Supporting Information

Fullerene Peapod Nanoparticles as Organic Semiconductor-Electrode Interface Layer

Jing M. Ren,[†a] Jegadesan Subbiah,[†b] Bolong Zhang,[b] Kenji Ishitake,[c] Kotaro Satoh,[c] Masami Kamigaito,[c] Greg G. Qiao,*[a] Edgar H. H. Wong,*[‡a] and Wallace W. H. Wong*[b]

[a]Department of Chemical and Biomolecular Engineering, The University of Melbourne,
Parkville, Victoria 3010, Australia.
[b]School of Chemistry, Bio21 Institute, The University of Melbourne, 30 Flemington Road,
Parkville, Victoria 3010, Australia.
[c]Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan.
‡Present address: Centre for Advanced Macromolecular Design and Australian Centre for
Nanomedicine, School of Chemical Engineering, The University of New South Wales,
Sydney, NSW 2052, Australia.
[†]These authors contributed equally to this study.

Correspondence: wwhwong@unimelb.edu.au; edgar.wong@unsw.edu.au;
gregghq@unimelb.edu.au

Contents

1. Experimental

1.1 Materials

The initiator, dimethyl 2-chloro-2,4,4-trimethylpentanedioate ($(MMA)_2$-Cl), was prepared using previously published synthetic methods.[1] RuCp*Cl($(PPh_3)_2$) was provided by Wako and used as received. Alumina (neutral), L-ascorbic acid (reagent grade), copper(I) chloride (CuCl, ≥ 99.995 %), copper(I) bromide (CuBr, 99.999 %), copper(II) bromide ($CuBr_2$, 99.999 %), ethyl vinyl ether (≥ 98 %), magnesium turnings (> 99.5 %), Grubbs catalyst (2nd Generation), lithium aluminum hydride ($LiAlH_4$, 95%), anhydrous dimethyl sulfoxide (DMSO, > 99.9 %), *t*-butylbromide (> 99 %), 2,2′-bipyridine (bpy, ≥ 99 %), 5-hexynoic acid (Sigma-Aldrich, 97%), iodine (I_2, ≥ 99.99%), 4-(dimethylamino)pyridine (DMAP, ≥ 98.0%), and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDCI, ≥ 98.0%) were purchased from Sigma-Aldrich and used as received. Metathesis catalyst, i.e. the pyridine-modified Grubbs catalyst (2nd Generation), was prepared according to the literature procedure.[2] All solid compounds were handled in a glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere ($H_2O < 0.1$ ppm and $O_2 < 0.1$ ppm). Methyl methacrylate (MMA, TCI, > 99.8 %), 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol ($PhC(CF_3)_2OH$, Wako, > 99 %), *n*-Bu3N (Wako, > 98%), dichloromethane (ChemSupply, AR) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99 %) were distilled from calcium hydride under reduced pressure before use. Toluene (Kishida, > 99 %) was distilled from sodium benzophenone ketyl and bubbled with dry nitrogen for 15 min before use. Norbornene carboxylic acid (Wako, 97 %), magnesium sulphate ($MgSO_4$, Scharlau, anhydrous, ≥ 99 %, sodium carbonate (Na_2CO_3, ChemSupply, AR), fullerene (C60, BulkyUSA, 99.5 %), potassium iodide (KI, Fisons, AR), sodium thiosulphate ($Na_2S_2O_3$, BHD, 97 %), sodium sulphate (Na_2SO_4, anhydrous ChemSupply, AR), ammonium chloride (NH_4Cl, BHD, 99.8 %), acetonitrile (MeCN, Shameleon Reagent, > 99.5 %), diethyl ether (DEE, ChemSupply, 98 %), ethyl acetate (EtOAc, ChemSupply, AR), *n*-hexane (TCI, > 99 %), and anhydrous methanol (MeOH, ChemSupply, > 99 %) were used as received.

1.2 Characterization

1.2.1 Nuclear magnetic resonance (NMR) spectroscopy

^1H and ^{13}C NMR spectroscopy measurements were conducted in $CDCl_3$ at 25 °C or 55 °C (polymer analysis) on a JEOL ECS-400 spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C, respectively. The triad tacticity of PMMAs was determined by the integration of area under the C=O carbon resonance at 175-180 ppm in the ^{13}C NMR spectrum.

1.2.2 Gel permeation chromatography (GPC)

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the product polymers were determined by GPC in THF at 40 ºC using two polystyrene gel columns [Shodex KF-805L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to Jasco PU-980 precision pump and a Jasco RI-2031 detector. The columns were calibrated against 10 standard PMMA samples (Agilent Technologies; M_p = 875–1677000 Da; M_w/M_n = 1.02–1.09).

1.2.3 Gel permeation chromatography coupled with multi-angle laser light scattering detector (GPC-MALLS)

GPC-MALLS was performed on a Shimadzu liquid chromatography system fitted with a Wyatt DAWN EOS multi-angle laser light scattering (MALLS) detector (690 nm, 30 mW) and a Wyatt OPTILAB DSP interferometric refractometer (690 nm), using three Phenomenex Phenogel columns (500, 10^4, and 10^6 Å porosity; 5 µm bead size) operated at 1 mL/min using THF as the mobile phase and with the column temperature set at 30 ºC. Astra software (Wyatt Technology Corp.) was used to process the data to determine the molecular weight of polymers based on the assumption of 100 % mass recovery of the polymer where the dn/dc value was unknown.

1.2.4 Preparative gel permeation chromatography (prep-GPC)

Prep-GPC was performed on a Shimadzu LC-20AP liquid chromatography system fitted with a Shimadzu SIL-10AP autosampler, Shimadzu RID-10 refractometer (L = 633 nm), and Shimadzu SPD-20 UV-Vis detector, using two Phenomenex Phenogel columns (300 × 21.2 mm, 10^6 Å porosity; 10 µm bead size) operating at 3 mL/min using THF as the mobile phase at ambient temperature.

1.2.5 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements were performed on a Wyatt DynaPro NanoStar instrument fitted with a 120 mW Ga-As laser operating at 365 nm; 100 mW was delivered to the sample cell. Analysis was performed at an angle of 90° and at constant temperatures of 25 or 77 ± 0.01 °C.

1.2.6 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images were taken using a Tecnai TF30 transmission electron microscope (FEI Co., Eindhoven, The Netherland) operated at 200 kV. Images were acquired digitally with Olympus MegaView III CCD (Olympus, Tokyo, Japan). The TEM samples were prepared by dissolving at a concentration of ca. 0.2 mg mL^{-1} and then spin-coating the sample solution on TEM copper grid (strong carbon film, 300 mesh).

1.2.7 Ultraviolet-Visible (UV-Vis) spectroscopy

UV absorbance spectra were obtained using Shimadzu UV-1800 Spectrophotometer and UVProbe software package. The wavelength range of 250–550 nm was selected with medium scan speed and sampling interval of 1 nm. Scan mode was set to 21 repeats with 3 min interval between scans.

1.3 Synthesis

Synthesis of *st*-PMMA-Cl via Ru-catalyzed stereospecific living radical polymerization (SLRP).

SLRP of MMA was performed according to the previously established procedure:[3] $RuCp^*Cl(PPh_3)_2$ (**2**, 254 mg, 0.32 mmol) was added to a dry round-bottom flask equipped with a 3-way stopcock in a glovebox, followed by the addition (under dry N_2) of solvent $PhC(CF_3)_2OH$ (**3**, 59.2 mL), MMA (17.0 ml, 160 mmol), n-Bu_3N (0.76 ml, 3.2 mmol) and initiator $(MMA)_2$-Cl (**1**, 1.60 mmol as a 663 mM stock solution in toluene). The reaction was carried out at 0 °C with samples taken periodically under N_2. The polymerization was terminated after 79 h by cooling the reaction to -78 °C, and a sample was then extracted for ^1H NMR spectroscopic analysis. The remaining product was precipitated twice in hexane, followed by drying *in vacuo* to give *st*-PMMA-Cl as a white powder, (9.08 g, 91 %); ^1H NMR: MMA conversion = 49 % ($M_n^{theo} = 5140$ g mol^{-1}); GPC: $M_n = 5350$ g mol^{-1}, $M_w/M_n = 1.12$, *mm*/*mr*/*rr* (%) = 2/24/74; ^{13}C NMR: *mm*/*mr*/*rr* (%) = 2/24/74 (-CO(O)-, 176.3-178.0 ppm). The GPC DRI chromatogram and ^1H NMR spectrum for *st*-PMMA-Cl is provided in **Figure S1**.

Preparation of *exo*-norbornene carboxylic acid (NB-COOH).

A mixture (*exo*/*endo*, 56 : 44 %) of *endo*- and *exo*-norbonene carboxylic acid (50 g, 0.36 mol) was dissolved in Na_2CO_3 solution (0.56 M, 580 mL) in a round-bottom flask equipped with a 3-way stopcock. To this solution, KI and I_2 (1.4 M and 0.44 M in distilled H_2O, respectively, 457 mL) was added dropwise via an additional funnel over 2 h. The reaction solution was stirred for further 1 h and washed with Et_2O (150 mL × 6). The aqueous layer was extracted, and to which aqueous $Na_2S_2O_3$ (10 wt%, 300 mL) and HCl (1M, 300 mL) was successively added. The mixture was then washed with Et_2O (100 mL × 8), and all the organic layers were combined, dried over Na_2SO_4, and evaporated to give a yellowish solid. The crude product was then purified via flash chromatography using Et_2O as eluent to give a white crystal (27.0 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.32-1.44 (*m*, 1H, -CHC***H***(H)CH- and 1H, bridge proton), 1.49-1.57 (*d*, 1H, -CHCH(***H***)CH-), 1.90-1.98 (*dt*, 1H, bridge proton), 2.21-2.29 (*m*, 1H, -CH_2C***H***(COOH)CH-), 2.89-2.95 (*br*, 1H, bridgehead), 3.07-3.13 (*br*, 1H, bridgehead), and 6.08-6.16 (*m*, 2H, C*H*=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 30.4 (-CH*C*H_2CH-), 41.7 (bridgehead), 43.3 (-CH_2***C***H(CHOOH)CH-), 46.5 (bridgehead), 46.8 (bridge carbon), 135.8 (***C***H=CH), 138.2 (CH=***C***H), and 183.2 (-CH***C***HOOH).

Preparation of *exo*-norbornene methanol (NB-CH$_2$OH).

$LiAlH_4$ (2.8 g, 0.74 mol) was dissolved in dry THF (20 mL) in a pre-dried round bottom flask. To the same round bottom flask, a solution of **NB-COOH** (1.1 M, 19 mL) was added dropwise over 30 mins, and the reaction solution was allowed to warm up to r.t. and stirred for a further 16 h. The reaction was terminated by quenching with saturated NH_4Cl and then filtered. The filtrate was washed with EtOAc (25 mL × 3), dried over Na_2SO_4 and evaporated *in vacuo* to give **NB-CH$_2$OH** as a colourless oil (1.8 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.07-1.14 (*dt*, 1H, -CHC***H***(H)CH-), 1.10-1.37 (*m*, 3H, -CH_2C***H***(CH_2OH)CH-, 1H-bridge proton, and -CHCH(***H***)CH-), 1.56-1.66 (*m*, 2H, 1H-bridge proton, and -O***H***), 2.70-2.86 (*d*, 2H, bridgeheads), 3.49-3.58 (*dd*, 1H, -CHC***H***(H)OH), 3.66-3.73 (*dd*, 1H, -CHCH(***H***)OH) and 6.03-6.13 (*m*, 2H, C***H***=C***H***). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 29.5 (-CH***C***H_2CH-), 41.5 (-CH_2***C***H(CH_2OH)CH-), 41.8 (bridgehead), 43.2 (bridgehead), 44.9 (bridge carbon), 67.5 (-CH***C***HOH), 136.4 (***C***H=CH), and 136.8 (CH=***C***H).

Synthesis of exo-norbonene methyl hex-5-ynoate

5-hexynoic acid (2.0 g, 18 mmol), DMAP (0.8 g, 6.5 mmol), and EDCI (4.2 g, 21.9 mmol) were dissolved in dry DCM (100 mL) in a round bottom flask. A solution of **NB-CH$_2$OH** in dry DCM (0.4 M, 36 mL) was then added dropwise over 15 min, and the reaction mixture was stirred at r.t. for 24 h. The product solution was washed with $NaHCO_3$ (sat. 50 mL x 2), HCl (2 M, 50 mL x 2), and NaCl (sat. 50 mL x 2). The organic layer was dried over $MgSO_4$, concentrated, and purified via flash chromatography using Et_2O/Hexane (1 : 9) as eluent to give **4** as a yellowish oil (2.98 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.10-1.40 (*m*, 4H, -CHC***H***$_2$CH- and bridge protons), 1.67-1.77 (*m*, 1H, -CHC***H***(CH_2)CH_2-), 1.81-1.91 (*q*, 2H, *J* = 7.2 Hz, -CH_2C***H***$_2$$CH_2$-), 1.96-1.99 (*t*, 1H, *J* = 2.1 Hz, -C≡C***H***), 2.23-2.32 (*dt*, 2H, *J* = 7.2 Hz, *J* = 2.1 Hz, -CH_2C***H***$_2$C≡CH), 2.43-2.51 (*t*, *J* = 7.2 Hz, -COOCC***H***$_2$$CH_2$-), 2.67-2.73 and 2.81-2.87 (*br*, 2H, bridgehead protons), 3.90-4.20 (*m*, -CHC***H***$_2$COO-), and 6.04-6.14 (*m*, 2H, C***H***=C***H***). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 17.8 (-CH_2***C***H$_2$C≡CH), 23.6 (-CH_2***C***H$_2$$CH_2$-), 29.5 (-CH***C***H$_2$CH-), 33.0 (-OOC***C***H$_2$$CH_2$-), 37.9 (-CH***C***H($CH_2$)$CH_2$-), 41.6 (1C, bridgehead), 43.6 (1C, bridgehead), 44.9 (bridge carbon), 68.3 (-CH***C***H$_2$COO-), 69.1 (-C≡***C***H), 83.3 (-***C***≡CH), 136.2 (***C***H=CH), 136.9 (CH=***C***H), and 173.1 (-CH_2***C***OO-).

Synthesis of *st*-PMMA-N_3 via the azidation of *st*-PMMA-Cl

st-PMMA-Cl (7.0 g, M_n = 5350, 1.31 mmol), NaN_3 (0.85 g, 13 mmol) and L-ascorbic acid (0.035 g, 0.20 mmol) were dissolved in CH_3CN/H_2O (9 : 1) in a round bottom flask, and the mixture was degassed by bubbling N_2 for 10 min. A standard catalyst solution of $CuCl/CuCl_2$/bpy (0.1/0.067/0.33 M in CH_3CN/H_2O (9 : 1), 7.85 mL) was then added and the reaction solution was stirred at 40 ºC for 24 h. The crude product solution was extracted with EtOAc (50 mL x 3), and the organic layers were collected, combined and then washed with HCl (1 M, 50 mL x 3) and H_2O (50 mL x 3). The solution was then concentrated (to ~ 50 mL), and passed through a short neutral alumina column before dried *in vacuo* to afford *st*-PMMA-N_3 as a white crystal (7.0 g, > 99%). GPC: M_n = 5400 g mol^{-1}, M_w/M_n = 1.11. The GPC DRI chromatogram and ^{1}H NMR spectrum for *st*-PMMA-Cl is provided in **Figure S1**.

Synthesis of *st*-PMMA-NB via click chemistry

st-PMMA-N_3 (6.9 g, M_n = 5400, 1.27 mmol), exo-norbonene methyl hex-5-ynoate (1.40 g, 6.39 mmol), and CuBr (0.91 g, 6.39 mmol) were added into a round bottom flask equipped with a 3-way stopcock in a glovebox. Degassed DMF (110 mL) and distilled PMDETA (1.10 g, 6.39 mmol) were subsequently added. The reaction mixture was stirred at r.t. for 10 min and then at 40 ºC for 24 h. The crude product was precipitated into H_2O (1 L), and extracted with EtOAc (100 mL x 5). The organic extracts were combined, washed with HCl (1M, 200 mL x 3) and H_2O (200 mL x 3), concentrated under reduced vacuum to ~ 100 mL. The product polymer was isolated by precipitation into hexane/Et_2O (9 : 1) and dried *in vacuo* to give *st*-PMMA-NB as a white powder (6.3 g, 91 %). GPC: M_n = 5500 g mol^{-1}, M_w/M_n = 1.15. The GPC DRI chromatogram and ^{1}H NMR spectrum for *st*-PMMA-Cl is provided in **Figure S1**.

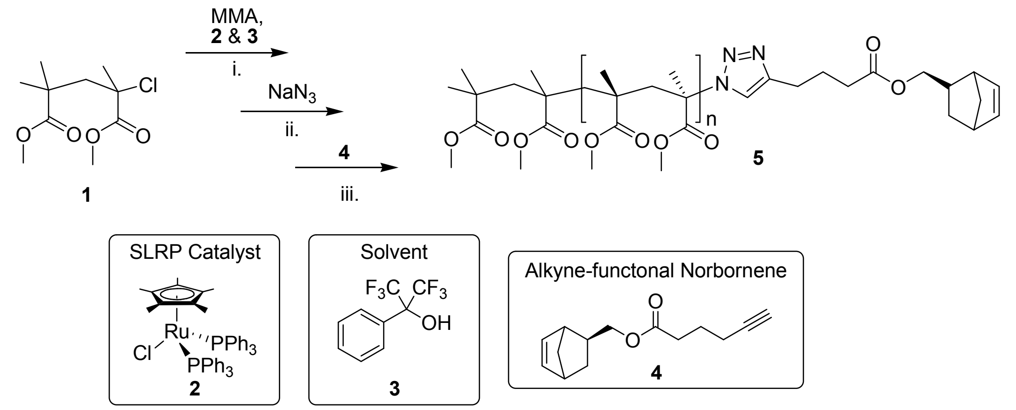
Synthesis of *st*-PMMA-BB via ring-opening metathesis polymerization (ROMP)

st-PMMA-BB (0.63 g, M_n= 5500, PDI = 1.15, 115 mmol) was dissolved in DCM (1.3 mL) in a pre-dried round bottom flask equipped with a 3-way stopcock. 0.10 mL of pyridine-modified 2nd generation Grubbs' catalyst (5 mM in DCM) was then added. The reaction was then stirred at r.t. with samples taken periodically under N_2. The reaction was terminated after 45 min (GPC-DRI: **5** conversion = 95 %) by the addition of ethyl vinyl ether (a few drops). The product polymer was first isolated via precipitation into MeOH (~20 mL), and purified via preparative GPC to afford *st*-PMMA-BB as a white powder (0.32, 51 %). GPC: M_n = 183700 g mol^{-1}, M_w/M_n = 1.38; GPC-MALLS: M_n = 815900 g mol^{-1}, M_w/M_n = 1.12. The GPC DRI chromatogram and ^{1}H NMR spectrum for *st*-PMMA-BB is provided in **Figure 1**.

Synthesis of *st*-PMMA/C60 stereocomplex.

st-PMMA/C60 was prepared according the previously published literature with slight modifications;[4] *st*-PMMA-BB (M_n = 815900 g mol^{-1}, PDI = 1.12, 20 mg, 193 μmol of MMA repeating units) was dissolved in MeCN (10 mL) in a 30 mL glass vial. C60 (100 mg, 139 mmol) was added to the solution, and the reaction mixture was then stirred at r.t. for 48 h. The reaction solution was centrifuged and passed through a syringe filter (0.45 μm) to remove any uncomplexed C60. The *st*-PMMA/C60 was kept in solution state, diluted (to 0.2 mg/mL) and characterized via UV-Vis spectroscopic analysis, DLS and TEM (particle size plots are provided in **Figure S2** and **S3**). UV-Vis: C60 loading = 1.9 wt% (26 C60s per complex) (**Figure S4**).

2. Supporting Figures and Results



Scheme S1. Schematic illustration for the preparation of *exo*-norbornene end-functionalized syndiotactic poly(methyl methacrylate) (***st*-PMMA-NB**) via i. stereospecific living radical polymerization (SLRP), ii. azidation, and iii. 'click' chemistry.

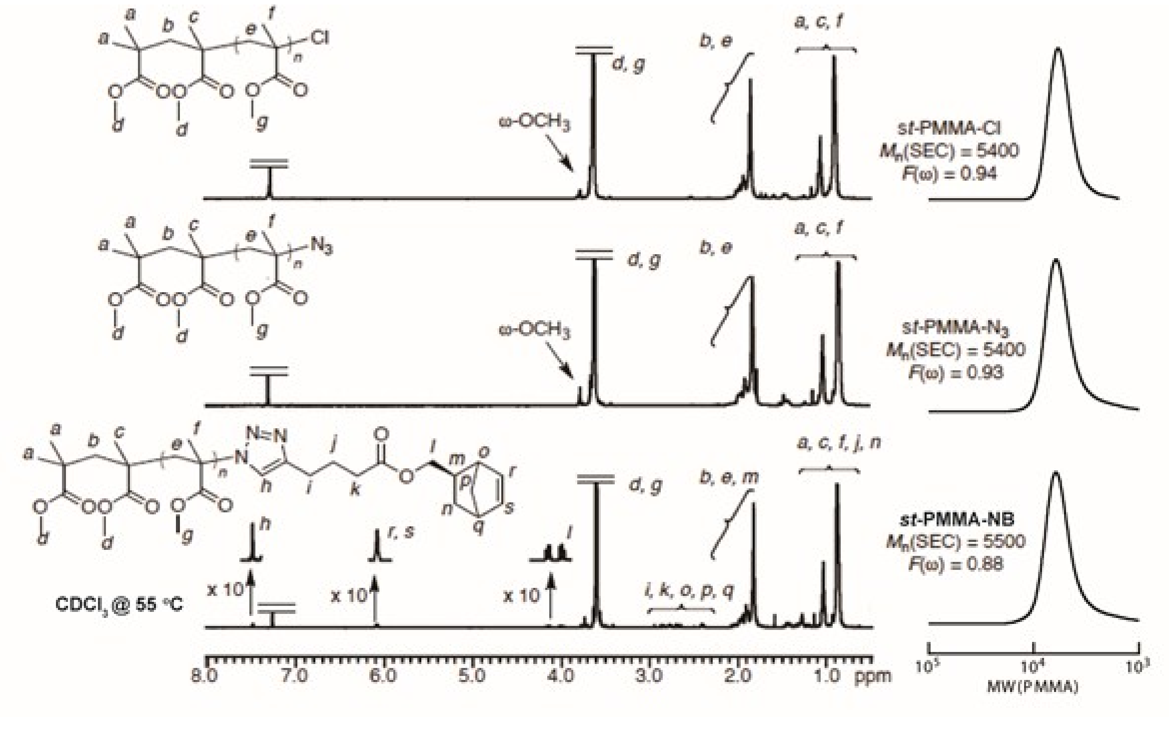


Figure S1. ^{1}H NMR spectra and GPC DRI traces of chloride (*st*-PMMA-Cl), azide (*st*-PMMA-N_3), and norbornene (*st*-PMMA-NB) chain-end functionalized syndiotactic poly(methyl methacrylate).

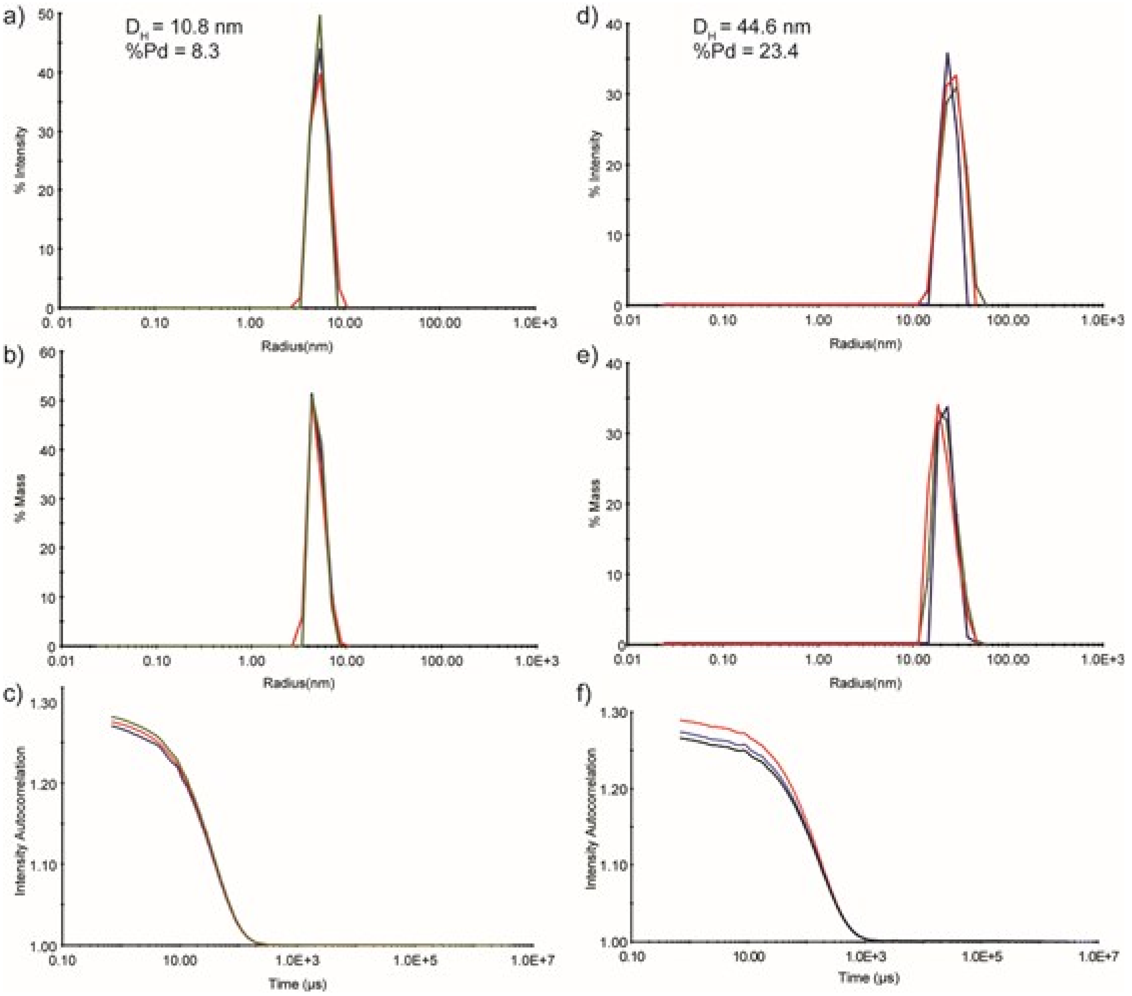


Figure S2. Dynamic light scattering (DLS) percentage intensity distribution, percentage mass distribution, and autocorrelation plots for *st*-PMMA-BB (a-c) and *st*-PMMA/C60 SC (e-f), respectively.

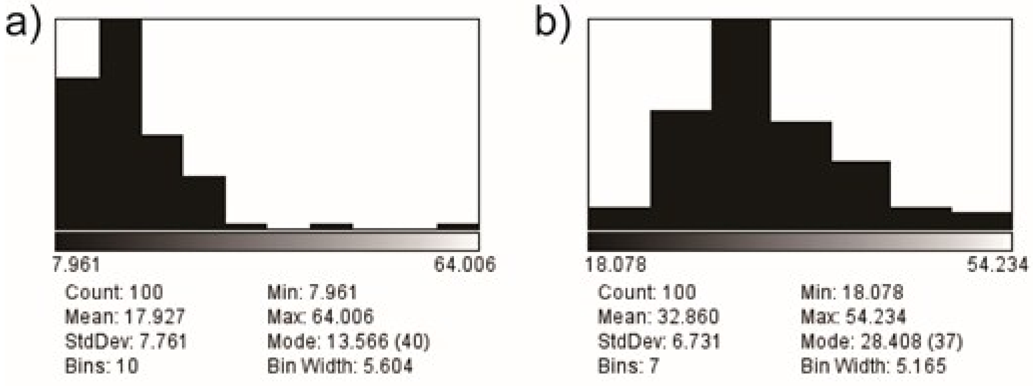


Figure S3. Particle size distribution graphs for a) syndiotactic poly(methyl methacrylate) bottlebrush polymer (*st*-PMMA-BB), and b) syndiotactic poly(methyl methacrylate) bottlebrush polymer/C60 stereocomplex (*st*-PMMA/C60 SC), generated from their respective TEM micrographs.

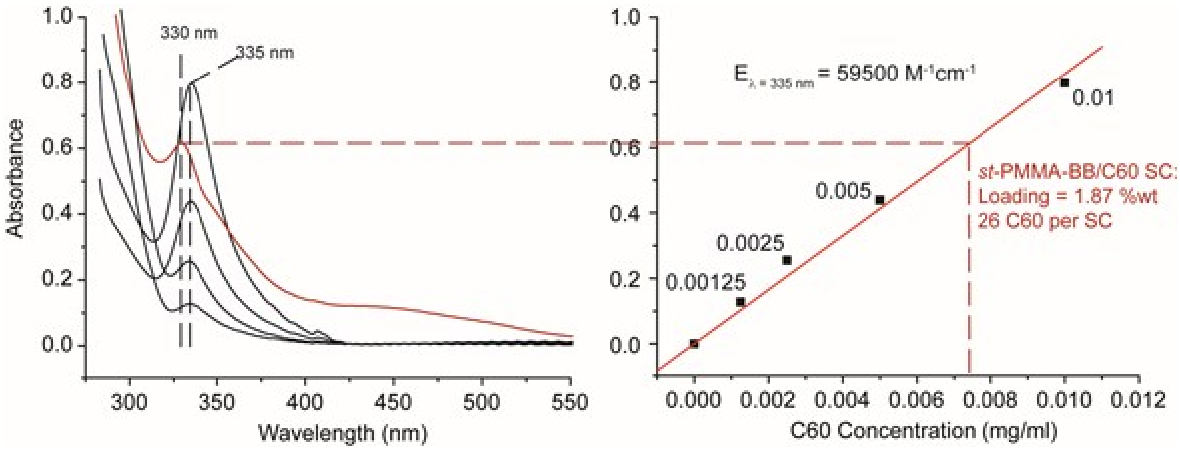


Figure S4. UV-vis spectra for syndiotactic poly(methyl methacrylate) bottlebrush polymer/C60 stereocomplex (*st*-PMMA/C60 SC) (MeCN) and C60 (Toluene), and calibration curve for C60 and determination of SC C60 loading.

Bulk heterojunction device fabrication and characterisation

Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. First, a thin layer of ZnO nanoparticle[5] was deposited on cleaned ITO substrate by spin-coating (3000 rpm) to form 30 nm of ZnO layer, followed by backing on a hot plate at 140 °C for 5 min. An ultra-thin interlayer of ***st*-PMMA-BB** or ***st*-PMMA/C60 SC** was spin coated on top of ZnO layer using an acetonitrile solution. Then, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was deposited by spin coating an 1,2-dichlorobenzene solution (1 ml) containing 10 mf of P3HT and 10 mg of $PC_{61}BM$ or 8 mg of PBDT-BT and 16 mg of $PC_{71}BM$. The active layer P3HT:$PC_{61}BM$ was annealed at 150 ºC for 10 min. The thickness of the active layers were measured as 140 nm for P3HT:$PC_{61}BM$ blend and 80 - 90 nm for PBDT-BT-$PC_{71}BM$ blend. MoO_3 (10 nm) and silver (100 nm) were thermally evaporated at ~a vacuum of 10^{-7} mbar on top of active layer as a anode. The area of the devices was 0.10 mm^2. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit (**Figure S5**). Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory. Device fabrication and characterizations were performed in a glove box without any encapsulation and multiple devices (at least 10 devices) of the same composition were tested for reproducibility. The current density versus voltage data for various devices are shown in Figure S5. The surface morphology of various interlayer films such as, ZnO, ZnO/*st*-PMMA-BB and ZnO/*st*-PMMA-C60 were examined using tapping mode atomic force microscopy (**Figure S6**).

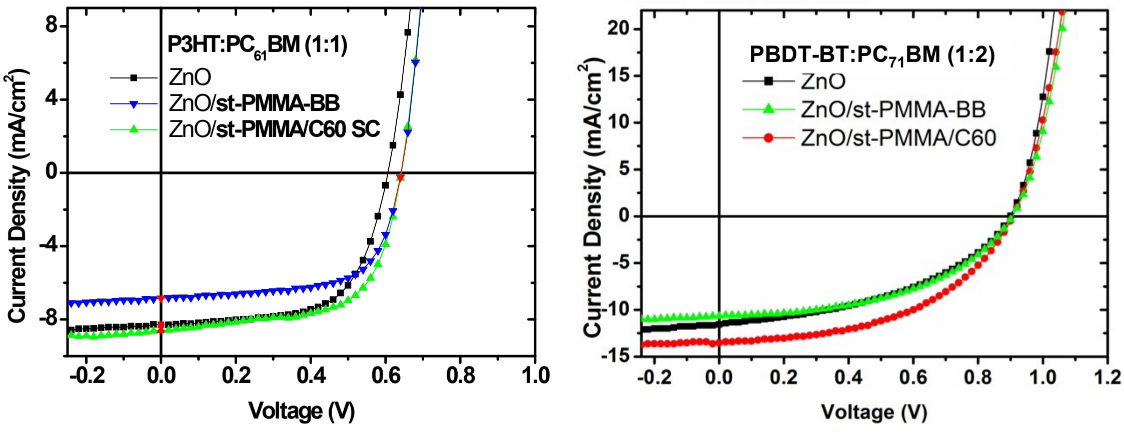


Figure S5. Current density - voltage curves of P3HT:PC$_{61}$BM (left) and PBDT-BT:PC$_{71}$BM (right) based solar cell devices with various interlayer ZnO, ZnO/*st*-PMMA-BB and ZnO/*st*-PMMA-C60.

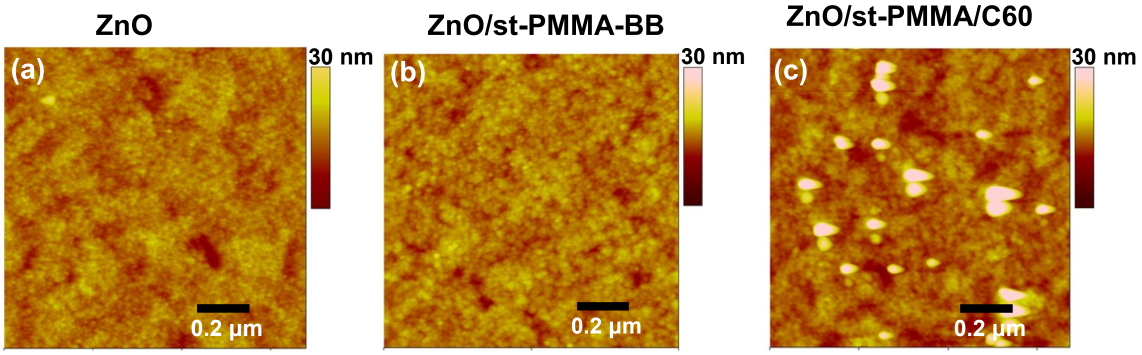


Figure S6. Surface morphology of various cathode interlayer (a) ZnO, (b) ZnO/*st*-PMMA-BB and (c) ZnO/*st*-PMMA-C60.

References

[1] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 2819-2824.

[2] M. S. Sanford, J. A. Love, R. H. Grubbs, *Organometallics* **2001**, *20*, 5314-5318.

[3] T. Shibata, K. Satoh, M. Kamigaito, Y. Okamoto, *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 3609-3615.

[4] M. Kawauchi, T. Kawauchi, T. Takeichi, *Macromolecules* **2009**, *42*, 6136-6140.

[5] G. Sarasqueta, K. R. Choudhury, J. Subbiah, F. So. *Adv. Funct. Mater.* **2011**, *21*, 167–171.