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Electronic Supplementary Information (ESI) for

Precise Synthesis of Double-Armed Polymers with Fullerene C_{60} at the Junction for Controlled Architecture

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SUPPORTING EXPERIMENTAL SECTION

Synthesis of PS_{36}-Br. ATRP was carried out in anisole using Cu(I)Br as a catalyst and dNbipy as a ligand. A mixture of St (25.0 g, 0.240 mol), EBiB (0.468 g, 2.40 mmol), dNbipy (11.8 g, 29.0 mmol), and anisole (35.8 g) was degassed under argon for 30 min at RT in a flask. Cu(I)Br (1.72 g, 12.0 mmol) and Cu(II)Br_2 (0.268 g, 1.20 mmol) were added to the mixture under argon and stirred for several minutes to allow for complexation between the copper salts and the ligand. The mixture was then heated to 110 °C. After 215 min, the polymerization mixture was quenched and poured into a large amount of methanol (MeOH). The precipitate obtained was collected by centrifugation, dissolved in $CHCl_3$, and then poured into a large amount of MeOH again. The precipitate was dissolved in $CHCl_3$, washed with aqueous ethylenediaminetetraacetic acid disodium salt dihydrate solution (2 wt%) and deionized water, and then concentrated under vacuum. Finally, the crude polymer was dissolved in $CHCl_3$ and then precipitated into MeOH for purification to yield PS_{36}-Br (4.58 g, 51.0%) as a white powder. Before the next reaction, PS_{36}-Br was purified by silica gel column chromatography (CH_2Cl_2) to completely remove any trace impurities. M_n (GPC, THF): 3.8×10^3, M_w (GPC, THF): 4.3×10^3, M_w/M_n (GPC, THF): 1.14. ^{1}H NMR (800 Hz, $CDCl_3$, Me_4Si, δ): 0.80–1.05 (9 H, -CH_3), 1.16–1.72 (2 36 H, -CH_2-), 1.72–2.30 (1 × 36 H, -CH-), 3.32–3.70 (2 H, m, -OC$H_2$$CH_3$), 4.35–4.58 (1 H, m, -CHPhBr), 6.24–6.87 (72

H, *m*-Ph), 6.87–7.23 (108 H, *o,p*-Ph). Bromine terminal functionality was determined using ^{1}H NMR spectroscopy by a comparison of peaks associated with the proton located on the carbon next to bromine at the growing polymer chain end (-C*H*Ph-Br, 1 H, multiplet) at 4.35–4.68 ppm and the methyl protons from the initiating isobutyryl and methyl group (CH_3CH$_2$O-C=O-C(CH_3)$_2$-, 9 H, multiplet) at 0.79–1.03 ppm according to the method of Lutz and Matyjaszewski.[S1] The bromine terminal functionality (x) can be calculated using Eq. 1,

$$x = \frac{(integral\ at\ 4.35 - 4.58\ ppm)}{(integral\ at\ 0.79 - 1.03\ ppm)/9} \quad (1)$$

The bromine terminal functionality of PS$_{36}$-Br was calculated to be 83%.

Synthesis of PS$_{73}$-Br. A mixture of styrene (10.0 g, 0.096 mol), EBiB (0.095 g, 0.49 mmol), Cu(I)Br (0.347 g, 2.42 mmol), Cu(II)Br$_2$(0.0536 g, 0.240 mmol), dNbipy (2.35 g, 5.76 mmol), and anisole (17.15 g) was heated to 100 °C. After 16 h, the polymerization was quenched and purified with the same work-up procedure as used for **PS$_{36}$-Br**. M_n (GPC, THF): 7.9 × 10^3, M_w (GPC, THF): 9.1 × 10^3, M_w/M_n (GPC, THF): 1.15. Bromine terminal functionality: 67%.

Synthesis of PS$_{390}$-Br. A mixture of styrene (20.0 g, 0.192 mol), EBiB (0.023 g, 0.12 mmol), Cu(I)Br (0.210 g, 1.46 mmol), dNbipy (1.18 g, 2.89 mmol), and anisole (21.4 g) was heated to 100 °C. After 20 h, the polymerization was quenched and purified with the same work-up procedure as used for **PS$_{36}$-Br**. Conv.: 22%. M_n (GPC, THF): 4.1 × 10^4, M_w (GPC, THF): 4.7 × 10^4, M_w/M_n (GPC, THF): 1.15. Bromine terminal functionality: 77%.

Synthesis of PAS_{54}-Br. A mixture of acetoxystyrene (20.6 g, 0.127 mol), EBiB (0.120 g, 0.627 mmol), Cu(I)Br (0.178 g, 1.24 mmol), and PMDETA (0.643 g, 3.71 mmol) was heated at 90 °C. After 40 min, the polymerization was quenched and purified with the same work-up procedure as used for **PS_{36}-Br**. Yield: 4.44 g, 80%, M_n (GPC, THF): 9.0×10^3, M_w (GPC, THF): 9.7×10^3, M_w/M_n (GPC, THF): 1.08. ^{1}H NMR (800 MHz, $CDCl_3$, Me_4Si, δ): 0.78–1.03 (9 H, -CH_3), 1.21–2.04 (2 × 50 H, -CH_2-), 2.20–2.33 (3 × 50 H, OAc), 3.40–3.70 (2 H, m, -OC$H_2$$CH_3$), 4.35–4.58 (1 H, m, -CHPhBr), 6.24–7.02 (78 H, Ph). Bromine terminal functionality: 59%.

Synthesis of 1,2-PS_{36}-C_{60}-H. A mixture of PS_{36}-Br (1.0 g, 0.25 mmol), C_{60} (0.54 g, 0.75 mmol), and water (0.045 g, 2.5 mmol) in ODCB (54.0 mL) was combined with a mixture of $CoCl_2$dppe (0.013 g, 0.025 mmol) and Mn (0.041 g, 0.75 mmol) in ODCB (25.0 mL). Reaction Yield: quant. Isolated yield: 0.25 g (22%). The low isolated yield was because of product loss during the sampling procedure.

Synthesis of 1,2-PS_{73}-C_{60}-H. A mixture of PS_{73}-Br (0.237 g, 0.030 mmol), C_{60} (0.065 g, 0.090 mmol), and water (0.0054 g, 0.30 mmol) in ODCB (6.5 mL) was combined with a mixture of $CoCl_2$dppe (0.0016 g, 0.0030 mmol) and Mn (0.0049 g, 0.09 mmol) in ODCB (630 mL) and reacted for 7 days. Reaction Yield: quant. Isolated yield: 0.235 g (91%).

Synthesis of 1,2-PS_{390}-C_{60}-H. A mixture of PS_{390}-Br (1.21 g, 0.030 mmol), C_{60} (0.065 g, 0.090 mmol), and water (0.0054 g, 0.30 mmol) in ODCB (6.5 mL) was combined with a mixture of

$CoCl_2$dppe (0.0016 g, 0.0030 mmol) and Mn (0.0049 g, 0.09 mmol) in ODCB (630 mL) and reacted for 7 days. Reaction Yield: quant. Isolated yield: 0.247 g (20%). The low isolated yield was because of product loss during the sampling procedure.

Synthesis of 1,4-PS_{36}-C_{60}-PS_{36}. A solution of *t*-BuOK (1.3 mg, 0.012 mmol, 3 eq) and $(n\text{-Bu})_4$NI (0.8 mg, catalytic) in THF (1.2 mL) was added to a solution of 1,2-PS_{36}-C_{60}-H (0.02 g, 0.004 mmol) and PS_{36}-Br (0.028 g, 0.008 mmol, 2 eq.) in THF (8.8 mL) with stirring under an argon atmosphere. The reaction mixture was stirred under reflux overnight, whereupon the solution formed a dark brown suspension. The mixture was diluted with $CHCl_3$, washed with distilled water, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by PGPC to afford 1,4-PS_{36}-C_{60}-PS_{36} as a brown solid (6.5 mg, 14%).

Self-Assembly of 1,4-PS_{73}-C_{60}-PHS_{54}. 1,4-PS_{73}-C_{60}-PHS_{54} was dissolved in THF (0.1 wt%) and mixed with an excess of toluene. The solution was gently evaporated to form a turbid solution consisting of mainly toluene.

Characterization. Transmission FT-IR spectra were recorded on a Nicolet 8700 FT-IR spectrometer (Thermo Fisher Scientific K.K., Yokohama, Japan) by the standard KBr pellet method at a sample concentration of 1 wt%, over a wavenumber range 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and a total of 36 scans. Dynamic light scattering (DLS) measurements were performed at 25 °C on a DLS-7000 photometer (Otsuka Electronics Co., Ltd., Osaka, Japan) with

a He-Ne laser as a light source. The scattering light intensity was measured at a scattering angle of 90°. Data analysis was performed by the histogram method, including non-negative least-squares analysis.

Calculation of Conversion and Concentration from GPC Measurements. We calculated the conversion of PS-Br (Figure 3) and the concentrations of PS-Br ($[\text{PS-Br}]_t$) and 1,2-PS-C_{60}-H ($[\text{1,2-PS-C}_{60}\text{-H}]_t$) (Figure S2) at different reaction times *t* during the Co-catalyzed radical addition reaction between PS-Br and C_{60}. An aliquot of the solution (about 1 mL) was removed with a syringe every day for 7 days, diluted with *o*-dichlorobenzene (ODCB), and analyzed by GPC (ODCB as an eluent; UV detector (λ = 400 nm)). The RI-detected profile of the reaction mixture at low elution times had the area $S_{\text{RI,polymer}}$, corresponding to the reactant PS-Br and the product 1,2-PS-C_{60}-H (Figure S1). The UV-detected profile of the reaction mixture at low elution times had the area $S_{\text{UV,PS-C60}}$, corresponding to the product 1,2-PS-C_{60}-H. Then, the measured areas were compared to the known RI value of PS ($S^0_{\text{RI,PS}}$) as a standard, enabling the conversion of PS-Br (*Conv.*(PS-Br)) and the concentrations of $[\text{PS-Br}]_t$ and $[\text{1,2-PS-C}_{60}\text{-H}]_t$ to be estimated according to the following equations:

$$Conv.\,(PS-Br) = \left(100 - \frac{S'_{RI,polymer} - k \cdot S'_{UV,PS-C60}}{S^0_{RI,PS}}\right) \times \frac{1}{f_{\%Br}} \qquad \text{(S1)}$$

$$[PS-Br]_t = \left\{ \frac{\left(S'_{RI,polymer} - k \cdot S'_{UV,PS-C60} \right) \cdot f_{\%Br}}{S^0_{RI,PS}} \right\} \times \frac{1}{M_n \cdot d} \quad \text{(S2)}$$

$$[1,2PSC_{60}H]_t = [PS-Br]_{t=0} - [PS-Br]_t \quad \text{(S3)}$$

where S', k, $f_{\%Br}$, M_n, and d are the GPC area normalized according to the sample concentration, the RI/UV ratio for the GPC detector, the bromine terminal functionality of the reactant PS-Br, the number-average molecular weight of the reactant PS-Br, and the density of ODCB (0.77×10^{-3} L g^{-1}), respectively.

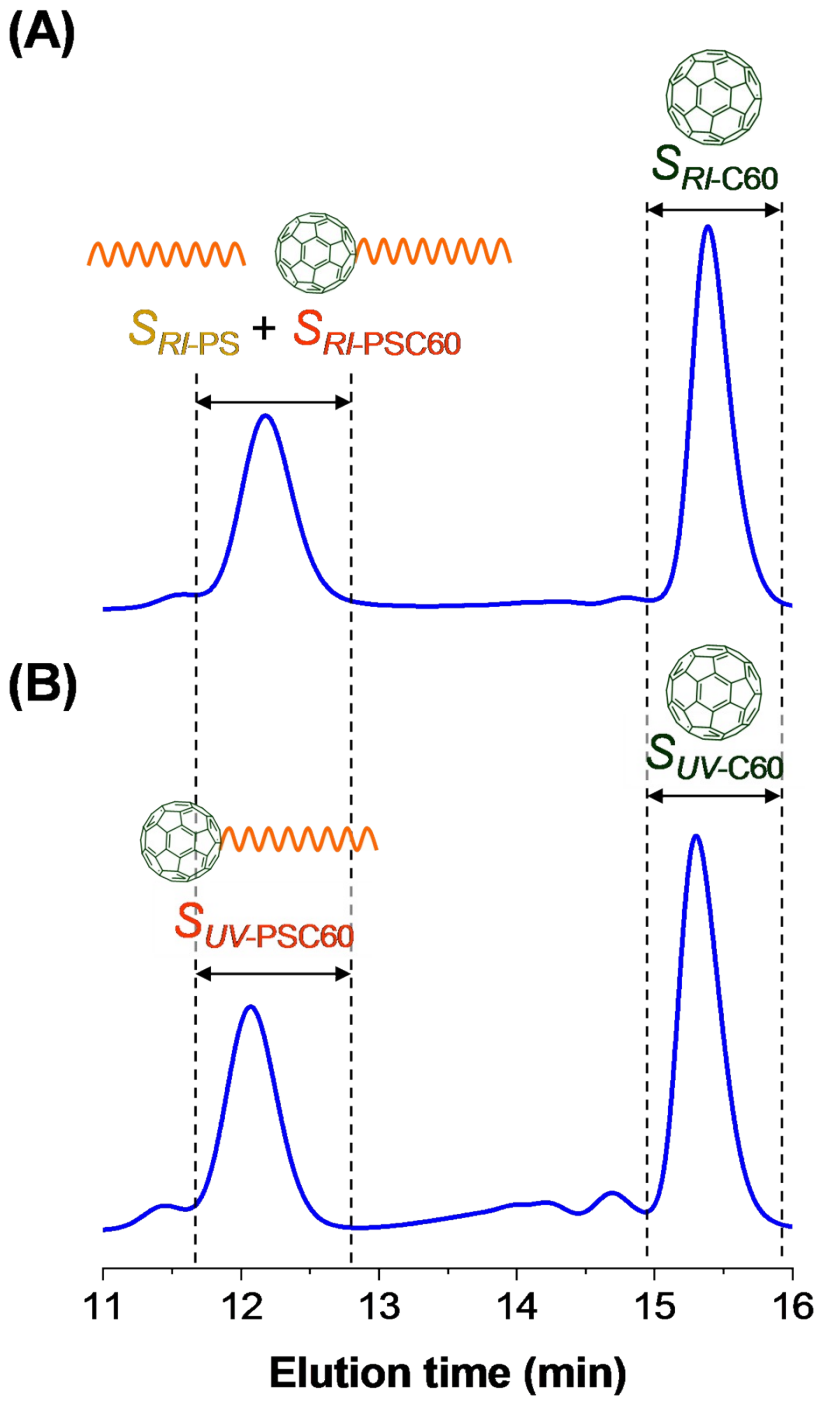

Figure S1. Representative GPC profiles for PS-Br/C_{60} reaction mixture; detector: (A) RI, (B) UV (λ = 400 nm); eluent: ODCB.

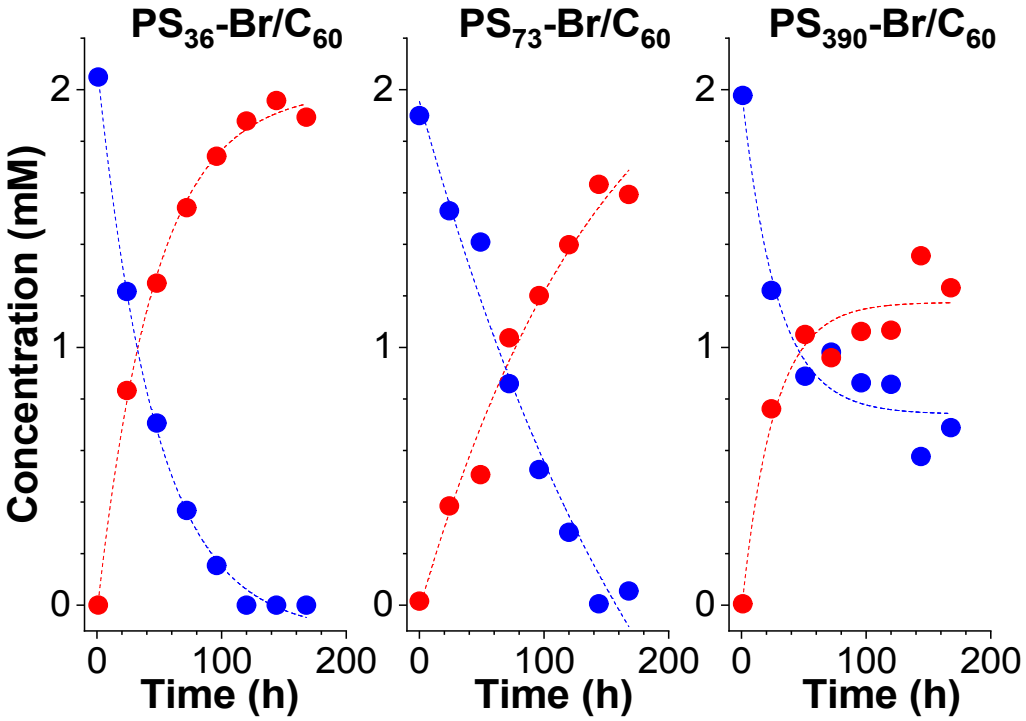

Figure S2. Molar concentrations of PS-Br (●) and 1,2-PS-C_{60}-H (●) in different PS-Br/C_{60} reaction mixtures, as estimated by GPC.

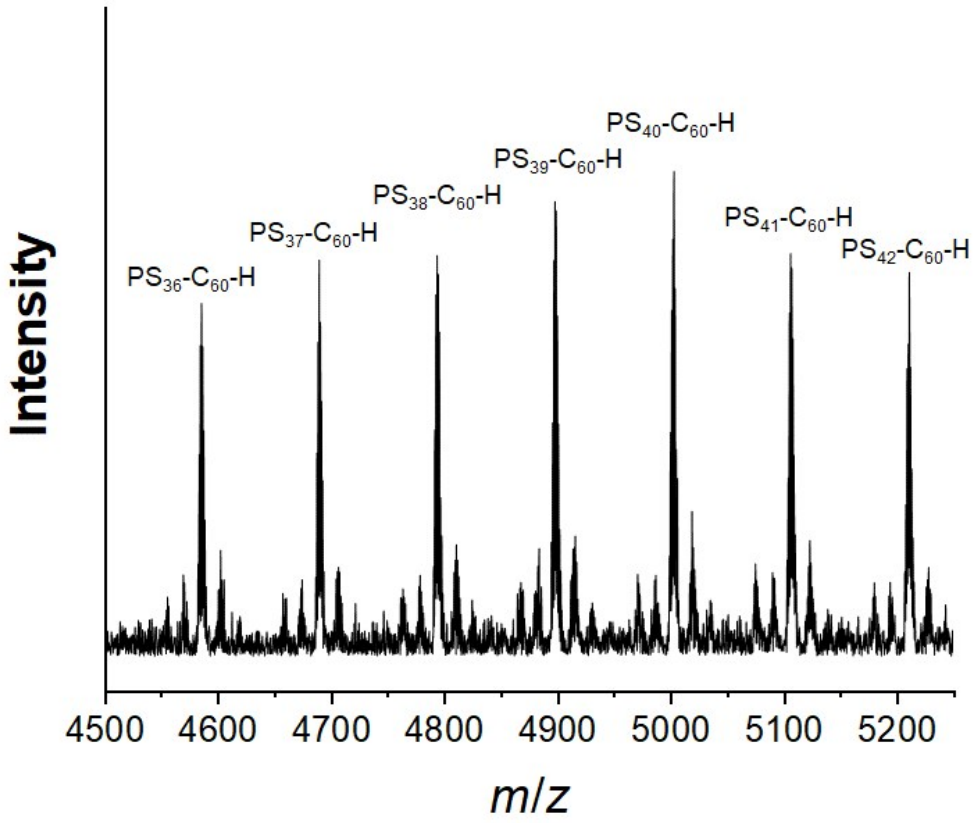

Figure S3. MALDI-FTICR-MS spectrum of 1,2-PS_{36}-C_{60}-H.

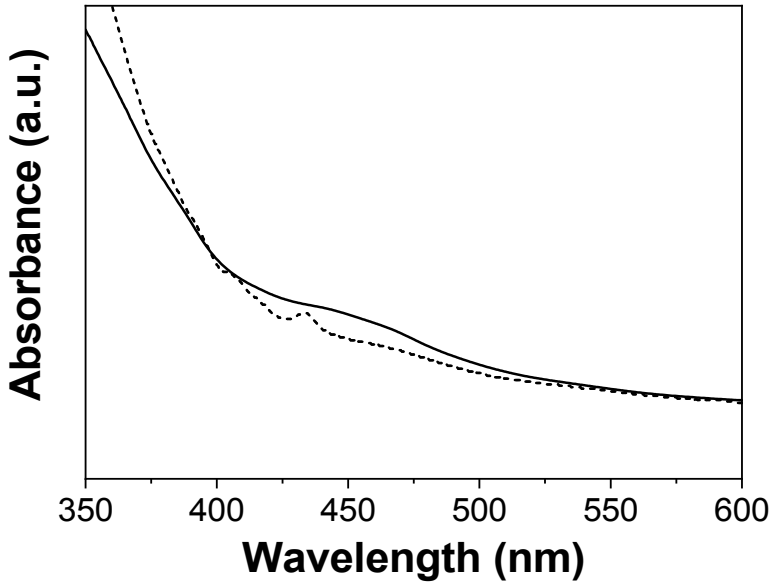

Figure S4. UV-vis spectra of 1,2-PS_{36}-C_{60}-H (broken line) and 1,4-PS_{36}-C_{60}-PS_{36} (solid line) in THF.

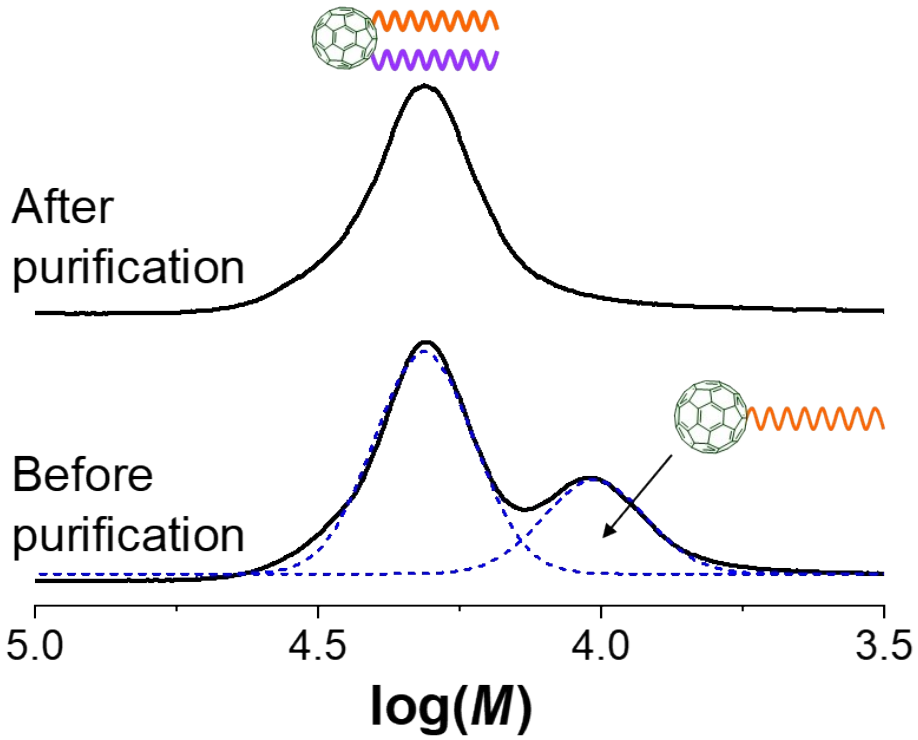

Figure S5. GPC charts before and after purification of 1,4-PS_{73}-C_{60}-PAS_{54} (detector: UV-vis (λ = 400 nm); eluent: ODCB; PS standards).

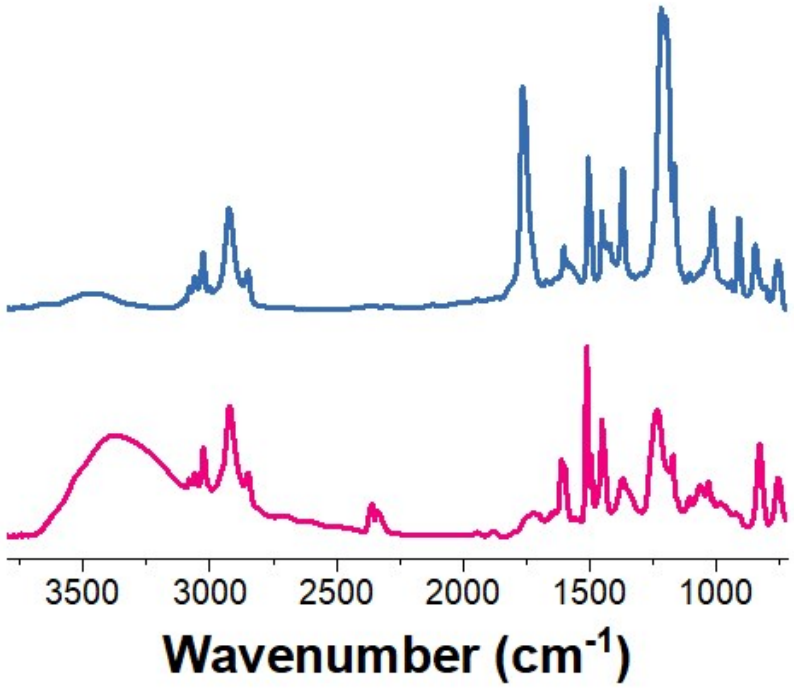

Figure S6. FT-IR spectra of 1,4-PS_{73}-C_{60}-PAS_{54} (upper, blue) and 1,4-PS_{73}-C_{60}-PHS_{54} (lower, red).

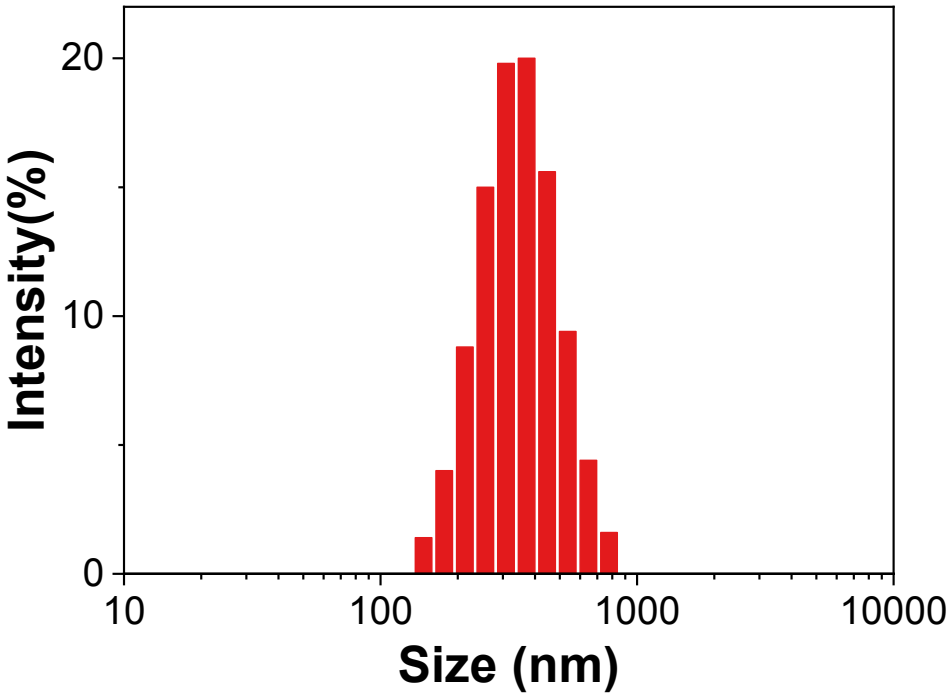

Figure S7. DLS result for the self-assembled 1,4-PS_{73}-C_{60}-PHS_{54} in a THF-toluene mixture.

Supporting References.

S1. Lutz, J.-F.; Matyjaszewski, K. Nuclear Magnetic Resonance Monitoring of Chain-end Functionality in the Atom Transfer Radical Polymerization of Styrene. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 897-910.