

Supporting Information

Synthesis and Characterization of Multicomponent ABC- and ABCD-Type Miktoarm Star-branched Polymers Containing Poly(3-hexylthiophene) Segment

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Materials.

The reagents (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium, distilled over LiAlH_4 under nitrogen, and then distilled from its sodium naphthalenide solution under high-vacuum conditions (10^{-6} Torr). Heptane and *tert*-butylbenzene were washed with concentrated H_2SO_4 , water, and aqueous NaHCO_3 , dried over P_2O_5 , and finally distilled from its 1,1-diphenylhexyllithium solution under high-vacuum conditions. Styrene, α -methylstyrene, and isoprene were washed with 5% NaOH aqueous solution, water, and then dried over MgSO_4 . After filtration of MgSO_4 , they were distilled over CaH_2 , and subsequently distilled from their Bu_2Mg solutions (ca. 3 mol%) under high-vacuum conditions. Styrene and α -methylstyrene were diluted with THF (ca. 1.0 M) and isoprene with *tert*-butylbenzene (ca. 3.5 M). **P3HT-C₄-Br**,¹ **PI-DPE**,² and **AB-DPE**³ were synthesized according to the literatures.

Synthesis of 4-trimethylsilylethynylbenzyl chloride.

Thionyl chloride (5.0 mL) was added to the Et_2O solution (5.0 mL) of 4-trimethylsilylethynylbenzyl alcohol (0.90 g, 4.40 mmol) under nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 2 h. After the removal of all volatile compounds, silica gel column chromatography using hexane as an eluent yielded 4-trimethylsilylethynylbenzyl chloride ($R_f = 0.18$) as a colorless oil in 92% yield (0.90 g, 4.04 mmol). ^1H NMR (300 MHz, CDCl_3): $\delta = 0.25$ (9H, s, $\text{Si}(\text{CH}_3)_3$), 4.56 (s, $-\text{CH}_2-$), 7.32 (2H, d, $J = 8.1$ Hz, C_6H_4), 7.46 (2H, d, $J = 8.1$ Hz, C_6H_4). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 0.08$ ($\text{Si}(\text{CH}_3)_3$), 45.9

(-CH₂-), 95.22 and 104.63 (alkyne), 123.44 (C₆H₄, C_{ipso}), 128.56 and 132.41 (C₆H₄), 137.79 (C₆H₄, C_{ipso}).

Synthesis of P3HT-N₃.

P3HT-C₄-Br (0.40 g) was dissolved in dry THF (5 mL), followed by the addition of trimethylsilyl azide (20 equiv. to the bromomethyl group) and Bu₄NF in THF solution (1.0 M, 20 equiv.). The reaction mixture was stirred at room temperature for 16 h. The objective **P3HT-N₃** was purified by precipitation into methanol twice and freeze-drying from its benzene solution (93% yield, 0.37 g). $M_{n\text{ RALLS}} = 8.37 \text{ kg mol}^{-1}$, $M_w/M_n = 1.08$. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.92$ (t, -CH₃), 1.22-1.55 (m, thiophene(Th)-CH₂-CH₂-(CH₂)₃-), 1.57-1.80 (m, Th-CH₂-CH₂-), 2.49 (3H, s, tolyl), 2.51-2.95 (m, Th-CH₂-), 3.33 (2H, t, 6.6 Hz, -CH₂-N₃), 6.99 (s, Th).

Synthesis of AB-alkyne.

A living PS was prepared by the living anionic polymerization of styrene (5.19 mmol) initiated with *sec*-BuLi (0.0569 mmol) in THF at -78 °C for 20 min, followed by addition of **PI-DPE** (0.56 g, 0.0533 mmol), which was pre-purified with Bu₂Mg (0.080 mmol). The reaction solution was allowed to stand for 4 h under the same conditions, and the resulting living polymer reacted with 4-trimethylsilylethynylbenzyl chloride (0.0912 mmol) in THF for 5 min. The PS-*b*-PI with a TMS-protected alkyne functionality between the blocks was isolated by preparative SEC and purified by precipitation into MeOH and freeze-drying from its benzene solution (68 % yield, 0.73 g). $M_{n\text{ RALLS}} = 19.5 \text{ kg mol}^{-1}$, $M_w/M_n = 1.02$. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.21$ -0.32 (m,

9H, Si(CH₃)₃), 0.53-0.79 (m, 6H, *sec*-Bu), 1.02-2.50 (broad, backbone), 4.70 and 4.77 (s, vinyl protons of 3,4-PI), 5.14 (s, vinyl protons of 1,4-PI), 5.34-5.44 (m, CH₂= of DPE), 6.29-7.24 (m, Ph).

The TMS group of the alkyne moiety was cleaved by the treatment of the obtained PS-*b*-PI with 10 equiv. of Bu₄NF in dry THF at room temperature for 16 h. The resulting **AB-alkyne** was purified in a similar manner as already mentioned (96% yield, 0.70 g). ¹H NMR (300 MHz, CDCl₃): δ = 0.53-0.79 (m, 6H, *sec*-Bu), 1.02-2.50 (broad, backbone), 4.69 and 4.77 (s, vinyl protons of 3,4-PI), 5.14 (s, vinyl protons of 1,4-PI), 5.34-5.44 (m, CH₂= of DPE), 6.29-7.24 (m, Ph).

Synthesis of ABC star.

CuBr (6.0 mg, 0.042 mmol) was added to a degassed THF solution (5 mL) of **P3HT-N₃** (0.071 g, 0.0085 mmol), **AB-alkyne** (0.15 g, 0.0077 mmol), and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 7.0 mg, 0.040 mmol). The reaction mixture was stirred at 50 °C for 12 h. CuBr was then removed by passing the reaction mixtures through a silica gel column. The objective **ABC star** was isolated by preparative SEC and purified in a similar manner as already mentioned (21% yield, 45 mg). *M_n*_{RALLS} = 30.7 kg mol⁻¹, *M_w*/*M_n* = 1.06. ¹H NMR (300 MHz, CDCl₃): δ = 0.33-2.45 (broad, backbone of PS and PI, Th-CH₂-(CH₂)₄-), 0.92 (t, -CH₃), 2.49 (3H, s, tolyl), 2.53-2.97 (m, Th-CH₂-), 4.69 and 4.77 (vinyl protons of 3,4-PI), 5.14 (vinyl proton of 1,4-PI), 6.26-7.24 (m, Ph), 6.99 (s, Th).

Synthesis of ABC-alkyne.

A living P α MS was prepared by the living anionic polymerization of α -methylstyrene (3.56 mmol) initiated with *sec*-BuLi (0.0450 mmol) in THF at -78 °C for 2 h, followed by addition of **AB-DPE** (0.36 g, 0.0187 mmol). The reaction solution was allowed to stand for 4 h under the same conditions, and the resulting living polymer reacted with 4-trimethylsilylethynylbenzyl chloride (0.0868 mmol) in THF for 5 min. The objective polymer was isolated by preparative SEC and purified in a similar manner as already mentioned (77 % yield, 0.41g). $M_{n\text{ RALLS}} = 30.3$ kg mol⁻¹, $M_w/M_n = 1.02$. ¹H NMR (300 MHz, CDCl₃): $\delta = -0.06$ -0.55 (Me of P α MS and Si(CH₃)₃), 0.55-0.79 (m, 6H, *sec*-Bu), 1.01-2.49 (broad, backbone), 4.69 and 4.77 (s, vinyl protons of 3,4-PI), 5.14 (s, vinyl protons of 1,4-PI), 6.26-7.24 (m, Ph).

The cleavage of the TMS group of the alkyne moiety and purification of the resulting polymer was carried out in the same manners as those for **AB-alkyne** (95% yield, 0.39 g). ¹H NMR (300 MHz, CDCl₃): $\delta = -0.06$ -0.55 (Me of P α MS), 0.55-0.79 (m, 6H, *sec*-Bu), 1.01-2.49 (broad, backbone), 4.69 and 4.77 (s, vinyl protons of 3,4-PI), 5.14 (s, vinyl protons of 1,4-PI), 6.24-7.24 (m, Ph)

Synthesis of ABCD star.

CuBr (5.0 mg, 0.035 mmol) was added to a degassed THF solution (5 mL) of **P3HT-N₃** (0.040 g, 0.00478 mmol), **ABC-alkyne** (0.20 g, 0.0066 mmol), and PMDETA (6.0 mg, 0.035 mmol). The reaction mixture was stirred at 50 °C for 12 h. Isolation and purification of the objective **ABCD star** was carried out in the same manners as those for **ABC star** (31% yield, 80 mg). $M_{n\text{ RALLS}} =$

44.0 kg mol⁻¹, $M_w/M_n = 1.05$. ¹H NMR (300 MHz, CDCl₃): $\delta = -0.11$ -0.55 (Me of P α MS), 0.55-2.44 (broad, backbone of PS and PI, Th-CH₂-(CH₂)₄-), 0.92 (t, -CH₃), 2.49 (3H, s, tolyl), 2.52-2.93 (m, Th-CH₂-), 4.69 and 4.77 (vinyl protons of 3,4-PI), 5.14 (vinyl proton of 1,4-PI), 6.25-7.23 (m, Ph), 6.98 (s, Th).

Measurements.

Molecular weights (M_n s) and molecular weight distribution (M_w/M_n) were measured on an Asahi Technion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three PS gel columns (Tosoh TSK_{gel} G5000H_{HR}, G4000H_{HR}, and G3000H_{HR}) were used. The relative molecular weights were determined by SEC with an RI detection using a standard PS calibration curve. The combination of viscometer, right angle laser light scattering detection (SEC-RALLS), and RI detection was applied for the online SEC system in order to determine the absolute molecular weights of polymers. The separation of the polymer mixtures was carried out by preparative SEC (KNAUER, smartline) equipped with an RI detector and four columns (Tosoh TSK_{gel} G5000H_{HR} x2 and G4000H_{HR} x2) using THF as a carrier solvent at a flow rate of 5.0 mL/min at room temperature. ¹H NMR spectra were measured on a Bruker DPX300 in CDCl₃. The chemical shifts were recorded in ppm downfield relative to CHCl₃ ($\delta = 7.26$) as standard. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C min⁻¹ for differential scanning calorimetry (DSC). UV-vis absorption spectra of the polymer solution and thin films (annealed at 150 °C for 10 min

(**ABC star**) and 170 °C for 5 min (**ABCD star**)) were recorded using a Hitachi U-4100 spectrophotometer. For the thin film spectra, polymers were first dissolved in toluene, followed with filtering through a 0.45 µm pore size PTFE membrane syringe filter, and then drop-casted onto quartz substrate. Tapping mode AFM observation was performed with an Agilent AFM 5500, using microfabricated cantilevers with a force constant of 34 N/m. The polymer samples were drop-cast onto Si wafers from toluene solutions, followed by annealing at 150 °C for 10 min (**ABC star**) and 170 °C for 5 min (**ABCD star**). The polymer samples for grazing incidence X-ray scattering (GIXS) experiments were prepared by drop-casting onto Si wafers from toluene solutions followed by annealing at 150 °C for 10 min (**ABC star**) and 170 °C for 5 min (**ABCD star**). GISAXS patterns were obtained at beamline BL46XU of SPring-8, Japan. The monochromated energy of the X-ray source was 10.314 keV ($\lambda = 0.12022$ nm) and the incidence angle α_i was 0.15°. GISAXS patterns were recorded with a 2D image detector (Pilatus 2M) with the sample-to-detector distances of 2981 mm. GIWAXS measurements were conducted at the beamline BL46XU of SPring-8, Japan. The sample was irradiated at a fixed incident angle α_i on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.398 keV (X-ray wavelength $\lambda = 0.10002$ nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300K) with the sample-to-detector distances of 174.1 mm. The scattering vectors q_y and q_z for GIXS are defined in Equation (1).⁴

$$(q_y, q_z) = (2 \pi (\sin \psi \cos \alpha_f) / \lambda, 2 \pi (\sin \alpha_f + \sin \alpha_i) / \lambda) \quad (1)$$

where ψ is out-of-plane angle, α_f is exit angle.

Comparison of ABC star and ABCD star.

The optical property of **ABC star** and **ABCD star** was compared by ultraviolet-visible (UV-vis) spectroscopy. The UV-vis spectra of both **ABC star** (Figure S12) and **ABCD star** (Figure S8) films show a shoulder at around 605 nm corresponding to the vibronic absorption from the intermolecular π - π interaction. They support the behavior of the phase separation even when the AB or ABC arm segments are covalently linked to the P3HT segment at the core.

In order to investigate the difference in the morphology of **ABC star** and **ABCD star** in detail, their thin films were investigated by GIXS. Figures S15(a) and S10(a) show the 2D GISAXS patterns, which were measured using the **ABC star** and **ABCD star** films coated on silicon substrates from toluene solutions. Based on these patterns, the out-of-plane and in-plane scattering profiles have been extracted and the resulting scattering profiles for **ABC star** and **ABCD star** are shown in Figures 15(b) and 10(b), respectively.

As can be seen in Figure S15(a), there is no diffraction peak for the **ABC star** film along both the in-plane and out-of-plane directions, indicating no periodicity for a phase-separated structure. On the other hand, the **ABCD star** film shows arc and anisotropic ring scatterings that correspond to the mean period distance of 22.4 nm (in-plane) and 23.4 nm (out-of-plane) (Figure 2(b)), as mentioned in the main text. The reason why **ABC star** does not show clear phase separation is still unclear; however, this difference is also supported by the difference in AFM images (**ABC star** (Figure S14) and **ABCD star** (Figure 3)).

The higher crystallinity of the **ABCD star** film is confirmed by the 2D grazing incidence wide angle X-ray scattering (GIWAXS) patterns (Figure S10). The **ABC star** film (Figure S15) shows only two visible arc and anisotropic ring scatterings; on the contrary, the **ABCD star** film shows three distinct arcs with a higher intensity along the q_z direction. These scattering features are

indicative of the well-ordered multilayer structure of P3HT with an “edge-on” orientation. The slightly smaller d -spacing values are obtained for **ABCD star** ($d_{(100)} = 1.61$ nm (out-of-plane) and $d_{(010)} = 0.376$ nm (in-plane)) than for **ABC star**, confirming the higher crystallinity of the P3HT segment more densely packed in the **ABCD star** film.

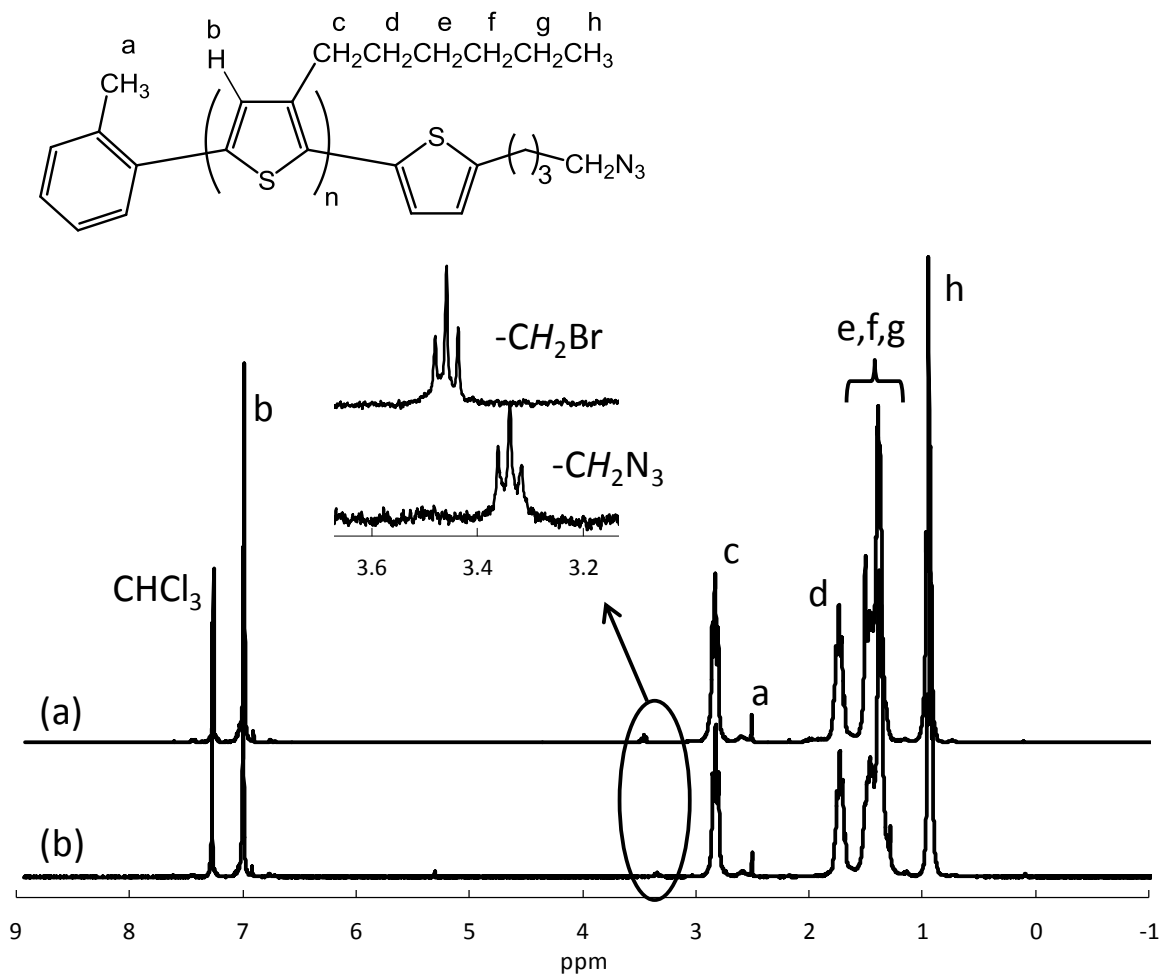


Figure S1. ^1H NMR spectra of (a) **P3HT-C₄-Br** and (b) **P3HT-N₃** in CDCl_3 .

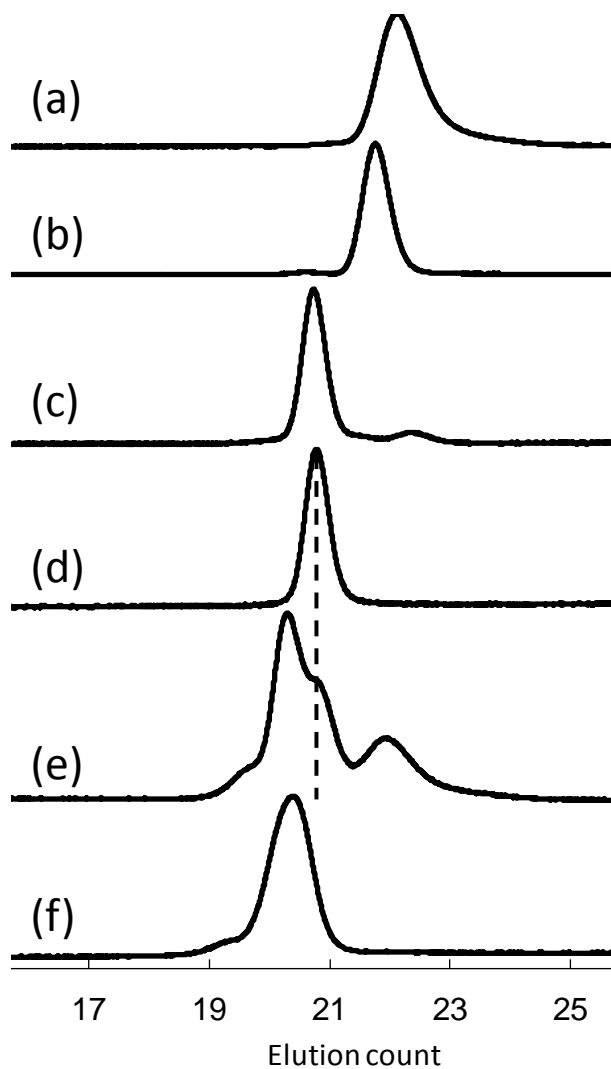


Figure S3. SEC RI curves of (a) **P3HT-N₃**, (b) **PI-DPE**, (c) **AB-alkyne** (before SEC fractionation), (d) **AB-alkyne** (after SEC fractionation), (e) **ABC star** (before SEC fractionation), and (f) **ABC star** (after SEC fractionation).

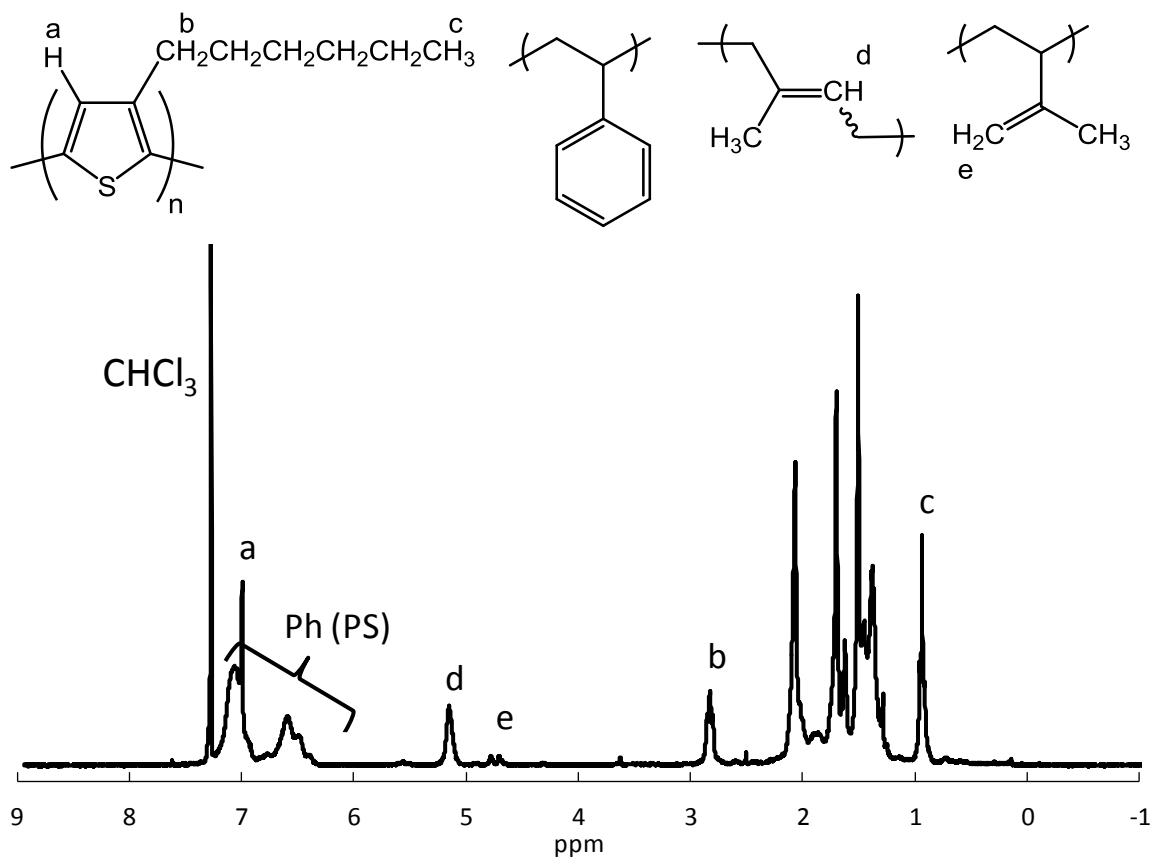


Figure S4. ^1H NMR spectrum of ABC star in CDCl_3 .

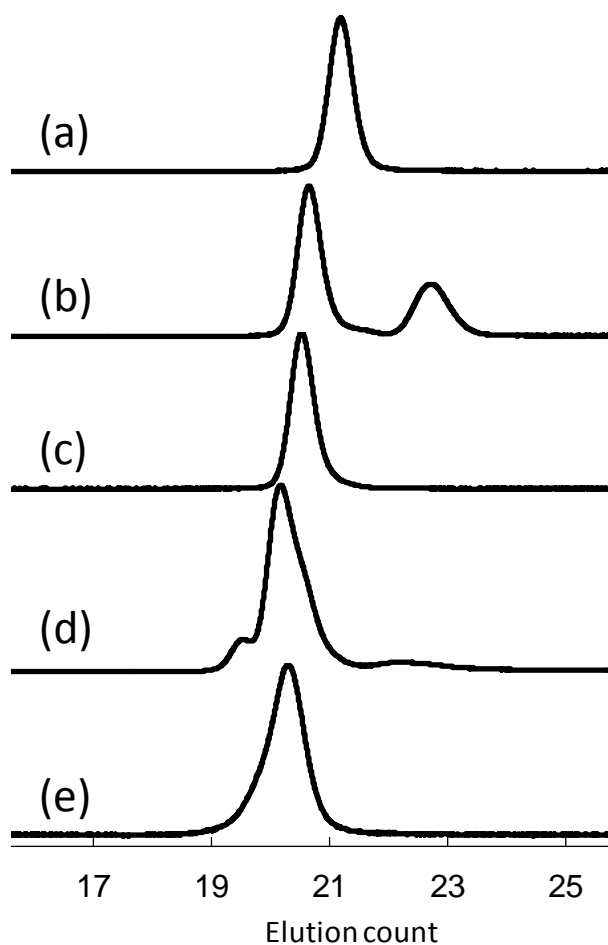


Figure S5. SEC RI curves of (a) **AB-DPE**, (b) **ABC-alkyne** (before SEC fractionation), (c) **ABC-alkyne** (after SEC fractionation), (d) **ABCD star** (before SEC fractionation), and (e) **ABCD star** (after SEC fractionation).

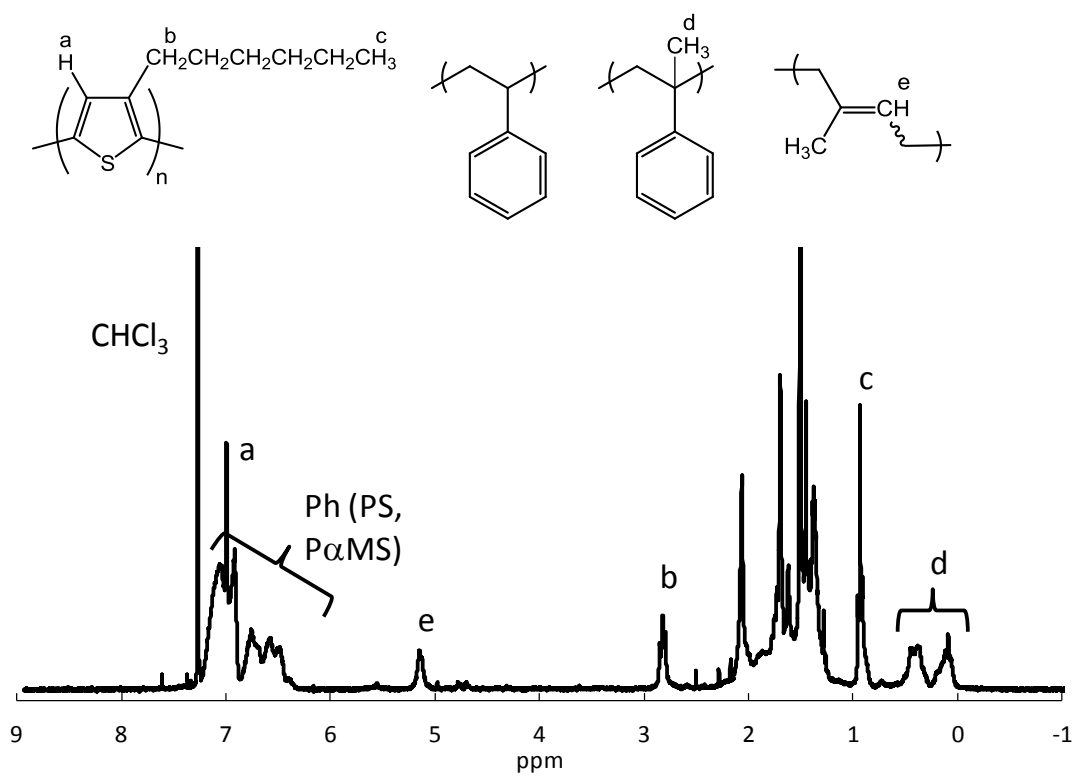


Figure S6. ^1H NMR spectrum of **ABCD star** in CDCl_3 .

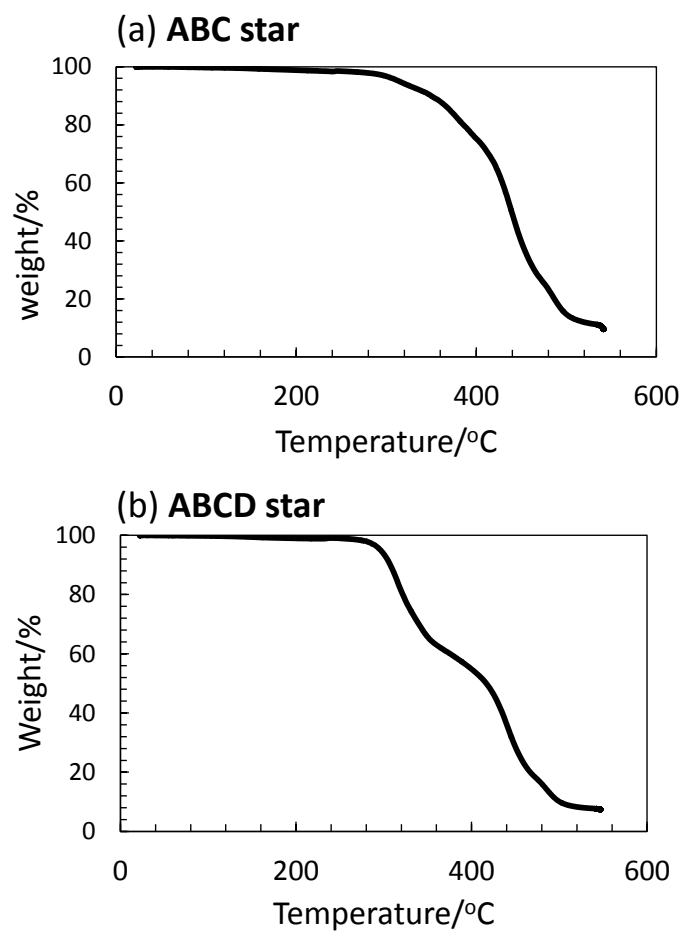


Figure S7. TG themograms of (a) **ABC-star** and (b) **ABCD star**.

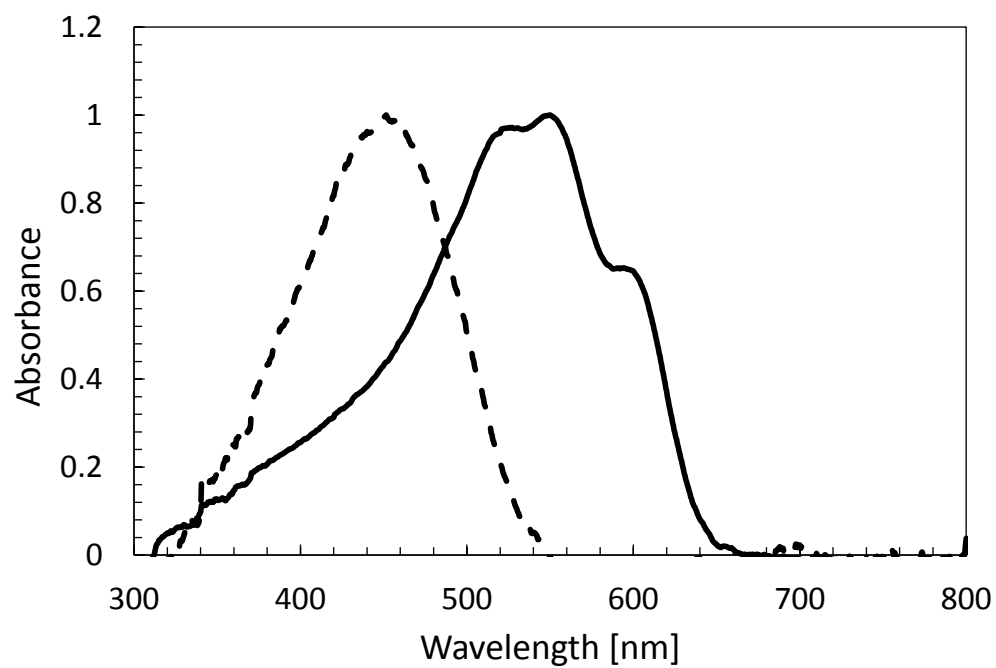


Figure S8. UV-vis spectra of the **ABCD star** thin film. Dotted line and solid line correspond to the solution state (in chloroform) and solid state, respectively.

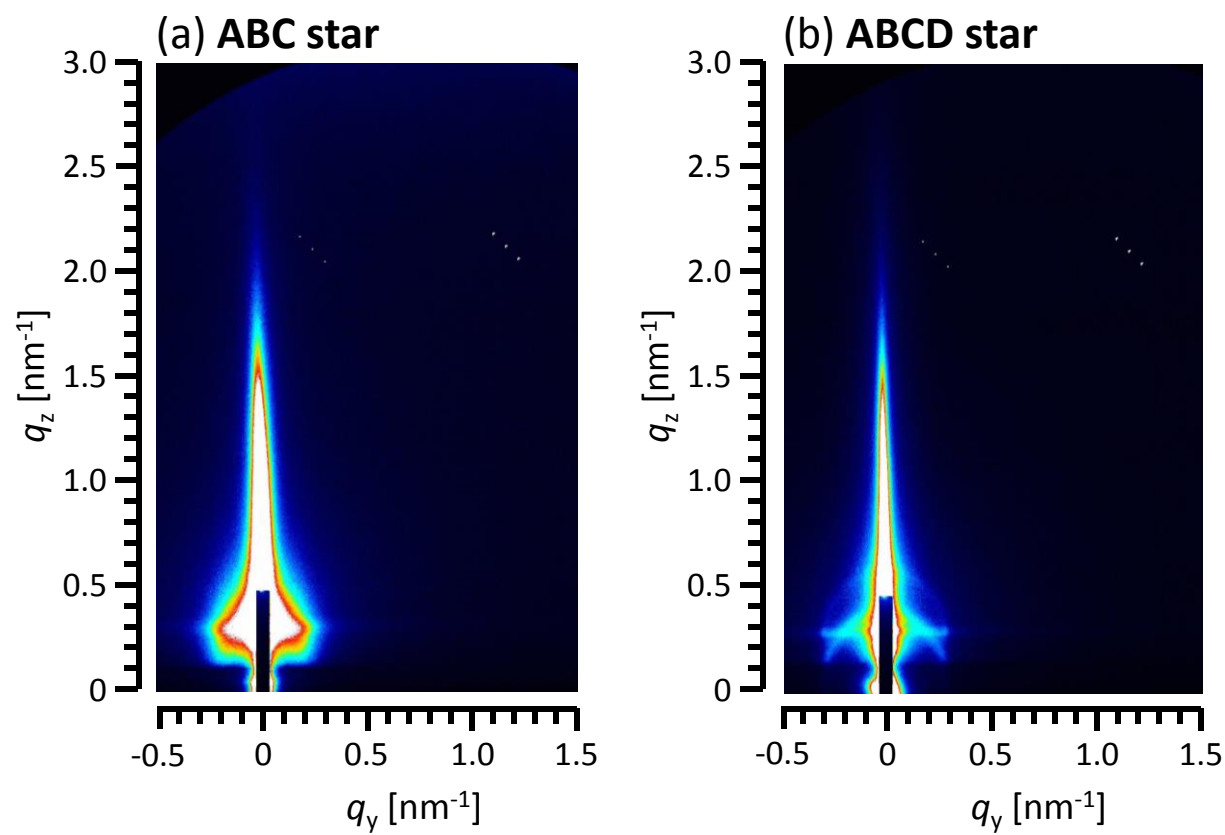


Figure S9. 2D GISAXS patterns of (a) **ABC Star** and (b) **ABCD Star**.

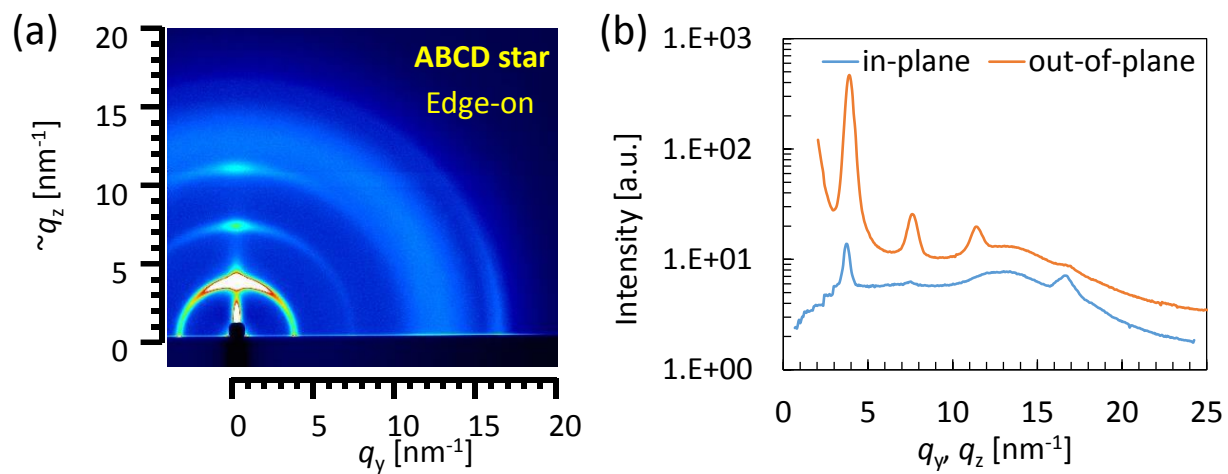


Figure S10. (a) 2D GIWAXS patterns of the **ABCD Star** film and (b) in-plane/out-of-plane GIWAXS profiles extracted along q_y/q_z direction from the 2D image measured for the **ABCD Star** film.

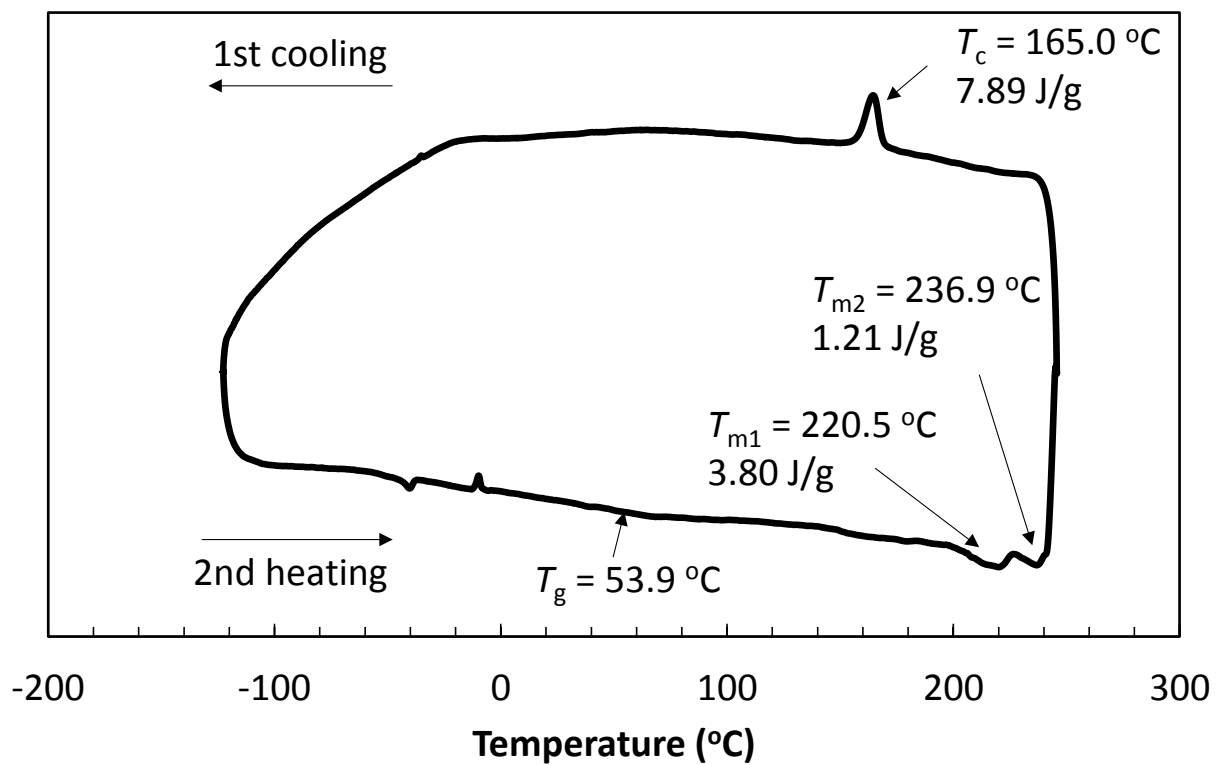


Figure S11. DSC thermogram of **ABC star** (20 $^{\circ}\text{C}/\text{min}$ for 1st cooling scan and 10 $^{\circ}\text{C}/\text{min}$ for 2nd heating scan).

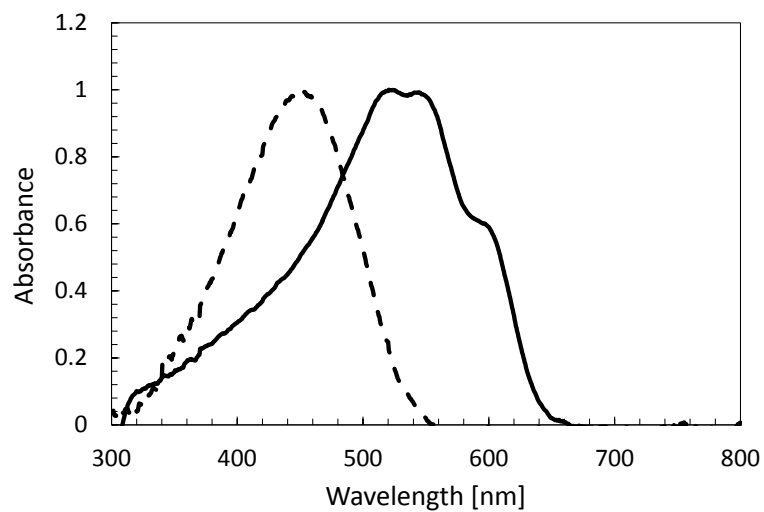


Figure S12. UV-vis spectra of the **ABC star** thin film. Dotted line and solid line correspond to the solution state (in chloroform) and solid state, respectively.

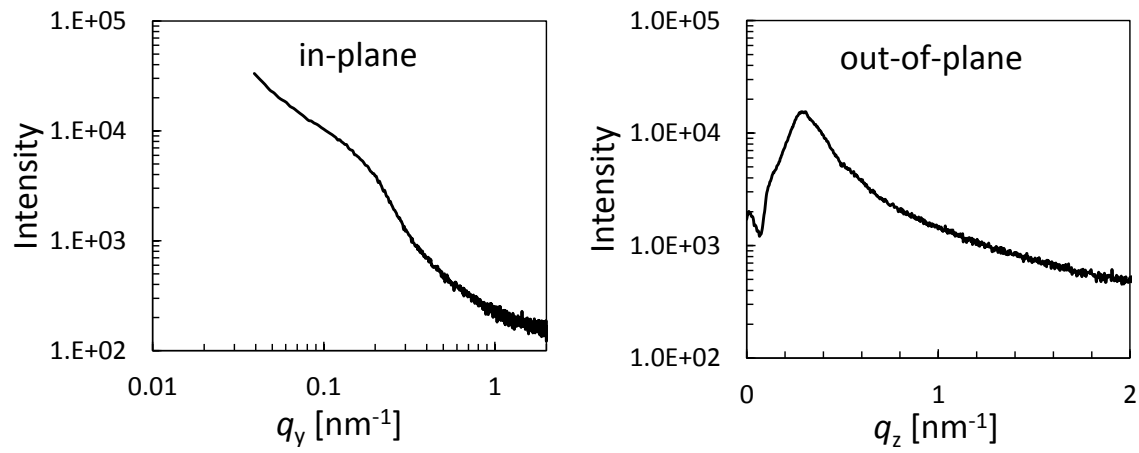


Figure S13. In-plane/out-of-plane GISAXS profile extracted along q_y/q_z direction at $q_z/q_y = q_z^0/q_y^0$ from the 2D image measured for the **ABC star** film. Here, q_z^0 and q_y^0 are defined as 0.384 and 0.100 nm⁻¹, respectively.

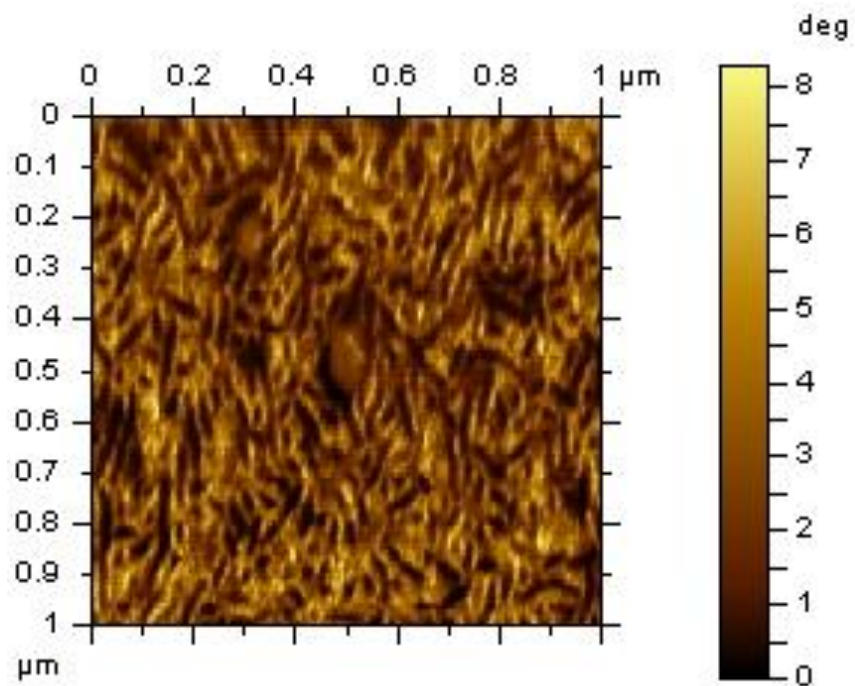


Figure S14. Tapping mode AFM phase image of the **ABC Star** film (annealed at 150 °C for 10 min).

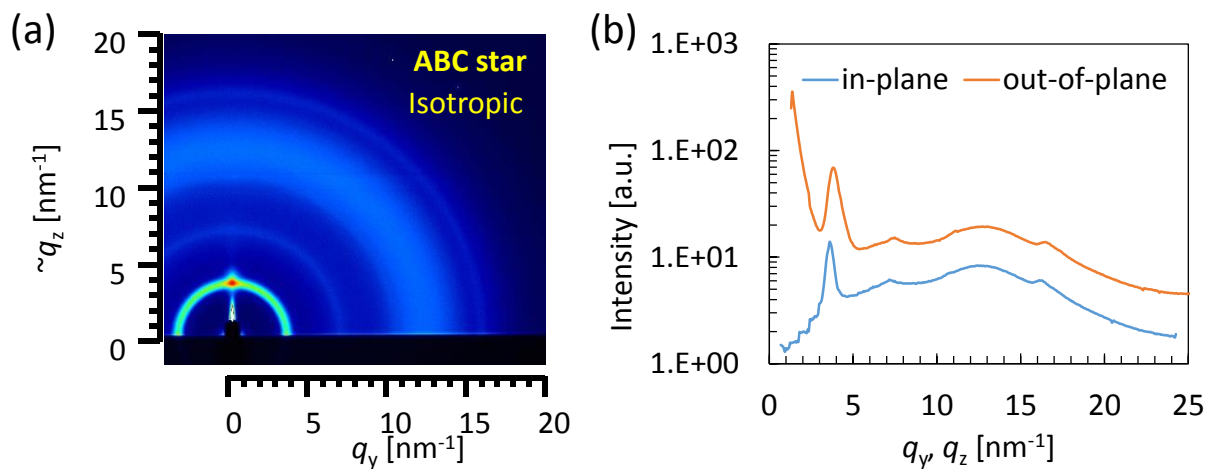


Figure S15. (a) 2D GIWAXS patterns of the **ABC Star** film and (b) in-plane/out-of-plane GIWAXS profiles extracted along q_y/q_z direction from the 2D image measured for the **ABC Star** film (annealed at 150 °C for 10 min).

References

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