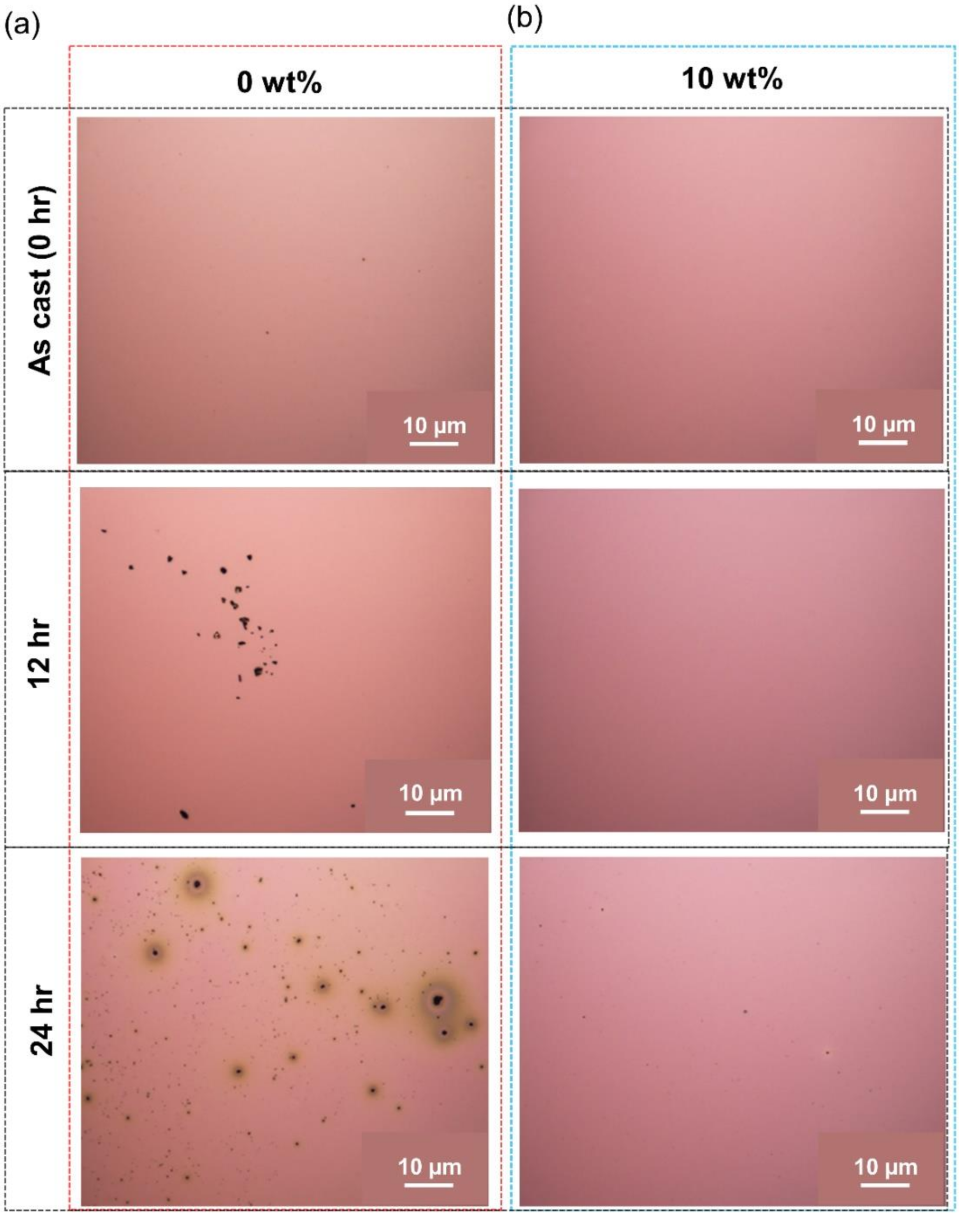


**Fig. S9.** OM images of the PBDB-T:$PC_{71}BM$ blends (a) without and (b) with 10 wt% compatibilizers. The films were annealed at 80 °C.

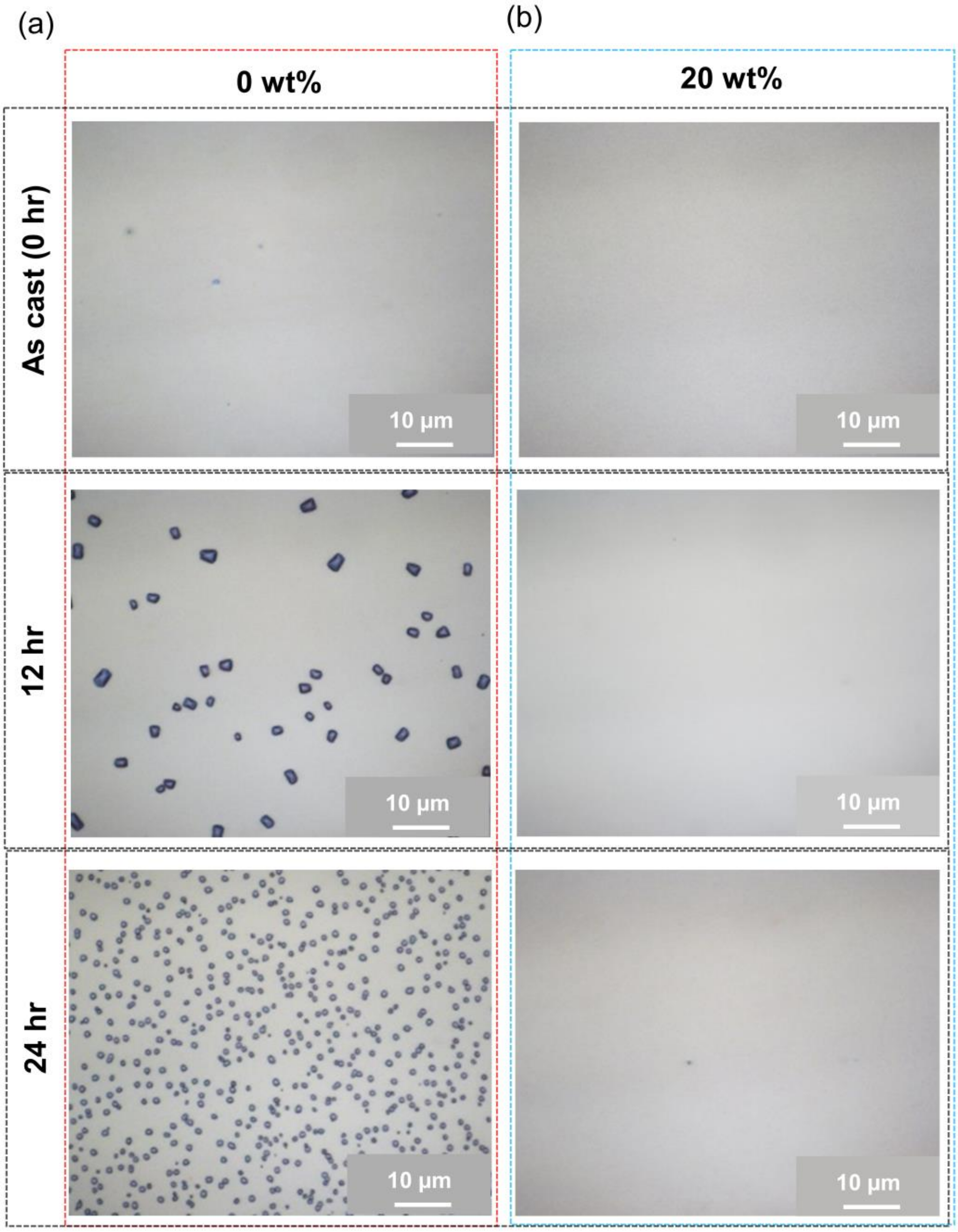


**Fig. S10.** OM images of the P3HT:PC$_{61}$BM blends (a) without and (b) with 20 wt% compatibilizer. The films were annealed at 150 °C.

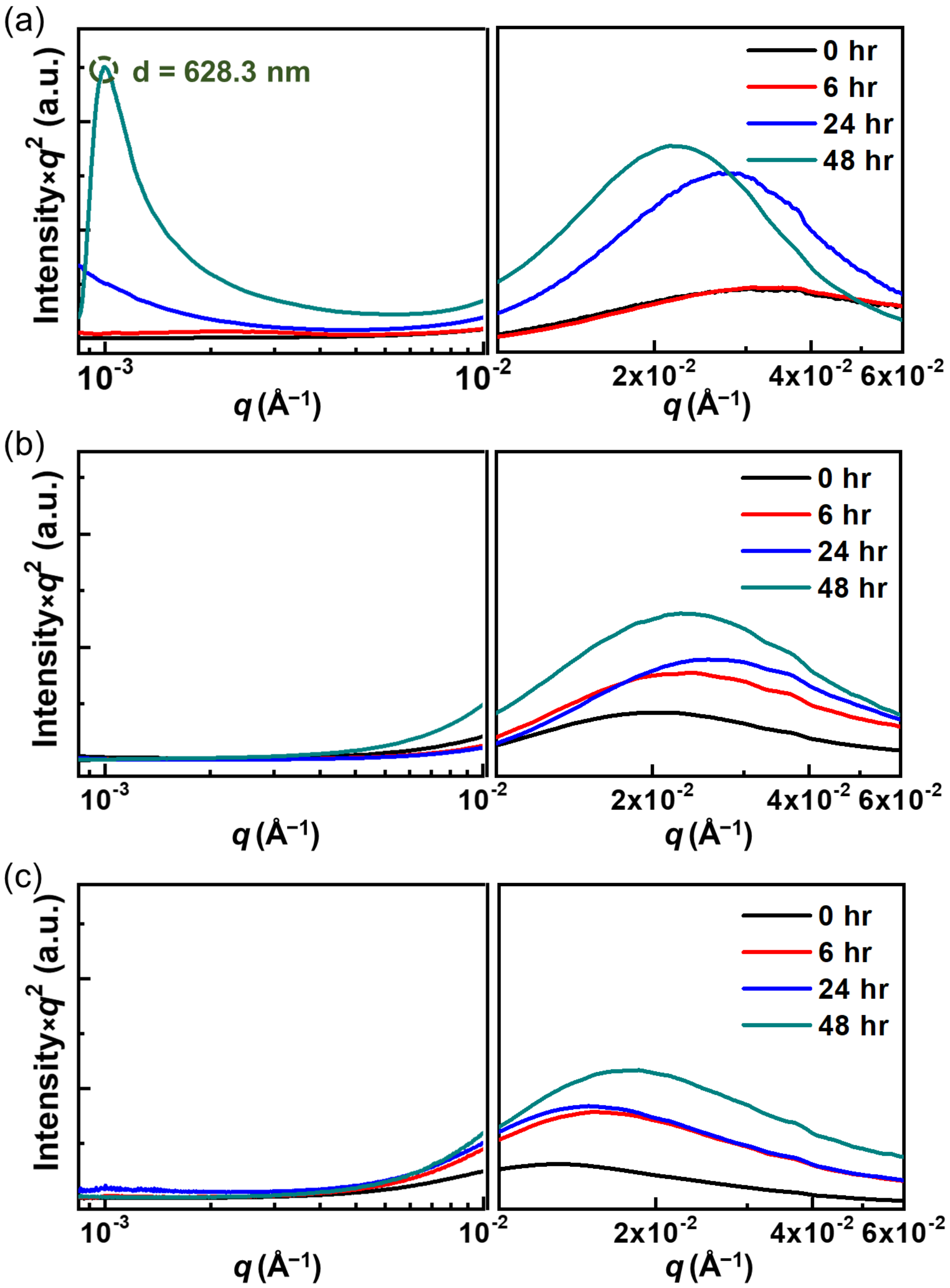


**Fig. S11.** RSoXS profiles of PBDB-T-Th:PC$_{71}$BM blends with (a) 0 wt%, (b) 5 wt%, and (c) 10 wt% 5TRh-PCBM.

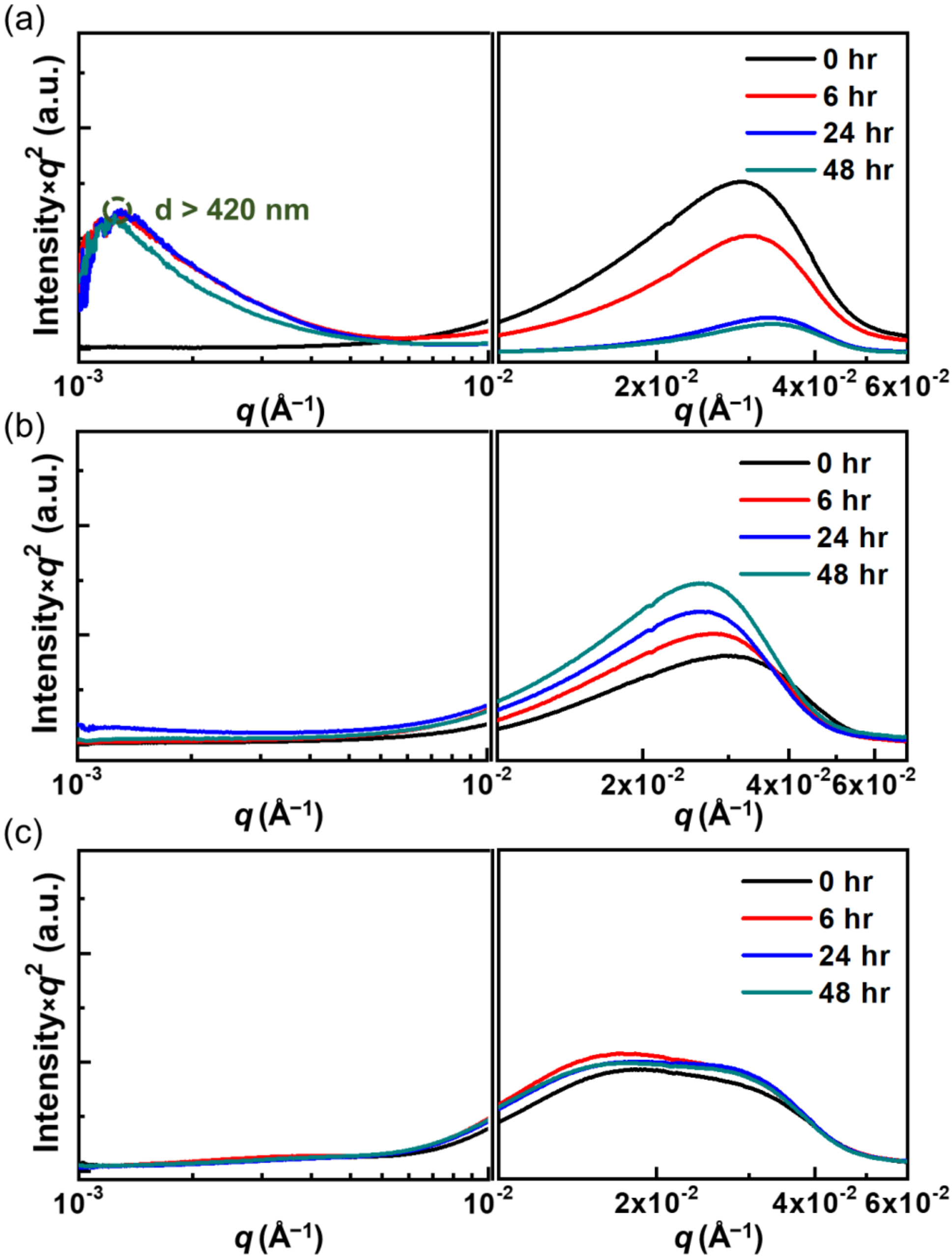


**Fig. S12.** RSoXS profiles of P3HT:PC$_{61}$BM blends with (a) 0 wt%, (b) 10 wt%, and (c) 20 wt% 5TRh-PCBM.

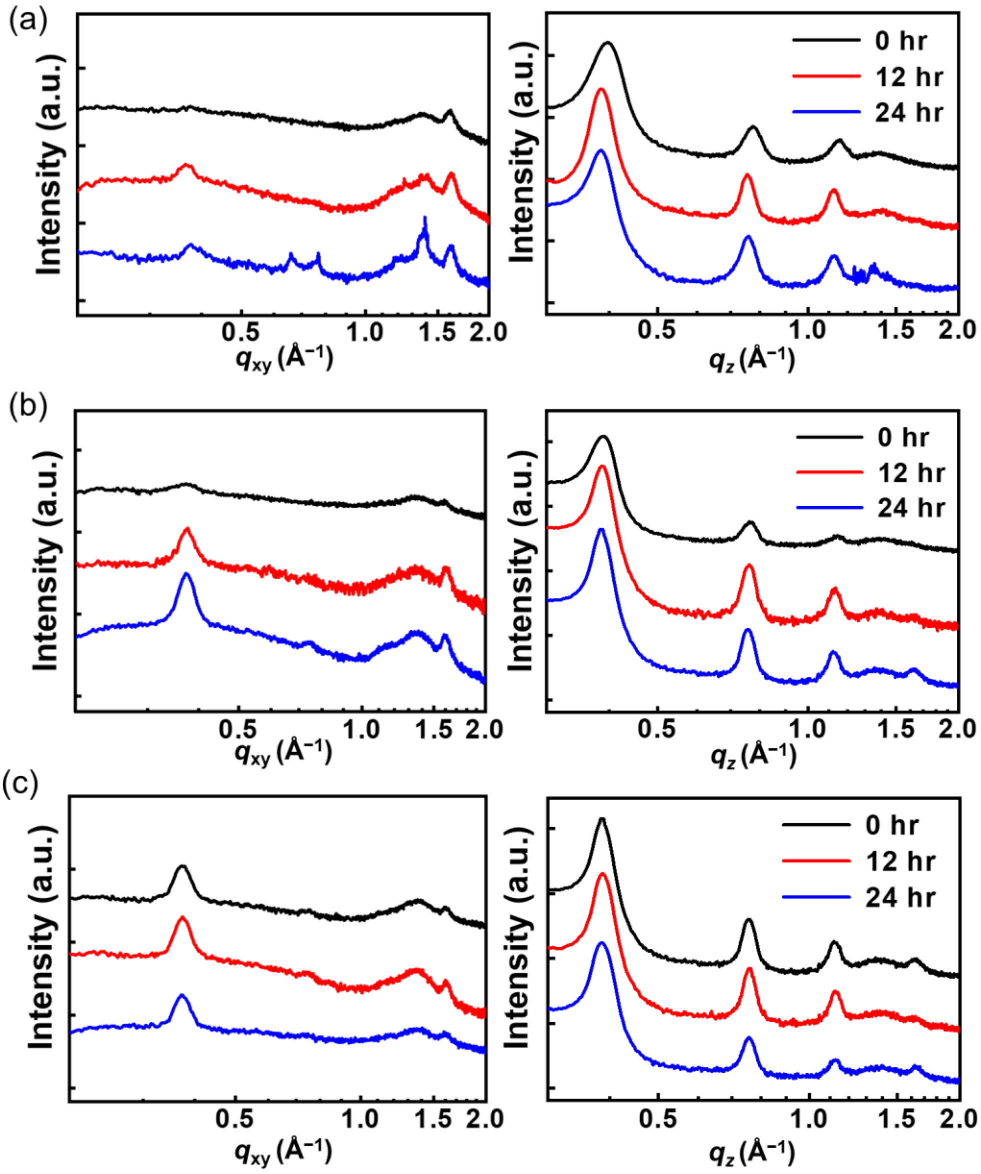


**Fig. S13.** In-plane and out-of-plane GIXS line-cuts of the P3HT:PC$_{61}$BM blend films with (a) 0 wt%, (b) 10 wt%, and (c) 20 wt% 5TRh-PCBM.

# References

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