Supplementary Information

Synthesis of a rod-coil block copolymer incorporating PCBM

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Experimental section

Solvents were of AR grade and were distilled before use. Styrene was purified by filtration through neutral alumina (70–230 mesh) to remove inhibitors and flash distilled immediately prior to use. Reagents were obtained from Terma USA (PCBM, 99%); Strem Chemicals, Inc (Tetrakis(triphenylphosphine)palladium); Aldrich (4-vinylbenzylchloride (90% - Note: there was no evidence from NMR for the presence of any ortho isomer), Phthalimide potassium salt (98%), hydrazine monohydrate (98%), di-tert-butyldicarbonate (99%), dimetylamoniopyridine (99%), 5,5'-dibromo-2,2'-bithiophene (99%), 9,9-dihexylfluorene-2,7-diboronicacid-bis(1,3-propanediol)ester (97%), Aliquat 336, potassium carbonate (99%), trifluoroacetic acid (99%) and heptanoyl chloride (99%)). The acid chloride of PCBM was synthesized as reported in literature. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) performed in tetrahydrofuran (1.0 mL/min) at 30°C using a Waters 2695 Separations Module, with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector, a series of four Polymer Laboratories PLGel columns (3 × 5μm Mixed-C and 1 × 3μm Mixed-E), and Empower Pro Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories EasiCal, MW from 264 to 256000), and molecular weights are reported as polystyrene equivalents based on the refractive index detector. Nuclear magnetic resonance spectra (NMR) were obtained with a Bruker AC200, AC400 spectrometer. Chemical shifts are reported in ppm from external tetramethylsilane. UV-vis absorption spectra were recorded on a Cary 5E spectrophotometer. Steady state fluorescence spectra were recorded on a Perkin Elmer LS50 fluorimeter. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer. Surface morphology analysis was performed using the Asylum Cypher atomic force microscope (AFM).

Synthesis of polymer 4

Styrene (10g, 96mmol), Vinylbenzyl chloride (1.6279g, 10mmol), RAFT agent 3 (0.1117g, 0.38mmol) and AIBN (0.0062g, 0.04mmol) were transferred into an ampoule which was degassed by three freeze-evacuate-thaw cycles, sealed and heated at 75 ± 1°C in a thermostated oil bath for 16 h. The ampoule was removed and cooled. The copolymer was precipitated into MeOH and conversion and ratio were calculated by ^{1}H-NMR and GPC. ^{1}H-NMR ($CDCl_3$, 200MHz): δ ppm 7.36-6.24 (br, *H*-Ar), 4.65-4.35 (br, ArCH_2Cl), 2.71-2.57 (br, S-CH_3), 2.35-1.67 (br, CH_2C*H*-Ar), 1.67-1.05 (br, CH_2CH-Ar). ^{13}C-NMR ($CDCl_3$, 50MHz): δ ppm, 145.28, 134.72, 127.95, 127.61, 125.70, 46.28, 40.37

	Conversion (%)	**Ratio (n:m)**	**Mn**	**Mw/Mn**
4	41	7:1	10935	1.15

Synthesis of polymer 5

Polymer 4 (4.1g, 3.8×10^{-4} mol), *N*-ethylpiperidine hypophosphite (0.6810g, 3.8×10^{-3} mol), initiator Vazo 88 (0.0371g, 1.52×10^{-5}mol) and toluene (15 mL) were placed into an ampoule, degassed with three freeze-evacuate-thaw cycles, sealed under vacuum and heated at 110°C for 4 hours. Afterwards, the organic phase was concentrated and the product precipitated in methanol several times. It was obtained 3.84g of a white solid. ^{1}H-NMR ($CDCl_3$, 200MHz): δ ppm 7.36-6.24 (br, *H*-Ar), 4.65-4.35 (br, $ArCH_2Cl$), 2.35-1.67 (br, CH_2CH-Ar), 1.67-1.05 (br, CH_2CH-Ar).

	Recovered (%)	Ratio (n:m)	Mn	Mw/Mn
5	94	7:1	10187	1.22

Synthesis of polymer 6

A mixture of polymer 5 (3.8g, 4.31×10^{-3} mol, 1 eq), potassium phthalimide (3.9917g, 2.15×10^{-2} mol, 5eq) and dry DMF (40mL) were stirred and heating at 80°C overnight under nitrogen atmosphere. The solvent was removed and the solid taken up with chloroform, washed with water (3 times) and dried over Mg_2SO_4. The organic phase was concentrated and precipitated into methanol. It was obtained 3.8g of polymer. ^{1}H-NMR ($CDCl_3$, 200MHz): δ ppm 7.92-7.57 (br, *H*-Ph), 7.34-6.16 (br, *H*-Ar), 4.88-4.55 (br, $ArCH_2$-Ph), 2.39-1.65 (br, CH_2CH-Ar), 1.65-1.10 (br, CH_2CH-Ar). ^{13}C-NMR ($CDCl_3$, 50MHz): δ ppm, 167.96, 145.06, 133.89, 132.19, 127.93, 125.61, 123.24, 41.28, 40.33.

	Yield (%)	Ratio (n:m)	Mn	Mw/Mn
6	89	7:1	10563	1.22

Synthesis of polymer 7

Polymer 6 (3.7g, 3.73×10^{-3} mol) was dissolved in THF (50mL) with the reaction mixture under reflux, ethanol (30mL) and hydrazine monohydrate (10mL) were added. The mixture was refluxed overnight under stirring. The solvent was removed under high vacuum; the residue was dissolved in the minimal amount of THF and precipitated into methanol 2 times. It was obtained 2.23g of polymer. ^{1}H-NMR ($CDCl_3$, 200MHz): δ ppm 7.34-6.22 (br, *H*-Ar), 3.89-3.56(br, $ArCH_2$-NH_2), 2.41-1.64 (br, CH_2CH-Ar), 1.64-1.10 (br, CH_2CH-Ar). ^{13}C-NMR ($CDCl_3$, 100MHz): δ ppm, 145.33, 140.61, 127.95, 127.70, 125.65, 46.27, 40.32.

	Yield (%)	Ratio (n:m)
7	69	7:1

Synthesis of polymer 8

In a dry flask containing polymer 7 (2g, 2.32×10^{-3} mol, 1.1eq) dissolved in 23mL of dry THF were added DIBOC (0.5569g, 2.55×10^{-3} mol, 1.1eq) and DMAP (0.0283g, 2.32×10^{-4} mol, 0.1eq). The reaction mixture was stirred overnight at room temperature. The solution was concentrated and the polymer precipitated into methanol. It was obtained 1.96g of polymer. ^{1}H-NMR ($CDCl_3$, 400MHz): δ ppm 7.22-6.20 (br, *H*-Ar), 4.78-4.48 (CH_2-N*H*-), 4.32-4.00(br, ArCH_2-NH), 2.35-1.12 (br, CH_3-C; CH_2C*H*-Ar; CH_2CH-Ar).

	Yield (%)	Ratio (n:m)	Mn	Mw/Mn
8	88	7:1	13560	1.26

The GPC trace of polymer **8** shows the appearance of a small shoulder (Figure 2A) at higher molecular weight following introduction of the Boc protection group. It was not present for polymer **6**. The exact reason for the appearance of the shoulder is not known but a possible explanation might be a side reaction during the synthesis and the formation of a urea bond via isocyanate (see ref. 1 below) to couple to another chain. However ^{1}H-NMR and FT-IR did not show any evidence of such chemical groups, which suggests if this reaction occurs it must only be a quite minor process and should not affect the final properties of the bulk material.

1. R. Dalpozzo, G. Bartoli, M. Bosco, P. Melchiorre, L. Sambri, *Curr. Org. Synth.*, 2009**,** **6**, 79

Synthesis of polymer 9

In a long neck flask were put 5,5'-dibromo-2,2'-bithiophene (0.303g, 9.26×10^{-4} mol), 9,9-dihexylfluorene-2,7-diboronica cid-bis(1,3-propanediol)ester (0.506g, 9.77×10^{-4} mol), $Pd(PPh_3)_4$ (0.0321g, 3 mol% based on bithiophene), Aliquot 336 (0.0395g, 10 mol% based on boronic ester) and dry toluene (6mL). The mixture was degassed for 20 min and then 3 mL of K_2CO_3 solution (2M) was added. The reaction mixture was stirred and degassed for another 20 min and then heated at 85°C for 16h. Afterwards, the polymer was end-capped by adding a degassed solution of **8** (1.50g, 15 mol% on boronic ester in 3 mL of dry toluene) and the reaction mixture was refluxed for 4h. The solution was cooled to room temperature and precipitated twice into methanol. The precipitate was washed with acetone resulting in a yellow-green solid. ^1H-NMR ($CDCl_3$, 400MHz): δ ppm 7.80-7.27 (br, *H*-Ar), 7.29-6.13 (br, *H*-Ar), 4.76-4.47 (br, $ArCH_2NH$-), 4.30-4.05 (br, CH_2NH), 2.34-1.23 (br, CH_3C, CH_2-FL, CH_2CH-Ar, CH_2CH-Ar), 1.23-0.84 (br, CH_2), 0.84-0.45 (br, CH_2CH_3).

	Conversion (%)	Ratio (p:x)	Mn	Mw/Mn
9	65	27:11	27214	2.06

Synthesis of polymer 10

0.5g of polymer 9 were dissolved and stirred at 35°C in 8 mL of chloroform. To this solution were added 8 mL of TFA. The reaction mixture was stirred at 35°C overnight. The solvent was removed in vacuum and the dark green residue neutralized with a 2M aqueous solution of NaOH. The solution was stirred for 3h at room temperature, then the yellow-green solid was filtered and washed with methanol. It was obtained 0.45g of a yellow solid. **^1H-NMR** ($CDCl_3$, 400MHz): δ ppm 7.80-7.29 (br, *H*-Ar), 7.29-6.13 (br, *H*-Ar), 3.94-3.54 (br, CH_2NH_2), 2.34-1.23 (br, CH_2-FL, CH_2CH-Ar, CH_2CH-Ar), 1.23-0.84 (br, CH_2), 0.84-0.50 (br, CH_2CH_3).

	Conversion (%)	Ratio (p:x)
10	98	27:11

Synthesis of polymer 11

In a dry flask polymer 10 was dissolved (0.4g, 1.89×10^{-4}mol) in 10mL of dry toluene and 1 mL of dry pyridine. To the flask was added under stirring a solution of PCBM-Cl in dry toluene (0.26g, 2.83×10^{-4} mol, 1.5eq, in 50mL of dry toluene). The black reaction mixture was stirred at reflux overnight under inert atmosphere, then 1 mL of water was added to convert the excess of PCBM-Cl in the corresponding acid. The solution was precipitated in methanol. The residue was dissolved in toluene, sonicated, centrifuged and the supernatant removed. The same procedure was repeated using THF and again toluene. The combined organic phases were concentrated and precipitated into methanol obtaining 0.55g of a yellow-brown powder. **^{1}H-NMR** ($CDCl_3$, 400MHz): δ ppm 8.11-7.27 (br, *H*-Ar), 7.29-6.13 (br, *H*-Ar), 4.51-4.09 (br, CH_2NHCO), 3.76-3.66 (br, CH_2NH_2), 3.02-2.81 (br, $CH_2CH_2CH_2CO$), 2.63-2.46 (br, $CH_2CH_2CH_2CO$), 2.45-1.19 (br, $CH_2CH_2CH_2CO$, CH_2-FL, CH_2CH-Ar, CH_2CH-Ar), 1.19-0.82 (br, CH_2), 0.82-0.50 (br, CH_2CH_3). **FT-IR** υ (cm-1): 3420 N-H, 1679 C=O (amide).

	Yield (%)	**Amount of C_{60} (%)[a]**
11	97	90

[a] calculated by ^{1}H-NMR

Synthesis of polymer 12

In a dry flask polymer 11 was dissolved (0.5g, 1.67×10^{-4}mol) in 70mL of dry toluene and 0.1 mL of dry pyridine. To the flask was added under stirring 0.1mL of heptanoyl chloride. The reaction mixture was stirred at reflux overnight under nitrogen. The solvent was concentrated and the polymer precipitated in methanol, heptanes, methanol and acetone obtaining 0.21g of a brown powder. **^{1}H-NMR** ($CDCl_3$, 400MHz): δ ppm 8.07-6.13 (br, *H*-Ar), 4.99-4.61 (br, CH_2NCOCO), 3.09-2.80 (br, $CH_2CH_2CH_2CO$), 2.75-2.46 (br,

$CH_2CH_2C\mathit{H}_2CO$), 2.45-1.19 (br, $CH_2C\mathit{H}_2CH_2CO$, CH_2-HP, $C\mathit{H}_2$-FL, $CH_2C\mathit{H}$-Ar, $C\mathit{H}_2CH$-Ar), 1.19-0.82 (br, CH_2), 0.82-0.41 (br, CH_2CH_3). **FT-IR** υ (cm-1): 1725 C=O (imide)

	Yield (%)	**Mn**	**Mw/Mn**
12	40	30373	2.36

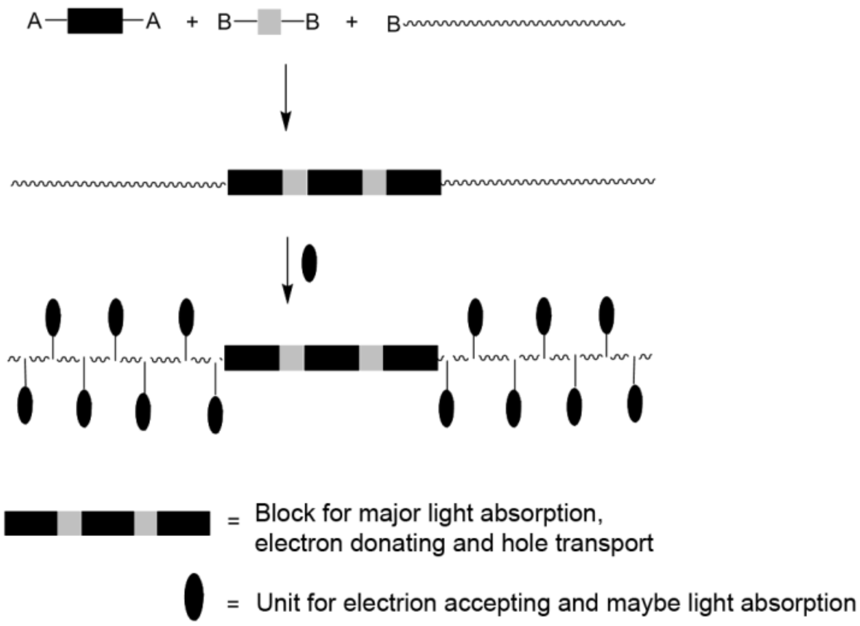

Figure SI 1. Synthetic strategy for the donor-accepter-donor tri-block copolymers (Note: instead of the AA/BB-approach illustrated here, the polycondensation reaction can also be performed by using an AB-approach). The mono-functional macro-monomer can be synthesised by the RAFT method using a B-functional RAFT agent.

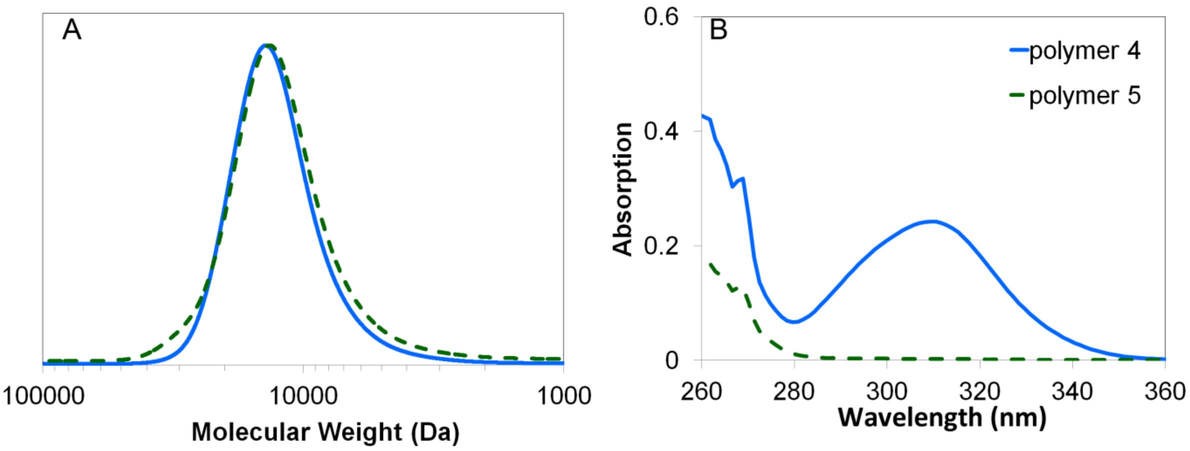

Figure SI 2 A – chromatograms of polymer 4 and 5; B – UV absorption spectra of the polymer at 27.35 min elution time before (polymer 4) and after (polymer 5) chemical removal of RAFT end group.

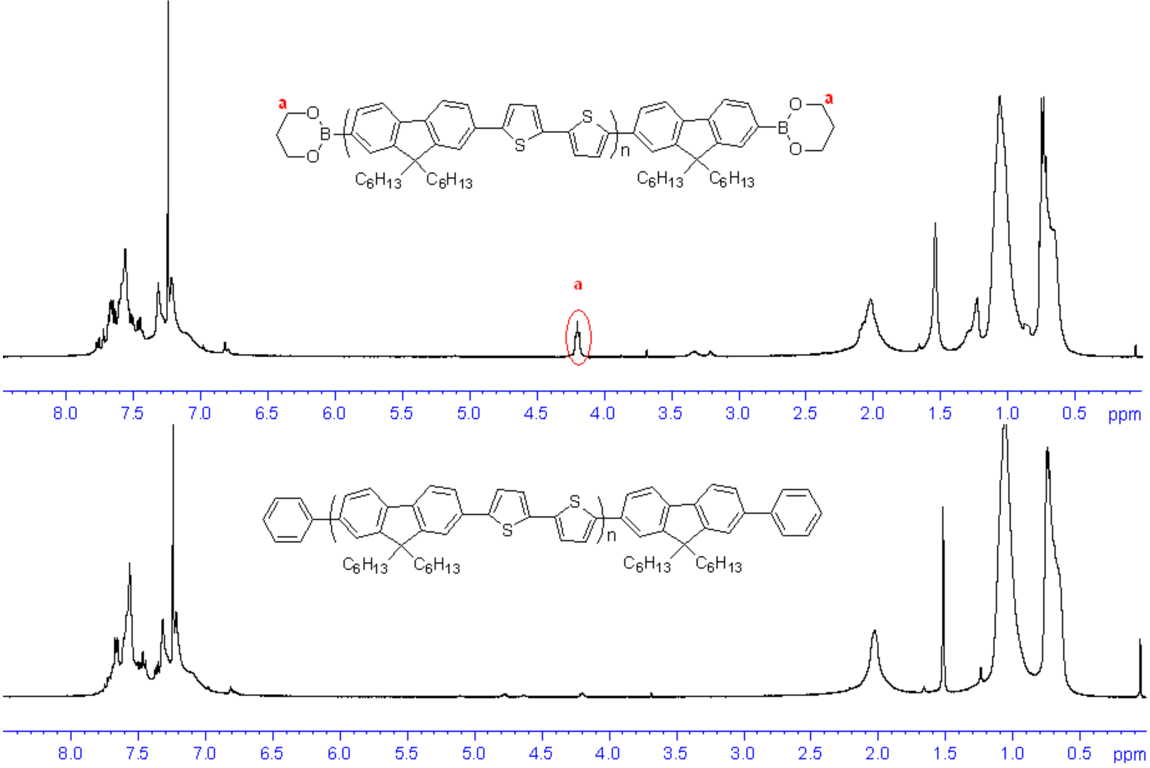

Figure SI 3 ^{1}H-NMR of a model reaction of polymer **F6T2** before and after endcapping

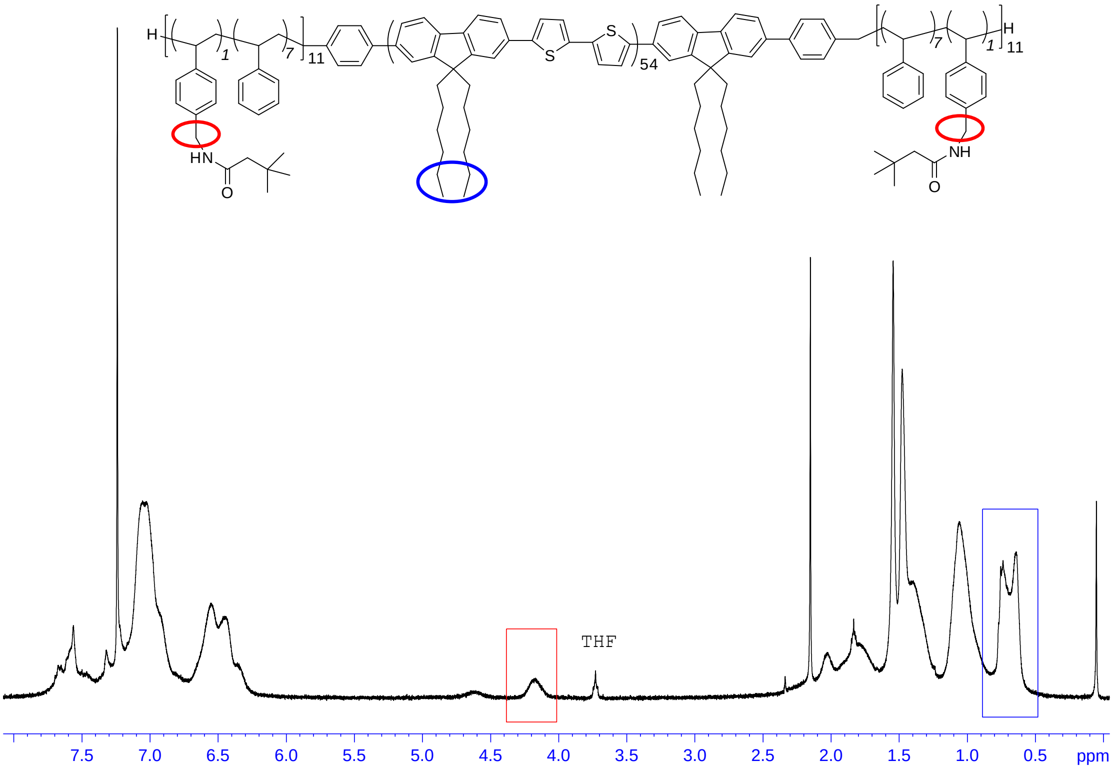

Figure SI 4 ^{1}H-NMR of polymer **9**

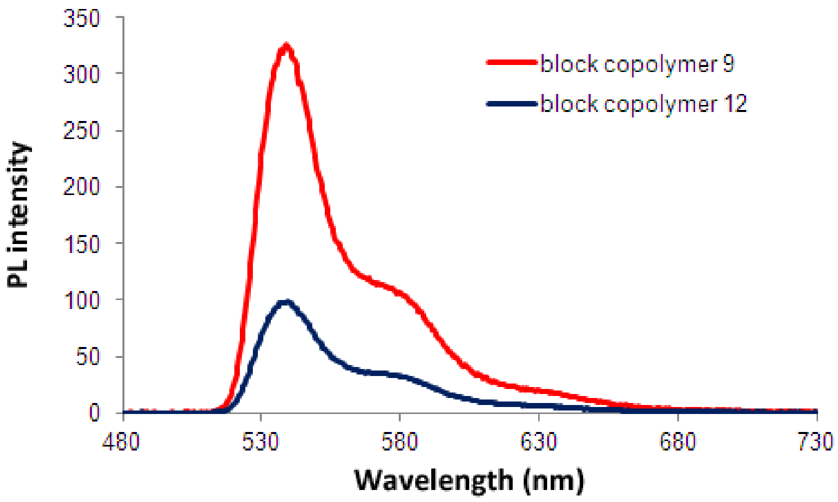

Figure SI 5 Photoluminescence spectra in THF solution at room temperature of polymer **9** (0.0013mg/mL), polymer **12** (0.0013 mg/mL) normalized by UV absorption at excitation wavelength (450nm).

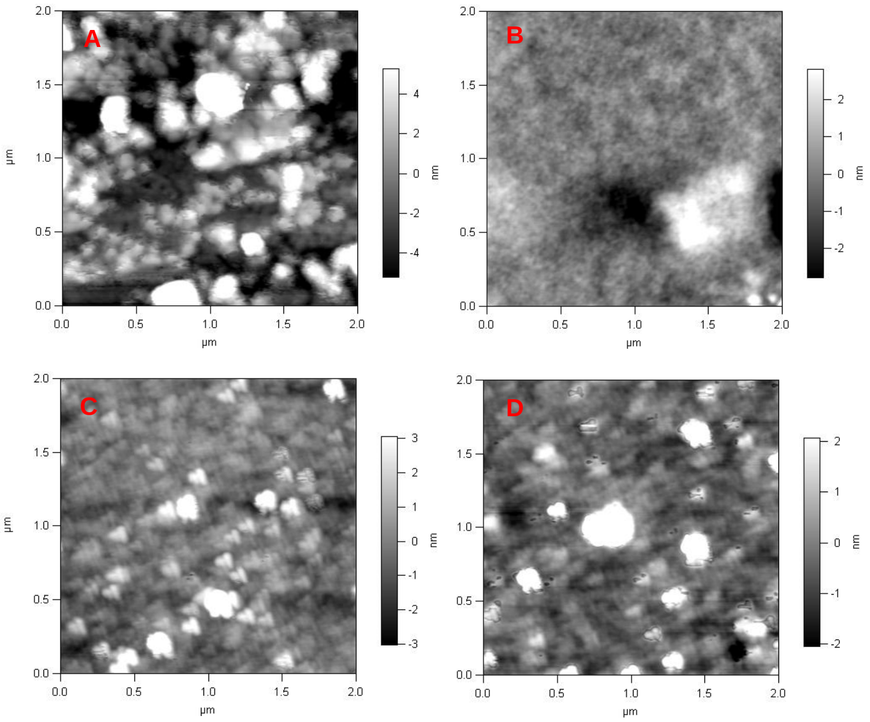

Figure SI 6 AFM phase images of spin-cast films on glass substrates for a mixture of F6T2-PCBM at (a) room temperature, (b) 150°C; and rod-coil block copolymer **12** at (c) room temperature and (d) 150°C. Films b and d were annealed for 10 minutes 2 times. The film samples were prepared by spin-casting from chlorobenzene solution on glass for 1min at 1200rpm and analyzed on the AFM operating in 'Tapping Mode'.